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In-line coagulation prior to UF of treated domestic wastewater – foulants removal, fouling control and phosphorus removal

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ABSTRACT

The present work investigated fouling control and phosphorus removal by applying in-line coagulation prior to ultrafiltration (UF) of treated domestic wastewater. Experiments were conducted in both lab- and pilot-scale under close to neutral pH condition. Lab-scale foulant removal tests showed that increasing the dosage of $FeCl_3$, $AlCl_3$ and polymeric aluminum chloride (PACl) can improve biopolymer removal. Specifically, PACl reduced preferentially the proteinaceous fraction of biopolymer while the other two coagulants showed no significant preference. The filterability of water samples was improved after coagulation, which is contributed to biopolymer removal and the formation of larger particles. Pilot UF experiments demonstrated that in-line coagulation improved the performance of UF to a large extent. Within 0.037–0.148 mmol Me^{3+}/L dosage range, adding more $FeCl_3$ and $AlCl_3$ slowed down the development of trans-membrane pressure (TMP) correspondingly, while changing PACl dosage showed little effect on the variation of TMP increase rate. Further investigations indicated that PACl related precipitates contributed to more irreversible fouling than that which the monomeric coagulants made. Fouling control is thus considered as a co-effect determined by foulant removal efficiency, fouling layer structure and the adherence of hydrolysis products/precipitates onto the membrane. With respect to phosphorus removal, dosing $FeCl_3$ and $AlCl_3$ achieved higher removal efficiency than using PACl. Based on lab- and pilot-scale results, dosing $FeCl_3$ and $AlCl_3$ at a relative dosage of over 2.5 mol Me^{3+} per mol total phosphorus (TP) in feedwater is necessarily required to keep the TP concentration under 50 μg/L in UF permeate.

1. Introduction

In tertiary treatment for wastewater reclamation, in-line coagulation with low-pressure membrane filtration is receiving increased attention. The application of in-line coagulation can: (i) reduce membrane fouling which is a major cost concern in advanced wastewater treatment using membranes, (ii) simultaneously remove nutrients (e.g., phosphorous) to meet strict water quality thresholds for certain reuse purposes (e.g., eutrophication control of receiving water body), and (iii) decrease the footprint of the treatment plant compared to employing conventional flocculation sedimentation processes.

Similar to the application of other pretreatment processes for fouling control, removing certain foulants from water is considered an important procedure using in-line coagulation [1]. Along with the identification of biopolymers (macromolecular proteins and polysaccharides) as the preliminary foulants in UF of secondary effluent (SE) [2–5], it is necessary to investigate the removal of these organics by in-line coagulation using different coagulants and compare the corresponding fouling control effect, which are the main objectives of the present study.

With respect to biopolymer removal, previous studies investigated this issue in conventional coagulation sedimentation procedures (as seen in [6]). Compared to that applied in those processes, in-line coagulation needs much shorter coagulation time and lower dosages [7]. This might lead to a different foulant removal behavior which is still unclear to date. In addition, increasing evidence shows that within biopolymers, macromolecular protein-like material might play a more important role than other fractions [8,9]. As proteins are preferentially removable by certain coagulants (e.g., PACl [10]), specific removal of proteinaceous biopolymers is expected to be achieved using PACl and thus, fouling control efficiency might be improved to a larger extent than dosing other coagulants. Nevertheless, the validity of this hypothesis has not been explored.

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For fouling control in membrane filtration, selection of suitable coagulation conditions (e.g., coagulant type, dose and feed water pH [11]) is important and requires both foulant removal analysis and pilot-scale tests. In conventional coagulation/sedimentation processes, foulant removal can be investigated using standard lab-scale jar tests. Higher removal efficiency leads to better performance of the subsequent membrane system [6]. But, using in-line coagulation the relationship is not straightforward because the hydrolysis products or precipitates of coagulants may also interact with membranes and contribute to fouling [12]. The severity of the effect depends mainly on the type of the coagulants [13,14]. Polymeric coagulants seem to cause more fouling related hydrolysis species than monomeric reagents do [14,15]. For this reason, the selection of suitable coagulation conditions should be determined through pilot-scale tests instead of only based on foulant removal results [12]. However, lab-scale experiments and foulant removal tests are popularly used because of its simplicity and time-saving character. In addition, monomeric reagents like $FeCl_3$ or $AlCl_3$ do not show obvious fouling effects as polymeric coagulants have [13]. Therefore, it is important to identify the relationship between foulant removal and fouling control in the UF process for certain commonly used coagulants and propose useful advices for practical operation. In this work, the effect of two commonly used monomeric inorganic coagulants ($FeCl_3$, $AlCl_3$) and polymeric PACl on foulant removal was studied. The relationship between biopolymer removal determined through lab-scale tests and the performance of a pilot UF was investigated. In the experiments, pH of SE was not modified to test the availability of in-line coagulation on fouling control under typical pH range in wastewater reclamation.

