Pre-coagulation and ultrafiltration of effluent impaired surface water for phosphorus removal and fouling control
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ABSTRACT
The process combination of in-line coagulation and subsequent membrane filtration is a suitable advanced treatment stage to achieve higher quality standards regarding pathogens and phosphorus in biologically treated wastewater prior to its discharge into sensitive water bodies. In this study a membrane pilot installation (capacity of 6 m³/h) was operated in dead-end configuration to investigate phosphorus removal and fouling behaviour depending on FeCl₃ dosage. In parallel, effects of in-line coagulation on the filtration behaviour were investigated in lab-scale filtration experiments.

The coagulation leads to the predominant reduction of dissolved organic macromolecular substances which are detected as biopolymer fraction by liquid chromatography-organic carbon detection. Besides the removal of dissolved organic molecules, the resulting filter cake plays a major role for the performance of ultrafiltration. In lab-scale filtration experiments the in-line coagulation results in positive effects on the filtration stability. In contrast, high coagulant doses lead to the loss of filtration performance during the pilot operation. The installed in-line coagulation, however, successfully reduced the orthophosphate concentration in permeate to values below 30 μgP/L when operated at a fixed molar ratio of FeCl₃ concentration to influent PO₄-P concentration of 6 (βPO₄-P-value).

Key words | fouling, hybrid process, phosphorus removal, surface water, ultrafiltration

INTRODUCTION
Among other processes, ultrafiltration (UF) is applied more and more in water reclamation to produce high quality water regarding the concentration of particles and pathogens from surface water or secondary effluent. An effective reduction of the irreversible deposition of foulants on the membrane material is essential for the economical operation of the process. Especially dissolved macromolecular substances are considered to be significant foulants in membrane filtration of surface water and biologically treated effluent (Halle et al. 2009; Zheng et al. 2009).

Frequent combinations of membrane processes consist of adequate pre-treatments, which are designed in dependence of process objectives and apply adsorption, pre-oxidation, pre-filtration or coagulation processes. Coagulation is the common technique to achieve an effective improvement of the filtration performance (Huang et al. 2009).

Simultaneously, the coagulation efficiently reduces the concentration of different dissolved water contaminants (e.g. phosphorus, taste and odour compounds (Farahbakhsh et al. 2004)). In Berlin, the removal of total phosphorus to a value below 100 μg P/L is envisaged for the discharge of secondary treated effluent in the local surface water to control eutrophication.

Coagulation leads to the build up of cake layers which bind colloidal or dissolved macromolecular compounds in particular (Haberkamp et al. 2007). The formed coagulation cake layer is attributed to ‘protect’ the membrane surface from smaller foulants (<membrane pore size), which
improves the overall UF performance (Howe et al. 2006). The aggregation of colloids and the binding of larger macromolecules due to the coagulation as well as the rapid formation of the filter cake are necessary to prevent direct pore clogging (Bagga et al. 2008). Lee et al. (2000) describe an increased porosity of the cake layer after coagulation which results in a reduced filtration resistance. Therefore the ratio of floc size to membrane pore size is an important parameter with regard to the optimisation of the filtration performance of low pressure membranes (Howe et al. 2006).

The current study investigates the process combination of pre-coagulation and membrane filtration to simulate the advanced treatment of secondary treated effluent in pilot plant experiments and short-term lab-scale filtration tests. Effluent impaired surface water [Landwehrkanal (LWK)] is used as a surrogate for secondary effluent. The raw water quality of the eutrophic surface water shows strong seasonal fluctuation with regard to particles and the concentration of phosphorus. In comparison to secondary effluent the range of biopolymer concentrations are comparable.

In the pilot plant operation, both, an efficient phosphorus removal as well as fouling control were investigated. The process performance was observed in dependence of dosed iron concentration. In the lab-scale filtration tests, which were conducted with the same type of membranes, the influence of in-line coagulation on the membrane filtration was investigated, in detail. The lab-scale filtration experiments consist of three parts: (a) investigation of the impact of surface water (LWK) particles on the membrane filtration and the efficiency of its removal during the backwash; (b) the influence of macromolecular compounds and their reduction by coagulation; (c) the influences of in-line coagulation on the filtration behaviour with optimised backwash efficiency.

