

Performance of Biological Ion Exchange Resin and Gravity-Driven Ceramic Membrane Hybrid Process for Surface Water Treatment

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Abstract

In this study, the performance of a biological ion exchange (BIEX) resin and gravity-driven ceramic membrane (GDCM) filtration hybrid process in terms of membrane permeate quality, flux, and membrane biofilm characteristics during river water treatment for drinking water was investigated. The hybrid process results were compared with those of the GDCM process without the BIEX pre-treatment. Three types of previously synthesized microfiltration membranes were used: M1 (100 wt% kaolin), M2 (75 wt% kaolin + 25 wt% alumina), M3 (50 wt% kaolin + 50 wt% alumina), and M4 (commercial ceramic microfiltration membrane). In terms of permeate quality, the BIEX column removed approximately 74% of the dissolved organic carbon (DOC) compared with the influent water, followed by 27% DOC removal using M3 compared with the BIEX column effluent on day 65 (6,240 BV), which was mainly due to the removal of humic and fulvic acids. BIEX removed turbidity of the influent water from 2.20 NTU to 0.77 NTU, which was further decreased to 0.09 NTU by membranes. The maximum stabilized flux of the membranes was approximately 5.7 LMH, which was almost doubled compared to GDCM without pre-treatment. The membrane biofilm showed lower thickness and roughness in the hybrid process than that in GDCM without pre-treatment. Higher extracellular polymeric substance (EPS) concentration and biological activity were observed for M3, the membrane with the highest stabilized flux and highest DOC removal efficiency.

The results indicate that the hybrid BIEEX + GDCM is a robust, high-performance, and easy-to-use process that can increase the flux and permeate quality of GDCM systems.

1 Introduction

Decentralized drinking water treatment systems are an appealing option for water supply of remote communities [1, 2]. However, given the lack of expertise available for maintenance and operation, such systems should be as passive as possible. Eliminating natural organic matter (NOM) in decentralized water treatment systems is a major challenge as most treatment options involve the use of chemicals such as coagulants, granular activated carbon (GAC), which has a limited capacity to absorb NOM, or high-pressure membranes processes. The abatement of NOM improves the organoleptic properties of water (color, taste, and odor) and mitigates the formation of organo-chlorinated disinfection byproducts [3]. An improved process targeting simultaneous passive disinfection and NOM removal from water is required to expand the deployment of decentralized drinking water systems.

Utilization of gravity-driven membrane (GDM) filtration is attractive because of its high particle removal performance, low energy consumption, reduced need for chemical or physical washing, and ability to reach a stabilized flux, making it suitable for long-term passive filtration [4, 5]. Typically, stabilized GDM flux varies between 4 to 10 LMH according to the influent water composition, and the transmembrane pressure is below 0.1 bar [6]. The two critical limitations of this process are its relatively low flux (compared with conventional low-pressure membrane filtration) and very low NOM removal [6]. To overcome these disadvantages, we propose that integrating a passive NOM pre-treatment process with ceramic membranes could benefit the development of GDM filtration in decentralized water systems.

The longevity of ceramic membranes during long-term filtration is considered an essential factor because it decreases the capital costs of a plant, despite high production costs. For example, Metawater, a Japanese company, has supplied ceramic membranes for 160

installations worldwide. In one plant, the membranes have been in operation since 1998 with no breakage events [7].

Kaolin-based ceramic membranes are cost-effective (capital / production cost) compared with other ceramic membrane types, primarily because of the lower calcination temperature required for kaolin, which is attributed to the membrane structure and starting materials. In certain cases, they are more cost-effective than polymeric membranes in term of total production cost [8].

Although ion-exchange resins with regular regeneration have shown good NOM removal performance, there are concerns regarding the challenges with the management of spent brine and transportation of regeneration chemicals [9]. Biological Ion Exchange (BIEX) is an ion-exchange resin process that operates with an infrequent regeneration to promote secondary ion exchange (IEX) (e.g., NOM displacing sulfate and bicarbonate). Elimination of the regeneration step results in the formation and growth of biofilms, which increase the biological activity of the media [10]. BIEX resins provide a suitable environment for the growth of microorganisms, although two recent studies [11, 12] state that the main NOM removal mechanism is IEX and not biodegradation.

The traditional coagulation, flocculation, and sedimentation chains are not considered an option in the small water treatment systems because of their limitations such as online injection of chemicals [13]. Therefore, researchers have widely suggested membrane filtration (MF/UF) processes in gravity driven mode (GDM) without pretreatment [13-15] or integrated with GAC and/or PAC, while integration of BIEX with GDM has not been developed yet. In the hybrid BIEX + gravity-driven ceramic membrane (GDCM) filtration process, BIEX is mainly responsible for NOM removal, whereas GDCM filtration (MF/UF) principally targets particulate removal. These two treatment strategies are relatively new. The effect of BIEX pre-treatment on the fouling of polymeric ultrafiltration membranes has also been investigated [16]. BIEX has been reported to remove 50% of the different types of NOMs, such as humic

substances, building blocks, and low-molecular-weight acids (from a pond water in Vancouver, Canada pre-filtered through 1 μm filters and diluted by tap-water to achieve 5 mg C/L of DOC), leading to a substantial reduction in total and irreversible UF fouling. However, the UF was conducted at a higher flux (50 LMH) than expected in the GCDM. In wastewater treatment applications, a hybrid process consisting of a biofilm reactor with submerged GDM can increase the flux compared to a single GDM process owing to improved organic matter removal [17]. Two studies have focused on integrating granular and powdered activated carbon with a GDM process developed for rainwater treatment [18, 19]. In these studies, a layer of granular and powdered activated carbon or sand was coated on the membrane surface. The presence of a granular activated carbon (GAC) layer increased the NOM removal by 25%; however, it decreased the stable flux (3.2 LMH) compared to that of the membrane without a coating layer (4.5 LMH). Finally, the effect of in situ coagulation on the performance of a GDM bioreactor intended for wastewater treatment enhanced the permeability by more than two-fold compared to the control process without coagulation. However, no flux stabilization was observed [20].

In summary, previous studies suggest that lowering the NOM is beneficial in reducing membrane fouling. However, the effect of BIEX pre-treatment on the stabilized flux achieved by GCDM filtration has not yet been investigated.

The general objective of this research was to study the performance of the BIEX + GDCM hybrid process for the decentralized treatment of river water with high NOM concentration. In this study, two original sub-objectives were pursued. Firstly, the impact of BIEX pre-treatment on the permeate water quality and stabilized GCDM flux was investigated. Secondly, ceramic membranes were selected in the GDM process according to their extended lifetime expectancy which is aligned with the decentralized water treatment requirements. To achieve these objectives, a commercial anionic exchange resin operated without regeneration was used as a pre-treatment prior to kaolin-based microfiltration (MF) ceramic membranes. The performance

of the hybrid process (BIEX + GDCM) was compared with that of a negative control consisting of only the GCDM step.

2 Materials and Methods

2.1 Membrane synthesis

Disk-shaped ceramic MF membranes with different kaolin and alumina contents were synthesized using a pressure casting and sintering method, as previously described [21]. Briefly, kaolin (Sheffield Pottery, Sheffield, MA, USA) and alumina (Fisher Scientific, Switzerland; Al_2O_3 , 40–300 μm , CAS: 1344-28-1, $M_w = 101.96 \text{ g mol}^{-1}$) in predefined proportions (M1–M3) were mixed with deionized water to prepare a dough that was transferred to a disk-shaped mold. After applying 7.3 MPa pressure (SPI low-pressure sensor, NJ, USA) and drying at room temperature (20 – 25 °C), the membranes were calcined at 1100 °C for 2 h. The previously published membrane characteristics are presented in Table 1. Briefly, the goniometer (OCA20, Dataphysics, Germany) equipped with a video camera was used to measure the contact angle by placing a water droplet on the membrane surface. Porosity was measured by determining the difference between wet and dry membrane weights. The membrane mean pore radius was calculated using the Guerout-Elford-Ferry equation [22] by measuring DI water flux at different pressure heads. Surface diameter of visible holes calculated using scanning electron microscopy (SEM) micrographs taken by Jeol, JSM-7600TFE, JEOL Ltd., Japan device using low electron voltages (5–10 kV) after sample preparation procedures. Minor and major crystalline phases appeared after membrane calcination procedure determined using a Brucker D8 Advanced X-ray diffraction (XRD) device by Cu-K α radiation at a rate of 0.2° per second. Three membranes of each type were used for all the characterization techniques except XRD (one sample was used). A commercial ceramic MF (0.8 μm $\text{ZrO}_2/\text{TiO}_2$, disk shape, area 16 cm^2 , Tami Industries, France, referred

hereafter as M4) was tested along the alumina/kaolin ones to compare the performance of the membranes.

Table 1. Membrane characterization results [21]

Membrane type	M1	M2	M3	M4
Membrane contents	100 wt% kaolin 0 wt% alumina	75 wt% kaolin + 25 wt% alumina	50 wt% kaolin + 50 wt% alumina	ZrO ₂ /TiO ₂
Contact angle	<5°	<5°	<5°	<5°
Porosity (%)	41.9 ± 2.48 ¹	43.6 ± 4.68	54.7 ± 5.21	21.2 ± 8.72
Mean pore radius (µm) (calculated)	0.43 ± 0.03	0.48 ± 0.05	0.98 ± 0.07	0.8 ²
Mean pore radius (µm) (from SEM)	0.37 ± 0.03	0.58 ± 0.09	0.98 ± 0.13	-
Pure water permeability (LMH/bar) at 90 mbar	101 ± 7.60	375 ± 45.07	3,851 ± 87.07	141 ± 12.91
Major phase ³	Boromullite	Aluminum borate	Aluminum borate	-
Minor phase ³	SiO ₂	SiO ₂	SiO ₂	-

¹ Mean ± 95% confidence interval

² According to the manufacturer

³ From the XRD analysis

2.2 Influent water characteristics

Approximately 400 L of Des Prairies River water was collected in March 2022 from the influent of the Pont-Viau water treatment plant (after traversing through the water screen and before low-pressure pumps), which is located in Laval (Canada). The water was stored at 4 °C in a refrigerator (20 buckets, 20 L capacity) for the whole operation period. During the operation, DOC, turbidity, UVA₂₅₄, pH, alkalinity and the anions were monitored carefully by testing an average of 25 samples. The 95% confidence interval of the distributions (or standard deviations) confirmed fairly stable properties of the influent water during the operation. Influent water (40 L) was removed from the fridge weekly and incubated at room temperature for at least 5 h before being added to the system. The physicochemical composition of the influent water was monitored approximately thrice per week. The mean composition of the influent water during the study is presented in Table 2. The water exhibited a substantial DOC concentration and aromaticity, moderate turbidity, and a low concentration of competitive anions such as sulfate and nitrate [23].