In addition to fouling control, phosphorus removal is also expected by using in-line coagulation. The removal of phosphorus from wastewater may become necessary when it is discharged to water bodies that are at risk of eutrophication [16]. In Berlin, future stringent phosphorus regulations are expected for wastewater discharge, aiming on a limit of TP at 50 μg/L in receiving surface water in order to prevent increased algae growth [17,18]. Noting the low dosage of coagulants applied using in-line coagulation prior to low-pressure membranes [7,12], it is of interest to investigate if such dosages are sufficient for fouling control and simultaneously effective for phosphorus removal ($TP < 50\ \mu g/L$ in UF permeate). Although a previous study showed that the molar ratio of added Al^{3+} or Fe^{3+} to TP must generally be larger than 1:1 to achieve efficient TP removal in wastewater reclamation [19], no precise ratio has been reported for this purpose using $FeCl_3$, $AlCl_3$ and PACl. The results are expected to be valuable for operating water reclamation using in-line coagulation combined with UF technology.

2. Methods and materials

2.1. Secondary effluent (SE)

Treated domestic wastewater used in the present work is SE from the Wastewater Treatment Plant (WWTP) Ruhleben (Berlin, Germany) with a treatment capacity of 250,000 m^3/d [20]. The treatment process of the full-scale plant includes conventional activated sludge process, biological nitrogen and phosphorus removal. To keep the TP concentration in SE below 0.5 mg/L, inorganic coagulants are added into the aeration tank to enhance phosphorus removal (Fig. 1 [20]). The effluent from the secondary clarifier was taken as feedwater to UF (Fig. 1). The average water quality of the feedwater during the experimental period is shown in Table 1.

Table 1
Average water quality of the secondary effluent during the investigation period ($n = 167–179$).

Parameters	Average value with standard deviation
DOC [mg/L]	11.5 ± 1.4
Biopolymer concentration [mg C/L]	0.57 ± 0.17
Biopolymer organic nitrogen [mg N/L]	0.15 ± 0.05
UV_{254} [$1\ m^{-1}$]	19.1 ± 2.3
Total phosphorus [mg/L]	0.27 ± 0.12
Ortho phosphate [mg/L]	0.17 ± 0.09
pH	7.0 ± 0.2
Conductivity [μS/cm]	1165 ± 227
Temperature [°C]	19.2 ± 2.5

2.2. Coagulants

For coagulation experiments, $FeCl_3$, $AlCl_3$ and PACl were used. Table 2 presents their basic characteristics. The dosage concentration range is selected based on the recommended range suggested by Crittenden et al. [21] and primary tests on phosphorus removal tests. Me^{3+} used here is a general symbol representing metal ions such as Fe^{3+} and Al^{3+}.

2.3. UF membrane filtration test

2.3.1. Lab-scale amicon UF test

2.3.1.1. General description of filterability test using Amicon filtration cell. The lab-scale Amicon cell filtration test is used to quantify the filterability of different water samples. Here, filterability is defined as normalized flux decline after filtering 500 mL of water. The filtration procedure is described by Zheng et al. [2] in detail. In brief, prepare water sample in a 4 L container is pressurized at one bar through an UF membrane installed in the Amicon cell (Amicon 8200, Millipore, U.S.A). After filtering 500 mL of water, the pure water flux of the fouled membrane is measured. The filterability is the ratio of pure water flux of the fouled membrane to that of the corresponding new one. In the present work hydrophilized polyethersulphone (PES) UF membrane (0.00287 m^2, NADIR® UP150, molecule weight cutoff (MWCO) 150 kDa, Germany), with similar material characteristics to the UF membrane of the pilot plant, is used. The preparation process of the membrane samples is described in detail by Zheng et al. [2].