**MATERIALS AND METHODS**

**Size exclusion chromatography-organic carbon detection**

Total organic compounds (TOCs) and dissolved organic compounds (DOCs) of raw water, permeate and backwash water samples were determined as a bulk parameter using a High TOC II (Elementar Analysensysteme GmbH). The chemical composition of the DOCs of these samples was characterised by liquid chromatography-organic carbon detection (LC-OCD). LC-OCD system by DOC-Labour Dr. Huber; column: HW55S (GROM Analytik + HPLC GmbH; detection limit of 10 μgL⁻¹; standard deviation <1%). The LC-OCD analyser includes a size exclusion chromatography with continuous UV254 nm and organic carbon detection. A typical LC-OCD chromatogram of surface water and secondary treated effluent consists of four principal fractions which elute from the SEC (size exclusion chromatography) column with decreasing molecular weight in the following sequence: (i) biopolymers (including extracellular polymeric substances, e.g. mainly protein-like and polysaccharide-like substances), (ii) humic substances, (iii) low-molecular-weight acids and (iv) low-molecular-weight neutrals.

**Pilot plant experiments**

In this study a membrane pilot installation was tested for phosphorus removal and fouling behaviour depending on FeCl₃ dosage. The UF pilot plant (SWT Memcor CMF-S unit) is located in the city centre of Berlin (Schleuseninsel, LWK) and consists of four SWT Memcor® submerged modified PVDF hollow fibre UF membrane modules with a capacity of 6 m³/h (total membrane area of 112 m²; constant flux of 54 L/m²h, Figure 1). The SWT Memcor® hollow fibre membranes (outside-in) are characterised by a nominal pore size of 0.04 μm. The pilot plant operated in a 20 min backwash interval. During the backwash the modules are aerated (approximately 45 m³/h for 45 s for all modules) in addition to the permeate backwash (backwash flux equal to filtration flux) to remove the filter cake from the membranes. Chemical cleanings of the membranes in between filtration experiments are conducted by a constant two step cleaning procedure. The cleaning chemicals are heated up to 30 °C inside the membrane tank.

The coagulation is realised by in-line coagulation including a static mixer (four mixing elements, coefficient of variation <0.05) and a subsequent coagulation time of approximately 50 s (including pipe coagulation and retention time in the membrane tank). Pilot filtration experiments were conducted at FeCl₃ concentrations between 0 and 2 mgFe/L. Both, dosing a fixed iron concentration and a dynamic iron
dosing according to a constant $\beta_{PO_4-P}$ value (molar ratio of coagulant concentration to influent $PO_4-P$ concentration) were performed. The pilot plant is equipped with an on-line $PO_4-P$ analyser (Bran + Luebbe, SPX Flow Technology Group) for the continuous detection of the orthophosphate removal performance and to realise a dynamic dosing control.

**Lab-scale filtration experiments**

Parallel to the pilot plant, a lab-scale membrane module equipped with the same type of SWT Memcor hollow fibre membranes was installed and operated either parallel to the pilot plant (bypass-configuration) or in batch configuration (Figure 1). In batch configuration the lab-scale module is used independently of the pilot plant as a stand-alone membrane unit. The lab-scale filtration unit operates in the cross-flow configuration at a constant trans-membrane pressure whereas the pilot plant operates in dead-end-configuration and at constant flux.

In case of the setup modification (batch configuration as stand alone filtration unit) the raw water circulates by passing the membrane module inside the batch system (Figure 1, batch configuration). The extracted permeate is collected and is periodically pumped back into a 10 L raw water storage tank to avoid an increase in concentration. In this setup only filtration tests with particle free waters (pre-filtered by 0.45 $\mu$m cellulose nitrate filters) are conducted.

