

The effect of pre-ozonation and subsequent coagulation on the filtration of WWTP effluent with low-pressure membranes

Cornelia Genz, Ulf Mieke, Regina Gnirß and Martin Jekel

ABSTRACT

The impact of a pre-treatment by pre-ozonation (2–10 mg O₃/L) and subsequent coagulation (FeCl₃; 2–6 mg Fe³⁺/L) on the performance of a polymeric ultrafiltration membrane was investigated in lab scale. The performance was assessed by monitoring the flux decline during filtration of secondary effluent in Amicon test cells. During the filtration process no free dissolved ozone was in contact with the membrane. It was observed that flux decline is reduced with increasing coagulant concentration as well as with increasing ozone dosage. This effect involves a reduction in the amount of biopolymers measured by size exclusion chromatography (LC-OCD). Moreover, multi-filtration cycles revealed that pre-ozonation leads to a significant increase in irreversible fouling that might be caused by increasing colloidal iron concentrations. Phosphorus in the permeate was successfully reduced to concentrations <60 µg/L.

Key words | coagulation, fouling, ozone, ultrafiltration

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INTRODUCTION

The European Water Framework Directive (2000/60/EG) aims at ensuring good surface water quality (Article 1). As a consequence, the Berlin Water Company (Berliner Wasserbetriebe) considers upgrading the wastewater treatment plant (WWTP) Ruhleben/Berlin with disinfection and advanced phosphorus removal. Effluent concentrations for phosphorus shall be reduced from nowadays 0.3–0.4 mg P/L down to a target concentration of 0.05–0.1 mg P/L.

Low-pressure membrane filtration of secondary effluent allows disinfection and, combined with chemical coagulation, advanced phosphorus removal. However, the loss of filtration performance due to membrane fouling is still a fundamental problem. Fouling by formation of a cake/gel layer on the membrane surface, pore blocking or in-pore adsorption results in a reduction of the membrane performance (Amy 2009). As a consequence, membranes have to be periodically cleaned applying physical (hydraulic water backwash) or chemical cleaning procedures, leading to a reduction in operation time.

Organic fouling is caused by colloids and by larger dissolved organic substances. Te Poele (2006) and Zheng

et al. (2009) found that biopolymers (BP) in the form of proteins and polysaccharides as well as colloids in the size of 10–450 nm are mainly responsible for fouling of low-pressure membranes. With regard to dissolved organic carbon (DOC), approximately 10% of the Ruhleben effluent DOC contributes to the fouling process (Laabs 2004). Using size exclusion chromatography (Liquid Chromatography – Organic Carbon Detection (LC-OCD)), these substances typically elute within the so-called ‘biopolymer peak’, consisting mainly of polysaccharides, organic colloids and proteins. Haberkamp *et al.* (2007) showed that coagulation partially removes the fouling-active BP as well as humic substances.

Another promising approach to reduce organic fouling and to improve the membrane filtration performance is the application of ozone, especially for ceramic membranes (Schlichter *et al.* 2004). The combination of coagulation and ozonation using low ozone dosages (1–2 mg/L) can lead to the formation of larger, more stable flocs as a result of the so-called ‘microfloculation effect’ (Jekel 1998), having a positive effect on the filtration performance of granular media

filters. Beyond this microfloculation effect, higher ozone dosages (10–12 mg O₃/L) lead to transformation of organic substances and micropollutants (Bahr et al. 2007).

This study investigates if a pre-treatment by ozonation would be suitable to improve the subsequent coagulation/membrane filtration process in lab scale. For that purpose, different concentrations of iron and ozone were applied and filtration performance as well as fouling potential (by BP analysis) was monitored during the filtration process. The combination of the two processes (ozonation/coagulation) was optimised in order to identify the most favourable ratio of ozone dosage and coagulant concentration.

MATERIAL AND METHODS

Ozonation and coagulation

Pre-ozonation was performed using an ozonation unit that produces gaseous ozone from pure oxygen using an ozone generator from WEDECO (type Modular 8HC, ITT WEDECO GmbH, Germany). The gaseous ozone provided by the ozone generator was directly introduced into the sample in a 4-L semi-batch stirred tank reactor. In-gas and off-gas ozone concentration, dissolved ozone and gas flow rate were measured continuously. For completion of the mass balance, the off-gas ozone was stripped with pure oxygen. Target ozone dosage was in the range of 2–10 mg O₃/L, corresponding to 0.2–0.9 mg O₃/mg DOC. Coagulation with FeCl₃ was conducted according to ‘technical rule DVGW W 218’ (DVGW 1998) using a differing beaker volume of 2 L instead of 4 L. Direct addition of FeCl₃ into the 4-L semi-batch stirred tank reactor was

followed by a stirring period of 30 s at 360 rpm with subsequent stirring at 60 rpm for 5 min.