2.3.1.2. Preparing raw and coagulated SE for filterability test. As dissolved organics in SE have been regarded as major fraction contributing to membrane fouling, the filterability test focused on the water samples after 0.45 μm filtration (cellulose nitrate membrane, Sartorius, Germany) of raw and coagulated SE. A jar test based on standardized method (DVGW-Worksheet W 218) was conducted to prepare coagulated SE. 1.8 L of water was filled into a 2 L beaker equipped with a magnetic stirrer operating at a turning speed of 400 rpm. After dosing coagulants into water and mixing for 30 s, the coagulated SE was filtered through. The overall coagulation time was controlled at around 120 s to simulate the short reaction time applied by in-line coagulation process. As soon as the coagulation process finished, the coagulated SE was filtered using the 0.45 μm filter. During coagulation due to the buffer effect of the water sample, the variation of pH was almost negligible except for dosing $FeCl_3$ at a dosage of 0.148 mmol Fe^{3+}/L, under which condition pH was decreased by around 0.3 pH units.

To identify the contribution of size fractionated foulants to filterability and their variation after coagulation, filters with pore size of 1.2 (Sartorius, Germany), 0.45 and 0.026 μm (NADIR® UP150) were used to fractionate water samples. The produced effluent was filtered using the same kind of UF membrane mentioned above.

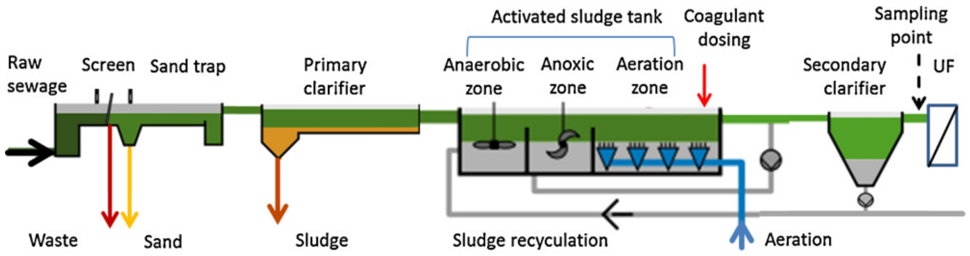

Fig. 1. Domestic wastewater treatment process in WWTP Ruhleben and the location of the UF pilot plant used in the present work. (adapted from [20] with simplifications)

The calculation of hydraulic resistance of different fractions is done according to Zheng et al. [2].

2.3.1.3. Reversibility test using multi-cycle UF. Multi-cycle UF tests are applied to compare the contribution of different coagulant hydrolysis products or precipitates to membrane fouling. The preparation of coagulation solution is as follows: 0.037 mmol Me^{3+}/L coagulant was added to 1.8 L salt solution ($CaCl_2$ 2.8 mmol/L, NaCl 5.4 mmol/L in pure water, conductivity around 1200 μS/cm which is similar to that of the water samples) and mixed as described above. During mixing, pH was controlled at around 7 by adding NaOH. Thereafter, 1.8 L coagulated water was filled into the feed reservoir ($V = 4$ L). Using the connected cell (Amicon 8200) the 500 mL water sample was filtered through the UF membrane (NADIR® UP150) under 1 bar using pressurized nitrogen gas. The fouled membrane was then turned around and backwashed using 100 mL salt solution at 1 bar. After measuring water flux by filtering 150 mL pure water, the unused coagulant solution in the reservoir was removed and 1.8 L freshly prepared solution was filled into it for the next filtration cycle. After three series of filtration and backwashing, the ratio of the pure water flux of the fouled membrane to that of its original value is calculated as the reversibility (%). The operation is conducted at room temperature (∼22 °C).