Table 2. Physico-chemical characterizations of the influent water

Parameters	Mean Value $\pm$ 95% confidence interval	Max Value	Min Value	Number of samples
DOC (mg C/L)	7.43 $\pm$ 0.05	7.67	7.12	27
Turbidity (NTU)	2.20 $\pm$ 0.07	2.72	1.89	27
pH	7.39 $\pm$ 0.06	7.62	7.14	27
Alkalinity (mg CaCO ₃ /L)	25.22 $\pm$ 0.37	28	24	27
UVA ₂₅₄ (cm ⁻¹)	0.25 $\pm$ 0.003	0.26	0.23	27
Nitrate (mg/L)	2.23 $\pm$ 0.18	3.02	1.73	19
Sulfate (mg/L)	4.53 $\pm$ 0.12	5.2	4.09	24
Chloride (mg/L)	4.78 $\pm$ 0.27	7.2	4.03	24

2.3 Biological ion exchange resin and gravity-driven filtration experiments

The experimental setup consisted of a BIEEX step followed by a GDCM step, as shown in Figure 1. The membranes described in section 2.1 were used in the GDCM section. In the BIEEX section, Purolite® A860, an anionic strong base resin, was packed into a transparent PVC column with a 63 cm height and 1.27 cm (0.5 inches) diameter. Approximately 42 cm of the column was filled with resin to obtain a total bed volume (BV) of 52 cm³. The empty-bed contact time (EBCT) was 15 min. The column was continuously fed with influent water at a constant filtration rate of 3.47 mL/min (~ 5L/d, 4 BV/h) for 65 days (6,240 BV). The resin column effluent was characterized for DOC, alkalinity, pH, UV absorbance, anions chromatography, and turbidity analyses daily in the first week of operation and twice per week for the remainder of the study.

To investigate the dynamic mechanism of exchange of different anions and NOM between the influent water and resin, the anion loading on the IEX resin charge was calculated using equation (1), where q (eq/L resin) is the cumulative anion loading on the resin, C_{inlet} and C_{outlet} are the concentrations (eq/L) of each anion in the influent/effluent of the resin column, V_{resin} is the total resin volume in the column (52 mL), Q is the flowrate (5 L/d), $\Delta t = (t_i - t_{i-1})$ is the time between each anion and DOC measurement (d), and i is the number of anion and DOC concentration measurements during the experiment. The loadings were calculated for chloride,

sulfate, bicarbonate, and nitrate, which are the major inorganic anions present in the influent water [24].

$$q = \sum_{i=1}^{24} \frac{(Average(C_{inlet, i}, C_{inlet, i-1}) - Average(C_{outlet, i}, C_{outlet, i-1})) \times Q \times (t_i - t_{i-1})}{V_{resin}}, \text{ Eq. (1)}$$

For converting the concentration from mg C/L to eq/L, the charge density of DOC (NOM) was considered to be 10 meq/g C at a pH of 6.5 [25]. Initially, the resin was loaded with chloride ions at a concentration of approximately 0.9 eq/L of resin.

In the GDCM step, the resin column effluent overflowed into a 10 L tank to maintain a constant transmembrane pressure of 90 cm (~ 93 mbar). To prevent algal growth in the system owing to natural light, the raw water tank, resin effluent receiver, and permeate containers were covered with an aluminum foil layer. Membrane holders were constructed from polyethylene equipped with a sight glass on top which allowed visually tracking of the biofilm growth and Optical Coherence Tomography (OCT) imaging without removing membranes from the holders. During the OCT imaging, the membrane holders were removed from the system for approximately 30 min and then installed back in place. The permeate was recovered in a covered container to minimize evaporation and weighed daily using an analytical balance (Ohaus Adventure Pro, Parsippany, NJ, USA). The temperature of the laboratory air conditioning system was set to 20 °C and the real temperature of air was monitored daily (21.5 °C ± 0.5)

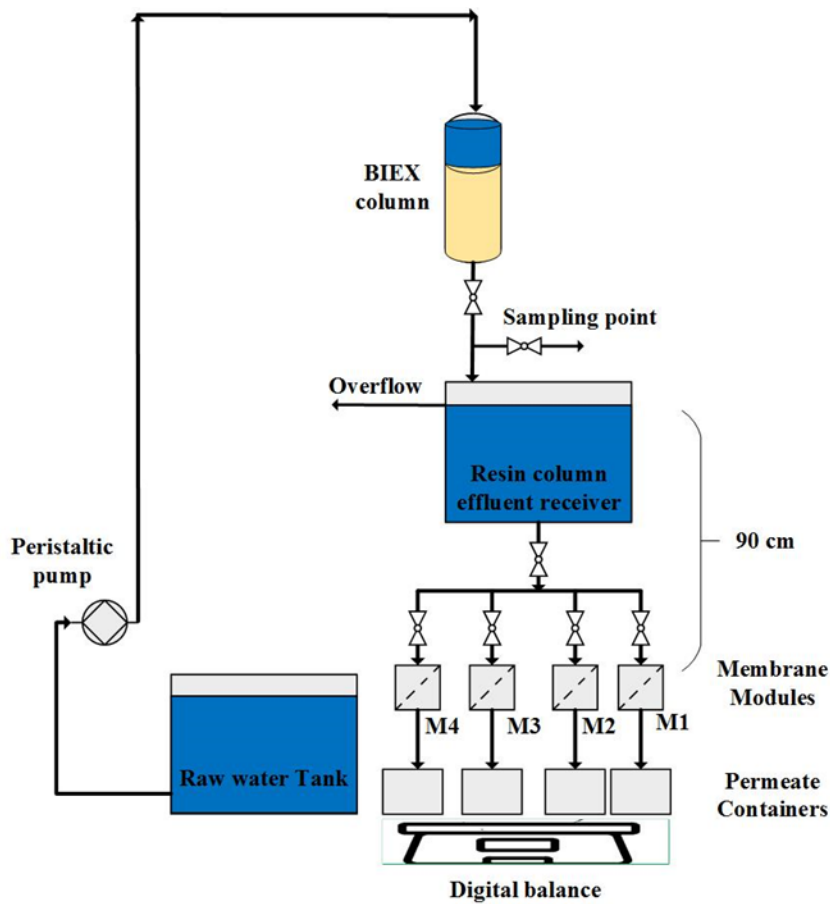


Figure 1. Schematic representation of the experimental setup showing two main sections of BIEEX and GDCM. Figure adopted from [21].

The membrane flux was measured and normalized to 20 °C by transforming the permeate weight to a volume corresponding to 20 °C and divided by the membrane area. Darcy's law was used to calculate membrane fouling resistance. Fouling resistance (biofilm and irreversible resistance) was determined by subtracting the clean membrane resistance from the total fouling resistance [26]. It is worth noting that the viscosity correction during calculation of fouling resistance in this study was negligible as the working temperature was fairly 20 °C. For experiments in the lower temperature, it is essential to consider such correction.

2.4 Analytical methods for water samples

DOC was measured by filtering samples through a prewashed 0.45 µm filter (PES, 0.45-µm, 47 mm, Pall Corporation, Washington, NY, USA) and then using an online TOC analyzer (Sievers M5310C, Trevose, PA, USA). The turbidity of the samples was measured using a

TL2300 (Hach, USA) turbidity meter after calibration with standard samples. A UV-visible spectrophotometer (Cary 100 Scan, Varian Inc., USA) was utilized to measure UVA₂₅₄ in a 1-cm quartz cells on filtered samples (0.45 µm filter, PES, 0.45-µm, 47 mm, Pall Corporation, Washington, NY, USA). A pH meter (Accumet AB 15 basic; Fisher Scientific, Waltham, MA, USA) was used to measure the pH after calibration with standard solutions. 50 mL of the sample was titrated using a 0.01 N H₂SO₄ solution to obtain a pH of 4.5, and then 4.2; alkalinity was calculated using Equation 2.

$$Alkalinity \left(\frac{mg}{l} CaCO_3 \right) = \frac{(2B-C) \times 0.01 \times 50,000}{V}, \text{ Eq. (2)}$$

Where B is the consumed volume of H₂SO₄ to reach a pH of 4.5, C is the total volume of H₂SO₄ consumed to reach a pH of 4.2, and V is the volume of the sample.

To measure the anions, water samples were filtered through 0.45 µm syringe filters and analyzed using an ion chromatography device (ICS 5000 AS-DP DIONEX, Thermo Scientific, Waltham, MA, USA).

A liquid chromatography organic carbon detection (LC-OCD) device (DOC Labor Huber, Stuttgart, Germany) with three detectors (UV absorbance at 254 nm, organic carbon, and organic nitrogen) was used to quantify the NOM fractions in the duplicate samples of influent water, BIEF column effluent, and membrane permeates [27]. The samples were filtered through a 0.45 µm filter before analysis.

