Elucidating the removal of organic micropollutants on biological ion exchange resins

Liu, Zhen ; Solliec, Morgan; Papineau, Isabelle; Lompe, Kim M.; Mohseni, Madjid ; Bérubé, Pierre R. ;
Sauvé, Sébastien ; Barbeau, Benoit

DOI
10.1016/j.scitotenv.2021.152137

Publication date
2022

Document Version
Final published version

Published in
Science of the Total Environment

Citation (APA)
Liu, Z., Solliec, M., Papineau, I., Lompe, K. M., Mohseni, M., Bérubé, P. R., Sauvé, S., & Barbeau, B. (2022). Elucidating the removal of organic micropollutants on biological ion exchange resins. *Science of the Total Environment*, *808*, 1-8. Article 152137. https://doi.org/10.1016/j.scitotenv.2021.152137

Science of the Total Environment 808 (2022) 152137

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Elucidating the removal of organic micropollutants on biological ion exchange resins

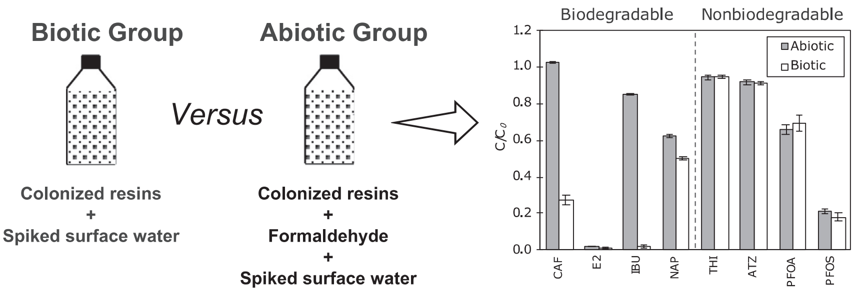
Zhen Liu [a,b,*], Morgan Solliec [b], Isabelle Papineau [b], Kim M. Lompe [c], Madjid Mohseni [d], Pierre R. Bérubé [e], Sébastien Sauvé [a], Benoit Barbeau [b]

[a] *Department of Chemistry, Université de Montréal, Montréal, QC H2V 0B3, Canada*
[b] *NSERC-Industrial Chair on Drinking Water, Department of Civil, Mining and Geological Engineering, Polytechnique Montréal, Montréal, QC H3T 1J4, Canada*
[c] *Department of Water Management, Delft University of Technology, 2600 GA Delft, the Netherlands*
[d] *Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada*
[e] *Department of Civil Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada*

HIGHLIGHTS

- BIEX resins were evaluated for micropollutant removal in batch tests.
- Both biodegradation and ion exchange contributed to micropollutant removal.
- Biodegradation contributes to the removal of caffeine, estradiol, and ibuprofen.
- Ion exchange contributes to the removal of naproxen, PFOA, and PFOS.
- Ion exchange resins can be used as biomass support in biofiltration.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 July 2021
Received in revised form 14 November 2021
Accepted 28 November 2021
Available online 2 December 2021

Editor: Dimitra A Lambropoulou

Keywords:
Ion exchange resins
Biological ion exchange (BIEX)
Biodegradation
Natural organic matter (NOM)
Micropollutants
PFAS

ABSTRACT

Biological ion exchange (BIEX) refers to operating ion exchange (IX) filters with infrequent regeneration to favor the microbial growth on resin surface and thereby contribute to the removal of organic matter through biodegradation. However, the extent of biodegradation on BIEX resins is still debatable due to the difficulty in discriminating between biodegradation and IX. The objective of the present study was to evaluate the performance of BIEX resins for the removal of organic micropollutants and thereby validate the occurrence of biodegradation. The removals of biodegradable micropollutants (neutral: caffeine and estradiol; negative: ibuprofen and naproxen) and nonbiodegradable micropollutants with different charges (neutral: atrazine and thiamethoxam; negative: PFOA and PFOS) were respectively monitored during batch tests with biotic and abiotic BIEX resins. Results demonstrated that biodegradation contributed to the removal of caffeine, estradiol, and ibuprofen, confirming that biodegradation occurred on the BIEX resins. Furthermore, biodegradation contributed to a lower extent to the removal of naproxen probably due to the absence of an adapted bacterial community (Biotic: 49% vs Abiotic: 38% after 24 h batch test). The removal of naproxen, PFOS, and PFOA were attributable to ion exchange with previously retained natural organic matter on BIEX resins. Nonbiodegradable and neutral micropollutants (atrazine and thiamethoxam) were minimally (6%–10%) removed during the batch tests. Overall, the present study corroborates that biomass found on BIEX resins contribute to the removal of micropollutants through biodegradation and ion exchange resins can be used as biomass support for biofiltration.

---

[*] Corresponding author at: Department of Chemistry, Université de Montréal, Montréal, QC H2V 0B3, Canada.
E-mail addresses: zhen.liu.1@umontreal.ca (Z. Liu), morgan.solliec@polymtl.ca (M. Solliec), i.papineau@polymtl.ca (I. Papineau), K.M.Lompe@tudelft.nl (K.M. Lompe), madjid.mohseni@ubc.ca (M. Mohseni), berube@civil.ubc.ca (P.R. Bérubé), sebastien.sauve@umontreal.ca (S. Sauvé), benoit.barbeau@polymtl.ca (B. Barbeau).

http://dx.doi.org/10.1016/j.scitotenv.2021.152137

1. Introduction

A large number of organic micropollutants such as pesticides, pharmaceuticals, steroidal hormones, and industrial chemicals enter surface waters via stormwater runoffs and treated wastewater discharge. As several of these micropollutants are persistent in the environment and recalcitrant to drinking water treatment processes, many have been detected in treated drinking water worldwide (Coupe and Blomquist, 2004; Wang et al., 2011; Husk et al., 2019). Although micropollutants are often found at trace concentrations (i.e., ng/L to μg/L) in drinking water, there has been a rising concern over the long-term effects on human health arising from the exposure to a mixture of micropollutants. Consequently, the number of micropollutants to be regulated in drinking water is on the rise. For example, the USEPA has recently announced its regulatory determinations for 8 micropollutants out of the 109 contaminants found on the Contaminant Candidate List 4 (USEPA, 2021).