2.3.2. UF pilot plant

A UF pilot plant (W.E.T., Germany) with hydrophilized polyethersulfone (PES) membrane (Dizzer 450, Inge AG, Germany) was used to filter different waters. The membrane module has a filtration area of 4.5 m^2 and the MWCO of the membrane is 100 kDa. Detail information about the membrane can be found in a previous study [22]. In the present work it was operated in dead-end filtration mode at a constant flux of 60 L/(m^2 h). After 20 min filtration the membrane was backwashed for 25 s using permeate water at a flux of 260 L/(m^2 h). Liquid coagulants were dosed into the feedwater pipe prior to the pressure pump. After mixing by the pump the coagulated water was pressured into the membrane module. The retention time (flow time from mixing point to the membrane surface) was kept at around 60 s (according to preliminary experiments). An experiment ended when the trans-membrane pressure (TMP) reached 600 mbar. After each experiment the module was cleaned with NaOCl and NaOH solution (60 mg/L active chlorine dissolved in distilled water at pH 12) and H_2SO_4 (pH 2) until the permeability of the membrane was restored to over 90% of the initial value (tested with tap water after temperature corrected to 20 °C). The time the plant operated from the beginning until the TMP reached 600 mbar was defined as the operating time (in days). During operation a 50 mL sample of the influent to the UF plant was taken each hour using an auto-sampler (7400 Tübingen-PP MOS 12/T, Germany). A daily composite sample was then analyzed in terms of DOC, UV_{254} and biopolymer content (per LC-OCD). Online pH (WTW740, Germany), conductivity and temperature meters (WTW 730, Germany) were set up in the feedwater tank and the analysis data was recorded hourly.

2.4. Analysis

2.4.1. Quantification of biopolymers using LC-OCD-UVD-OND system

The LC-OCD-UVD-OND system (DOC-LABOR Dr. Huber, Germany) is equipped with a size exclusion column HW55S (GROM Analytik + HPLC GmbH, Germany) and online dissolved organic carbon (OCD), UV_{254} (UVD) and dissolved organic nitrogen (OND) detectors. The liquid chromatograph (LC) unit separates organic compounds according to their molecular size and the separated compounds are detected by online detectors. Using the software FIFIKUS®, the corresponding peak area can be converted into concentrations of mg C/L, mg N/L and UVA_{254} absorbance in 1 m^{-1}, respectively. The biopolymer concentration in the present study is given in mg C/L. The identification of the various fractions, including biopolymers, is described by a recently published study [23]. In the present work, DOC and UV_{254} were quantified using LC-OCD by integrating its by-pass peaks.

2.4.2. Quantification of phosphorus content

Concentration of total phosphorus and ortho-phosphate were quantified using flow injection analysis system FIAstar® 5000 (Foss, Hillerød, Denmark) based on standardized methods (ISO/DIN 15681:2001 part 1,[18]). The standard deviation was determined

Table 2
Types and dosage of the coagulants used in the experiments.

Coagulant	Type	Me^{3+} content [g Me^{3+}/L]	Basicity [%]	Strength [% w/w]	Supplier	Dosage
$FeCl_3$	Inorganic monomer	200	0	40 ($FeCl_3$)	CVB Albert Carl GmbH & Co KG (Germany)	0.037, 074, 0.148 mmol Me^{3+}/L for all the investigated coagulants
$AlCl_3$ LiquiFloc-30®	Inorganic monomer	42.6	30	7 (Al_2O_3)	Ludwig Schulz GmbH (Germany)	
PACl LiquiFloc-80®	Inorganic polymer	42.6	80	12 (Al_2O_3)	Ludwig Schulz GmbH (Germany)	