2.5 Membrane Biofilm characterization

2.5.1 Biofilm growth by optical coherence tomography

The OCT device, method of analyzing images, and correlation between real and imaged biofilm thicknesses have been described comprehensively in a previous study [21]. Briefly, a commercial 1310-nm OCT equipped with a Thorlabs SL1310V1, Newton, USA laser (with resolution of 8.1 µm) and a balanced detector imaging module were used. Three random areas (~ 7 mm × 4 mm) were selected for each membrane type during each OCT B-scan. Then, using

a developed MATLAB code, the raw images were processed and then analyzed using ImageJ software (NIH, USA) to obtain the optical biofilm thickness (Z_f in μm) which was subsequently used to calculate the physical (real) biofilm thickness (Z_i in μm) by considering the refractive index (n_f) equal to 1.333 due to the high water content of the biofilm [28].

$$Z_i = \frac{Z_f}{n_f} \text{ Eq. (3)}$$

Finally, mean physical biofilm thickness ($\bar{Z}$ in μm), absolute (R_a in μm) roughness, and relative ($\bar{R}_a$) roughness coefficient were calculated using equations 4-6.

$$\bar{Z} = \frac{1}{n} \sum_{i=1}^n Z_i \text{ Eq. (4)}$$

$$R_a = \frac{1}{n} \sum_{i=1}^n (|Z_i - \bar{Z}|) \text{ Eq. (5)}$$

$$\bar{R}_a = \frac{1}{n} \sum_{i=1}^n \left(\frac{|Z_i - \bar{Z}|}{\bar{Z}} \right) \text{ Eq. (6)}$$

2.5.2 Biological activity of biofilm

At the end of the overall experiment, six sonication cycles (40 W power and 20 KHz, Cole-Parmer Ultrasonic processor, Canada) were performed on a piece of membrane, and each cycle was performed in 50 mL of phosphate buffered saline to ensure biofilm detachment from the membrane surface. Thereafter, 90 mL of the composite sample was obtained by mixing 15 ml supernatant from each sonicated subsample. A portion of the composite sample was then filtered through a syringe filter (0.2- μm , Quench-Gone, DIS-SFQG-25, LuminUltra, USA) to maintain microorganisms on the filter to measure the extracellular ATP. Intracellular ATP in the biofilm was then quantified by lysing a portion of the composite samples using Ultralyse 7 solution (LuminUltra, USA). Finally, using a luminometer (PhotonMaster, LuminUltra, USA) and sterilized test tubes, the luminescence (RLU/s) was read and then converted to ng ATP/ cm^2 using a calibration curve prepared with a standard Ultracheck solution (1000 pg/ml, LuminUltra, USA) [9].

2.5.3 Extracellular polymeric substances in the biofilm

EPS were extracted from the biofilm using sonication and centrifugation [29]. The sonication step is described in section 2.5.2. Next, 45 mL of the composite sample was centrifuged twice (Avanti JXN-26; Beckman Coulter, Indianapolis, IN, USA) at $4000 \times g$ for 20 min. The supernatants were collected for EPS quantification. The total EPS content in the extract was determined using protein (PN) and polysaccharide (PS) measurements [30]. The enhanced test tube protocol for the bicinchoninic acid (BCA) assay (Thermo Fisher Scientific, Waltham, MA, USA) was used for protein quantification, with bovine serum albumin as the standard solution. Polysaccharides were measured using the classic phenol-sulfuric acid method, with glucose as the standard solution [31].

2.6 Statistical analysis of data

Membranes with the highest mean stabilized flux, the lowest mean permeate turbidity, DOC, and UVA_{254} were identified as control and then the values were compared to the other membranes using an analysis of variance (ANOVA) with Tukey multiple comparison tests in GraphPad Prism ® 10.0. 2 software to determine whether the differences were statistically significant at $p = 0.05$.

2.7 Gravity-driven ceramic membrane filtration without pre-treatment

To investigate the effect of BIEEX pre-treatment on membrane flux, permeate quality, and biofouling layer characteristics formed on the membrane surface, the results of the hybrid BIEEX + GDCM process (present study) were compared to those of the GDCM process without pre-treatment as a negative control (from the previous study of the authors, which was conducted using the same types of membranes, influent water, and conditions [21]).

3 Results

3.1 Dynamic of ion exchange on the resin

Figure 2a shows the dynamics of anion exchange for chloride, sulfate, bicarbonate, nitrate, and DOC (NOM) in relation to the operation time and cumulative waterbed volume. The fresh resin

capacity (on day 0 and 0 BV) was approximately 0.9 eq/L in the chloride form. Prior to 2,000 BV (~ day 21), chloride continuously exchanged with NOM from the influent water leading to a decrease in resin chloride loading from 0.9 to 0 eq/L resin, which causes exhaustion of resin according to the pre-charged anion (chloride). This can be considered an endpoint for primary IEX and initiation of secondary IEX, referred to as the BIEEX mode. Meanwhile, the bicarbonate, sulfate, and nitrate concentrations on the resin increased to 0.78, 0.18, and 0.04 eq/L resin at 2,000 BV (day 21), respectively. The resin capacity was therefore completely exhausted from the chloride form by mostly bicarbonate and sulfate.

After 2,000 BV (~ day 21), the resin began exchanging bicarbonate and sulfate with the NOM present in the influent (BIEEX mode). Therefore, the NOM loading on the resin continuously increased, whereas the bicarbonate and sulfate concentrations on the resin decreased. At the end of operation (6,240 BV = day 65), the anion loadings of NOM, chloride, bicarbonate, sulfate, and nitrate were 0.36, 0, 0.57, 0.12, and 0 eq/L resin, respectively. In this study, the experiment was not continued until the total resin exhaustion time (secondary exhaustion due to bicarbonate and sulfate). However, if the experiment continues to the exhaust point in the secondary IEX region (0 eq/L resin for bicarbonate and sulfate), the DOC of the resin effluent can reach the same level as that of the influent water [23]. It is worth noting that between 1,920 – 6,240 BV, the total anion loading on the resin was approximately 1.1 eq/L resin which was slightly higher than that of the obtained fresh resin capacity. This could be firstly related to the higher experimental error associated with our bicarbonate measurements compared to the other anions and DOC. Moreover, swelling of polymeric matrix of the resin which is described as the process of penetration of the influent water into a polymer matrix causing a change in the volume due to endosmosis phenomenon (diffusing water molecules from outside to inside the resin matrix). Therefore, a resin with greater swelling will demonstrate an increased rate of anion diffusion into the matrix core, resulting in a reduced reaction time and enhanced chemical

conversion efficiency [32]. The alkalinity and pH trends of the influent water and BIEX column effluent are shown in Figure 2b. Prior to 2,300 BV (day 24), in the primary IEX region, the BIEX column effluent alkalinity varied in a lower range than that of the influent water, which confirmed the uptake of bicarbonate by the resin. Accordingly, pH showed a lower range (4.3 – 6.5) compared to that of the influent water. After 2,300 BV (day 24), in the secondary IEX region, the BIEX column effluent alkalinity increased and exceeded that of the influent water, confirming the release of bicarbonate by the resin (bicarbonate exchange with NOM in the influent water).

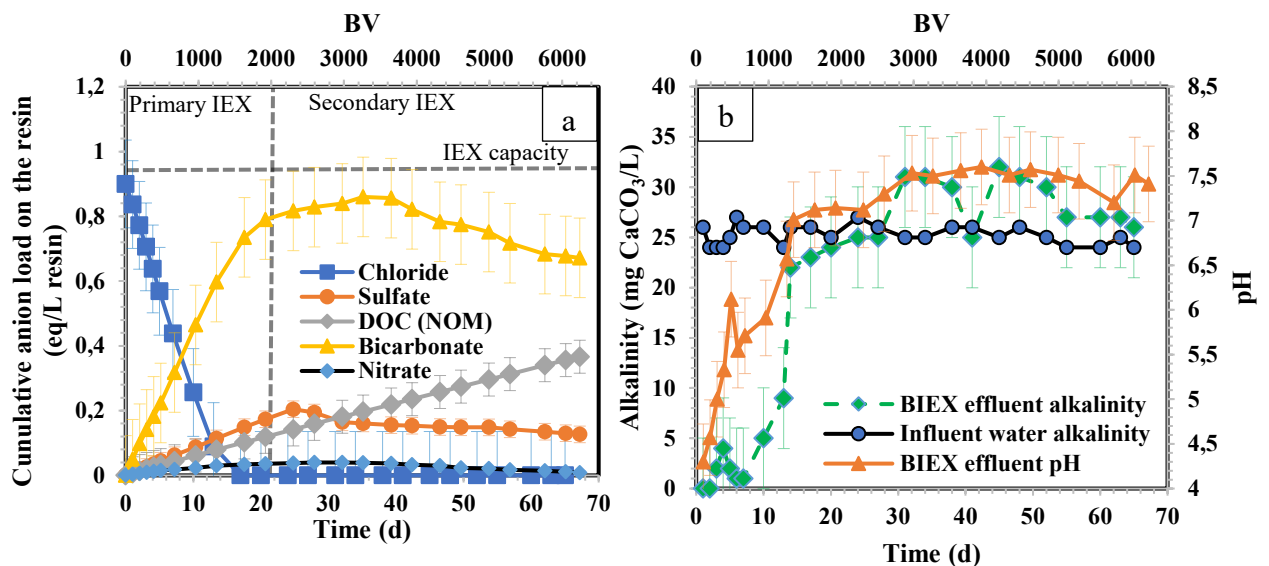


Figure 2. Variation of a) chloride, sulfate, DOC, bicarbonate, and nitrate concentration on the resin by operating time and bed volume, b) alkalinity and pH of BIEX column effluent, and alkalinity of influent water during the operation period. Error bars show 95% confidence intervals.

3.2 Effluent quality of BIEX column and membranes

3.2.1 Dissolved organic carbon removal

The DOC of the BIEX column effluent and membrane permeates are presented in Figure 3a. In the primary IEX region (prior to day 24 and 2,300 BV), the DOC concentration was at 0.57 mg C/L (~ 92% removal), then rose progressively and peaked at 2.03 mg C/L (~ 73% removal) at 2,304 BV. Until day 5 (480 BV), the chloride release was stable at 24–26 mg/L (Figure 3c). The chloride release then dropped markedly from 26 to 5.9 mg/L by day 24 (2,300 BV).

Simultaneously, a breakthrough in the DOC of the BIEEX column effluent was observed (2.03 mg C/L – 73% removal). This breakthrough in the DOC concentration indicates the end of the primary IEX region (chloride exchange with NOM), where the chloride concentration in the resin is almost completely released [9, 23, 24]. In the secondary IEX region (from 2,300 to 6,240 BV), the DOC concentration of the BIEEX effluent initially decreased because of bicarbonate and sulfate ion exchange with NOM. The concentration then fluctuated until approximately 4,000 BV before increasing again at 2.05 mg C/L (~ 74% removal) at the end of the experiment (day 65, 6,240 BV). In summary, BIEEX pre-treatment provides an effective treatment option to remove NOM for 65 d without any regeneration.

