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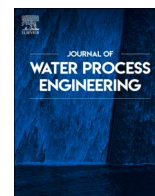To cite this publication, please use the final published version (if applicable).
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Ultrafiltration (UF) and biological oxygen-dosed activated carbon (BODAC) filtration to prevent fouling of reversed osmosis (RO) membranes: A mass balance analysis

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ABSTRACT

(Bio)fouling is the most common problem in membrane processes used in water production. It is also a reported unavoidable problem, with mitigation strategies being frequently ineffective in addressing this problem. An ultrapure water plant (UPW) in Emmen (The Netherlands), fed with secondary effluent, comprises the following subsequent treatment steps: ultrafiltration (UF), biological oxygen-dosed activated carbon (BODAC) filtration and reverse osmosis (RO). The BODAC filters were designed to prevent fouling in RO membranes, and for ten years, they have been operated without significant fouling issues. The present work aims to provide insight into the role of the full-scale UF + BODAC in fouling prevention, by conducting a mass balance (MB) analysis to assess the removal/release of common fouling precursors. Positive MB results were noticed for particulate organic compounds, iron (*Fe*) and manganese (*Mn*) meaning their constant removal in the UF + BODAC. The UF + BODAC was shown to be an effective nitrification system, effectively converting all the ammonium and nitrite to nitrate. In conclusion, the combined removal of organics, *Fe*, and *Mn* species and nitrification by UF + BODAC is most likely an important factor in downstream fouling prevention, making this system an attractive process for fouling prevention. Nevertheless, further investigations to discover the mechanisms involved are needed.

1. Introduction

Natural freshwater reserves are increasingly stressed due to climate change, urbanization, pollution, and rising freshwater demand [1]. Water reclamation and reuse can mitigate this but relies on efficient water purification technology [1]. Water reclamation plants typically make use of membrane technology, e.g., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [2–4], because of the reliability and high-quality effluent [2,3].

The main drawback of membrane processes is (bio)fouling. (Bio) fouling is the unwanted deposition of inorganic, organic substances and/ or biological on the membrane's surface or pores. (Bio)fouling results in

an increased transmembrane pressure (TMP) and a decreased water flux across the membrane. (Bio)fouling can be mitigated by frequent physical and/or chemical membrane cleaning and by membrane replacement [2,4]. Thus, the overall operation costs will increase due to fouling mitigation [5–7]. There are three methods to prevent or minimize membrane (bio)fouling [2]. Firstly, by applying pre-treatment to remove fouling precursors from the feed water. Reducing the substrate and nutrient (carbon, nitrogen and phosphorus compounds or C, N and P) concentrations will limit microbial growth and thus biofilm formation on the membranes [3,8]. Reducing dissolved organic carbon and humic substances in the membrane influent is widely applied, using pre-treatments such as biological activated carbon (BAC) [9–13], filters

using diverse media [14], and other membrane processes [9,10,15]. Limiting the phosphate [3,8,16] or adjusting the C:N:P ratio [17] in the feed water which can inhibit microbiological growth. Applying a disinfection method, such as ozonation, to inactivate planktonic cells can also reduce biofouling [2,3]. Secondly, modification of physico-chemical membrane surface properties to make the membrane less prone to fouling by limiting microbial attachment [2,18]. And finally, fouling can be minimized through the engineering of the membrane unit, by creating unfavourable hydrodynamic conditions [3].

At *Puurwaterfabriek* (Emmen, The Netherlands) [19,20] ultrapure water (UPW) is being produced from secondary effluent from a waste-water treatment plant (Fig. S1). The UPW plant comprises the following subsequent treatment steps: drum sieve with a pore size of 1 mm, aerated ultrafiltration (UF) with a pore size of 0.04 μm, biological oxygen-dosed activated carbon (BODAC) filtration, reverse osmosis (RO) and electro-deionization (EDI). The BODAC filters, which were designed to prevent biofouling [21], are a type of BAC filter that is periodically backwashed and supplied with pure oxygen, maintaining the oxic conditions throughout the filter. The BODAC filters have been in operation for over ten years without replacement or regeneration of the carbon. The RO membranes have been in operation for over ten years, near continuously, as well, without significant fouling issues. The original membranes are still in use, and cleaning (backwashing + chemical cleaning) is conducted only twice a year. This indicates that UF followed by BODAC filtration (hereafter denoted as UF + BODAC) is effective in preventing downstream fouling [19,20], acting as pre-treatment to remove fouling precursors. UF followed by a form of activated carbon (AC) filtration, as pre-treatment for RO, is rarely reported [22]. Both UF alone [15,21] and AC filtration alone [23] are not effective in preventing fouling in RO units [15,21,23].

The present study aims to identify the key fouling precursors and their removal, by performing a mass balance analysis over the combination of the UF + BODAC system as a pre-treatment. This analysis comprises the monitoring of organic and inorganic constituents related to fouling (*COD, TOC, tN, PO_4^{3-}, Mn, Fe, Ca, K, Mg, Si, TIC*) in all the influent and effluent streams of the UF + BODAC systems, and to evaluate whether their occurrence and removal are related to the effective fouling prevention in the UPW. (Bio)fouling prevention is essential for the cost effectiveness of a full-scale treatment to upgrade wastewater treatment plant effluent for reuse [24], yet generally very difficult to accomplish [25,26]. Hence, the full scale UF + BODAC system is a very interesting case to study.

2. Materials and methods

2.1. UF + BODAC filters

The UF is aerated with compressed air and has pore sizes of 0.04 μm. Two BODAC filters are operated in series: a pre-filter (BODAC 1) and a polishing filter (BODAC 2). BODAC 1 and 2 have different volumes, 50 m³ and 100 m³, respectively, and different empty bed contact times (*EBCT*): 10 min and 20 min, respectively. BODAC 1 is backwashed approximately every 48 h and BODAC 2 every 10 to 12 days, depending on the season. Periodical backwashing (BW) is key to controlling the biofilm growing on the activated carbon granules [19]. The back-washing program for BODAC 1 comprises 5 min air scouring, followed by 5 min water flushing, and then again 5 min air scouring, followed by 5 min water flushing (total time: 20 min). The backwashing program for BODAC 2 comprises 5 min of air scouring followed by 13 min of water flushing (total time: 18 min).

2.2. Sampling campaign and sample preparation

The sampling campaign was designed to understand better how the fouling precursors are removed prior the RO units, and to cover a complete backwash cycle of BODAC 2. Triplicate samples, at the same

time, were taken at the sampling points depicted in Fig. 1 on August 4 (04/08), 11 (11/08), and 14 (14/08), 2020. On these days, BODAC 1 was backwashed, while BODAC 2 was backwashed on 04/08 and 14/08. The backwash water was sampled at five-time points during the back-washing program: for BODAC 1 at 0 (just before BW was started), 7.5, 10, 17.5, and 20 min, and for the BODAC 2 at 7.5, 10, 12.5, 15, and 18 min. The samples collected during backwashing were taken from top of the BODAC filters since the backwash water flowed upwards. The sol-uble fractions of the samples were obtained by 0.45 μm syringe filtra-tion. Both filtered (soluble fraction) and non-filtered (total) samples were analyzed according to the methods described in Section 2.3.