Filtration tests

Filtration tests were performed according to Zheng et al. (2009) using Amicon filtration cells in dead end mode without stirring. The experimental set-up is illustrated in Figure 1. The sample was filled into the feed reservoir and pressurised with a constant pressure of 1 bar using nitrogen gas. In order to prevent the flocs from settling in the feed reservoir the sample was slowly stirred. The permeate weight increase over time was recorded using an electronic balance. Each filtration cycle experiment was performed until 500 mL cumulative permeate was obtained. For discussion of results, normalised flux J/J_0 (permeate flux/pure water flux) was plotted over permeate volume. Since the applied pressure was 1 bar, the absolute values of flux (L m⁻² h⁻¹) and permeability (L m⁻² h⁻¹ bar⁻¹) are identical for all performed tests. Prior to the experiments, membranes were soaked in pure water for at least 24 h and subsequently filtrated with 2 L pure water in order to remove wetting agents and production residues and to achieve a stable permeate flux. For determination of the pure water flux J_0 of each membrane, 100 mL of pure water was filtered immediately before starting the experiment. For all performed experiments, the maximum deviation in pure water flux was 20%. The experiments were conducted at room temperature (22.9 ± 1.5 °C). The investigated UF membrane (NADIR[®] UP150, MICRO-DYN-NADIR GmbH, Germany) is made of permanent hydrophilised polyethersulphone (PES) with a molecular weight cut-off (MWCO) of 150 kDa. Secondary effluent from WWTP Ruhleben (Berlin) was used as test water for all experiments.

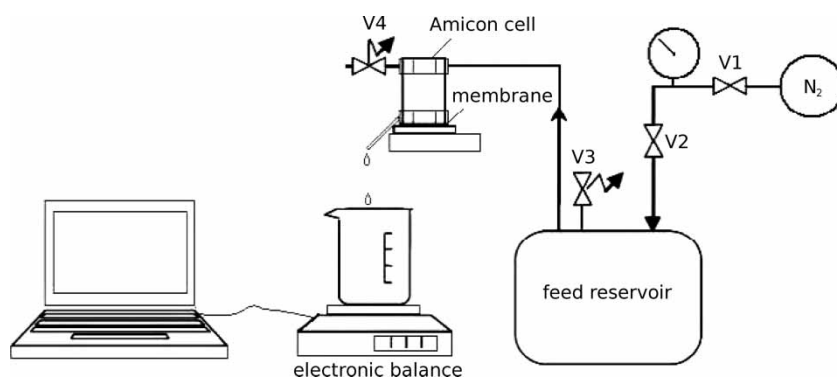


Figure 1 | Schematic set-up for trials with the Amicon test cell (adapted from Zheng 2010).

Multi-filtration trials

Multi-filtration trials were performed to study the membrane fouling potential. For that purpose, samples treated by coagulation only (4 mg Fe³⁺/L) were compared to samples treated by pre-ozonation (0 and 6 mg O₃/L) and subsequent coagulation (4 mg Fe³⁺/L). The trials were performed following Jermann *et al.* (2008) and based on the description in the previous section. Deviating from Jermann *et al.*, the number of filtration cycles amounted to five instead of three cycles. Only the first run was performed with a new membrane but all following runs with the same membrane. After each cycle, the membrane was backwashed using 50 mL of the previously generated permeate at a pressure of 1 bar. Additionally, the flux of the used membrane was again determined with 100 mL of pure water prior to each filtration cycle.

Analytics

The global parameters Ultraviolet Absorbance at 254 nm (UVA 254), measured with a photometer (Lambda 12, Perkin-Elmer, Germany) and DOC, according to EN 1484 (1997) using a HighTOC analyser (Elementar, Germany) were determined. The effect of the two pre-treatment steps on the character of DOC, especially the BP fraction, was investigated by the use of size exclusion chromatography with subsequent organic carbon detection (LC-OCD) according to Zheng *et al.* (2009). Additionally to these parameters, Total Soluble Phosphorus (P_{T,f}) was analysed by flow injection analysis (FIAstar 5000, FOSS, Germany) and residual iron concentration defined as total iron after 0.45 µm filtration was measured by atomic absorption spectroscopy (Atomic Absorption, Spectrometer SpectrAA400, Graphite Tube Atomizer GTA 96, Varian Deutschland GmbH, Germany). The standard parameters temperature, pH and electric conductivity were also determined.