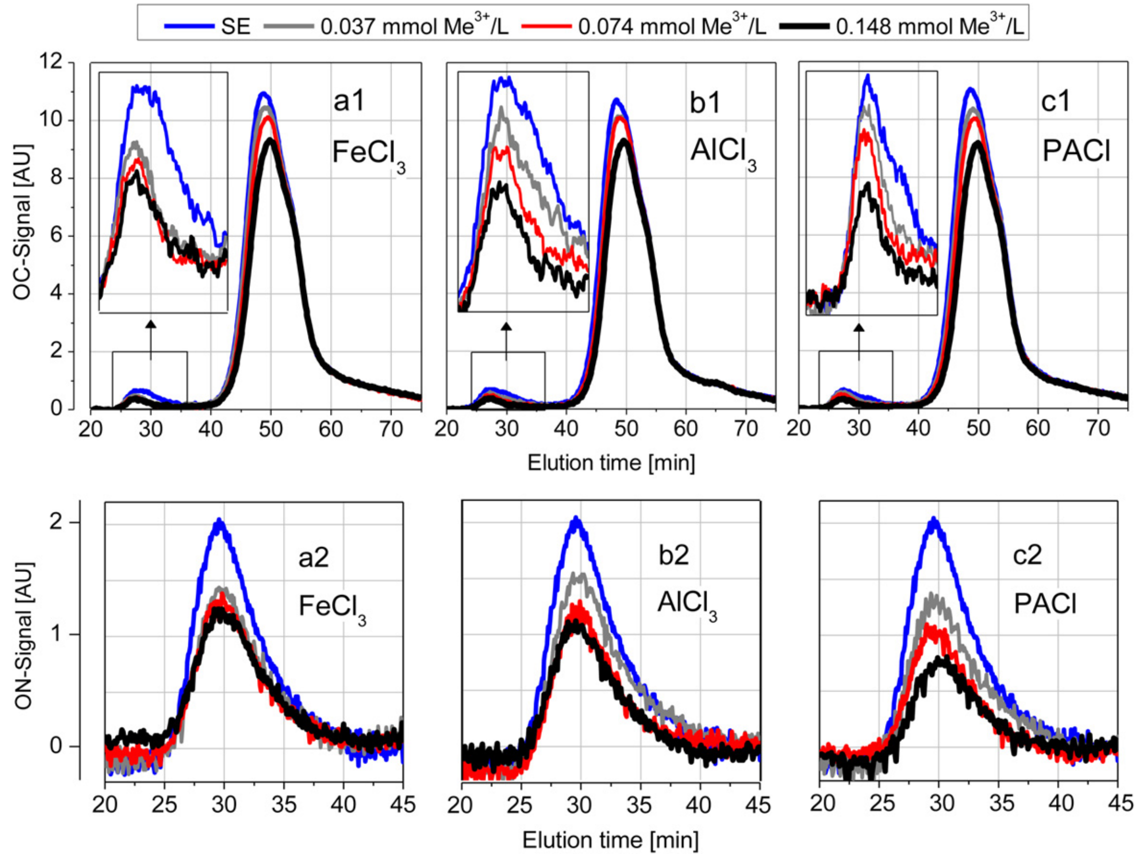

Fig. 2. Influence of dosing coagulants on the change of LC-OCD-OND chromatograms. Influence of dosing $FeCl_3$ on the removal of (a1) biopolymer carbon, (a2) biopolymer nitrogen; $AlCl_3$ on the removal of (b1) biopolymer carbon, (b2) biopolymer nitrogen; PACl on the removal of (c1) biopolymer carbon, (c2) biopolymer nitrogen.

to be 4.8% at a mean concentration of 0.016 mg/L P with a detection limit of 3 μg/L. Two calibration ranges including 0–100 μg/L and 0.01–1 mg/L were used to quantify phosphorus concentration in water [24]. For the measurement of ortho-phosphate in SE, the sample was first pre-filtered using cellulose nitrate membrane (pore size 0.45 μm, Sartorius). The treatment of water sample for total phosphorus measurement was conducted according to ISO 6878:1998.

3. Results and discussion

3.1. Biopolymer removal in lab scale coagulation experiments

Fig. 2 shows the change of LC-OCD chromatograms of SE before and after coagulation in jar tests. As shown, adding each kind of coagulant reduced the content of biopolymers (the peak at elution time 25–40 min). At low dosage level (0.037 mmol Me^{3+}/L), $FeCl_3$ presented the highest biopolymer removal in the three reagents (Figs. 2a1 and 3a). Increasing the dosage up to 0.148 mmol Me^{3+}/L, biopolymer removal can be improved from 33% to 42% by using $FeCl_3$ (Fig. 3a), while from 12% to 44% and 17% to 41% by dosing $AlCl_3$ and PACl, respectively (Fig. 3a).

The elimination of biopolymer nitrogen-containing substances is shown in Figs. 2 and 3. At 0.037 mmol Me^{3+}/L, $FeCl_3$ reduced 35% of biopolymer N content while $AlCl_3$ and PACl achieved only 20 and 25% removal, respectively. An increase of $FeCl_3$ dosage to 0.148 mmol Me^{3+}/L cannot improve the effect significantly (Fig. 2a2). Increasing PACl to this dosage level led to almost 60% removal of organic N (Fig. 3b) and a corresponding increase of C/N ratio in biopolymers from 5 to around 7.5 (w/w), which are the highest achievements in using these three coagulants.