The DOC concentration of the membrane permeate followed the general trend of the BIEEX effluent. However, incremental DOC removal was achieved in all four membranes investigated. At the beginning of the experiment, membranes M1, M2, and M3 exhibited similar DOC concentrations. However, M3 (50 wt% kaolin and 50 wt% alumina) exhibited the best DOC removal performance at the end of the experiment. At the end of filtration (day 65), the DOC concentrations in the M1, M2, M3, and M4 permeates were 1.82, 1.71, 1.48, and 1.82 mg C/L, respectively, which corresponded to approximately 10%, 16%, 27%, and 10% DOC removal calculated against the DOC of the BIEEX column effluent. According to Figure 4a, the mean DOC concentration of the M3 permeate (1.23 ± 0.11 mg C/L, mean $\pm$ 95% confidence interval) was statistically different compared to that of other membrane types (M1 = 1.45 ± 0.15 mg C/L, mean $\pm$ 95% confidence interval, p (M3 – M1) < 0.001; M2 = 1.38 ± 0.15 mg C/L, mean $\pm$ 95% confidence interval, p (M3 – M2) = 0.003; M4 = 1.38 ± 0.12 mg C/L, mean $\pm$ 95% confidence interval, p (M3 – M4) = 0.006). We attribute this performance to the enhanced sorption provided by the higher alumina content of membrane M3. The hybrid BIEEX + GDCM (using M3) process removed approximately 81% of DOC from the influent water at the end of the experiment.

3.2.2 UVA₂₅₄ reduction

UVA₂₅₄ in the BIEEX effluent and membrane permeate are shown in Figure 3b. The general trend was the same as that of DOC in both the primary and secondary IEX regions. Regarding the BIEEX effluent, in the primary IEX region (prior to 2,300 BV, day 24), UVA₂₅₄ increased continuously as the operation commenced (day 0, 0.003 cm⁻¹) to 960 BV (day 10, 0.023 cm⁻¹) and then fluctuated before peaking at only 0.024 cm⁻¹ on day 24 (2,300 BV). Similarly, the breakthrough in UVA₂₅₄ confirmed the end of the primary IEX region (the endpoint of chloride release). Considering the constant UVA₂₅₄ for the influent water (0.25 cm⁻¹ ± 0.003, mean ± 95% confidence interval) during the experiment, the UVA₂₅₄ removal at the end of the primary IEX region was approximately 90%. In the secondary IEX region (from days 24 to 65/ 2,300 to 6,240 BV), the removal initially increased due to the exchange of sulfate and bicarbonate anions with the DOC from the influent water. UVA₂₅₄ stabilized from 2,500 to 4,300 BV (days 27 to 45) before increasing to 0.031 cm⁻¹ at the end of the operation (6,240 BV on day 65, with a corresponding removal of ~ 88%).

At the start of the experiment, the UVA₂₅₄ in the membrane permeates was approximately the same as that in the BIEEX effluent. The membrane long-term permeation decreased UVA₂₅₄ below that of the BIEEX effluent. UVA₂₅₄ were 0.023, 0.024, 0.016, and 0.027 cm⁻¹ in the permeates of M1, M2, M3, and M4, respectively, on day 65, corresponding to 25%, 22%, 48%, and 13% UVA₂₅₄ removal compared to the BIEEX. As shown in Figure 4b, the mean UVA₂₅₄ of M3 (0.012 ± 0.002 cm⁻¹, mean ± 95% confidence interval) was lower than that of the other membranes and BIEEX column effluent. However, the obtained value by M3 was not statistically different compared to the other membrane types. In contrast, it was significant when compared to the BIEEX column effluent (0.02 ± 0.002 cm⁻¹, mean ± 95% confidence interval, *p* < 0.001). The resins showed good UVA₂₅₄ removal in both the primary and secondary IEX (BIEEX mode) regions. At the end of the experiment, the UVA₂₅₄ abatement using the BIEEX + GDCM (M3) hybrid process was approximately 94%.

3.2.3 Turbidity removal

The effluent turbidities of the BIEX and GDCM sections are shown in Figure 3d. Regarding BIEX effluent, the trend started with a sharp decrease from 1.1 NTU to 0.55 NTU at approximately 1,250 BV (day 14). The BIEX effluent turbidity then increased from 0.55 NTU to 0.75 NTU at 3,000 bed volume filtration (day 31) before stabilizing at approximately 0.77 NTU $\pm$ 0.06 (mean $\pm$ 95% confidence interval) until the end of the experiment.

A similar trend was observed for the membrane permeate turbidity. The turbidity of all permeates started at 0.12 – 0.16 NTU and declined to 0.05, 0.07, 0.08, and 0.06 NTU for M1, M2, M3, and M4, respectively, on day 4. The trend then increased and fluctuated toward a stable value of 0.09 – 0.11 NTU. At the end of experiment (day 65), the permeate turbidities were 0.11, 0.10, 0.09, and 0.11 NTU for M1 – M4, respectively. These performances were consistent with the expected turbidities for low-pressure membrane processes, which are required to provide turbidities lower than 0.15 NTU [33].

To compare the membrane performance in term of turbidity removal, a bar graph representing the mean of turbidity measurements during the operation was prepared (Figure 4c). M2 with 0.09 NTU $\pm$ 0.007 turbidity (mean $\pm$ 95% confidence interval) was lower than that of the other three membranes, although the difference was only statistically different when compared to M4 with 0.11 NTU $\pm$ 0.008 turbidity (mean $\pm$ 95% confidence interval, $p = 0.006$).

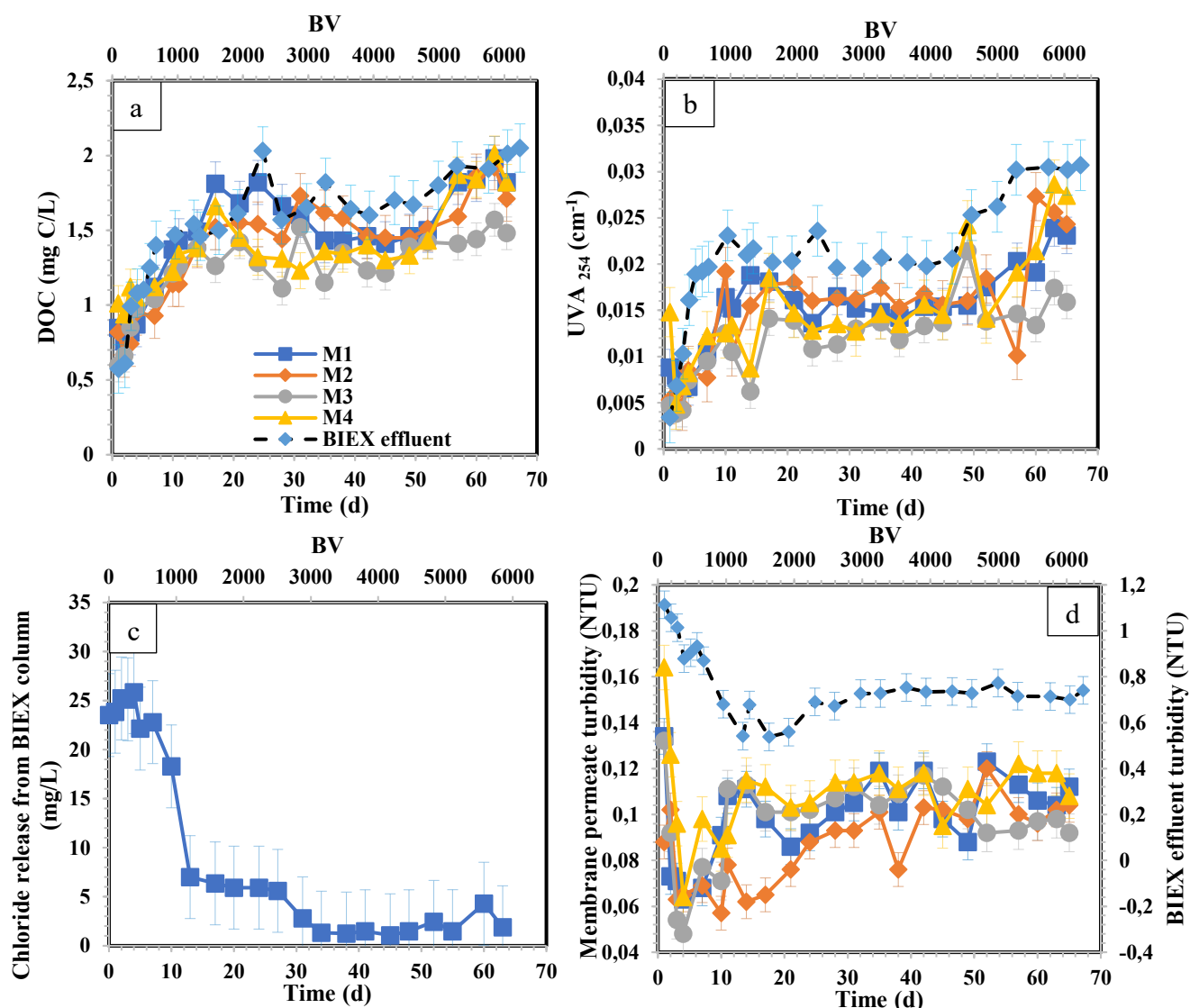


Figure 3. The variations of a) DOC, b) UVA₂₅₄, c) chloride release from the resin, and d) turbidity by M1 (100 wt% kaolin), M2 (75 wt% kaolin, 25 wt% alumina), M3 (50 wt% kaolin, 50 wt% alumina), M4 (0.8 μ m commercial), and BIEX column effluent during the operation period. UVA 254₀ = 0.25 cm⁻¹ $\pm$ 0.003, DOC₀ = 7.43 mg C/L $\pm$ 0.05, Turbidity₀ = 2.20 NTU $\pm$ 0.07. Error bars show 95% confidence intervals.