2.3. Analytical methods

Chemical oxygen demand (*tCOD* or *$tCOD_{Cr}$*) was analyzed using the closed reflux method, with potassium dichromate as oxidant [27]. Total-N (*TN*) was measured using the Koroleff (peroxydisulfate) digestion and photometric detection with 2,6-dimethylphenol [28]. *COD* and *tN* ana-lyses were done for both filtered and unfiltered samples. The soluble fraction (*sCOD, sN*) was obtained from the filtered samples, the partic-ulate fractions (*pCOD, pN*) from the difference between the filtered and unfiltered samples. The total carbon (*TC*), total organic carbon (*TOC*), and total inorganic carbon (*TIC*) content of filtrated samples were measured according to Standard Methods [29], using the *Shimadzu TOC-L TOC analyzer*. The minerals (*Ca, Mg, K, Fe, Mn,* and *Si*) content of filtered samples was measured by inductive coupled plasma optical emission spectrometry (ICP-OES) using a *Perkin Elmer Optima 5300 DV*. Phosphate (*PO_4^{3-}*), ammonium (*NH_4^+*), nitrite (*NO_2^-*), and nitrate (*NO_3^-*) in filtered samples were analyzed by ion chromatography (IC) using *Metrohm AG IC 761*.

To better understand the removal of organics in the UF + BODAC filters, and to understand its relevance for fouling prevention, four fractions of organic matter were quantified according to Huber and co-workers [30]: biopolymers (*Biopolymers*), humic substances (*Humics substances*), acidic low molecular weight organics (*LMW Acids*), and neutral low molecular weight organics (*LMW Neutrals*). The fractions were quantified with liquid chromatography organic carbon detection (LC-OCD, Model 8 with OCD-detector *Siemens Ultramat 6*), the quanti-fication was by carbon content (*Biopol C, Humics C, LMW Acids, LMW Neutrals*) and or by nitrogen content (*Biopol N, Humics N*).

2.4. Mass balances (MB)

In this study, we present for several elements the mass flows at the UF, BODAC 1 and BODAC 2 inlets and outlets. The mass flows are ob-tained by multiplying the concentration by both the flow and by the relative duration, as described in Eq. (2), of the flow (information on the individual in and outlet flows is presented in Table S1 of the Supple-mentary materials). The mass flows were averaged based on triplicate samples at each sampling point (Fig. 1) and the standard deviation was also calculated based on the triplicate samples. This approach will not only show the difference between influent and effluent, but also quantify the washout with the UF concentrate or BODAC backwash water. Therefore, it will also indicate net accumulation or washout. To get further insights, the constituents making up the total carbon and total nitrogen were also analyzed.

MB analysis was performed on each unit (UF, BODAC 1, and BODAC 2) of the UPW plant. For the calculation of the *MB* to an x compound for the UF unit, Eq. (1) was used [31].

$$MB_x = Q_I \times c_{Ix} - Q_P \times c_{Px} - Q_C \times c_{Cx} \tag{1}$$

where Q_I, Q_P, and Q_C represent the flow of influent, permeate, and concentrate streams, respectively, and c_{Ix}, c_{Px}, c_{Cx}, represent the con-centration of a given compound, x, in each stream.

The *MB* to each BODAC filter, expressed in mass unit per time unit,
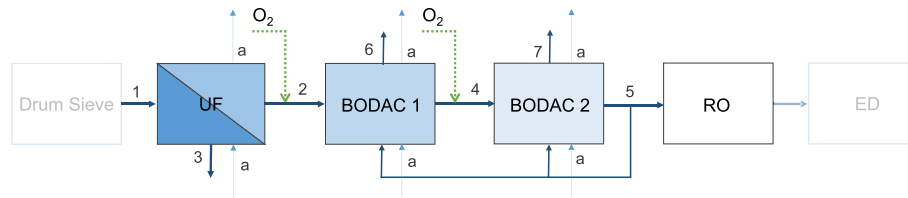
**Fig. 1.** Sampling points in the UF + BODAC system, where UF is the ultrafiltration unit, BODAC 1 is the BODAC pre-filter, BODAC 2 is the BODAC polishing filter, and the numbers represent the sampling points. 1: UF feed; 2: UF permeate; 3: UF concentrate; 4: BODAC 1 effluent; 5: BODAC 2 effluent; 6: BODAC 1 backwash water; 7: BODAC 2 backwash water; a: air scouring (part of BODAC backwash program and UF aeration).
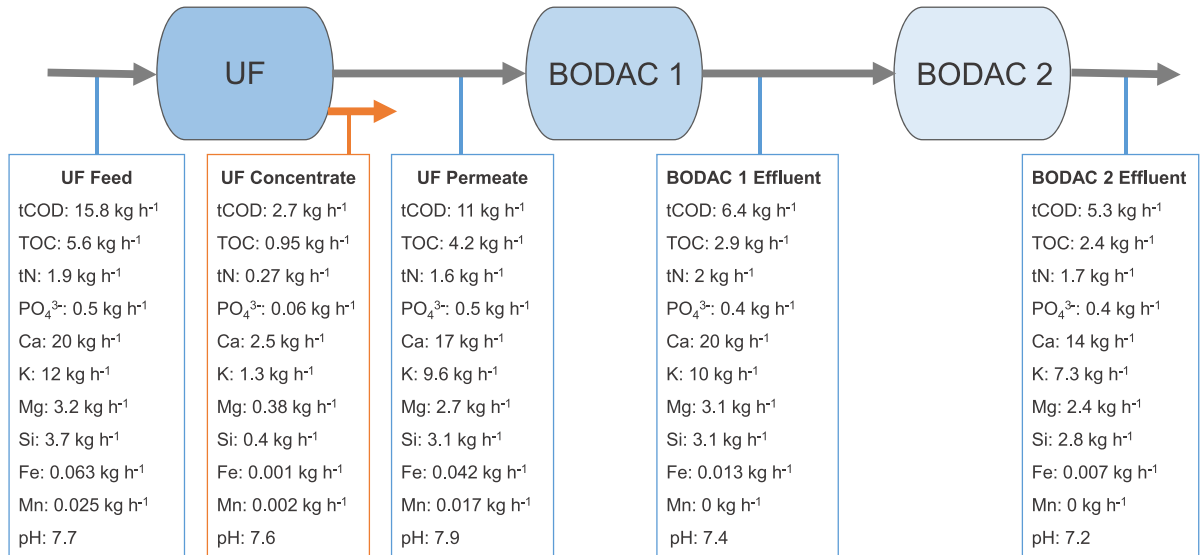
Fig. 2. Mass flows of the monitored constituents, and the pH, for the UF + BODAC system, represented as averages based on triplicate samples for two sampling days.

were calculated using Eq. (2) [31],

$$MB_x = Q_{MI} \times c_{Mix} + \left(Q_{BWI} \times d_{BW/f}\right) \times c_{BWIx} - Q_{ME} \times c_{Mex} \\ - \left(Q_{BWE} \times d_{BW/f}\right) \times c_{BWEx}$$

(2)

where Q_{MI}, Q_{ME}, Q_{BWI}, Q_{BWE} represent the flow of main stream influent, main stream effluent, backwashing stream influent, and backwashing stream effluent, respectively, and c_{Mix}, c_{Mex}, c_{BWIx}, c_{BWEx} represent the concentration of a given compound in each stream, d_{BW}, is the duration of each backwash expressed in minutes, and f is the frequency of backwash, also expressed in minutes.