RESULTS AND DISCUSSION

Temperature, pH and electric conductivity

pH was measured before and after each treatment process. Due to a high buffer capacity of the WWTP effluent, pH showed only an increase from 7.3 ± 0.1 before to 7.9 ± 0.0 after pre-ozonation with 2 mg O₃/L and 8.0 ± 0.1 after pre-treatment with 10 mg O₃/L. Increases in pH during

ozonation occurred most likely due to stripping of inorganic carbon. Conductivity also showed a small variance and was approximately 1,126 ± 138 µS/cm, depending on the predominant weather conditions. Initial values of UVA 254 for the secondary effluent without pre-treatment were approximately 28.05 ± 1.38 m⁻¹. DOC of the secondary effluent varied slightly during the project and was 10.9 ± 0.8 mg/L.

Total soluble phosphorus (P_{T,f})

Concentrations of Total Phosphorus (P_T) in the secondary effluent varied between 188 µg P/L and 763 µg P/L during the project period. The average concentration of P_T was 338 ± 175 µg/L, whereas average P_{T,f} concentration of the effluent amounted to 126 ± 50 µg P/L. Figure 2 shows the P_{T,f} concentrations in the permeate as a function of the P_{T,f} concentrations in the WWTP effluent and in dependence on different coagulant concentrations (2, 4 and 6 mg Fe³⁺/L). For the permeate, P_{T,f} is identical to P_T. No impact of pre-ozonation was observed. In Figure 2 the effect of different coagulant dosages is shown. It is visible that for approximately 80% of the data points coagulant concentrations of 2 mg Fe³⁺/L result in phosphorus concentrations <60 µg P/L. A further increase in coagulant concentration to 4 mg Fe³⁺/L leads to a reduction in P_{T,f} to concentrations <50 µg P/L. Application of even higher coagulant concentrations (6 mg Fe³⁺/L) does not lead to a further reduction in concentrations of P_{T,f}. Application of 2 mg Fe³⁺/L leads to an average P_{T,f} concentration after UF of 50 ± 13 µg P/L, whereas 4 and 6 mg Fe³⁺/L result in an additional reduction of P_{T,f} concentrations after UF and average values of 32 ± 5 µg P/L and 39 ± 18 µg P/L were obtained, respectively.

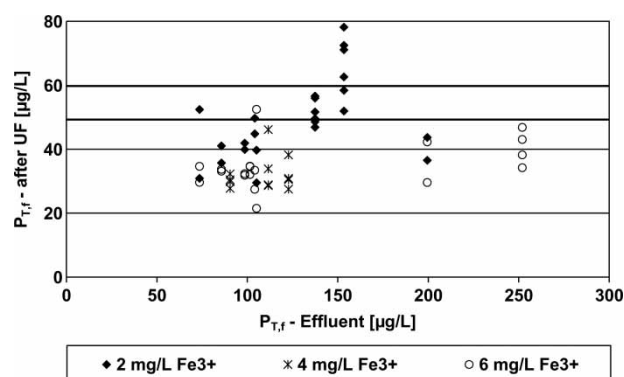


Figure 2 | P_{T,f} concentration in the permeate against P_{T,f} concentrations in the WWTP effluent for different coagulant concentrations.

Flux decline and filtration time

The average normalised flux decline for all investigated WWTP effluent samples without any additional treatment amounted to 90% (after filtration of 500 mL). As visible in Figure 3, flux decline decreased significantly by means of coagulation and pre-ozonation/coagulation. Oxidation effects on the surface of the membrane can be excluded because of complete stripping of the residual ozone with pure oxygen prior to the filtration step. Normalised flux at the end of filtration was improved to 21% by coagulation (6 mg Fe³⁺/L) and to 30% by pre-ozonation/coagulation (10 mg O₃/L and 6 mg Fe³⁺/L) compared to 9% without any treatment. In general, the flux decline decreased with increasing dosages of FeCl₃ and O₃ (Figure 3(a) and 3(b)). The combination of pre-ozonation/coagulation led to further improvements compared to the sole application of coagulant. When keeping the coagulant dosage constant, increasing ozone dosages led to a stepwise increase in flux with the above mentioned maximum at 10 mg O₃/L and 6 mg Fe³⁺/L.