3.2. Fouling control effect

3.2.1. Improvement of filterability contributed by dissolved fraction in SE due to coagulation

Filterability of dissolved fraction in SE (after 0.45 μm filtration) before and after coagulation was tested (the samples also used for LC-OCD measurement shown in Fig. 2). It is shown that dosing 0.037 mmol Me^{3+}/L $FeCl_3$ improved the filterability from 0.24 to 0.39 (Fig. 4a1). A fourfold increase in dose (to 0.148 mmol Me^{3+}/L) only resulted in slight improvement of the filterability from 0.39 to 0.42. The hydraulic resistance results confirmed the insignificant

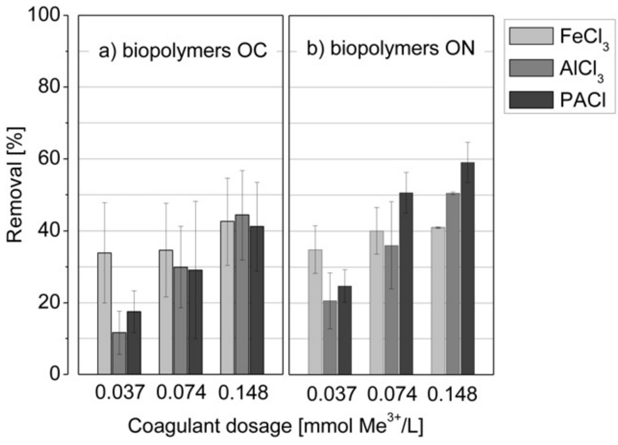

Fig. 3. Effect of dosing different coagulants on the removal of (a) biopolymer carbon content, (b) biopolymer nitrogen content ($n = 2–9$, pH ≈ 7).