The lab-scale membrane module has a total membrane area of 220 cm$^2$ (30 fibres by a length of 30 cm) and is periodically backwashed. The permeate backwash is initiated in a 20 min interval. Optionally, air bubbles overflow the membranes during the backwash to produce shear forces for an effective solids removal (aerated backwash, compressed air flow comparable to the settings of the pilot plant installation). The aerated backwash at the lab-scale module was used in the experiment series (a) and (c).

For each filtration experiment a new membrane module was potted by a self-developed procedure. Prior to use, the new membranes were rinsed with pure water and a
hydrogen peroxide solution (5 g/L) to wash out production residues. After rinsing the initial permeability of each lab-scale membrane module was determined. Pure water permeabilities at 345 mbar and 20 °C reached a mean value of 243 ± 11 L/m² h bar (standard deviation).

Test waters in lab-scale experiments and their pre-treatment

All test waters were pre-filtered by a 300 µm stainless steel filter. For the investigation of the impact of surface water particles (a) and the influence of in-line coagulation (c) experiments were conducted in bypass configuration without further pre-treatment. For the investigation of the influence of macromolecular compounds and their reduction by coagulation (b) the test waters were pre-treated by coagulation at concentrations of 2 and 5 mgFe/L and by filtration of 0.45 µm cellulose nitrate filters prior to membrane filtration. For this experiment series the different waters were collected and pre-treated within one day (period August–September). After their pre-treatment the waters can be mainly distinguished by different concentrations of macromolecular compounds (according to the LC-OCD). Additionally, minor differences can be found in the concentration of humic substances. The waters were stored at 4 °C and warmed up to room temperature before the experiments.

Coagulation batch experiments

Coagulation jar tests were performed according to DVGW standard W218 with LWK water in the following procedure: (i) 1.8 L raw water; (ii) dosing of coagulant and 30 s rapid mixing (400 rpm, equal to $G = 1143$ s⁻¹; (iii) 1.5 min coagulation time (60 rpm, equal to $G = 70$ s⁻¹; (iv) subsequent filtration by 0.45 µm cellulose nitrate filter. The pH-values during the coagulation tests ranged between 7.5 and 7.2.

RESULTS AND DISCUSSION

DOC characterisation of surface water

The composition of DOC in the LWK water is influenced by DOC sources in the catchment area of the surface water (natural and anthropogenic allochthonous sources, e.g. secondary effluent, rain water discharge) and microbial processes (production and degradation) (Sachse et al. 2005). Table 1 characterises the seasonal variability of the DOC composition (according to the LC-OCD). The concentration of biopolymers fluctuates within a wide range. The primary production during periods of increasing microbial activity plays an important role in the concentration of biopolymers (Sachse et al. 2005). Both, extracellular and intracellular (due to cell lyses) compounds are present during growing periods. The biopolymer concentration of secondary treated effluent changes within a comparable range of 0.13–0.78 mgC/L (Zheng et al. 2010) during the seasonal variation. However, the highest biopolymer concentrations of secondary effluent are reached during winter season, whereas the LWK water shows the highest biopolymer peaks in late summer (Table 1(d)), probably because of the release of algae metabolic products (Sachse et al. 2005).

Preliminary experiments

In preliminary jar coagulation experiments the reduction of DOCs was observed. Coagulation jar experiments were repeated with LWK water of different compositions (five

| Table 1 | LWK water parameters during seasonal variations |
|---------------------------------|-----------------|-----------------|
| LWK (feed) | | |
| Temperature | 1–24 °C | |
| pH | 7.5–8.0 | |
| PO₄-P | 18–215 µg/L | |
| TOC [mg/L] | DOC [mg/L] | |
| February–September | 7.5 ($±0.37; n = 32$) | 6.8 ($±0.24; n = 37$) |
| Biopolymers [mg C/L] | Humic substances [mg C/L] | |
| (a) Beginning of Feb.– end of March | 0.26 ($±0.02; n = 9$) | 4.08 ($±0.23; n = 9$) |
| (b) Mid of April – beginning of June | 0.44 ($±0.02; n = 8$) | 4.67 ($±0.26; n = 8$) |
| (c) Mid of June – end of July | 0.58 ($±0.05; n = 12$) | 4.65 ($±0.09; n = 10$) |
| (d) Mid of Aug. – beginning of Sep. | 0.96 ($±0.05; n = 6$) | 5.38 ($±0.16; n = 7$) |
jar test series in the period February–August). In average, the coagulation reduces dissolved macromolecular substances by $17 \pm 7\%$ per mgFe/L ($n = 15$) according to LC-OCD. In comparison, humic substances were reduced by $5 \pm 2\%$ ($n = 15$) and the total DOC by $3 \pm 1\%$ ($n = 15$) (average removals were tested within a range of 0–4 mgFe/L). Different fractions of DOC are linearly reduced as a function of coagulant dosage within the tested range of the ferric chloride concentration.