3. Results and discussion

3.1. Mass balances and removal efficiencies

The *MB* analysis starts with assessing the mass flows at the inlets and outlets of the UF + BODAC system. Fig. 2 shows the mass flows for the different constituents (calculated the *MB*, according to Eqs. (1) and (2) in average of the different elements assessed, during the sampling campaign. On last day of the sampling campaign (14/8) the due to weather conditions (rain) the concentrations were not representative. The detailed mass flows for each sampling day and respective *MB* for each unit process, can be found in Tables S2, S3, and S4 of Supplementary materials. The contribution of the backwash water to the mass flows was <1 %, therefore these values were not included in Figs. 3 through 6 The interpretation guide of the mass balances can be found in

Supplementary materials. A *MB* is considered closed when the result of Eqs. (1) or (2) is zero, meaning no net removal or release for the particular treatment unit. A positive result means removal, a negative result means release.

The mass flows for all the parameters measured were decreasing after the treatment of UF, BODAC 1 and BODAC 2, except for *tN, Ca, K, Mg*, and *Si* where their mass flows were fluctuated along the treatment processes (Fig. 2). Positive *MB* results were noticed for *tCOD, Fe*, and *Mn* meaning their constant removal in the UF, BODAC 1 and BODAC 2 (Tables S2, S3 and S4). In the UF, the *MB* calculated for *tCOD, Fe*, and *Mn* were ~2.7, ~0.01, and ~0.006 kg h^{-1}, respectively. In the BODAC 1, the *MB* calculated for *tCOD, Fe*, and *Mn* were ~4.5, ~0.04, and ~0.02 kg h^{-1}, respectively. In the BODAC 2, the *MB* calculated for *tCOD, Fe*, and *Mn* were ~0.68, ~0.001, and 0.00 (no further removal) kg h^{-1}, respectively. The potential removal mechanisms and dynamics of each parameter is further discussed in the following sections.

Regarding *tN*, the *MB* values calculated for the UF unit were positive, with the mass flow in the UF feed of 1.9 kg h^{-1}, UF permeate of 1.6 kg h^{-1}, and UF concentrate being ~0.27 kg h^{-1}. However, the *tN* mass flows in the BODAC 1 and 2 effluent were fluctuated without showing a net removal/release. The close to null value for the *MB* in BODAC 1 and 2 of the *tN* lead to a N speciation study which is discussed in Section 3.3.

The *MB* to the PO_4^{3-} obtained was very close to 0 kg h^{-1} in all units and days evaluated during the sampling campaign, which indicates that no removal of release of PO_4^{3-} was observed in the overall system. The values can be consulted in Tables S2, S3, and S4 of the Supplementary materials and the discussion will follow in Section 3.4.

Regarding the other element usually connected to (bio)fouling in RO membranes, *K, Mg*, and *Si* mass flows do not change significantly