The increase of filtration performance and especially the positive effect of pre-ozonation become even more obvious in Figure 3(c) and 3(d) showing the filtration times needed for each sample (500 mL) corresponding to trials of Figure 3(a) and 3(b). The combination of 10 mg O₃/L and subsequent coagulation with 2 mg Fe³⁺/L reduced the filtration time by 51% compared to the effluent without treatment (Figure 3(c)). Applying the same pre-ozonation dosage followed by

coagulation with 6 mg Fe³⁺/L (Figure 3(d)) resulted in a reduction in filtration time of 61%. Comparing coagulated samples and samples treated with a combination of pre-ozonation and subsequent coagulation, filtration time is further reduced by a maximum of 28% (2 mg Fe³⁺/L) and 33% (6 mg Fe³⁺/L), respectively, compared to the filtration time of samples which were only pre-treated by coagulation.

Behaviour of BP

BP are known as main foulants during UF (Zheng et al. 2009). Figure 4 shows the BP fraction of WWTP effluent with and without pre-treatment for coagulant concentrations of 2 mg Fe³⁺/L and different ozone dosages (0–10 mg O₃/L), eluting approximately between 33 and 48 min. BP peaks before UF are depicted in Figure 4(a), whereas Figure 4(b) shows BP peaks after UF.

The BP fraction shows a significant decrease for the samples treated with coagulant only (Figure 4(a)). A further decrease in the amount of BP and a shift to smaller molecules is observed with increasing dosages of ozone. There is an overall change in the quantity of BP as the amount of BP eluting with the main BP peak around 38 min decreases clearly, whereas the amount of BP eluting around 48 min only increases slightly. Ozone seems to transform BP to smaller BP fragments with longer retention times. This increase is also observed for the samples after UF (Figure 4(b)). The smaller BP are not retained by the

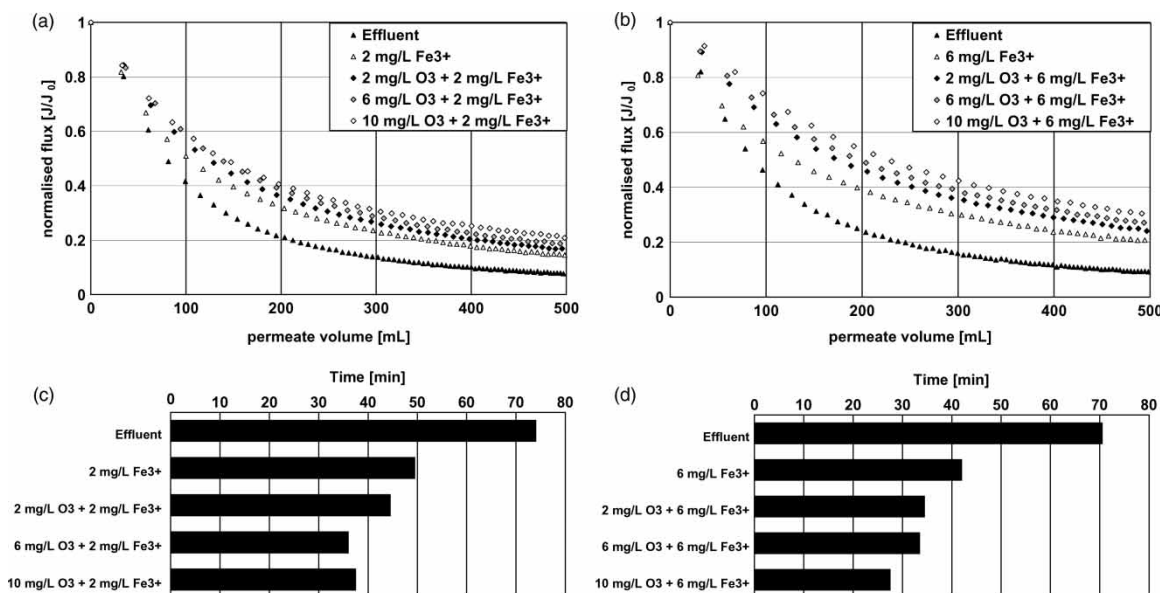


Figure 3 | Flux decline curves and filtration times for different ozone dosages of 0–10 mg O₃/L and a constant FeCl₃ addition of 2 mg Fe³⁺/L (a and c) and 6 mg Fe³⁺/L (b and d).