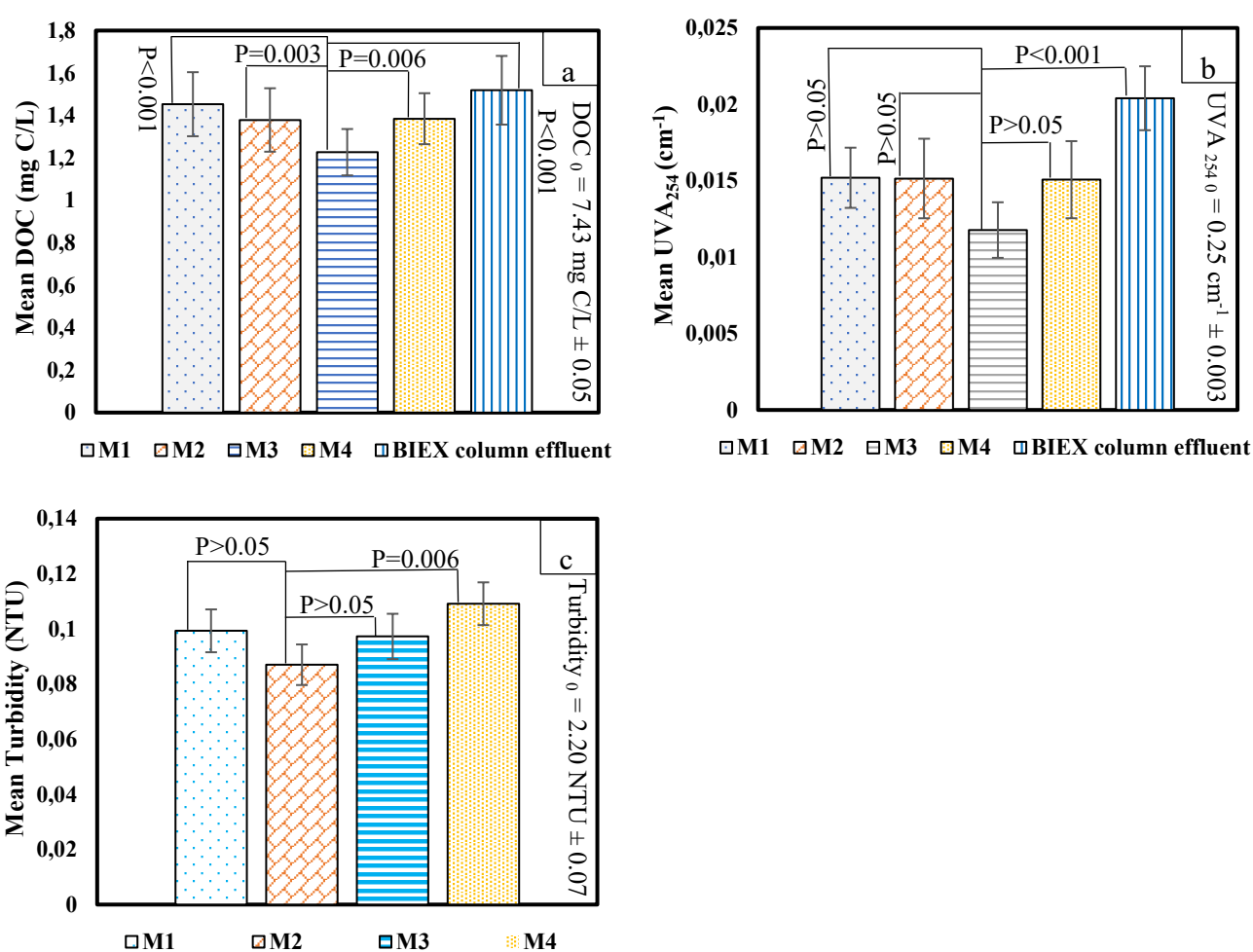


Figure 4. a) mean DOC b) mean UVA₂₅₄ c) mean turbidity measurements for M1 (100 wt% kaolin), M2 (75 wt% kaolin, 25 wt% alumina), M3 (50 wt% kaolin, 50 wt% alumina), M4 (0.8 μ m commercial), and BIEF column effluent during the operation period (number of samples = 23 in 65 days of operation). The numbers indicate the p-values. Error bars show 95% confidence intervals.

3.2.4 Removal of NOM fractions

The different NOM fractions present in the influent water, BIEF column effluent, and membrane permeates on days 15 (1,440 BV, primary IEX region), 36 (3,456 BV, secondary IEX region), and 65 (6,240 BV, secondary IEX region) of operation are shown in Table 3 and Figure S1. As expected, humic substances (HS) were the predominant fraction of NOM in the influent water, with a concentration of 5,127 μ g/L $\pm$ 299 (mean $\pm$ 95% confidence interval) which were completely removed by the BIEF column and membranes on days 15 and 36. On day 65, the HS concentration reached 293 μ g/L $\pm$ 72 in the BIEF effluent, which was retained

by all membranes. The concentration of biopolymers (BP) was $273 \mu\text{g/L} \pm 112$ in the influent water. The BIEEX effluent showed a slightly higher concentration of BP ($295 \mu\text{g/L} \pm 40$ on day 15); however, the M3 and M4 permeates contained less BP (187 ± 40 and $126 \mu\text{g/L} \pm 36$ on day 15, respectively). The M3 permeate showed remarkable BP removal at $69 \mu\text{g/L} \pm 27$ and $79 \mu\text{g/L} \pm 12$ on days 36 and 65, respectively, compared with the BIEEX effluent and influent water. Based on previous results [21], the noticeably higher BP removal of M3 was due to BP biodegradation in the biofilm, as evidenced by the higher biological activity and biofilm thickness. The building blocks (BB) concentration in the influent water was $1,074 \mu\text{g/L} \pm 270$ which was substantially higher than that in the BIEEX column effluent ($163 \mu\text{g/L} \pm 27$ on day 15) and membrane permeates ($248 - 320 \mu\text{g/L}$ on day 15). BB concentration was generally slightly higher in the membrane permeate than that of the BIEEX column effluent (except for M3 on day 36). The concentration of low molecular weight acids (LMW acids) was slightly higher in the BIEEX column effluent and membrane permeates than that of the influent water. The hybrid BIEEX + GDCM was used continuously without any cleaning of the foulants; therefore, high-molecular-weight compounds (such as HS) could be retained and accumulated on the membrane surface. Such accumulated biomass can be hydrolyzed to low-molecular-weight compounds by bacteria and living organisms in the biofouling layer [34], which could lead to the higher LMW acids in the BIEEX and membrane effluent. Finally, the influent water contained $476 \mu\text{g/L} \pm 130$ LMW neutrals, which were decreased to approximately 294 ± 36 and $272 \mu\text{g/L} \pm 40$ on days 15 and 65, respectively, by the BIEEX resin. LMW neutrals content of membrane permeates were generally in the same range ($250 - 350 \mu\text{g/L}$). In summary, the hybrid BIEEX + GDCM process removed the total HS because of its high molecular weight ($350 - 10,000 \text{ g/mol}$) and charge density [27, 35]. BB was the second-most-removed NOM fraction in the primary ($\sim 84\%$) and secondary IEX regions (day 65, $\sim 77\%$) in the resin effluent, whereas BP and LMW acids showed no or low removals in either IEX region.

Table 3. Fractions of NOM (Mean $\pm$ 95% confidence interval) in the influent water, BIEC column effluent, M1 permeate (100 wt% kaolin), M2 permeate (75 wt% kaolin, 25 wt% alumina), M3 permeate (50 wt% kaolin, 50 wt% alumina), and M4 permeate (0.8 μ m commercial) on days 15 (1,440 BV, primary IEX), 36 (3,456 BV, secondary IEX), and 65 (6,240 BV, secondary IEX).

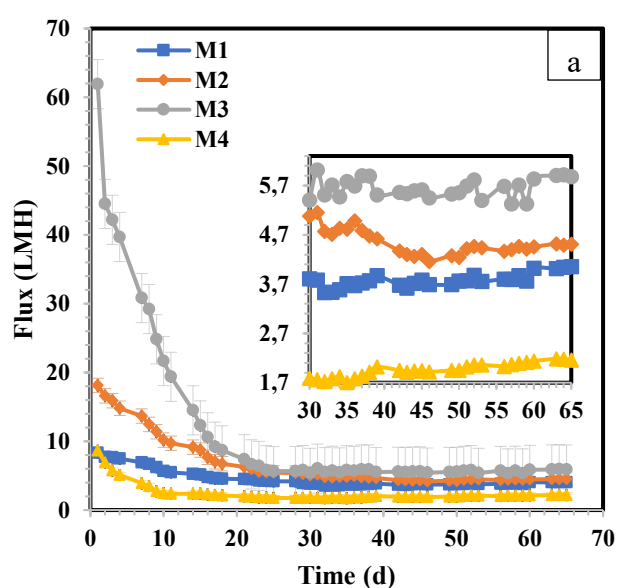
	Total DOC (μ g/L)			BP (μ g/L)		
	Day 15	Day 36	Day 65	Day 15	Day 36	Day 65
Influent water	7,137 $\pm$ 202	-	-	273 $\pm$ 112	-	-
BIEC	1,022 $\pm$ 144	1,170 $\pm$ 193	1,414 $\pm$ 386	295 $\pm$ 40	346 $\pm$ 36	272 $\pm$ 148
M1	1,182 $\pm$ 27	1,052 $\pm$ 67	1,216 $\pm$ 292	263 $\pm$ 31	229 $\pm$ 54	247 $\pm$ 36
M2	1,235 $\pm$ 18	1,208 $\pm$ 22	1,107 $\pm$ 126	316 $\pm$ 45	296 $\pm$ 58	219 $\pm$ 85
M3	1,028 $\pm$ 72	791 $\pm$ 99	940 $\pm$ 180	187 $\pm$ 40	69 $\pm$ 27	79 $\pm$ 12
M4	1,525 $\pm$ 103	947 $\pm$ 148	1,126 $\pm$ 220	126 $\pm$ 36	128 $\pm$ 27	215 $\pm$ 54
	HS (μ g/L)			BB (μ g/L)		
	Day 15	Day 36	Day 65	Day 15	Day 36	Day 65
Influent water	5,127 $\pm$ 299	-	-	1,074 $\pm$ 270	-	-
BIEC	n.d.	n.d.	293 $\pm$ 72	163 $\pm$ 27	232 $\pm$ 24	251 $\pm$ 63
M1	n.d.	n.d.	n.d.	320 $\pm$ 58	271 $\pm$ 85	311 $\pm$ 72
M2	n.d.	n.d.	n.d.	279 $\pm$ 49	260 $\pm$ 54	286 $\pm$ 45
M3	n.d.	n.d.	n.d.	248 $\pm$ 49	178 $\pm$ 72	253 $\pm$ 58
M4	n.d.	n.d.	n.d.	289 $\pm$ 85	271 $\pm$ 54	314 $\pm$ 40
	LMW acids (μ g/L)			LMW neutrals (μ g/L)		
	Day 15	Day 36	Day 65	Day 15	Day 36	Day 65
Influent water	188 $\pm$ 117	-	-	476 $\pm$ 130	-	-
BIEC	271 $\pm$ 40	286 $\pm$ 54	327 $\pm$ 63	294 $\pm$ 36	396 $\pm$ 49	272 $\pm$ 40
M1	280 $\pm$ 94	287 $\pm$ 90	367 $\pm$ 108	320 $\pm$ 31	265 $\pm$ 54	291 $\pm$ 76
M2	298 $\pm$ 49	295 $\pm$ 40	340 $\pm$ 85	344 $\pm$ 58	358 $\pm$ 22	263 $\pm$ 81
M3	278 $\pm$ 18	294 $\pm$ 54	333 $\pm$ 72	316 $\pm$ 45	250 $\pm$ 54	276 $\pm$ 130
M4	285 $\pm$ 67	292 $\pm$ 76	335 $\pm$ 90	826 $\pm$ 220	256 $\pm$ 45	262 $\pm$ 36