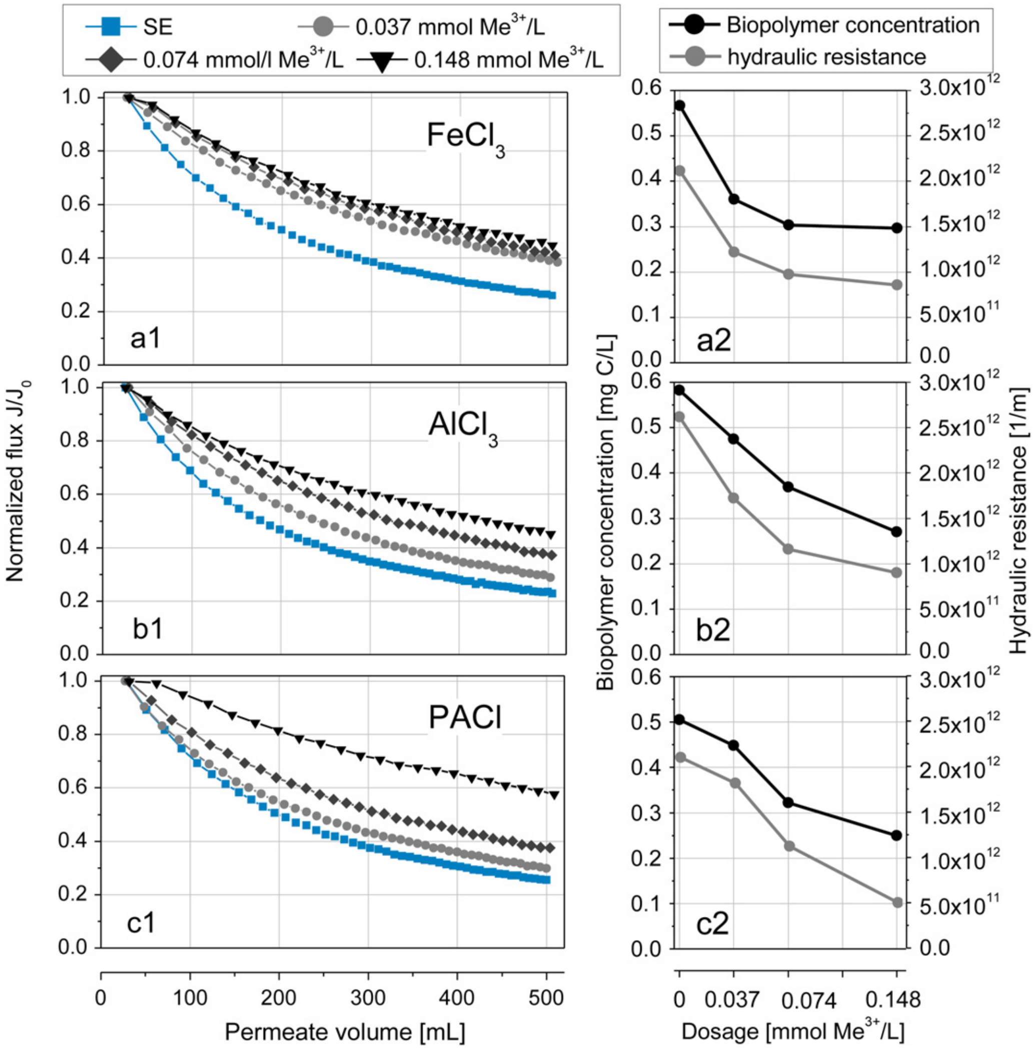

Fig. 4. Filterability improvement of dissolved fraction of SE by dosing different coagulants at dosages from 0.037 to 0.148 m mol $Me^{3}+/L$ (a1–c1) and the relationship between residual biopolymer concentration and hydraulic resistance (a2–c2).

improvement (Fig. 4a2) and were consistent with biopolymer removal (shown in Fig. 2a1). For $AlCl_3$ and PACl, increasing the dosage from 0.037–0.148 mmol Me^{3+}/L led to significant rise of the filterability from 0.24 to 0.45 and 0.24 to 0.59, respectively (Fig. 4b1 and c1). This was in accord with the decrease of hydraulic resistance (Fig. 4b2 and c2) and the significant removal of biopolymers (Fig. 2b1 and c1). These results indicate that biopolymers are the major organics influencing the filterability of dissolved substances in SE. Removing biopolymers through coagulation is the major reason improving the filterability.

3.2.2. *Variation of hydraulic fouling resistance due to coagulation*

The influence of coagulation on hydraulic resistance in UF of SE is shown in Fig. 5. It is evident that after coagulation the total hydraulic resistance caused by fouling was reduced, and higher dosage resulted in further reduction (Fig. 5). With respect to the resistance contributed by size fractioned material, it is shown that coagulation changed the resistance of the substances smaller than 0.026 μm only slightly, but reduced that contributed by the foulants in the size range of 0.026–0.45 μm significantly (mainly due to removal of biopolymers, Section 3.2.1). A slight increase of the resistance caused by the large colloids (size range from 0.45 to 1.2 μm) is

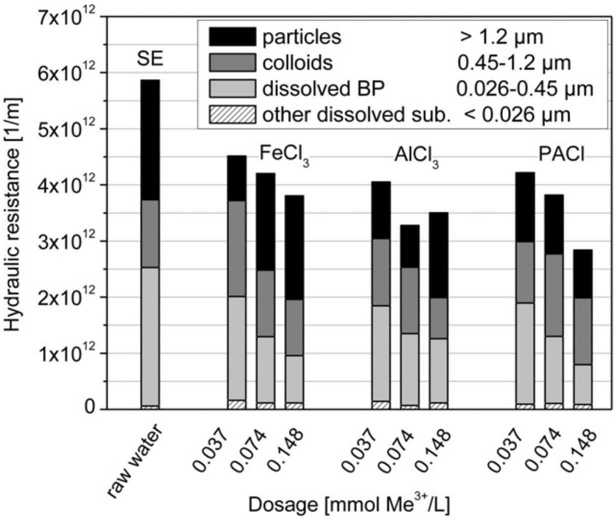

Fig. 5. Contribution of size fractionated substances to hydraulic resistance during UF after dosing coagulants (BP: biopolymers).

observed. It seems that the colloidal content increased after coagulation, which is in agreement with the observation found in another study [1]. This phenomenon might be caused by the formation of fine colloids (e.g., metal hydroxides [25]) due to short mixing time after coagulation [21]. For the large particles (>1.2 μm), their contribution to hydraulic resistance was reduced using each kind of coagulant, implying the formation of larger and more porous particles.

3.2.3. *The performance of the UF pilot plant*

The effect of coagulant dosage and type on the performance of the UF pilot plant was investigated from February to May 2009. During this period, temperature of the SE varied from 16 to 22 °C (Table 3). The average removal of DOC and UV_{254} using the UF pilot plant with and without in-line coagulation is shown in Fig. 6. It is evident that UF itself can remove some organic constituents (e.g., removal of DOC: 5%, UV_{254}: 2%). Increasing the dosage of each coagulant improved the removal of organic substances (Fig. 6). Compared to Al-based coagulants, $FeCl_3$ was less effective in removing UV-active organics within all the applied dosage ranges (Fig. 6b). Dosing PACl achieved the most significant reduction of both DOC content and UV_{254} absorbance at neutral pH range (Table 3), indicating that PACl is superior over the monomeric coagulants in removing these organics [14].