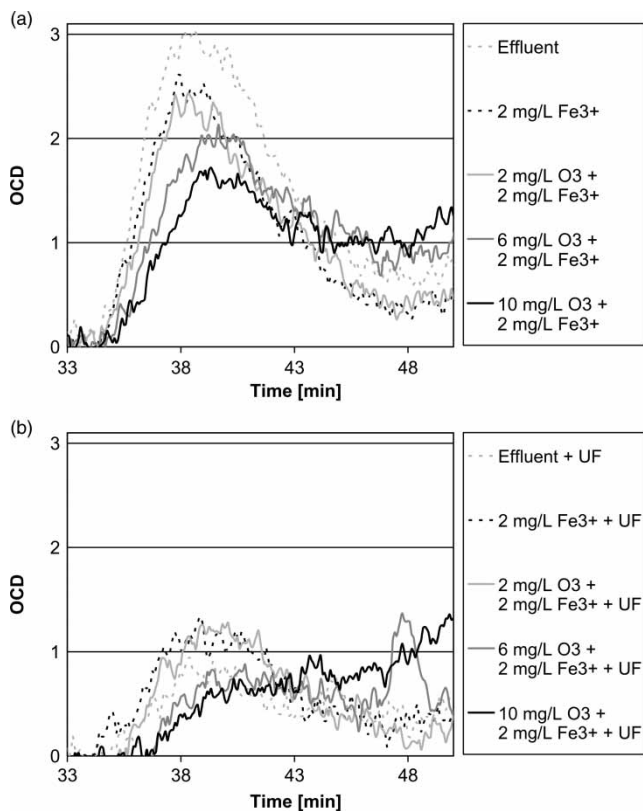


Figure 4 | Biopolymer peak of secondary effluent analysed by LC-OCD with a coagulant concentration of 2 mg Fe³⁺/L and different ozone dosages (0–10 mg O₃/L) before (a) and after UF (b).

UF and therefore do not contribute to reversible membrane fouling. In contrast, the amount of BP eluting around 38 min (higher molecular size) decreases significantly after UF. Thus this BP fraction is retained to a great extent by the UF, leading to a decline in flux.

Residual iron

Residual iron concentrations of the WWTP effluent after 0.45 μm filtration were 33 ± 10 μg/L. Independent of the applied pre-treatment, the average concentration of residual iron after UF was 30 ± 20 μg/L. In contrast, residual iron concentration after 0.45 μm filtration increased due to coagulation. Thus colloidal iron in the range of 0.026–0.45 μm is formed, which is retained by the membrane. Residual iron concentration after coagulation was 23–356 μg/L. Average concentrations were higher with low coagulant dosing of 2 mg Fe³⁺/L compared to 6 mg Fe³⁺/L. Results indicated a trend to even higher residual iron concentrations after pre-ozonation, in particular when applying high ozone dosages. Since ozonation is well

known for the formation of organic acids, this increase might be caused by the formation of colloidal organo-metal complexes (Jekel 1994). As a consequence, less iron might be provided for the coagulation process and more colloidal iron would be retained by the membrane.

Multi-filtration trials

Flux decline curves and filtration times for the coagulated effluent (4 mg Fe³⁺/L) and the corresponding pre-ozonated sample (6 mg O₃/L) are shown in Figure 5. Significant differences in flux at the end of the filtration cycles are only visible after the first filtration cycle. Irreversible fouling (defined as the difference between J/J_0 after backwash (BW) compared to $J/J_0 = 1$) increases significantly with the application of ozone. A maximum is reached after four BW cycles (51% irreversible fouling in contrast to 22% for the coagulated sample). In both cases (coagulation and pre-ozonation/coagulation), main constituents of irreversible fouling originate from the first and second filtration cycles. One possible explanation for the increased irreversible fouling after pre-ozonation might be an increased