n.d. = not detected

3.3 Flux and fouling resistance

The fluxes and fouling resistances of the membranes are shown in Figure 5. The fouling dynamics (Figure 5a) evolved in two stages. The first stage was a steep flux decline that lasted up to 10 – 30 days, depending on the membrane. The fouling resistance of the membranes is linked to their flux, as shown in Figure 5b. The fouling resistance showed a trend reversal similar to that of the flux. During the first 30 days, the flux of M1, M2, M3, and M4 declined from approximately 8.3 LMH to 3.8 LMH, 18.1 LMH to 5.1 LMH, 60 LMH to 5.4 LMH, and

8.6 LMH to 1.8 LMH, respectively. Subsequently, the fluxes stabilized such that at the end of the experiment (day 65), M1, M2, M3, and M4 fluxes were 4.1, 4.5, 5.9, and 2.2 LMH, respectively. The highest mean stabilized flux (day 30 – 65) was obtained for M3 (50 wt% kaolin + 50 wt% alumina, the membrane with enhanced adsorption capacity) which was significant compared to the other three membranes ($5.65 \text{ LMH} \pm 0.07$, mean $\pm$ 95% confidence interval, $p < 0.001$, Figure 5c). This is related to the larger mean pore size of M3 compared to those of the other three membranes ($0.98 \mu\text{m}$). Moreover, according to [26, 36], presence of a biofilm on the membrane surface can improve the permeate flux, as in 3.4.1 and 3.4.2. In these studies, flux development pattern was reported because of the combined effect of an increased biofilm thickness in dead – end GDM filtration and presence of bacterial activity and predation in the biofouling layer which are capable of altering biofilm morphology resulting in a more heterogeneous structure. The biofilm on M3 showed the highest mean biofilm thickness and biological activity. These results are consistent with previous findings, in which M3 showed the best stabilized flux in the GDCM process without pre-treatment [21]. Therefore, a higher flux was achievable without compromising turbidity and NOM removal.



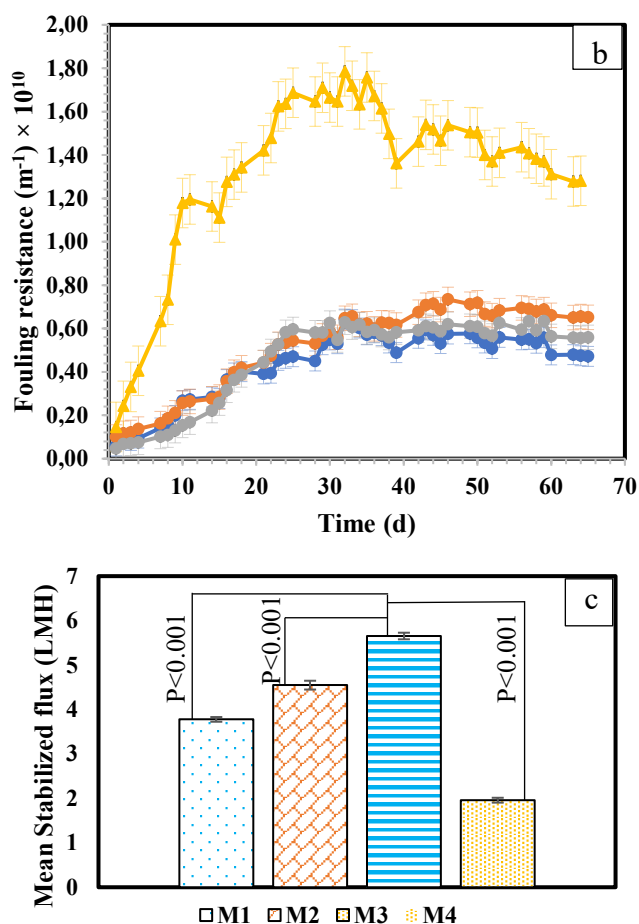


Figure 5. a) Flux – time, b) fouling resistance – time, and c) Statistical compare of mean stabilized flux data from day 30 (flux stabilization day) to day 65 for M1 (100 wt% kaolin), M2 (75 wt% kaolin, 25 wt% alumina), M3 (50 wt% kaolin, 50 wt% alumina), M4 (0.8 μm commercial). The numbers indicate the p-values. Error bars show 95% confidence intervals.

3.4 Biofouling layer characterization

3.4.1 Concentration of active microorganisms and extracellular polymeric substances in the biofouling layer

To quantify the active microorganisms present in the membrane biofilm, ATP concentrations were measured on the surface of each membrane type (Figure 6a). Significant differences ($p < 0.001$) in ATP concentration ($5.0 - 40 \text{ ng/cm}^2$) were observed between membrane types. The highest and lowest ATP concentrations were observed for membranes M3 ($40.26 \text{ ng/cm}^2 \pm 2.57$, mean $\pm$ 95% confidence interval, $p < 0.001$) and M1 ($5.87 \text{ ng/cm}^2 \pm 0.23$, mean $\pm$ 95% confidence interval), which also had the highest and lowest DOC removal rates, respectively.

596 Membrane M3 was made of 50% (by weight) alumina, while M1 was 100% kaolin. Given that
597 the M3 membrane has a higher porosity than M1, the increased performance of the M3
598 membrane lies in the synergy of alumina with biofilm growth. We have previously reported
599 that the use of alumina increases NOM sorption, which appears to be beneficial to biofilm
600 activity, as evidenced by the higher ATP concentrations [21]. A wide range of ATP
601 concentrations have been reported in the literature for the bioactivity of the biofilm
602 accumulated on filtration media working under gravity-driven mode. For example, rainwater
603 filtration for recycling purpose by a GDM system showed approximately 80 mmol ATP/m² (~
604 40×10^5 ng/cm²) [37] which is far higher than the data obtained in this study while gravity-
605 driven ultrafiltration of different surface water types and diluted wastewater showed a constant
606 22 ng/cm² of ATP in the biofouling layer [38] which is in the range of the ATP obtained in this
607 study. Moreover, biomass accumulated on the submerged GDM reactor during filtration of
608 secondary wastewater effluent with two different concentrations showed ~ 4 – 6 ng ATP/cm²
609 according to concentration of feed solution [39].

610 EPS concentrations (PN and PS) in the biofouling layers of the synthetic and commercial
611 membranes are shown in Figure 6b. Smaller differences in EPS/protein content were observed
612 in cakes recovered from the four membranes compared to ATP. However, membrane M3 had
613 the highest PS and protein content ($1.55 \text{ mg/cm}^2 \pm 0.13$ of total EPS concentration, mean $\pm$
614 95% confidence interval) which was statistically different compared to other membrane types,
615 except protein concentration in M2. The membrane with the enhanced adsorption capacity (M3
616 = 50 wt% kaolin + 50 wt% alumina) showed the highest biofilm activity, EPS concentration,
617 BP rejection, and maximum biofilm thickness among the tested membranes. Likewise, EPS
618 showed a wide range of values in previous research. In a previous study [40], ATP and EPS
619 concentrations were measured in biofilms formed on a biological activated carbon (BAC) filter
620 during river water treatment using hybrid activated carbon and membrane filtration (UF). ATP

concentration of BAC filter reported as 58.9 ng ATP/g dry BAC. PN and PS showed a concentration of 8.1 and 5.1 mg/g dry BAC, respectively. ATP showed approximately the same range, whereas the EPS concentration was higher than that reported in this study. In another study [37], 2.48 g/m² (0.248 mg/cm²) of EPS during rainwater filtration in a GDM process was reported while lake water filtration using a submerged GDM system showed 200 – 400 g/m² (20 – 40 mg/cm²) of EPS [41].

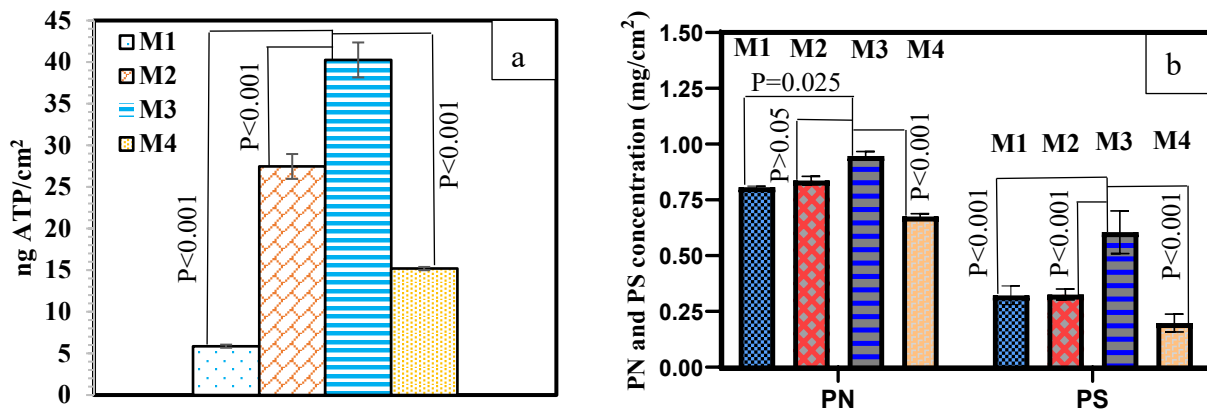


Figure 6. a) ATP concentration (active microorganisms), and b) EPS (PN=Proteins and PS=Polysaccharides) concentration in the biofilm of M1 (100 wt% kaolin), M2 (75 wt% kaolin, 25 wt% alumina), M3 (50 wt% kaolin, 50 wt% alumina) and M4 (0.8 μm commercial). Error bars show 95% confidence intervals.