Biologically active filtration (i.e., biofiltration) has been investigated as a treatment option for the removal of organic micropollutants because it is a simple and environmentally friendly process (Zearley and Summers, 2012; Benner et al., 2013; Piras et al., 2020; Peterson and Summers, 2021). Granular filters loaded with adsorptive media (e.g., granular activated carbon) or non-adsorptive media (e.g., sand and anthracite) gradually convert into biofilters when no disinfectants are used during the operation, that is, microorganisms will establish themselves on the surface of filtration media and develop a biofilm (Zearley and Summers, 2012). Upon filtration, micropollutants can sorb onto the biofilm present on the granular media surface and be subjected to biodegradation by direct catabolism or cometabolism (Benner et al., 2013). For instance, a wide variety of organic micropollutants proved to be amenable to biofiltration, such as 2-methylisoborneo, geosmin, caffeine, carbamazepine, diclofenac, and 2,4-D (Nerenberg et al., 2000; Reungoat et al., 2011; Zearley and Summers, 2012; Nord and Bester, 2020).

In 2017, we proposed a novel biofiltration process using ion exchange (IX) resins as biomass support for natural organic matter (NOM) removal (Schulz et al., 2017). Specifically, when operating fixed bed IX filters without regeneration, microorganisms colonize the surface of resins and develop a biofilm. This novel approach, referred to as biological ion exchange (BIEX), has been demonstrated to achieve a higher NOM removal than conventional biological activated carbon (BAC) filters in a lab-scale study (BIEX: 56% vs BAC: 15%) (Winter et al., 2018) and in a pilot-scale study (BIEX: 62% vs BAC: 5%) (Amini et al., 2018). The superior performance achieved by BIEX was later primarily attributed to ion exchange with sulfate and, to a lesser extent, biodegradation (Liu et al., 2020; Zimmermann et al., 2021). Additionally, our previous study demonstrated that ion exchange resins can support more biomass compared to granular activated carbon (Liu et al., 2021a). Such result was possibly due to the smaller bead size of ion exchange resins and the electrostatic interaction between bacteria and ion exchange functional groups (Edgar and Boyer, 2021). However, given that previous studies were devoted to investigating the performance of BIEX for NOM removal, its performance for the removal of organic micropollutants has not yet been explored.

Mass balance studies were conducted for the BIEX filters to elucidate the mechanisms that come into play (Amini et al., 2018; Liu et al., 2020). The authors reported that biomass contribution accounts for a maximum of 30% of NOM removal in BIEX filters. However, the mechanism for such contribution is still open to debate. Winter et al. (2018) reported that resins harvested from the BIEX filters were biologically active, but the relation between biological activities and the removal of NOM was not verified. Furthermore, DNA sequencing tests conducted with BIEX resins suggested that heterotrophic bacteria are abundant in the BIEX filter (Edgar and Boyer, 2021), but a direct proof of their contribution to the overall organic matter removal is yet to be made.

The overall objective of the present study was to evaluate the removal of organic micropollutants by BIEX resins and thereby validate the biodegradation of organic micropollutants on BIEX resins. Biotic and abiotic IX resins were used for lab-scale batch tests where biodegradable and nondegradable micropollutants with different charges (neutral vs anionic) were spiked into batch reactors. Such test helps elucidate the removal mechanisms for organic micropollutants with different characteristics. Suspect screening of the transformation products was performed using ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC-HRMS), which allows validating the biodegradation of organic micropollutants through the search of biotransformation products. The present study reports the first investigation of the performance of BIEX resins for organic micropollutants removal.

2. Materials and methods

2.1. Biological ion exchange (BIEX) resins characteristics

Exhausted ion exchange resins were harvested from a pilot plant at the Pont-Viau drinking water treatment plant (Laval, Canada) (Liu et al., 2021a). The pilot plant consists of a fixed bed IX filter loaded with polyacrylic type I macroporous strong base anion exchange resins (Purolite® A860, Purolite, Philadelphia, USA). The IX filter was continuously fed with untreated surface water from the Des Prairies River (Laval, Canada) and was operated without regeneration of the resins. After 5 months of operation, resins were harvested from the IX filter at the depth of 10 cm. Upon IX resins harvesting, no anion release (e.g., chloride or sulfate) was observed in the effluent at the harvesting location (data not shown), confirming that the resin capacity was fully exhausted at the depth of extraction, and the IX resins used in the present study were mainly loaded with NOM (Liu et al., 2021a). Moreover, a ^{14}C glucose respiration rate test conducted on the extracted resins revealed that the resins had a heterotrophic biomass density of approximately 15 μg C/mL resins (typical values for BAC are 9–14 μg C/mL) (Liu et al., 2021a), demonstrating that resins used in the present study were biologically active.

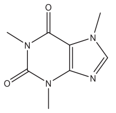
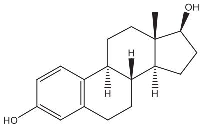
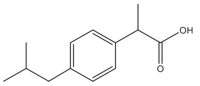
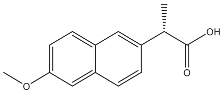
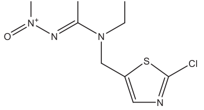
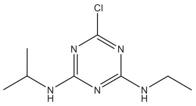
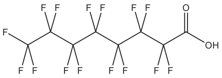
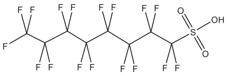
2.2. Raw water characteristics

Surface water from the Des Prairies River was filtered in the lab through 0.45 μm disk membrane (Supor® 450 PES, PALL, Port Washington, USA) and stored in the dark at 4 °C before use. The water demonstrated a moderate dissolved organic carbon (DOC) concentration (7.0 mg C/L), a neutral pH, and low anion concentrations (chloride: 6.6 mg/L; sulfate: 5.6 mg/L). Other information on raw water characteristics can be found in Table S1.