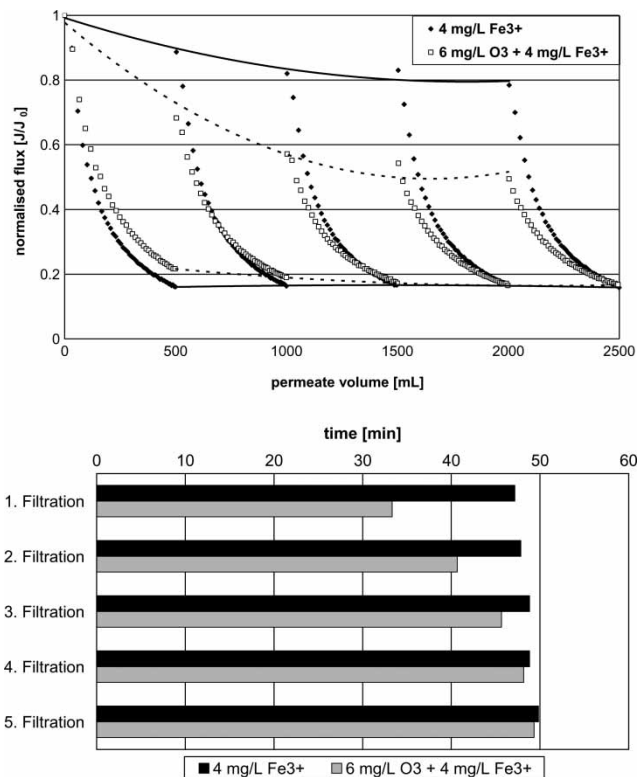


Figure 5 | Flux decline curves of BW experiments and corresponding filtration times comparing coagulated effluent (4 mg Fe³⁺/L) and effluent pre-treated with 6 mg O₃/L and 4 mg Fe³⁺/L.

in-pore adsorption of generated iron colloids or generated smaller BP. The observed different flux declines correspond with filtration times. For the coagulated sample, only a slight increase of the filtration time over four cycles was observed, whereas a strong increase was found for the sample treated by pre-ozonation/coagulation (from 33 to 49 min). Although an increase in irreversible fouling was observed due to pre-ozonation, the corresponding filtration times are significantly reduced – for the first and second filtration cycle by 14 and 7 min respectively. With growing number of filtration cycles, the filtration times converge and stay nearly constant after the fourth cycle.

When assessing the observed effect of an increased irreversible fouling after pre-ozonation, it has to be considered that BW conducted in these test trials differs strongly from BW procedures in pilot plants. Furthermore, no chemical BW was tested. Beyond these differences in BW, Zheng (2010) found that high filtration pressures of approximately 1 bar result in more compact BP fouling, which is more difficult to be hydraulically backwashed.

CONCLUSION

The results of this study suggest that combining pre-ozonation and coagulation is a promising pre-treatment process to reduce the fouling of organic membranes, without the necessity of applying free dissolved ozone onto the membrane surface. Pre-treatment by coagulation and pre-ozonation/coagulation enables effective phosphorus removal from WWTP effluent. Coagulation with 2 mg Fe³⁺/L leads to P_{T,f} concentrations <60 µg P/L. While coagulation (without pre-ozonation) already increases the flux compared to the effluent without pre-treatment, a further improvement of the filtration performance can be achieved by combining pre-ozonation and coagulation. This synergistic effect is more pronounced for higher coagulant concentrations.

Lower amounts of biopolymers after pre-treatment correlate with flux increase during filtration. Different mechanisms are considered as reasons for the improved performance after pre-ozonation and subsequent coagulation. An increase in ozone dosage leads to a decrease of the amount of biopolymers eluting with the main peak at around 38 min, leading to an increase in flux. Higher ozone dosages (>6 mg/L) additionally seem to induce disintegration of biopolymers and a shift to smaller organic compounds which pass through the membrane. Thus, the latter probably have a lower impact on fouling. Pre-

ozonation seems to change characteristics of the foulants. As a consequence, pre-ozonation resulted in an increased irreversible fouling during multi-filtration trials. In spite of lower initial fluxes, filtration times of pre-ozonated samples are significantly reduced for the first and second filtration cycles. The increase of irreversible fouling might be explained by the formation of colloidal iron and/or by the formation of small BP generated during ozonation, which can lead to in-pore adsorption and thus increase the irreversible fouling.

To confirm the outcomes of this study experiments at pilot scale are planned. These experiments will include operation at lower trans-membrane pressures, chemical cleaning and testing of different UF membranes to minimise irreversible fouling.

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