3.4.2 Physical characteristics of the biofilm and cake layer formed on the membrane surface

To monitor biofilm growth, OCT images were captured after 10, 25, 38, 52, and 65 days of operation (Figure S2 presents the images). Although the observed layer is a mixture of microorganisms as well as organic and inorganic foulants, we will refer to it as biofilm. Figure S3 shows the progression of biofilm on the membrane surface from days 10 to 52. Figure 7 presents the mean biofilm thickness, absolute biofilm roughness, and relative biofilm roughness coefficient calculated from these images. Mean biofilm thickness increases linearly with time and reaches approximately 200-230 μm after 52 days. The final sampling campaign on day 65 showed a decline in cake accumulation thickness. This has been reported previously

in [17, 26] and can be attributed to the upper layer detachment of the biofilm (aging biofilm) from the membrane surface because of the shear stress exerted by the transmembrane pressure, water pushing force, and interaction between particles.

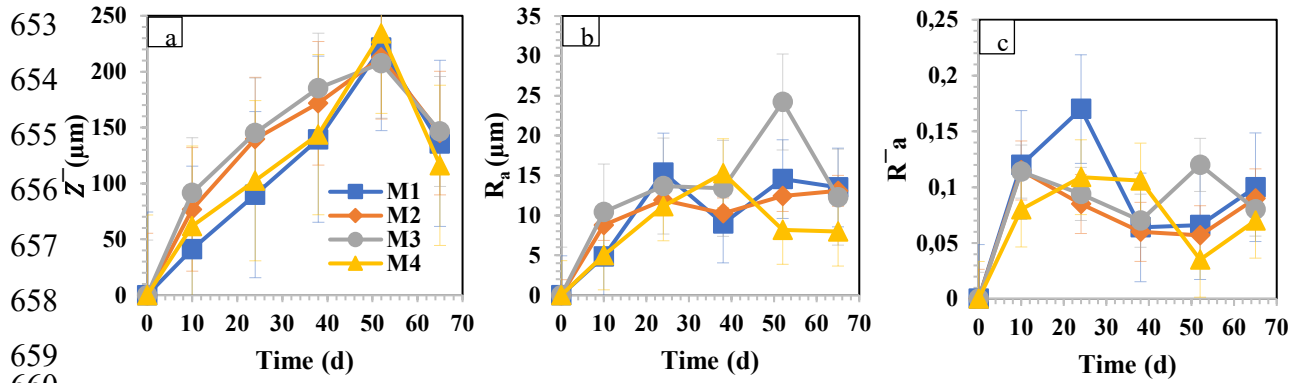


Figure 7. a) Mean biofilm thickness ($\bar{Z}$, μm), b) Absolute biofilm roughness (R_a , μm), and c) Relative biofilm roughness coefficient ($\bar{R}_a$) during the filtration time for M1 (100 wt% kaolin), M2 (75 wt% kaolin, 25 wt% alumina), M3 (50 wt% kaolin, 50 wt% alumina) and M4 (0.8 μm commercial). The error bars show 95% confidence intervals.

The mean biofilm thicknesses on day 65 were 136, 145, 146, and 116 μm for M1, M2, M3, and M4, respectively. The maximum mean biofilm thickness obtained in this study was higher than the ones reported by Akhondi et al. 2015 [26] (max mean thickness $\sim 80 \mu\text{m}$) during seawater pretreatment by a UF membrane in gravity-driven mode. However, the mean biofilm thickness in the present study is in the range of the thickness obtained during treating primary wastewater [42]. The higher thickness and less bioactivity associated to the biofouling layer formed on the membranes surface in this study, could be attributed to a decreased ratio of viable microorganisms (alive organic cells in the biofilm) to total accumulated biomass (alive + dead organic cells) in the biofilm layer. Young and thin biofilm layer containing higher alive organic cells has been shown to improve the permeate quality due to the degradation of organic fractions such as biopolymers, while aged biofilm comprising less alive organic cells could deteriorate the permeate quality by hydrolysis of organics into smaller-size materials that can permeate through the membrane [36].

As shown in Figure 7 b and c, the absolute roughness and relative roughness coefficient exhibit fluctuating trends. Absolute roughness of the biofilm was 4.85, 8.8, 10.42, and 4.99 μm in the case of M1 to M4, respectively. After relatively high fluctuations, it reached approximately 13 μm for the synthetic membranes (M1, M2, and M3) and 8 μm for M4 by the end of filtration. An opposite trend was observed for the relative roughness coefficient of the synthetic membranes. Relative roughness coefficient was calculated approximately to be 0.11 on day 10 for M1, M2, and M3, and then it varied from 0.07 to 0.10 toward the end of the filtration. According to the results, the absolute roughness and relative roughness coefficient of the biofilms in the first and last imaging events (days 10 and 65) were approximately equal, despite fluctuations occurring in the middle of the operation.

4 Discussions

4.1 Impact of BIEX pre-treatment on the flux and permeate quality of the membrane section

To improve the membrane permeate quality and flux, the GDCM process was integrated with resin pre-treatment operated without regeneration to achieve secondary IEX (BIEX mode). In the hybrid process, the BIEX column mainly removed NOM, and the GDCM retained the turbidity of the influent water while providing additional NOM retention. The BIEX column removed approximately 74% of DOC based on data from day 65, and the membranes retained 10%–27% of the remaining DOC, which was mainly in the form of HS and BB. DOC removal improves mainly because of primary and secondary IEX and biodegradation (Amini, Papineau et al. 2018). Regarding turbidity data of day 65, BIEX resin decreased the turbidity of influent water from 2.20 NTU to 0.77 NTU, and it was further decreased to 0.09 – 0.11 NTU using different membrane types. Compared to our previous study using the same membranes and influent water in the GDCM process without BIEX pre-treatment (negative control) [21], the permeate quality of the hybrid process increased markedly. In GDCM without pre-treatment,

the best DOC removal performance (after the initial and temporary high DOC removal periods), M3, was approximately 6% (influent water DOC = 6.51 mg C/L. M3 permeate DOC = 6.12 mg C/L, Figure S4a, Figure 8). Turbidity removal in the hybrid process also improved compared to that in GDCM without pre-treatment. Higher turbidity values were observed in the initial filtration days in the process without pre-treatment. Furthermore, at the end of the filtration, the stable turbidity of the GDCM process without BIE X pre-treatment was approximately 0.25 NTU, which is approximately twice that of the hybrid process (Figure S4b, Figure 8). Biologically aerated filters (filled with either granular activated carbon or shredded hollow fiber membranes) combined with PVDF hollow fiber ultrafiltration membranes were developed to treat polluted reservoir water [43]. Under optimal conditions, DOC removal and effluent turbidity were approximately 80% and 1 – 3 NTU, respectively, after biologically aerated filtration. Subsequent ultrafiltration membranes provided permeate DOC reduction of 7% and final turbidity of 0.3 NTU compared to that of the effluent of biological filtration. The results of organic removal and turbidity in the present study are fairly similar to the aforementioned research in the pre-treatment sections (BIE X for the present study and biologically aerated filters for the published study). However, in the membrane section, the present study showed a better performance in NOM and turbidity removal.

Regarding the membrane fluxes, the BIE X resin improved the stabilized fluxes approximately two folds compared with the GDCM process without pre-treatment. The membrane stabilized fluxes were reported at 2.5 – 3.0 LMH in GDCM without BIE X pre-treatment, while it was increased to 3.8 – 5.7 LMH using the hybrid process. Notably, flux stabilization occurred approximately on day 24 of filtration in GDCM-only, whereas, in the BIE X + GDCM process, it shifted to day 30, a week longer (Figure S4c, Figure 8). This could be related to the effective removal of high molecular weight NOM, such as HS, from the influent water and the reduced fouling effect in the subsequent membrane sections.

The present study results showed that BIEEX resin can be a robust, inexpensive, and easy-to-operate pre-treatment method for enhancing the flux in the subsequent membrane section and for increasing the quality of the produced permeate.

4.2 Effect of BIEEX pre-treatment on the characteristics of biofilm of the membranes

The previous study of the authors [21] using the same membranes, influent water and condition in GDCM process without a pre-treatment (negative control) showed a higher biofilm thickness (Maximum biofilm thickness: M1 = 371 μm , M2 = 224 μm , M3 = 315 μm) compared to that in the BIEEX + GDCM hybrid process (Maximum biofilm thickness: M1 = 221 μm , M2 = 212 μm , M3 = 207 μm). In the hybrid process, the maximum absolute roughness (R_a) and relative roughness coefficient ($\overline{R_a}$) were markedly lower than those in the GDCM process without BIEEX pre-treatment. Maximum R_a and $\overline{R_a}$ in GDCM-only were 104 μm and 0.28, 70 μm and 0.31, 173 μm and 0.55 for M1, M2 and M3, respectively. In BIEEX + GDCM process, according to section 3.4.2, maximum R_a and $\overline{R_a}$ of 15.4 μm and 0.17, 13.1 μm and 0.12, 12.3 μm and 0.08, 7.97 μm and 0.07 for M1, M2, M3, and M4 were obtained, respectively. In the hybrid process, BIEEX resin pre-treatment eliminated NOM from influent water via two mechanisms: ion exchange and biodegradation. Biomass accumulation and biodegradation in BIEEX columns have been reported to remove approximately 50% of the NOM and DOC [9, 44]. Nevertheless, IEX is the main NOM removal mechanism [11, 12].