2.3. Target micropollutants

Organic micropollutants were selected according to their biodegradability and charge state at pH 7. Biodegradable and nonbiodegradable micropollutants were selected to study the effect of biodegradation. The biodegradability was predicted by the linear regression model and the non-linear regression model, that is, BIOWIN and BIOWIN2 (EnviroSim Associates limited, Hamilton, Canada). Generally, biodegradation probability ranges from 0 to 1 in the BIOWIN and BIOWIN2 models, with 0 suggesting the organic micropollutant is unlikely biodegradable and 1 suggesting the organic micropollutant is easily biodegradable (Howard et al., 1992). In the present study, micropollutants with a probability smaller than 0.5 were defined as nonbiodegradable and those having a probability greater than 0.5 were defined as biodegradable. Furthermore, neutral and negatively charged micropollutants were included in each group, because molecules with higher affinity to the resin than previously retained anions can potentially be exchanged onto IX resins even though the resin capacity is exhausted (Liu et al., 2020). Therefore, 8 organic micropollutants including steroid hormones, pharmaceuticals, pesticides, and poly- and perfluoroalkyl substances (PFAS) were selected (Table 1). Based on the selection metrics, these micropollutants were divided into four groups: biodegradable and neutral (caffeine and estradiol), biodegradable and negative (ibuprofen and naproxen), nonbiodegradable and neutral (atrazine and thiamethoxam), as well as nonbiodegradable and negative (perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic (PFOS)).

Table 1
Organic micropollutants selected for the present study.

Compound	Structure	pKa[a]	Biowin1/Biowin2[b]	Classification (pH = 7)
Caffeine (CAF)		−1.16 (strongest basic)	0.6551/0.5625	Biodegradable and neutral
17β-Estradiol (E2)		10.33	0.8178/0.6452	
Ibuprofen (IBU)		4.85	0.8314/0.8672	Biodegradable and negative
Naproxen (NAP)		4.19	0.8972/0.9611	
Thiamethoxam (THI)		0.4 (strongest basic)	0.0789/0.0014	Nonbiodegradable and neutral
Atrazine (ATZ)		14.48	0.0045/0.0000	
Perfluorooctanoic acid (PFOA)		−4.2	-/0.0000	Nonbiodegradable and negative
Perfluorooctanesulfonic acid (PFOS)		−3.32	-/-	

-: not available.

[a] Acid dissociation constant (pKa) data is cited from chemicalize.com (2020).

[b] Data predicted using Estimation Programs Interface Suite (US EPA, 2020).

2.4. Batch tests

Raw water was spiked with analytical grade organic micropollutants (Sigma Aldrich, St. Louis, USA) to achieve a concentration of 10 μg/L for each selected micropollutant. Blank tests demonstrated that micropollutant concentrations remained unchanged throughout the test (24 h), suggesting that selected micropollutants were stable in the raw water (data not shown).

Batch tests were respectively conducted under two conditions, that is, **(1) biotic condition:** 15 mL BIEX resins were suspended in 241 mL spiked water within a 250 mL sterilized amber glass bottle; **(2) abiotic condition:** 15 mL BIEX resins were first incubated with 1.2 mL formaldehyde (37% w/v) in a 250 mL sterilized amber glass bottle for 3 h prior to the addition of 240 mL spiked water. Our pretests demonstrated that formaldehyde inhibited microbial glucose respiration by 98% subsequent to a 3-hour incubation using a volume ratio (media:formaldehyde) of 12.5 (Liu et al., 2021a). Notably, formaldehyde is a neutral substance that is not exchangeable on the BIEX resins during the incubation.

For each condition of the batch test, 8 amber glass bottles were prepared corresponding to 6 contact times (i.e., 1, 3, 10, 30, 240, 1440 min), 1 quality control (QC) (i.e., a replicate for t = 1440 min) and 1 blank reactor (only containing spiked water). All bottles were shaken at 200 rpm on a horizontal shaker at room temperature (22 °C). When reaching the desired contact time, samples were immediately filtered through 0.22-μm pore size glass fiber syringe filters (Kinesis KX, Vernon Hills, USA) and stored at 4 °C prior to micropollutant analyses. Glass fiber filters were selected over other types of filters due to their superior recovery of the target micropollutants (Fig. S1).

2.5. Analytical methods

Raw water and water samples after the batch tests were analyzed using on-line solid phase extraction (SPE) followed by ultra-high-performance liquid chromatography equipped with a reverse-phase column (C18, 100 mm × 2.1 mm, dp = 1.9 μm) coupled with high-resolution mass spectrometry (UHPLC-HRMS) (Q-Exactive Orbitrap mass spectrometer, Thermo Fisher Scientific, Waltham, USA). The results were used to calculate micropollutant removal during batch tests and identify transformation products. More details on the analytical method used for micropollutants analysis can be found in the Supplementary materials. All analyses were conducted in duplicate, and only mean values are reported in this paper as data demonstrated a low variability (average relative standard deviation < 3%).

2.6. Data analysis

2.6.1. Micropollutant removal kinetics

Batch tests data were fitted to a pseudo-first-order kinetics (commonly used to describe biodegradation removal) and a pseudo-second-order kinetics (commonly used to describe removal by sorption) through nonlinear regression. The normalized pseudo-first order kinetics model can be expressed as:

$$\frac{C}{C_0} = C_n = e^{-k_1 t} \tag{1}$$

where C_0 and C are the initial micropollutant concentration (μg/L) and the micropollutant concentration subsequent to the reaction time t (min), respectively; C_n is the normalized micropollutant concentration; k_1 is the pseudo-first-order rate constant (min^{-1}).

Normalized sorption pseudo-second-order kinetic model can be expressed as follows.

$$k_2 t = \frac{(1 - C_n)}{(C_n - C_{eq}/C_0)(1 - C_{eq}/C_0)} \tag{2}$$

where C_0 and C_{eq} are the initial micropollutant concentration and the concentration at equilibrium (μg/L), respectively; C_n is the normalized concentration; k_2 is the pseudo-second order kinetics rate constant (μg/(g·h)).

2.6.2. Suspect screening of transformation products

The identification of transformation products related to the selected organic micropollutants was carried out following the same procedures as in our previous study (Solliec et al., 2021). Briefly, an in-house database was first developed based on published scientific literature and includes 37 known transformation products related to the spiked micropollutants (Table S2). Then, Xcalibur software was used to investigate the raw data spectra and identify the transformation products based on the exact mass, the isotopic pattern, the fragmentation pattern, and the retention time. Thereafter, the exact masses and MS/MS spectra of the potential transformation products were compared with spectral database (i.e., METLIN and Mass Bank) or a MS-spectrum prediction software (i.e., CFM-ID 3.0 - University of Alberta, Edmonton, Canada). This identification process leads to a confidence level of 2 according to Schymanski et al. (2014). Finally, the concentration of identified transformation products was estimated by semi-quantitation with the help of the calibration curve of parent compounds. More details on the identification process are available in the Supplementary materials.