The LC-OCD analysis confirms a predominant reduction of dissolved macromolecular substances, which are measured as biopolymer fraction (Haberkamp et al. 2007). These substances are bound in the flocs and are retained by the filtration step.

**Lab-scale membrane filtration experiments**

The filtration performance in lab-scale membrane tests is displayed as the normalised permeability (standardised to 20 °C) after the backwash based on the initial permeability ($J_{sp}/J_{sp,0}$) and represents the part of the flux reduction which cannot be recovered with the backwash (hydraulically irreversible flux reduction).

**Influence of particles**

Larger particles are not expected to influence the filtration behaviour of the lab-scale membrane unit due to its operation in cross-flow configuration. The cross-flow velocity governs the flow profile inside the membrane module and controls the transport of particles along the membrane surface. However, the results show that it is essential to produce additional shear forces through aeration during the backwash (Figure 2(a)). An insufficient backwash results in an accumulation of particles on the membrane surface and inside the hollow fibre bundle. As the result particles of the 300 μm pre-filtered LWK water cause a rapid loss of the filtration performance (approximately 50% after a permeate volume of 25 L). Contrary, effective backwashing (aerated permeate backwash) results in a considerable lower gradient of the filtration curve.

**Retention characteristic**

LC-OCD analysis of raw water, permeate and backwash water samples confirm a predominant retention of organic compounds, which elute within the biopolymer peak (Figure 2(b)). Considering smaller molecular sizes, the chromatograms of feed and permeate water are almost identical, showing that humic-like compounds are retained to a minor extent. This agrees with the considered fouling potential of biopolymers. Retained organic macromolecular substances which are removed from the membrane during the backwash can be found in the backwash water (Figure 2(b), BP peak).

**Influence of dissolved macromolecular substances**

The filtration performance (loss of permeability) decreases as a function of the permeate volume during the filtration

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**Figure 2**
(a) Normalised permeability (standardised to 20 °C) after periodical backwash for 300 μm pre-filtered LWK water; (-) permeate backwash, (+) aerated permeate backwash; lab-scale unit in parallel configuration: $J_0 = 82$ L/h m², TMP = 380 m bar, $v_{cross-flow} = 0.18$ m/s, $t_{ filtration} = 20$ min, $J_{backwash} = 96$ L/h m² (mean), $p_{backwash} = 1.0$ bar, $c_{BP} = 0.77$ mgC/L (mean) turbidity (LWK 300 μm) = 6.1 NTU, pH = 7.5. (b) OC-signal of LC-OCD-chromatograms of LWK water, permeate and backwash water (permeate backwash); samples are filtered by 0.45 μm prior analysis; BP, biopolymers, HS, humic substances (diluted three-fold).
of pre-coagulated and raw LWK waters (Figure 3(a)). The test waters are pre-screened by 0.45 μm and defined as particle free. With regard to the cut-off characteristic of the membrane (cp. Figure 2(b)) the pre-filtered test waters differ mainly in the concentration of biopolymers (see preliminary experiments).

The filtration of 25 L raw water (pre-filtered by 0.45 μm) leads to an irreversible reduction of the permeability by 10–15%. The filtration of the coagulated waters results in a comparable relative low improvement of the filtration performance, which was unexpected considering the reduced biopolymer concentration of the pre-treated waters (>50%). Apart from slight differences in the initial filtration phase the normalised permeabilities of treated and untreated test waters decline at the same rate.