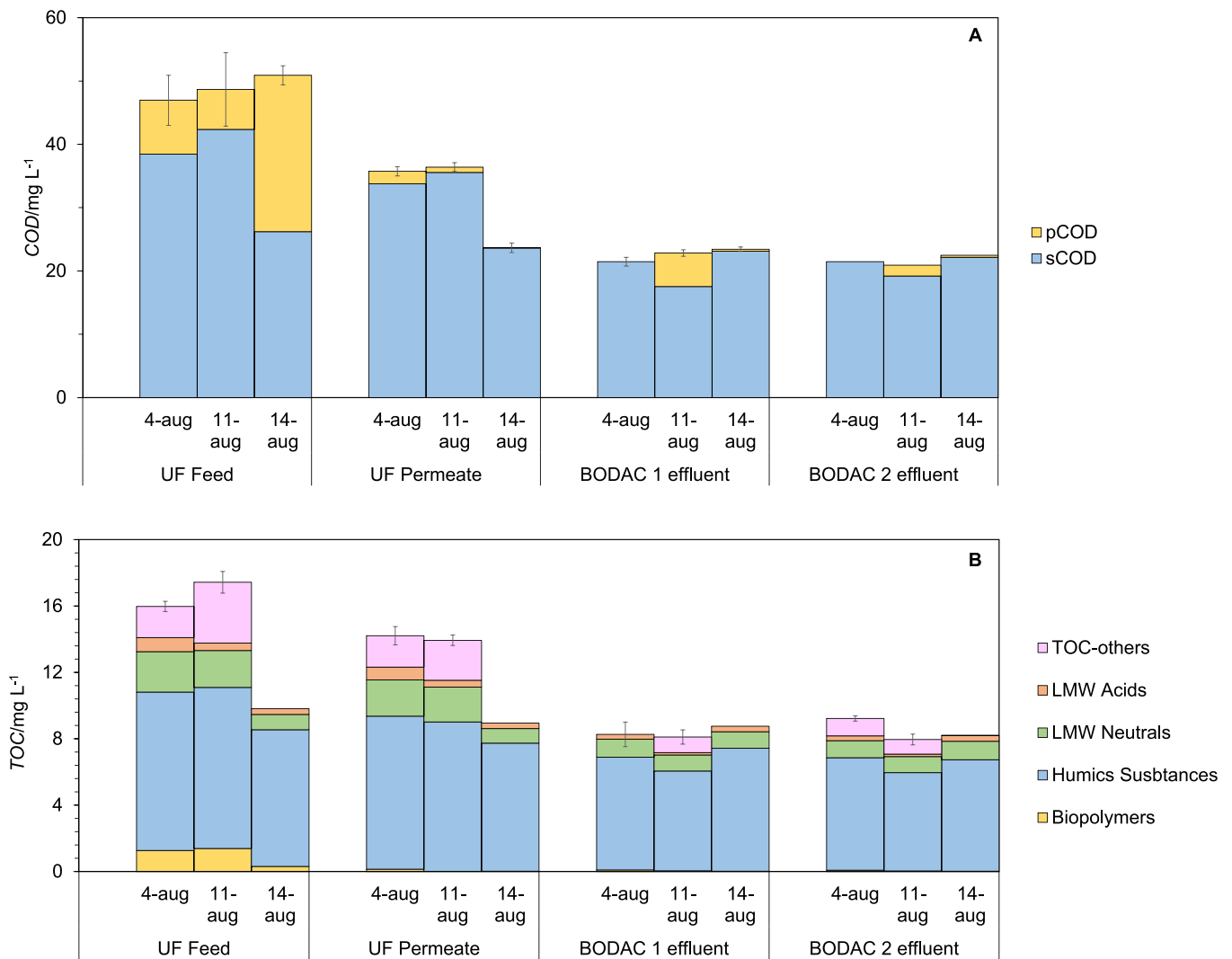**Fig. 3.** *COD* (A) and *TOC* (B) species concentrations in the UPW plant, for three independent days of sampling and triplicate samples were taken for each sampling point.
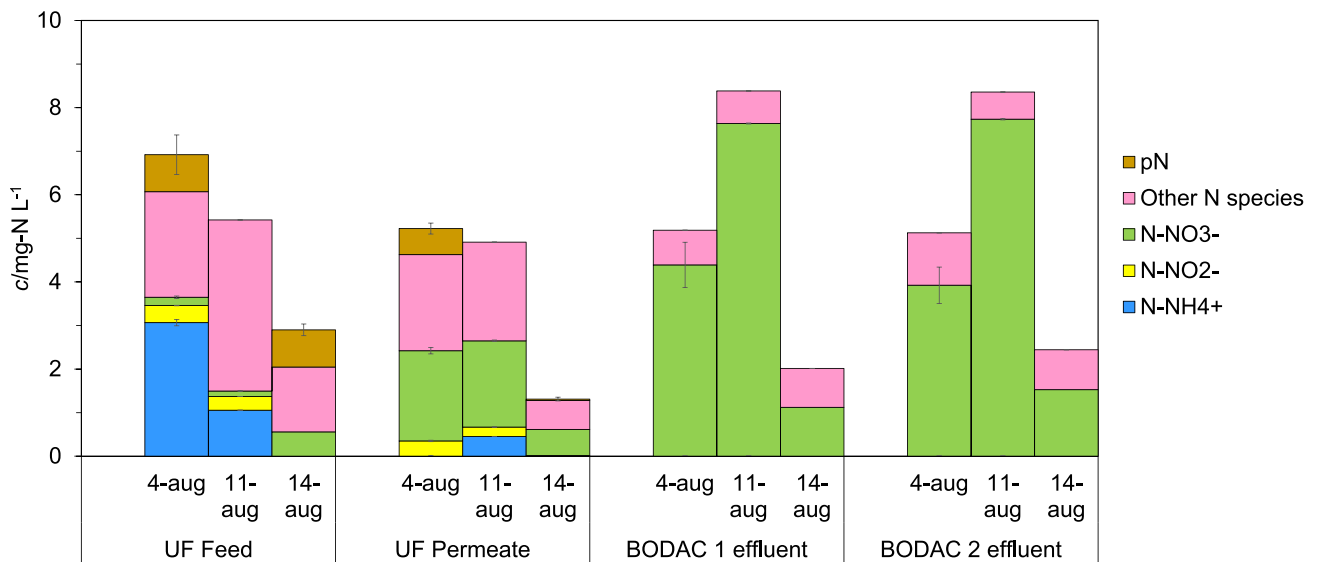

Fig. 4. The concentration of N species (N-NH_4^+, N-NO_2^-, N-NO_3^-, other N species) in the UPW plant, for three independent sampling days and triplicate samples were taken for each sampling point.
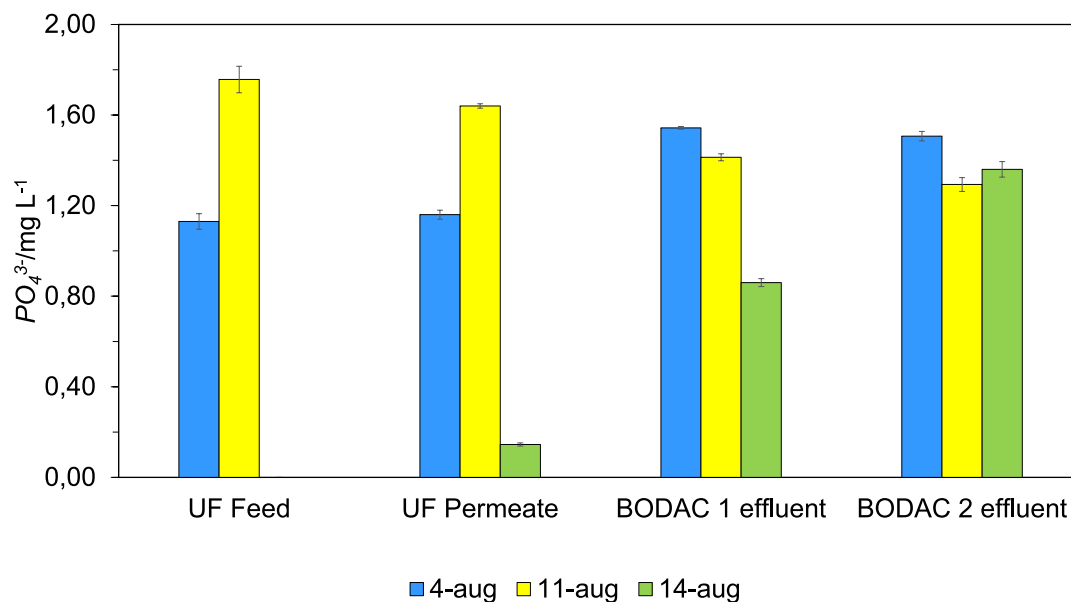
Fig. 5. The phosphate concentration (PO_4^{3-}) between subsequent treatment steps for three independent sampling days and triplicate samples were taken for each sampling point.

(Fig. 2), which hints for a closed mass balance. The *Ca* mass flow increased, which will be further discussed in Subsection 3.5. The pH slightly decreased throughout the process but remained stable around 7–8.

3.2. Total organic carbon speciation and COD

Considering the lack of fouling of the RO membranes working on the UPW, it is necessary to investigate the removal of the organics in the system. Both soluble and particulate organic matter can create an initial fouling layer on the membrane [2,3,32] and be used as substrates by microorganisms attached to the membrane surface to grow and excrete extracellular polymeric substances (EPS) [33,34].