3. Results and discussion

3.1. Organic micropollutant concentrations in the raw water

Raw water was monitored monthly to investigate the background concentrations of selected organic micropollutants. Overall, prior to resin harvesting, caffeine, ibuprofen, atrazine, PFOA, and PFAS were detected in raw water with a range of 4–166 ng/L whereas 17β-estradiol, naproxen, and thiamethoxam were below detection limit (Table 2). The presence of some biodegradable micropollutants in the source water likely resulted in the development of microbial communities on BIEX resins which could degrade these micropollutants (Rolph et al., 2019). For example, as IX resins were exposed to caffein-containing raw water during several months of operation, caffeine-degrading bacteria may have been developed on the BIEX resins. By contrast, as naproxen was absent in the raw water, bacteria adapted to naproxen degradation were less likely to be present on the BIEX resins.

Table 2
Micropollutant concentrations in the raw water prior to resin harvesting. Values and error bars respectively correspond to average and standard deviation of monthly measurements.

Groups	Micropollutants	Concentration in raw water (ng/L)
Biodegradable and neutral	Caffeine (CAF)	166 ± 7
	17β-Estradiol (E2)	<0.1
Biodegradable and negative	Ibuprofen (IBU)	128 ± 4
	Naproxen (NAP)	<0.1
Nonbiodegradable and neutral	Thiamethoxam (THI)	<0.09
	Atrazine (ATZ)	4 ± 2
Nonbiodegradable and negative	PFOA	4 ± 1
	PFOS	50 ± 5

3.2. Micropollutant removal during batch tests

Fig. 1 summarized the removal of micropollutants in the biotic condition (i.e., BIEX with active biomass) and the abiotic condition (i.e., BIEX media with inactivated biomass) during the batch test. Concentrations at different contact times were normalized to the concentration of blank samples (C/C_0). Data were fitted to pseudo-first-order and pseudo-second-order kinetics to determine fitted rate constants and coefficients (Table 3). In the following text, the analysis of organic micropollutant removal is grouped according to the class of micropollutants.

3.2.1. Biodegradable and neutral micropollutants

No caffeine removal was observed under the abiotic condition whereas a gradual decrease of caffeine was observed under the biotic condition. The biotic removal of caffeine could be effectively modeled with a pseudo-first-order kinetics ($R^2 = 0.93$). Given the fact that the only difference between the biotic and abiotic conditions was the microbial activity, the results indicate that the removal of caffeine by the exhausted BIEX resins was due to biodegradation. High caffeine removal through biodegradation has also been reported for other types of biofilters (e.g., slow sand filtration) (Zhang et al., 2019; Hermes et al., 2019).

By contrast, estradiol was gradually removed over time under both abiotic and biotic conditions. Estradiol removal under abiotic and biotic conditions were well described with a pseudo-second-order kinetics (R^2 = 0.68–0.69) even though estradiol removal under the abiotic condition was better described with a pseudo-first-order kinetics ($R^2 = 0.92$). A faster removal (k_2: 0.34 vs 0.06) was observed under the biotic condition compared to the abiotic condition, suggesting that microbial activities contributed to the removal of estradiol through biodegradation. Abtahi et al. (2018) reported a similar result where estradiol was removed to a higher extent under biotic conditions than abiotic conditions for a moving bed biofilm reactor. Furthermore, complete estradiol removal was observed under the abiotic condition at the end of the batch test (24 h), revealing that the abiotic mechanism (i.e., sorption) also came to play. As estradiol is a neutral compound, mechanisms other than IX must have contributed to its removal. Previous studies reported that estradiol can be directly adsorbed onto IX resin surface through Van der Waals forces or hydrophobic interaction (Zhang and Zhou, 2005).

3.2.2. Biodegradable and negative micropollutants

Minimal removal (i.e., 14% after 24 h) was observed for ibuprofen under the abiotic condition, even though ibuprofen is a negatively charged compound. Meanwhile, complete removal was observed after 24 h in the biotic reactor. The removal of ibuprofen under the biotic condition could be effectively modeled with a pseudo-first-order kinetics ($R^2 = 0.99$) whereas the removal under the abiotic condition could be modeled with a pseudo-second-order kinetics ($R^2 = 0.74$). The greater extent of removal under the biotic condition compared to the abiotic condition demonstrated that biodegradation is the main mechanism for the removal of ibuprofen on BIEX resins whereas sorption/IX processes did not significantly contribute to the removal of ibuprofen. This is possibly due to its low affinity for the resins. Past studies also demonstrated that ibuprofen was removed to a greater extent in biofilters than their abiotic counterparts (Paredes et al., 2016), suggesting that biodegradation is a viable approach for removing ibuprofen from water.

Naproxen was removed to a similar extent under the abiotic and biotic conditions (normalized concentration at 24 h = 0.51–0.62). The removals of naproxen under biotic and abiotic conditions were effectively modeled with a pseudo-second-order kinetics (R^2 = 0.95–0.97). The similar removal in the biotic and abiotic conditions suggests that abiotic processes played a major role in the removal of naproxen on BIEX resins. Given that the molecule is negatively charged, the removal of naproxen is attributed to ion exchange with previously retained NOM on the resins. Microbial activity had a minor contribution even though naproxen was initially defined as biodegradable in the present study. We hypothesized that the low biodegradation of naproxen was due to the absence of an adapted microbial community on