The relatively high biopolymer concentration of the untreated LWK water \(c_{BP,0} = 0.83 \text{mgC/L} \) results in an unexpected low decline of the permeability during the filtration. The observation in lab-scale membrane tests (Figure 3(a)) indicates that a relatively large part of LWK originating biopolymers has a good hydraulic reversibility during backwash. Extracted algogenic organic matter of blue-green algae contains a high hydrophilic fraction (Her et al. 2004), which may be responsible for the observed behaviour.

**Influence of pre-treatment by in-line coagulation**

In contrast to the preceding results, the in-line coagulation has a more significant influence on the filtration behaviour of the LWK water (Figure 3(b)). A distinct initial filtration phase is identified in case of the untreated raw LWK water, which is characterised by a rapid loss of permeability. Wang & Tarabara (2008) characterise the initial filtration phase by a rapid decline of filtration performance because of pore clogging due to colloids and macromolecules. After a permeate volume of 20 L the filtration is cake layer dominated and shows a smaller decline of the permeability.

The in-line coagulation as pre-treatment achieves a lower and nearly constant gradient in loss of permeability during the entire duration of the experiment. In particular, the direct pore clogging at the beginning of the filtration is prevented because of the described colloids aggregation and binding of larger organic molecules (Howe et al. 2006). Thus, the coagulation leads to a fast transition to the cake-dominated filtration (Bagga et al. 2008).

**Pilot plant operation**

Filtration data of the pilot plant operation including biopolymer concentrations are plotted in Figure 4. The filtration experiments with a dosed FeCl₃ concentrations of 1 mgFe/L do not show a decisive effect on the filtration behaviour and do not imply a positive effect of the in-line coagulation on the filtration performance (average decline of permeability of 9 L/m²h bar per day in contrast to 7 L/m²h bar per day without coagulation). Furthermore, iron concentrations higher than 1 mgFe/L lead to an increase of the filtration resistance. This is obvious for the operation period in
Phosphorus removal

The dynamic coagulant dosing combines the influent orthophosphate concentration and the concentration of FeCl₃. Its aim is to avoid an overdosing of coagulant with respect to orthophosphate removal. The concentration of FeCl₃ is adapted according to the influent orthophosphate concentration during the operation by a fixed $\beta_{PO₄-P}$ value (molar ratio of the FeCl₃ concentration to $c_{PO₄-P}$) of 6 which equates to FeCl₃ doses within a range of 1–2 mgFe/L. The FeCl₃ concentration is adjusted by the measurement interval of orthophosphate analysis (30 min). During the period June–August the orthophosphate influent concentration shows a distinct diurnal variation (range of 100–210 µgPO₄-P/L). At a $\beta_{PO₄-P}$ value of 6, the process combination reduces the orthophosphate concentration in permeate to values below 50 µgPO₄-P/L. In this case the average orthophosphate removal achieves values of approximately 87%.

In comparison to a fixed coagulant dose of 2 mgFe/L (based on influent $c_{PO₄-P}$ of 190 µgPO₄-P/L) the amount of coagulant could be reduced by approximately 34% due to dynamic dosing at a $\beta_{PO₄-P}$ value of 6.

CONCLUSION

In-line coagulation/UF pilot plant experiences in phosphorus removal and fouling control were supplemented with results of lab-scale UF experiments. With regard to the lab-scale membrane unit (cross-flow mode), it is assumed that inhibition of direct pore clogging and a fast formation of the coagulation filter cake are mainly responsible for the improvement of the filtration performance. In contrast, the coagulation/UF pilot plant (submerged modules) displays sensitivity regarding higher coagulant doses. An increase in the filtration stability cannot be verified while dosing 1 mgFe/L. However, the process successfully reduced the orthophosphate concentration to values below a desired effluent concentration of 50 µgPO₄-P/L. A moderate impact of the concentration of LWK source biopolymers, which is in contrast to results with secondary effluent, was obvious in both, lab-scale cross-flow filtration tests and the pilot plant operation.

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