The average *tCOD* removal by the UF + BODAC on the three sampling days was around 57 %. *pCOD* was almost totally removed (~61 % on the UF unit and the rest on BODAC 1) (Fig. 3A). Looking through the mass flows represented in Tables S2, S3 and S4 of Supplementary materials, it is noticeable that the *pCOD* was oxidized, since the value for this parameter in the permeate is low. In the three days assessed, the *tCOD* measured was quite similar in the feed, although, on 14/08, there was a clear difference in the fractioning: half of the *tCOD* is *pCOD*, while in the other two days, *sCOD* is the dominant fraction. Despite the variation, the *tCOD* concentrations at the BODAC 1 and 2 effluent were quite stable, which is a characteristic of mixed bioreactors, in which the effluent quality is determined by the SRT. The removal of *sCOD* fluctuated more during the three days evaluated. The maximum removal was observed on 11/08 (55 %), while the minimum was observed on 14/08 (15 %). The fluctuations in removal rates are attributed to the composition of the feed, as seen in Fig. 3.

Similar *COD* removal efficacies in another biological activated carbon (BAC) system for secondary effluent treatment was reported by Pradhan and co-workers [13]. The removal of *sCOD* may be carried out by various processes, namely adsorption onto GAC, biological degradation, and/or abiotic oxidation related to pure oxygen dosing, which cannot be distinguished in the current approach. In the BODAC 2, no net *COD* removal was observed for any of the sampling days. Besides oxidation or adsorption in the reactors, *COD* can be removed from the BODAC filters during the process of periodical backwashing (see Section 3.6).

The *TOC* removal in the UF + BODAC filters described in this study was 48 ± 8 %. Several studies [11,12,35,36] reported *TOC* removal of ~20 % by BAC filtration for treating secondary effluent and could be increased up to 30 % by adding a pre-treatment, such as ozone and/or membrane filtration. These studies recommended combining a pre-treatment step and BAC for fouling minimization in subsequent membrane processes.

Despite the relatively high *TOC* removal in the UF + BODAC filters (Fig. 3B), its concentration in the effluent of BODAC 2 was still around 9 mg L^{-1}, and similar concentrations can be found in the literature for the effluent of common BAC filtration [17,37]. Microbial growth and biofouling of RO membranes are reported at such a *TOC* concentration [17,37,38]. However, the type of organic matter also matters since not all organics can be readily used for microbial growth [37,38].

The *TOC* conversion to *TIC* coincided with the *COD* removal in BODAC 1 (Figs. 3B and 6B) for 04/08 and 14/08, which is consistent with the *MB* analysis. The increase of *TIC* in BODAC 1 was most likely due to the mineralization of dissolved organics that remained after the WWTP or accumulated in the BODAC 1 filter itself.

Biopolymers, such as residual EPS, and humic substances are well-known foulants [9,10,12,39]. The average biopolymers removal for the three subsequent treatment steps together was 95 ± 2 %, and they were mainly removed in the UF unit, which is consistent with their size (≥20 kDa).

The overall removal of *Humic substances*, which are also known foulants [9,10,12], in the UF + BODAC filters was 34 ± 7 % (Fig. 3B), of which the majority (30 ± 5 %) took place in BODAC 1. The humic substances removal in UF was only about 5 %, which is similar to the findings of Kennedy et al. [39]. The removal observed in BODAC 1 can be attributed to accumulation in the filter and removal by periodical backwash. In contrast, BAC processes were described to remove *Humic substances* up to 50 % [9,10]. To prevent membrane fouling issues, the literature reports [9,10,12] that the removal of *Humic substances* should be at least 60 % (Table 1). *Humic substances* are complex molecules and are not easily bio-assimilable by microorganisms [30]. Therefore, one of the hypotheses for effective fouling prevention, is that, even though these compounds are still present in relatively high concentrations, remaining humic substances are not used as a substrate for microbial growth. *Humic substances* can also accumulate in the membranes surface,
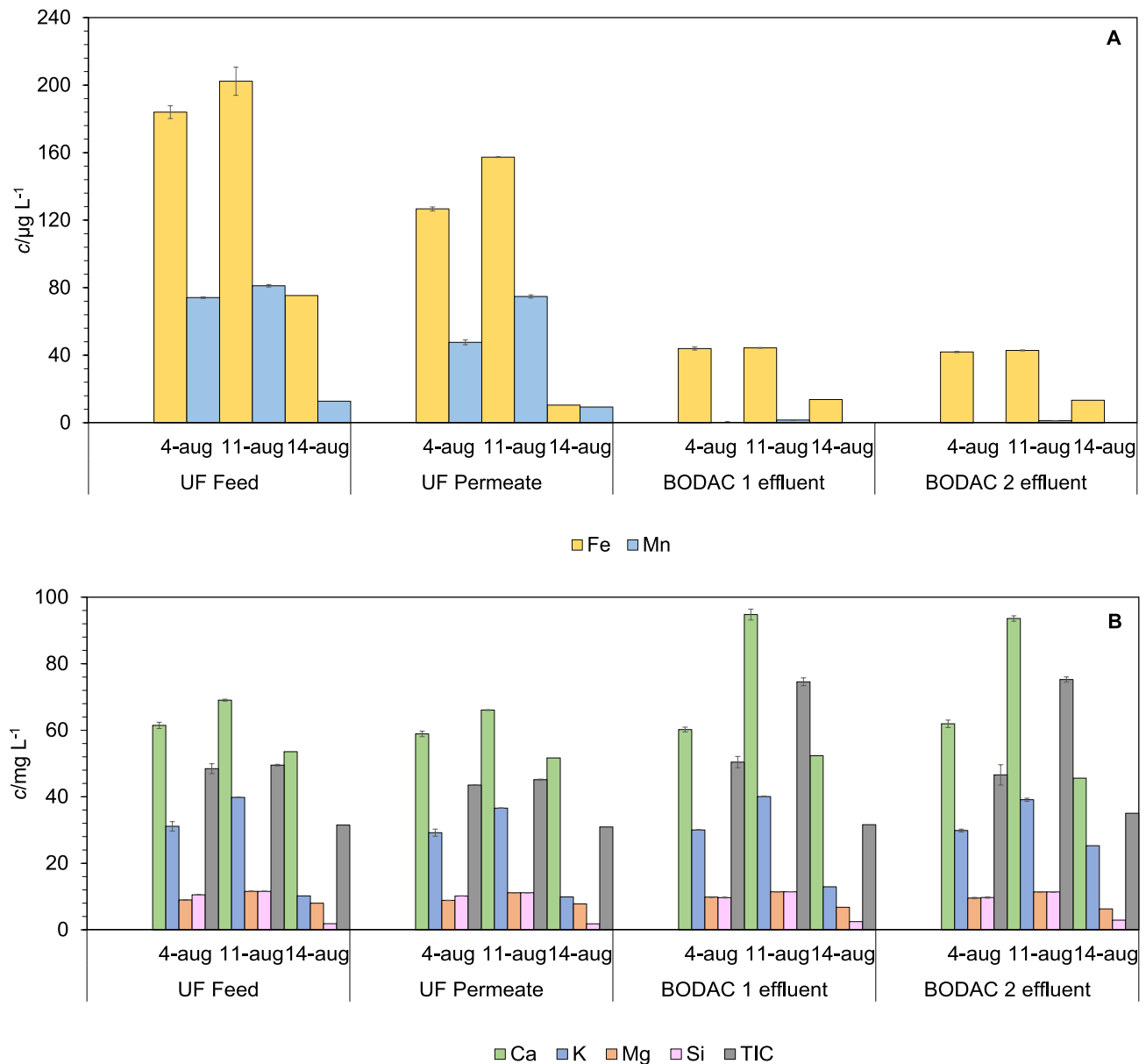
Fig. 6. Iron (*Fe*) and manganese (*Mn*) (A), calcium (*Ca*), potassium (*K*), magnesium (*Mg*), and silicon (*Si*), and total inorganic carbon (*TIC*) (B) concentration in UPW plant, for three independent sampling days and triplicate samples were taken for each sampling point.

causing organic fouling, however, it does not seem to be the case in the present work.