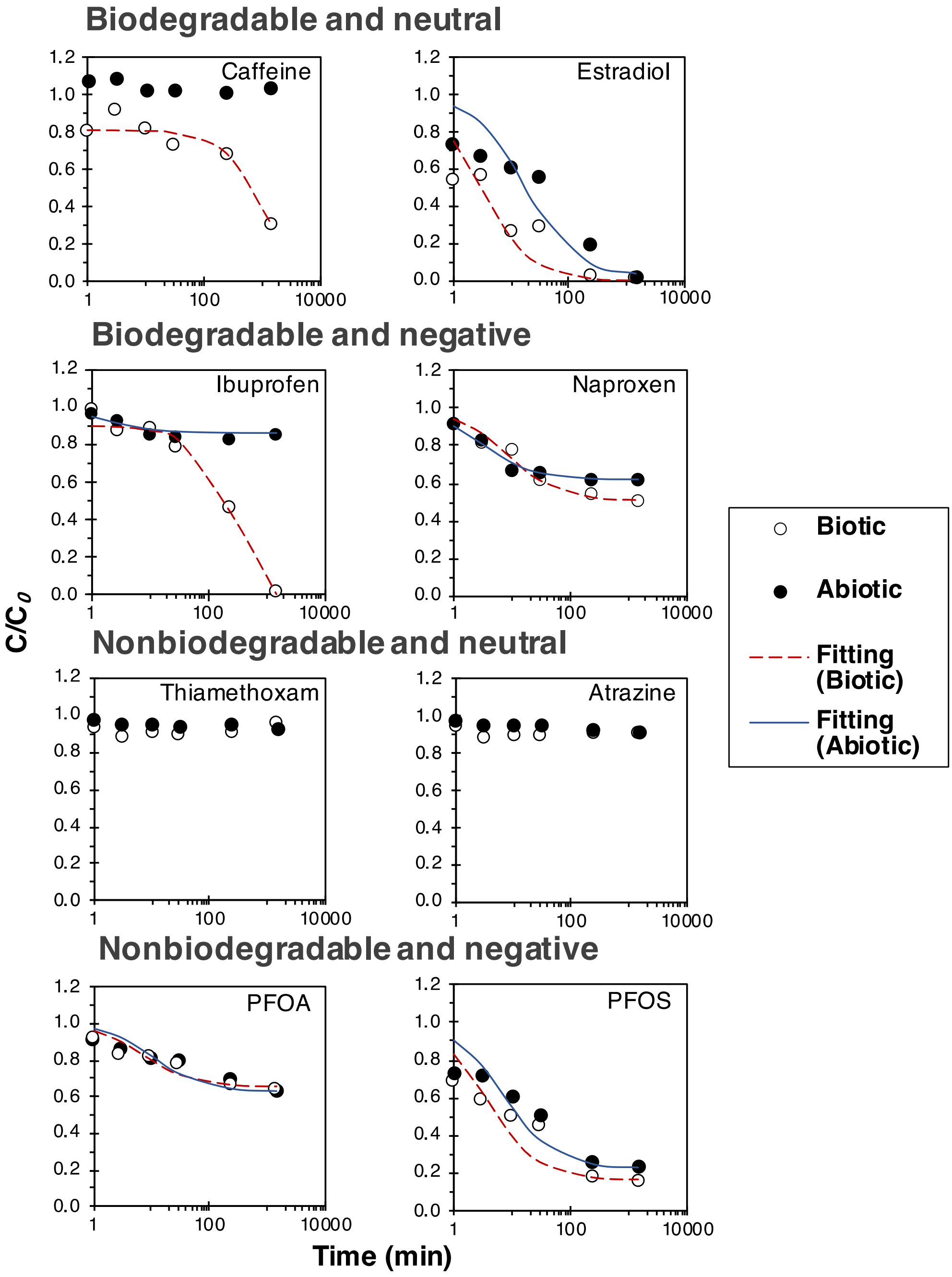


Fig. 1. Micropollutants removal during batch tests under biotic and abiotic conditions. Trendlines correspond to the kinetic model (pseudo-1st or pseudo-2nd order) fitted to the data. Kinetic parameters of the fitted models are summarized in Table 3. Error bars were omitted due to overlapping with data points. The initial concentration was approximately 10 μg/L for each organic micropollutant.

the BIEX resins which is consistent with the fact that naproxen was not detected in the raw water. In summary, biodegradation contributed to the removal of caffeine, estradiol, and ibuprofen but contributed minimally to the removal of naproxen on the BIEX resins, revealing that the biodegradation of micropollutants on the BIEX resins simultaneously depends on the characteristics of organic micropollutants and the microbial communities colonizing the media.

3.2.3. Nonbiodegradable and neutral micropollutants

For both biotic and abiotic conditions, low removals (6%–10%) were observed during batch tests for thiamethoxam and atrazine. Neither pseudo-first-order or pseudo-second-order kinetics could be fitted to the data. The observed removal was unlikely due to IX, as these compounds are neutral. Therefore, the minimal removal was attributed to sorption processes. Previous studies also reported limited removal of thiamethoxam and atrazine when using biofiltration for drinking water treatment (Halle et al., 2015; Gomez-Herrero et al., 2020), suggesting that alternative treatment (e.g., ozonation) would be needed to remove these micropollutants (Mathon et al., 2021).

3.2.4. Nonbiodegradable and negative micropollutants

Similar patterns were observed for PFOA removal under abiotic and biotic conditions which suggests that abiotic processes were the dominant removal mechanism. PFOA data under abiotic and biotic conditions were better modeled with a pseudo-second-order kinetics, respectively (R^2 = 0.74–0.83). Similarly, PFOS was removed to a similar extent under the

Table 3
Rate constants (k) and coefficients of determination (R^2) for the kinetic models of micropollutant removal during batch tests. Fitting with R^2 lower than 0.25 was designated as not available.

Micropollutants	Test condition	Pseudo-first order		Pseudo-second order	
		k_1 (min^{-1})	R^2	k_2 (μg/(g·h))	R^2
Caffeine	Biotic	0.0007	0.93	0.002	0.49
	Abiotic	Not available		Not available	
Estradiol	Biotic	0.002	0.63	0.34	0.68
	Abiotic	0.003	0.92	0.06	0.69
Ibuprofen	Biotic	0.003	0.99	0.008	0.95
	Abiotic	Not available		4.2	0.74
Naproxen	Biotic	0.0003	0.46	0.24	0.95
	Abiotic	Not available		0.85	0.97
Thiamethoxam	Biotic	Not available		Not available	
	Abiotic	Not available		Not available	
Atrazine	Biotic	Not available		Not available	
	Abiotic	Not available		Not available	
PFOA	Biotic	0.0002	0.52	0.41	0.83
	Abiotic	0.0002	0.66	0.26	0.74
PFOS	Biotic	0.0008	0.58	0.32	0.70
	Abiotic	0.0007	0.59	0.18	0.77

biotic and abiotic conditions. The removals of PFOS under abiotic and biotic conditions were also better modeled with a pseudo-second-order kinetics, respectively (R^2 = 0.70–0.77). As expected, biodegradation offered a minimal contribution to the removal of PFOA and PFOS due to their strong resistance to biodegradation (Liou et al., 2010; Li et al., 2019). On the other hand, ion exchange is well known to be an effective method to remove PFOA and PFOS (Dixit et al., 2019). Therefore, the removal of PFOA and PFOS is most likely achieved through ion exchange due to their higher affinity than previously retained NOM on the resins. In summary, batch tests with nonbiodegradable micropollutants confirmed that negative micropollutants can be removed by BIEX resins through ion exchange if the contaminants have a higher affinity than previously retained anions on the resin.