In the GDCM process without BIEEX pre-treatment, the biological activities of the M1, M2, and M3 biofilms were approximately 2.4, 11.2, and 46 ng ATP/cm², respectively (Figure 8, Figure S5), whereas, in the BIEEX + GDCM hybrid process, the biological activities were roughly 5.8, 28, and 40 ng ATP/cm² (Figure 8). According to these results, after BIEEX pre-treatment, the biological activity of the M3 biofilm in the hybrid process decreased marginally compared to the GDCM-only process, whereas the biological activities of the M1 and M2 biofilms in the hybrid process were more than two times higher than that of the GDCM process

without pre-treatment. A lower ATP concentration was expected in the biofilm of all membranes subjected to BIEX pre-treatment because of the lower influent NOM. However, an opposite trend was observed. We suspect that the BIEX mostly removed the poorly biodegradable fractions of NOM (i.e., HS). LMW acids contain biodegradable organic matter. BIEX pre-treatment increased this fraction compared to raw water, which may explain the higher observed biofilm activity on membranes treated with BIEX-pretreated water [35].

4.3 Relevance to the industry

The hybrid BIEX + GDCM process, which is intended to be used in the decentralized small water treatment systems, showed high performance in terms of stabilized flux (Max flux ~ 5.7 LMH) and permeate quality (effluent turbidity ~ 0.1 NTU, max DOC removal ~ 81%, effluent DOC < 2.0 mg C/L) in the long-term operation during treatment of a colored, turbid, and high NOM content river water. Comparing DOC removal, BIEX previously showed [9] a significant higher performance (~ 62% of DOC removal in warm water condition) compared with GAC and BAC (granular activated carbon under biological mode, ~ 7% of DOC removal in long-term) when treating the same source water as in the present study. Although IEX (ion exchange resin under frequent regeneration) revealed better DOC removal performance (~ 80% DOC removal) than that of BIEX, it cannot be considered as an interesting option in the decentralized systems, because of the chemical use, produced spent brine, and enhanced maintenance requirements, which are undesired characteristics.

The resin manufacturers generally recommend the regeneration after every 48 – 72 h of operation to maintain the resin capacity and control biomass growth on the resin [9]. In this study however, the regeneration process was not performed on the resin during the operation time to promote the BIEX mechanism (secondary IEX) during NOM removal. If a traditional regeneration process was performed on the system, assuming a 72-h regeneration frequency (during 65 days / 6,240 BV of total operation) with a 100 g/L dose of NaCl and 3 BV of the

brine consumption during each regeneration process (according to the supplier), 1.06 kg of NaCl per each m³ of treated water would be required while 10.58 m³ of spent brine per 1000 m³ of treated water would be produced. The calculated amount of salt consumption and produced brine (if regeneration was performed) is high enough to increase the operating expense markedly for decentralized applications. In this context, the proposed BIEX+GDCM process represents an opportunity. Likewise, membrane manufacturers advise regular backwash/chemical cleaning to avoid biomass fouling on the membrane surface, while in this GDCM process, the backwash and chemical cleaning are not performed regularly. In the GDCM process without pretreatment [21], M3 (50 wt% kaolin + 50 wt% alumina) with the highest mean biofilm thickness (315 µm) and microorganism activity (46 ng ATP/cm²) achieved the highest stabilized flux (~ 3 LMH). Promoting biofilm layer on the membrane surface has previously been shown to improve the organic removal by approximately 80% [36] and affect the stabilized flux positively [26]. Overall, operating resin and membrane processes in a biologically enhanced mode would lead to a substantial reduction in operating expenses while increasing the permeate quality, flux, and sustainability toward the decentralized water treatment systems.

Some challenges are associated with the proposed hybrid process when applies to the practical application in the decentralized water treatment systems. Schmutzdecke phenomenon in which a dense and difficult-to-break-up biological layer forms on the upper side of the column, considered as one of the issues in BIEX resin section. Air injection has been proposed to break this layer. Furthermore, a DOC breakthrough at the end of the primary IEX for a short period of time, could be considered as another issue [9]. In the GDCM section, a low stabilized flux and decreased NOM removal could be alleviated by selecting BIEX resin as a pretreatment process as shown in this study.

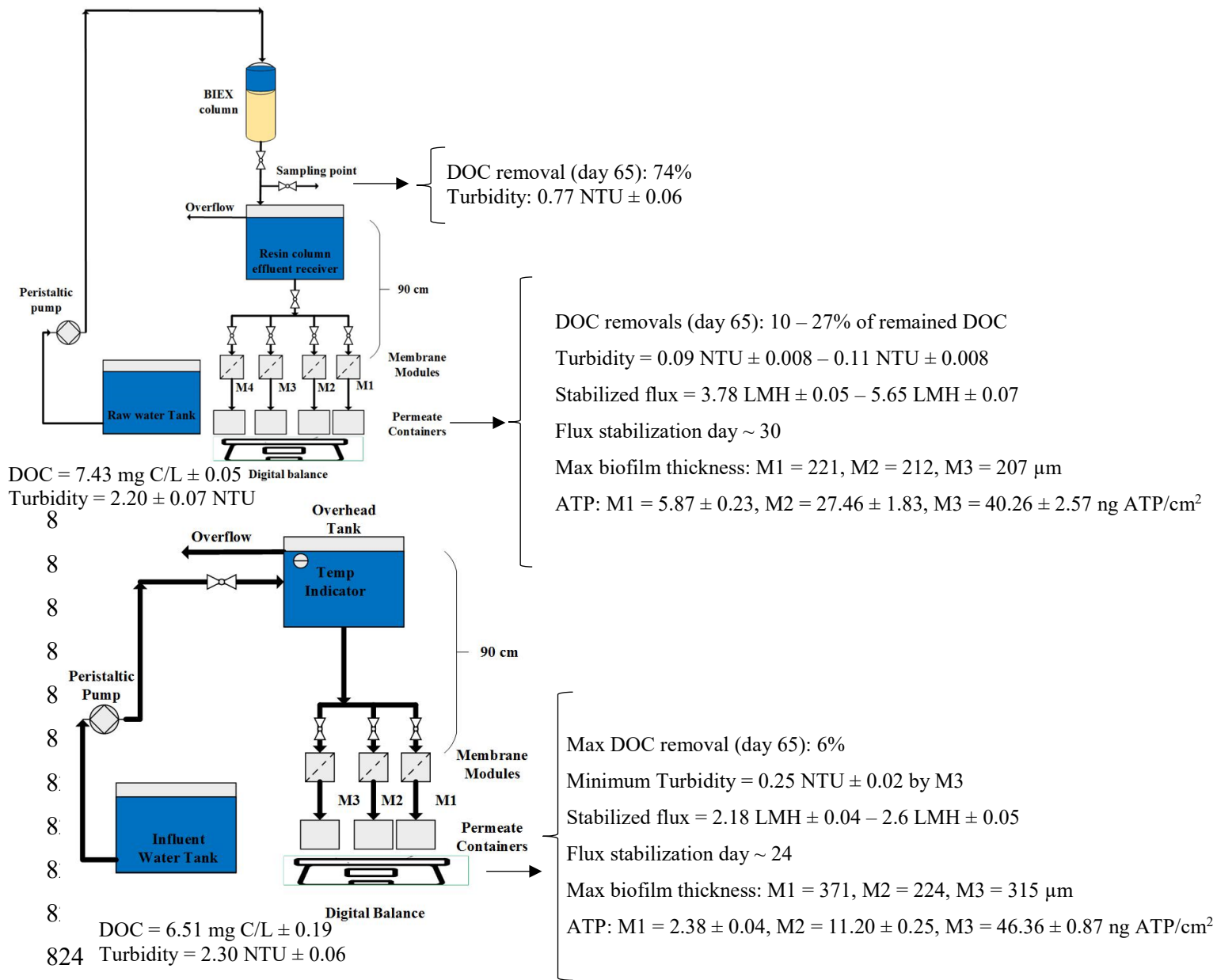


Figure 8. Impact of BIEX pre-treatment on the flux, permeate quality and biofilm properties of the membranes. Figure adopted from [21]. Values show mean $\pm$ 95% confidence intervals.

5 Conclusions

In this study, a hybrid BIE X + GDCM process was investigated to treat colored and turbid river water for drinking water applications. The performance of BIE X filtration as a pre-treatment stage for the subsequent GDCM process was investigated in terms of water effluent quality, membrane flux, and physicochemical characterization of the biofilm formed on the membrane surface. The following results were obtained:

- NOM removal was primarily achieved by BIE X pre-treatment. Sustained ($> 74\%$ during 65 days = 6,240 BV) NOM removal (mostly HS and BB) was achieved during BIE X pre-treatment without any regeneration.
- Of the four ceramic membranes tested, membrane M3, made of 50% kaolin and 50% alumina, provided the best performance, with an additional 27% removal of DOC at the end of the operation. This is due to the effective removal of the HS fraction. Compared to GDCM without pre-treatment (maximum DOC removal $\sim 6\%$), DOC removal by the membranes increased markedly using the hybrid process (maximum DOC removal $\sim 27\%$).
- Membrane M3 (which had the highest clean water flux) provided an equivalent turbidity (approximately 0.09 NTU) and a higher stabilized flux (approximately 5.7 LMH) than the other three membranes. Notably, M3 membrane exhibited the best DOC removal performance with the highest stabilized flux.
- Mean stabilized fluxes of membranes with BIE X pre-treatment were roughly 3.8 – 5.7 LMH, approximately two-fold higher compared to that of GDCM without a BIE X pre-treatment.
- The physical characteristics of the biofilm on the membranes, such as mean thickness and roughness, were considerably lower in the hybrid process than in the GDCM without the pre-treatment. However, the ATP concentration was higher in the

membrane biofilm that received BIEX-pretreated water, possibly due to the biodegradation of the weakly biodegradable fraction of NOM (HS and BB) by BIEX.

6 Credit authorship contribution statement

Yaser Rasouli: Design of experiments, Conducting experiments, Data analysis, Writing, Review, and Editing **Raphaël Maltais-Tariant:** Taking OCT images, Developing a method for analyze of OCT images, Analysis of OCT images, Review & Editing. **Benoit Barbeau:** Supervision, Data analysis, Writing, Review, and Editing, Funding acquisition. **Sigrid Peldszus:** LC-OCD device ownership, Interpretation of LC-OCD chromatograms and results. **Caroline Boudoux:** OCT imaging device ownership, Developing a method for analyze of OCT images, Funding acquisition. **Dominique Claveau-Mallet:** Supervision, Data analysis, Writing – review, and Editing, Funding acquisition.

7 Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that may have influenced the work reported in this study.

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