LMW organics, depending on their size, can clog membrane pores. Huber and co-workers [30] defined that LMW organics include small sugars, small organic acids (e.g., acetic and propionic acid), alcohols, aldehydes, ketones, amino-sugars, and amino acids. These compounds can contribute to microbiological growth [30] and, consequently, contribute to biofouling formation. The removal of the *LMW* organics by UF + BODAC was >50 % (Fig. 3B). The removal occurred mainly in BODAC 1 (52 % removal of the *LMW Neutrals* and 63 % removal of the *LMW Acids*). In the UF, the *LMW* organics removal was low (≤6 %), which can be expected since the UF pores are larger than the LMW molecules [39]. The LMW organics removal percentage in BODAC 1 was similar to the removal percentage found by others: Pramanik et al. [9] reported 70 % LMW organics removal by a BAC filter and correlates that to membrane fouling prevention, and Naidu et al. [38] reported 41 % *LMW* organics removal by a BAC filter.

3.3. Nitrogen species

Nitrogen is a basic component of the biopolymers and biomolecules that constitute microbial cells; thus, its availability can greatly influence biofouling [17]. During UF, *pN* was largely removed, as seen in Fig. 4. The sum of the other nitrogen species remained more or less constant throughout the UF + BODAC system (the mass balances to *tN* were close to zero), however, the speciation did change. Also in the UF, ammonium was oxidized to nitrate. In BODAC 1, the remaining nitrogen species were largely oxidized to nitrate as well (Fig. 4). In BODAC 2, the water composition regarding the *N*-species remained nearly constant. In comparison, Pradhan and co-workers [13] achieved a removal of $N-NO_2^-$ of 70 %, while Kalkan and co-workers [40] reported a removal of NH_4^+ removal up to 65 %. Both studies indicated that the *tN* removal depended on the *DO* concentration (3 mg L^{-1} to 4 mg L^{-1}). In this study, the oxidation of (party) reduced N-species was complete, however there was no observable denitrification, presumably due to the higher *DO* levels (6

Table 1

Comparison of secondary effluent treatment processes using BAC-type filters to prevent downstream fouling and to remove organic compounds.

Study	Processes involved	Pre-treatment	*EBCT*/ min	Organic carbon removal	Nitrogen removal	Phosphate removal	Other remarks
This work	Two BODAC filters in series	UF 0.04 μm, oxygen dosing	BODAC 1: 10 BODAC 2: 20	*DOC*: 48 % *Biopolymers*: 95 % *Humic substances*: 35 % *LMW*: ~50 %	*tN*: ~0 %	No consistent removal, effluent concentration of ~1.4 mg L⁻¹	The full-scale UF + BODAC filters prevented RO membrane fouling for ten years.
[11]	BAC filter	–	40	*DOC*: ~30 % *Biopolymers*: 54 % *Humic substances*: 56 % *LMW*: 70 %	N/A	N/A	The removal of biodegradable organics such as LMW was highlighted to reduce the biofouling potential in RO membrane.
[9,13]	BAC filter	Coagulation/ flocculation	a) 20 b) 40 c) 60	*DOC*: a) 42 % b) 58 % c) 65 %	N/A	N/A	BAC and GAC filters were compared, where less irreversible fouling was found with BAC than GAC pre-treatment.
[52]	BAC filter	Sand-filter	18	*DOC* removal: 38 % to 54 %	N/A	N/A	–
[53]	BAC filter	Sand-filter	18	*DOC* removal: 65 %	N/A	N/A	–

Note: N/A = not available.
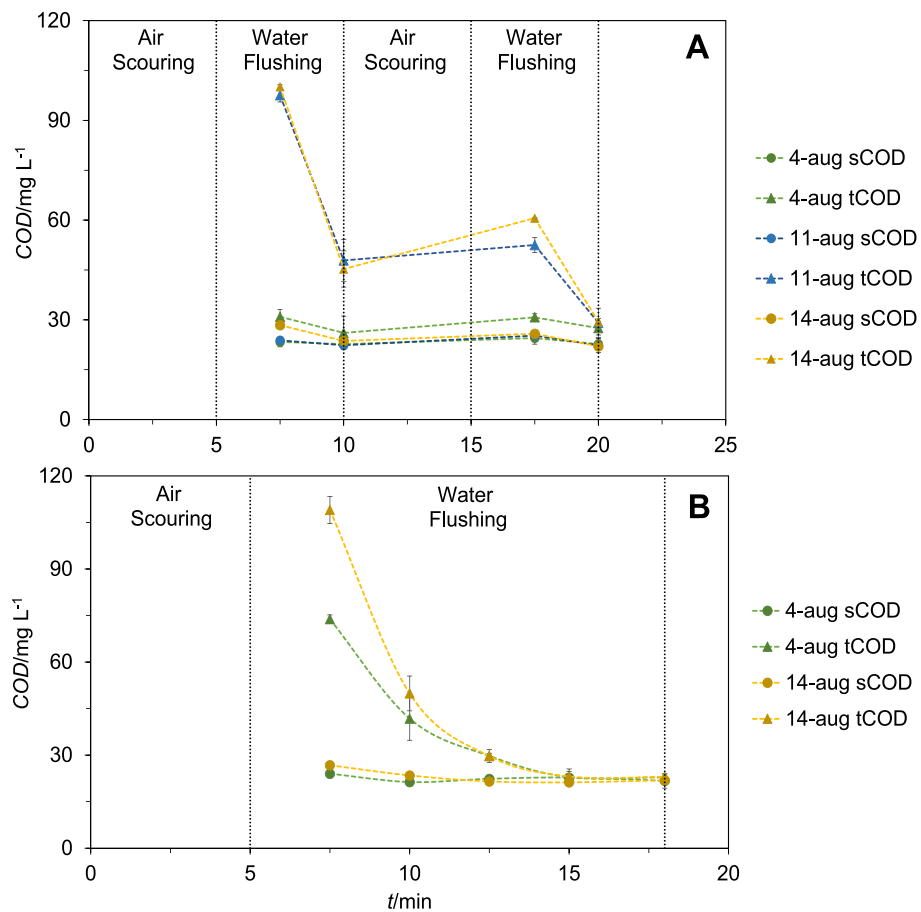
Fig. 7. The total (*tCOD*) and soluble (*sCOD*) chemical oxygen demand of the backwash water during the backwashing program, for the BODAC 1 for three independent sampling days (A), and the BODAC 2 for two independent sampling days (B). Triplicate samples were taken for each sampling point.

mg L^{-1} to 7 mg L^{-1}).