Micropollutant concentrations after 24-h batch test are summarized in Fig. 2. Due to sorption, estradiol was removed to a great extent under either abiotic or biotic conditions. Caffeine and ibuprofen were only efficiently removed under the biotic condition (normalized concentration: 0.3 and 0.02, respectively) thanks to the presence of acclimated biomass on the BIEX resins. Minimal difference in removal was observed for naproxen, PFOA, and PFOS between biotic and abiotic conditions, suggesting that negatively charged micropollutants can still be exchanged onto ion exchange resins even though BIEX resins were fully loaded with NOM and colonized with biomass. Given that the chloride/sulfate resin capacity was exhausted, it is hypothesized that a fraction of the NOM sorbed on the resins was exchanged for organic micropollutants with higher affinities for the resin. Atrazine and thiamethoxam were not amenable to removal using BIEX resins as sorption processes, biodegradation, and ion exchange were all inactive on these compounds. Overall, the order of organic micropollutant removal extent under the biotic condition was estradiol > ibuprofen > PFOS > caffeine > naproxen > PFOA > atrazine > thiamethoxam.

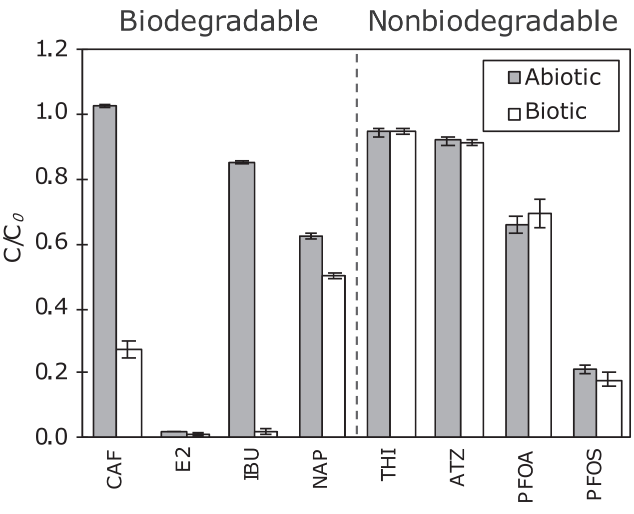


Fig. 2. Micropollutant concentrations after 24 h batch test. Error bars correspond to the minimum and maximum values between test groups and controls. CAF: caffeine; E2: estradiol; IBU: ibuprofen; NAP: naproxen; THI: thiamethoxam; ATZ: atrazine; PFOA: perfluorooctanoic acid; PFOS: perfluorooctanesulfonic acid.

The results after 24-h batch test also allows elucidating the contribution of biodegradation and ion exchange to the removal of studied micropollutants. The removal of caffein solely depends on biodegradation as no removal was observed in the abiotic condition. The removal of ibuprofen benefits primarily from biodegradation (85%), and to a much lesser extent, from ion exchange (15%). Finally, the removal of naproxen, PFOA, and PFOS was mainly due to ion exchange as minimal acclimated biomass presented on BIEX resins.

3.3. Suspect screening of transformation products

Two transformation products were identified from the in-house database using the suspect screening approach (Figs. S2–7). The concentrations of theobromine and 1-hydroxyibuprofen during the batch test were estimated using the standard curve of the parent ions (i.e., caffeine and ibuprofen) (Table 4). Theobromine was identified as a potential biotransformation product of caffeine as it mainly results from biodegradation processes (Suzuki and Waller, 1984). Theobromine was not found in the raw water and the abiotic condition except for the contact time of 1440 min (i.e., 24 h) whereas it was observed throughout the batch test conducted under the biotic condition. No clear trend was observed for the variation of theobromine under the biotic condition, hypothetically owing to the low concentrations measured. The contrasting results of theobromine under the abiotic and biotic conditions corroborate that biodegradation is an active mechanism for the removal of caffeine on the BIEX resins.

By contrast, 1-hydroxyibuprofen was observed under both biotic and abiotic conditions (Table 4). Previous studies reported that 1-hydroxyibuprofen was a biotransformation product of ibuprofen (Salgado et al., 2020). In the present study, the presence of 1-hydroxyibuprofen in the abiotic condition was due to the biodegradation of ibuprofen in the raw water (i.e., before micropollutant spiking) according to our suspect screening results. No significant difference can be observed between the abiotic and the biotic condition ($p > 0.05$) possibly due to the fast biodegradation of 1-hydroxyibuprofen under the biotic condition. Rutere et al. (2020) also reported minimal concentration detected for 1-hydroxyibuprofen in their ibuprofen biodegradation study, suggesting that 1-hydroxyibuprofen is a biotransformation intermediate of ibuprofen.

Table 4
Estimated concentrations of theobromine and 1-hydroxyibuprofen during the batch test.

Transformation products	Contact time (min)	Estimated concentration (ng/L)	
		Abiotic condition	Biotic condition
Theobromine	1	Not found	7 ± 3
	3	Not found	3 ± 2
	10	Not found	8 ± 1
	30	Not found	3 ± 5
	240	Not found	1 ± 1
	1440	3 ± 3	5 ± 2
1-Hydroxyibuprofen	1	20 ± 5	37 ± 3
	3	29 ± 3	25 ± 4
	10	16 ± 1	38 ± 6
	30	31 ± 8	26 ± 6
	240	31 ± 20	50 ± 3
	1440	36 ± 8	34 ± 24

3.4. Implication on the application of ion exchange resins

Conventional use of ion exchange resins for NOM removal implies frequent regeneration with high concentration of NaCl solution (8%–12% w/v). The regeneration produces a highly concentrated brine of which the disposal can be costly and difficult (Levchuk et al., 2018; Liu et al., 2021b). Operating ion exchange resins with a lower regeneration frequency, i.e., in biological ion exchange (BIEX) mode, is an alternative to the conventional strategy of operation for NOM removal applications. This is because 1) NOM can still be removed through secondary ion exchange (i.e., exchange with sulfate) subsequent to the exhaustion of primary ion exchange capacity (i.e., exchange with chloride) (Liu et al., 2020; Edgar and Boyer, 2021; Zimmermann et al., 2021; Liu et al., 2022); 2) with less frequent regeneration, microbial communities can fully develop on the resin surface and contribute to the removal of biodegradable micropollutants; 3) operating ion exchange resins in BIEX mode can reduce the salt usage and brine production compared to conventional mode. Overall, ion exchange resins are a promising alternative to conventional media (e.g., activated carbon) as a biomass support in biofiltration processes. Future studies will need to systematically compare the cost-efficiency of using ion exchange resins as biomass support compared to conventional media for biofiltration. The first full-scale application of BIEX has been put in operation in Middle River (BC, Canada) in 2019. Monitoring its performance is underway to confirm the superiority of BIEX over BAC filtration for both NOM as well as organic micropollutant removal.

4. Conclusions

The present study evaluated micropollutant removal using biological ion exchange (BIEX) resins. Results indicate that biodegradation contributes to the removal of caffeine, estradiol, and ibuprofen, corroborating that biodegradation contributes to the removal of organic substance on BIEX resins. However, the extent of biodegradation also depends on the presence of an adapted microbial community on the resin surface given that we observed a lower contribution of biodegradation for the removal of naproxen (Biotic: 49% vs Abiotic: 38% after 24 h batch test) which was not present in the source water. The removals of naproxen, PFOA, and PFOS were attributable to ion exchange with previously retained natural organic matter (NOM) on the resins. Finally, nonbiodegradable and neutral compounds, that is thiamethoxam and atrazine, were not effectively removed by the BIEX resins (6%–10%), suggesting that alternative treatment options should be considered to target these molecules. Future study should compare the cost-benefit of IX resins versus the other traditional media (e.g., sand, anthracite, and activated carbon) used for biofiltration.

CRediT authorship contribution statement

Zhen Liu: Methodology, Data curation, Writing – original draft, Visualization. **Morgan Solliec:** Software, Data curation, Writing – review & editing. **Isabelle Papineau:** Conceptualization, Writing – review & editing. **Kim M. Lompe:** Conceptualization, Writing – review & editing. **Madjid Mohseni:** Writing – review & editing. **Pierre R. Bérubé:** Writing – review & editing. **Sébastien Sauvé:** Writing – review & editing, Supervision. **Benoit Barbeau:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to thank the technical support of Sung Vo Duy, Jacinthe Mailly, Julie Philibert, and Yves Fontaine. This work was completed at part of the NSERC-Industrial Chair in Drinking Water at Polytechnique Montréal with the financial support of its partners, namely City of Montréal, Veolia Water Technologies Canada Inc., City of Laval, City of Longueuil and the City of Repentigny. All experiments were completed at CREDEAU laboratories, a research infrastructure supported by the Canadian Foundation for Innovation (CFI).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152137.

References

Abtahi, S.M., Petermann, M., Juppeau Flambard, A., Beaufort, S., Terrisse, F., Trotouin, T., Joannis Cassan, C., Albasi, C., 2018. Micropollutants removal in tertiary moving bed biofilm reactors (MBBRs): contribution of the biofilm and suspended biomass. Sci. Total Environ. 643, 1464–1480.

Amini, N., Papineau, I., Storck, V., Berube, P.R., Mohseni, M., Barbeau, B., 2018. Long-term performance of biological ion exchange for the removal of natural organic matter and ammonia from surface waters. Water Res. 146, 1–9.

Benner, J., Helbling, D.E., Kohler, H.-P.E., Wittebol, J., Kaiser, E., Prasse, C., Ternes, T.A., Albers, C.N., Aamand, J., Horemans, B., 2013. Is biological treatment a viable alternative for micropollutant removal in drinking water treatment processes? Water Res. 47 (16), 5955–5976.

Coupe, R.H., Blomquist, J.D., 2004. Water-soluble pesticides in finished water of community water supplies. J. Am. Water Works Assoc. 96 (10), 56–68.

Dixit, F., Barbeau, B., Mostafavi, S.G., Mohseni, M., 2019. PFOA and PFOS removal by ion exchange for water reuse and drinking applications: role of organic matter characteristics. Environ. Sci. Water Res. Technol. 5 (10), 1782–1795.

Edgar, M., Boyer, T.H., 2021. Removal of natural organic matter by ion exchange: comparing regenerated and non-regenerated columns. Water Res. 189, 116661.

Gomez-Herrero, E., Lebik-ElHadi, H., Ait-Amar, H., Tobajas, M., Rodriguez, J.J., Mohedano, A.F., 2020. Thiamethoxam removal by Fenton and biological oxidation. J. Chem. Technol. Biotechnol. 95 (4), 913–921.

Halle, C., Huck, P.M., Peldszus, S., 2015. Emerging contaminant removal by biofiltration: temperature, concentration, and EBCT impacts. J. Am. Water Works Assoc. 107 (7), E364–E379.

Hermes, N., Jewell, K.S., Schulz, M., Muller, J., Hubner, U., Wick, A., Drewes, J.E., Ternes, T.A., 2019. Elucidation of removal processes in sequential biofiltration (SBF) and soil aquifer treatment (SAT) by analysis of a broad range of trace organic chemicals (TOrCs) and their transformation products (TPs). Water Res. 163, 114857.

Howard, P.H., Boethling, R.S., Stiteler, W.M., Meylan, W.M., Hueber, A.E., Beauman, J.A., Larosche, M.E., 1992. Predictive model for aerobic biodegradability developed from a file of evaluated biodegradation data. Environ. Toxicol. Chem. 11 (5), 593–603.

Husk, B., Sanchez, J.S., Leduc, R., Takser, L., Savary, O., Cabana, H., 2019. Pharmaceuticals and pesticides in rural community drinking waters of Quebec, Canada - a regional study on the susceptibility to source contamination. Water Qual. Res. J. Can. 54 (2), 88–103.

Levchuk, I., Rueda Marquez, J.J., Sillanpaa, M., 2018. Removal of natural organic matter (NOM) from water by ion exchange - a review. Chemosphere 192, 90–104.

Li, F., Duan, J., Tian, S., Ji, H., Zhu, Y., Wei, Z., Zhao, D., 2019. <sb:contribution><sb:title>Short-chain per-and polyfluoroalkyl substances in aquatic systems: occurrence, </sb:title></sb:contribution><sb:host><sb:issue><sb:series><sb:title>impacts and treatment</sb:title></sb:series></sb:issue></sb:host>. Chem. Eng. J. 380, 122506.