On 11/08, the NO_3^- concentration in the influent of BODAC 1 and 2 was higher than on the other sampling days, furthermore, the *tN* was in the effluent of BODAC 1 and 2 was higher than the BODAC 1 influent. This increased concentration was also observed with the *TIC* and *Ca* data (Fig. 7B). A possible explanation could be that some biofilm was released/broken off from the granules, which was subsequently oxidized to form TIC and nitrate.

Since there was almost no *tN* removal in the UF + BODAC system, the BODAC 2 effluent still contained considerable amounts of nitrate and other N species, enough for cell proliferation and biofilm development to be possible [17]. Therefore, the successful fouling prevention cannot be explained by reduction in bioavailable N.

3.4. Phosphate

Phosphorous, in the water phase present as phosphate, is another nutrient required for biomass growth and thus biofilm formation [17]. Typically, phosphate is present at relatively low concentrations and therefore a limiting nutrient [17,41]. Phosphate can also cause inorganic fouling issues as it can precipitate with cations such as Ca^{2+} and Mg^{2+}. For these two reasons, limiting the phosphate in the RO feed is a widely used fouling prevention technique [3,42]. Fig. 5 presents the change of the orthophosphate (PO_4^{3-}) concentration, between subsequent treatment steps of the UPW plant, for three independent sampling days. The release of phosphate in the BODAC be attributed to two factors: the first, the physical-chemical dissolution equilibrium and the biotic degradation by microorganisms, where phosphate can be released due to biofilm detachment and degradation [41].

Despite the variation of PO_4^{3-} concentration at the inlet of the UF and BODAC filters, the concentration in the BODAC 2 effluent was relatively constant during the sampling campaign, the average phosphate concentration in the BODAC 2 effluent was 1.4 ± 0.1 mg L^{-1}. The relatively similar PO_4^{3-} concentration in the BODAC 2 effluent suggests the ability of this filter to act as a buffer for this compound. The BODAC filters stored PO_4^{3-} when the influent concentration was high and released it when the influent concentration was low. This observation may lead to the hypothesis that the PO_4^{3-} can accumulate in the BODAC filters as a precipitate, and that this precipitate dissolves again if the PO_4^{3-} concentration drops below 1.4 ± 0.1 mg L^{-1}.

On 11/08, there was net uptake of PO_4^{3-} and on the other two sampling days, there was a net release of PO_4^{3-}. Similar to the previous discussed organic carbon and nitrogen, the phosphate concentration in the BODAC 2 effluent was sufficient for cell proliferation and biofilm development to be possible [17]. This data also supports the hypothesis that the absence of biofouling in the RO membrane unit was caused by something other than phosphorous deficiency.

The pH in the BODAC system gradually dropped from 7.9 ± 0.3 in the UF Permeate to 7.2 ± 0.2 in the BODAC effluent, presumably due to the build-up of carbonic acid produced from the oxidation of organic matter. However, during the periodic air scouring the accumulated carbonic acid can be expected to be largely stripped out again as CO_2. These pH dynamics can affect the precipitation or dissolution of insoluble phosphate species, but it did not result in variations in the phosphate concentration in the BODAC 2 effluent, which remained constant at 1.4 ± 0.1 mg L^{-1}.

3.5. Other minerals

As previously mentioned, mineral depositions (*Ca, Mg, Si, Mn,* and *Fe*) may also cause fouling and scaling problems on RO membrane surfaces [2,3]. Additionally, biofilm can contain the mentioned minerals, including *K*, in their matrixes [43]. Fig. 6 represents the minerals of interest (*Ca, Mg, K, Si, Mn,* and *Fe*) and *TIC* removals in the UF + BODAC system. In general, the removals/releases of minerals were modest, hinting at closed mass balances (Tables S2, S3, and S4, Supplementary

material), apart from *Mn* and *Fe*.

Regarding *Fe* and *Mn*, their average removal in the UF + BODAC system was ~79 % and near 100 %, respectively. Most of the removal of these two minerals did occur in BODAC 1, where ~69 % of the *Fe* and 99 % of the *Mn* were removed (Fig. 6A). Some of the *Mn* left the BODAC 1 via backwashing (maximum mass flow of 3 g h^{-1} or ~ 17 % of mass flow in the BODAC 1), as seen in Tables S2, S3 and S4 in the Supplementary material. This suggests that *Mn* could be likely incorporated into the biofilm matrix and attached to the surface of carbon granules (Fig. S2, Table S5), in which biofilm and *Mn* are released into the water during backwash due to the shear forces. The retention of *Mn* in the biofilm matrix was potentially induced by chemoautotrophic bacteria through the formation of manganese oxides [44], as can be seen in Fig. S2. In the BODAC system, the *Mn* removal was achieved six months after its initial operation in 2010 and was relatively stable for ten years [19–21].

This *Mn* removal pattern was also demonstrated in ripened sand filters [45], where the *Mn* removal can be caused by the activity of microorganisms. Filters with manganese oxides showed an ability to mediate the abiotic degradation of persistent organics in water via catalytic and direct oxidation processes [46]. Therefore, further research should elucidate the role of manganese oxide on the GAC granules in organic matter degradation. Nevertheless, it is important to be noted that oxygen was being dosed to the BODAC filters (can be up to 40 mg L^{-1}); thus, the abiotic oxidation of soluble manganese into insoluble manganese was also probable, resulting in its precipitation on the surface of carbon granules (Fig. S1).

Fe was found to be associated with bacterial growth on the RO membrane [47]. It is also known that *Fe* can support biofilm formation in the BODAC filters [48,49]. In contrast to the *Mn*, *Fe* was not removed during backwash. The speciation calculations (data not shown) made on BODAC 2 showed that the majority of the *Fe* in this stream was in the form of oxidized Fe(III) and/or precipitated Fe(OH)$_3$ (bernalite). The oxidized and precipitated forms of *Fe* were supported by the fact that oxygen was dosed at a high concentration that precedes BODAC filters. According to the *Pourbaix* diagram (Fig. S3, Supplementary material), at circumneutral pH and a moderate redox state, the formation of precipitated *Fe* is favourable. This excludes the formation of iron phosphate complexes, which limit the amount of bioavailable dissolved *Fe*, and their formation could justify the absence of biofouling in the RO membrane. The *Fe* and *Mn* retention in BODAC 1 was in line with the EDX results that both of the minerals were found on the AC granules' surface (Table S5, Supplementary material).