Liou, J.S., Szostek, B., DeRito, C.M., Madsen, E.L., 2010. Investigating the biodegradability of perfluorooctanoic acid. Chemosphere 80 (2), 176–183.

Liu, Z., Lompe, K.M., Mohseni, M., Berube, P.R., Sauve, S., Barbeau, B., 2020. Biological ion exchange as an alternative to biological activated carbon for drinking water treatment. Water Res. 168, 115148.

Liu, Z., Papineau, I., Mohseni, M., Peldszus, S., Bérubé, P.R., Sauvé, S., Barbeau, B., 2021a. Operating bicarbonate-form versus chloride-form ion exchange resins without regeneration for natural organic matter removal. ACS ES&T Water 1 (6), 1456–1463. https://doi.org/10.1021/acsestwater.1c00040 2021.

Liu, Z., Haddad, M., Sauvé, S., Barbeau, B., 2021b. Alleviating the burden of ion exchange brine in water treatment: from operational strategies to brine management. Water Res. 205, 117728.

Liu, Z., Mills, E.C., Mohseni, M., Barbeau, B., Bérubé, P.R., 2022. Biological ion exchange as an alternative to biological activated carbon for natural organic matter removal: impact of temperature and empty bed contact time (EBCT). Chemosphere 288, 132466.

Mathon, B., Coquery, M., Liu, Z., Penru, Y., Guillon, A., Esperanza, M., Miege, C., Choubert, J.-M., 2021. Ozonation of 47 organic micropollutants in secondary treated municipal effluents: direct and indirect kinetic reaction rates and modelling. Chemosphere 262, 127969.

Nerenberg, R., Rittmann, B.E., Soucie, W.J., 2000. Ozone/biofiltration for removing MIB and geosmin. J. Am. Water Works Assoc. 92 (12), 85.

Nord, N.B., Bester, K., 2020. Can the removal of pharmaceuticals in biofilters be influenced by short pulses of carbon? Sci. Total Environ. 707.

Paredes, L., Fernandez-Fontaina, E., Lema, J.M., Omil, F., Carballa, M., 2016. Understanding the fate of organic micropollutants in sand and granular activated carbon biofiltration systems. Sci. Total Environ. 551, 640–648.

Peterson, E.S., Summers, R.S., 2021. Removal of effluent organic matter with biofiltration for potable reuse: a review and meta-analysis. Water Res. 199, 117180.

Piras, F., Santoro, O., Pastore, T., Pio, I., De Dominicis, E., Gritti, E., Caricato, R., Lionetto, M.G., Mele, G., Santoro, D., 2020. Controlling micropollutants in tertiary municipal wastewater by O3/H2O2, granular biofiltration and UV254/H2O2 for potable reuse applications. Chemosphere 239, 124635.

Reungoat, J., Escher, B., Macova, M., Keller, J., 2011. Biofiltration of wastewater treatment plant effluent: effective removal of pharmaceuticals and personal care products and reduction of toxicity. Water Res. 45 (9), 2751–2762.

Rolph, C.A., Villa, R., Jefferson, B., Brookes, A., Choya, A., Iceton, G., Hassard, F., 2019. From full-scale biofilters to bioreactors: engineering biological metaldehyde removal. Sci. Total Environ. 685, 410–418.

Rutere, C., Knoop, K., Posselt, M., Ho, A., Horn, M.A., 2020 Augg. Ibuprofen degradation and associated bacterial communities in hyporheic zone sediments. Microorganisms 8 (8), 1245.

Salgado, R., Brito, D., Noronha, J.P., Almeida, B., Bronze, M.R., Oehmen, A., Carvalho, G., Barreto Crespo, M.T., 2020. Metabolite identification of ibuprofen biodegradation by Patulibacter medicamentivorans under aerobic conditions. Environ. Technol. 41 (4), 450–465 Feb 10.

Schulz, M., Winter, J., Wray, H., Barbeau, B., Berube, P., 2017. Biologically active ion exchange (BIEX) for NOM removal and membrane fouling prevention. <sb:title>Water Sci. Technol. Water Supply</sb:title><sb:volume-nr></sb:volume-nr> 17 (4), 1178–1184.

Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., Hollender, J., 2014. Identifying Small Molecules Via High Resolution Mass Spectrometry: Communicating Confidence. ACS Publications.

Solliec, M., Roy-Lachapelle, A., Storck, V., Callender, K., Greer, C.W., Barbeau, B., 2021 Augg. A data-independent acquisition approach based on HRMS to explore the biodegradation process of organic micropollutants involved in a biological ion-exchange drinking water filter. Chemosphere 1 (277), 130216.

Suzuki, T., Waller, G.R., 1984. Biodegradation of caffeine: formation of theophylline and theobromine from caffeine in mature Coffea arabica fruits. J. Sci. Food Agric. 35 (1), 66–70.

USEPA, 2020. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA.

USEPA, 2021. Announcement of Final Regulatory Determinations for Contaminants on the Fourth Drinking Water Contaminant Candidate List, pp. 12272–12291 Washington, DC, USA.

Wang, C.A., Shi, H.L., Adams, C.D., Gamagedara, S., Stayton, I., Timmons, T., Ma, Y.F., 2011. Investigation of pharmaceuticals in Missouri natural and drinking water using high performance liquid chromatography-tandem mass spectrometry. Water Res. 45 (4), 1818–1828.

Winter, J., Wray, H.E., Schulz, M., Vortisch, R., Barbeau, B., Berube, P.R., 2018. The impact of loading approach and biological activity on NOM removal by ion exchange resins. Water Res. 134, 301–310.

Zearley, T.L., Summers, R.S., 2012. Removal of trace organic micropollutants by drinking water biological filters. Environ. Sci. Technol. 46 (17), 9412–9419.

Zhang, L., Carvalho, P.N., Bollmann, U.E., Ei-Taliawy, H., Brix, H., Bester, K., 2019. Enhanced removal of pharmaceuticals in a biofilter: effects of manipulating co-degradation by carbon feeding. Chemosphere 236, 124303.

Zhang, Y., Zhou, J.L., 2005. Removal of estrone and 17beta-estradiol from water by adsorption. Water Res. 39 (16), 3991–4003.

Zimmermann, K., Wright, J., Bérubé, P., Barbeau, B., Mohseni, M., 2021. Biological ion exchange capable of sulphate-based secondary ion exchange during long-term DOC removal. Water Res. 117036.