The *Ca, K, Mg,* and *Si* remained relatively constant over the subsequent treatment steps, as can be seen by their removals in Fig. 6B, even though high removal rates were reported for these elements in other BAC filters [36]. *Ca* and *Mg* cations are known fouling precursors, commonly found in biofouling layers [3,50,51] and are essential for biofilm formation and attachment to surfaces [43]. Similar to nitrogen and phosphate, *Ca* and *Mg* were not or hardly removed in the UF + BODAC system during the sampling campaign (Figs. 2 and 6B) and, thus, remained present in the RO feed. On 11/08, *Ca* release was observed together with the release of ~65 % of *TIC* (Fig. 7B). The CO_2 increase resulting from both oxidation and backwashing can react with $CaCO_3$ present in the filter and form $Ca(HCO_3)_2$, which is highly soluble, and so, detected by the analytical methods used (TOC, IC, and ICP). This suggests that *Ca* was immobilized in a matrix that also contained carbon and NO_3^- and later (partly) disintegrated on that sampling day. The dynamics of these elements seem to be independent of the phosphate since the release of PO_4^{3-} occurred on a different sampling day (14/08).

3.6. Backwashing of BODAC filters

Backwashing consists of air scouring to detach the biofilm (mainly composed of microbial cells and EPS) from the granules by creating agitation and subsequent water flushing with the BODAC 2 effluent. Based on the *MB* analysis (Tables S2, S3 and S4, Supplementary

material), the backwash water only contained a minor percentage for each organic and mineral parameter. Fig. 7 presents the *tCOD* and *sCOD* in backwash water for BODAC 1 and BODAC 2.

The *sCOD* was relatively constant because the effluent used for backwashing already contained 20 mg L^{-1}. In contrast, the *pCOD* quickly increased as soon as the air scouring started ($t = 7.5$ min and $t = 17.5$ min for the BODAC 1, and $t = 7.5$ min for the BODAC 2) and gradually decreased during water flushing, as the water in the system was progressively replaced with the almost-particle-free BODAC 2 effluent. However, the removal of organics via backwash represents only a minor component (up to 0.02 kg h^{-1}) in the *COD* mass balance (Tables S2, S3, and S4, Supplementary material).

The difference in *tCOD*, for BODAC 1 at $t = 7.5$ min, between the two sampling days can be explained by the difference in time since the last backwash, which was one day on 04/08, and two days on 11/08 and 14/08; new biomass, that could be detected as *tCOD*, had less time to develop on 04/08.

3.7. Comparison of BODAC to other BAC filters to prevent biofouling in membrane systems

A comparison between UF + BODAC and other recent studies using BAC filtration to treat secondary WWTP effluent is presented in Table 1. It summarizes the removal of the main nutrients (C, N, P) known to cause biofouling. BAC filtration has been shown to help mitigate fouling when applied as a pre-treatment to membrane processes [9], reducing the problems associated with irreversible (bio)fouling. In several studies [9–12], the absence of biofouling in RO membranes was reported to be attributed to the *DOC* removal, such as biopolymers and humic substances. The removal of *DOC* in UF + BODAC was within the range of the removal found in the studies mentioned in Table 1, and was in a higher percentage with a lower EBCT of 30 min (both BODAC 1 and 2 filters) compared to that reported in other studies. However, the removal of humic substances in the UF + BODAC was lower, compared to the results obtained by Pramanik et al. [10,11], and Hamid et al. [12]. These studies correlated the absence of (bio)fouling in the membranes with the removal of humic substances, where a higher concentration of humic substances in the membrane feed resulted in a higher flux drop, while a lower concentration resulted in an increase in membrane permeability. The humic substances concentration in the BODAC 2 effluent was relatively high (5–7 mg L^{-1}), however, fouling was still prevented.

Pradhan et al. [13] reported a high removal of *tN*, while in UF + BODAC systems, we did not see any removal of *tN*, possibly due to the continuous oxic condition preventing denitrification. The phosphate removal was low both for the BAC system reported in the literature [13], and in the present study.

Apart of the high removal of *tCOD*, *Fe*, and *Mn*, there was no significant removal of any of the other common (bio)fouling precursors and scalants in the UF + BODAC systems. Take for example phosphate, known for triggering both scaling and biofouling: a common strategy to mitigate biofouling is to limit this nutrient [3,8,16,17]. However, this study shows that limiting phosphate is not necessarily needed to prevent fouling.

(Bio)fouling is inevitable in membrane processes [26]. Nevertheless, the right tailoring of the pre-treatment, either by the macro- and micronutrient limitation, disinfection, or any other fouling mitigation method, will help to extend the lifespan of the membranes. The UF + BODAC shows an excellent performance for effective fouling prevention and to further organic removal from secondary wastewater effluent, similar to the other studies mentioned.

4. Conclusions

The UF + BODAC filters at the UPW plant in Emmen (The Netherlands) helped to prevent fouling of the downstream RO membranes. The present study found that:

1. The mass balance approach elucidated that two types of fouling precursors, i.e., biopolymers and micronutrients, were effectively removed, and their removals were thought to contribute to the negligible fouling issues in the RO membranes. Biopolymers were removed in the UF and the micronutrients *Fe* and *Mn* were removed in the BODAC filters.
2. The UF and BODAC 1 form an effective nitrification system, where nearly all nitrogen-species are converted to NO_3^-, a recalcitrant compound that entered the RO membrane.
3. The BODAC filters also acted as a PO_4^3 buffer, i.e. the PO_4^3 concentration in BODAC 2 effluent was constant, independently of the feed concentration. The always presence of PO_4^3 in the BODAC 2 effluent, suggesting that this compound was not the main reason of the RO membranes fouling prevention.
4. The elements *Fe* and *Mn* were effectively removed in BODAC 1: part of the retained *Mn* subsequently left the filter via the backwash water, while *Fe* was mainly retained in the carbon granules.

The mass balance analysis approach is a first step toward understanding the underlying physical, chemical and biological processes taking place in a UF + BODAC system preventing downstream fouling. However, from the current study it is already clear that a BODAC type system can be considered as an effective pretreatment, before RO, especially when the feed contains *Fe* and *Mn*. We intend to elucidate the underlying mechanisms in subsequent studies.

CRediT authorship contribution statement

Sara Ribeiro Pinela: Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Amanda Larasati:** Data curation, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Roel J.W. Meulepas:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Funding acquisition, Writing – original draft, Writing – review & editing. **Maria Cristina Gagliano:** Data curation, Formal analysis, Supervision, Writing – original draft. **Robbert Kleerebezem:** Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Harry Bruning:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Huub H.M. Rijnaarts:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2023.104648.

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