The performance of the UF pilot plant in terms of operating time under different coagulant conditions is summarized in Fig. 7. The average SE water quality for each experiment is presented in Table 3. The results show that under any coagulation condition there was significant improvement of the UF performance compared to filtering raw SE directly. Nevertheless, the effect on TMP development is different with respect to the coagulant type and dosage. Except at a dosage of 0.074 mmol Me^{3+}/L by using $AlCl_3$ (interpretation in the following paragraph), $FeCl_3$ performed generally better than $AlCl_3$ and PACl in TMP control. Within the explored dose range, increasing $FeCl_3$ obtained generally a progressive positive effect on fouling control. Although employing PACl achieved the highest removal of protein-like biopolymers (Fig. 3), DOC and UV-active organics (Fig. 6), this selection presented the lowest effect on TMP control at each dosage level compared to using the other two coagulants.

With respect to $AlCl_3$, it appears that adding more coagulant resulted in some increase of operating time of the UF pilot plant. The unexpected longer duration achieved at 0.074 mmol Al^{3+}/L than at a higher dosage can be attributed to significant feedwater quality variation. Due to heavy precipitation, lower biopolymer concentration and conductivity than usual in the feedwater was recorded during that period (Fig. 8a and b). The dilution effect of rainwater led to a reduced foulant load to the membrane [3] and enhanced backwash efficiency because of decreased ion strength (Fig. 8b [26]).

3.3. *Mechanisms involved in fouling phenomena and its control*

Chemical cleaning effect (NaOH/NaOCl followed by H_2SO_4) on the fouled membrane under different coagulation conditions is compared in Fig. 9. It is evident that when a membrane was fouled by filtering SE without coagulation, around 90% of the permeability could be recovered by using NaOH (pH 12) and NaClO (active Cl 60 mg/L). Using H_2SO_4 (pH 2) the permeability was further improved slightly. These phenomena indicate that fouling was mostly caused by organic substances instead of by inorganic materials [22]. When membranes were fouled during the application of $FeCl_3$ as a coagulant, fouling seemed to be more resistant to chemical cleaning as the permeability recovery was only 75% (Fig. 9). H_2SO_4 showed a little higher effect on foulant removal compared to its performance in cleaning SE fouled membranes, implying increased contribution of inorganic materials to

Table 3
Secondary effluent water quality during pilot-scale experiments.

Coagulant	$FeCl_3$				$AlCl_3$				PACl			
	0[a]	0.037[a]	0.074[a]	0.148[a]	0[a]	0.037[a]	0.074[a]	0.148[a]	0[a]	0.037[a]	0.074[a]	0.148[a]
Biopolymer [mg C/L]	0.51 $n = 1$	0.56 ± 0.1 $n = 12$	0.54 ± 0.1 $n = 10$	0.54 ± 0.1 $n = 21$	0.46 ± 0.05 $n = 2$	0.59 ± 0.1 $n = 11$	0.5 ± 0.07 $n = 12$	0.55 ± 0.06 $n = 11$	0.99 $n = 1$	0.77 ± 0.2 $n = 7$	0.85 ± 0.1 $n = 9$	0.79 ± 0.1 $n = 7$
C/N in biopolymer	n.a.	n.a.	n.a.	4.5 ± 1 $n = 21$	n.a.	5.5 ± 0.9 $n = 11$	n.a.	n.a.	5.6 $n = 1$	5 ± 0.4 $n = 7$	5.3 ± 0.5 $n = 9$	5.3 ± 0.4 $n = 7$
Conductivity [μS/cm]	1223 ± 11	1220 ± 35	1206 ± 49	1132 ± 189	1232 ± 8	1178 ± 44	1159 ± 116	1267 ± 21	916 ± 45	1078 ± 159	1078 ± 134	1150 ± 116
Temperature [°C]	22.2 ± 0.1	22.3 ± 0.2	21.8 ± 0.3	17.7 ± 1	19.8 ± 0.1	16.2 ± 0.3	16.6 ± 0.8	19.7 ± 0.6	18.2 ± 0.1	20.6 ± 0.5	20.7 ± 0.8	20.4 ± 0.7
pH	7 ± 0.02	7.3 ± 0.1	7.3 ± 0.05	7 ± 0.2	7 ± 0.04	n.a.	6.8±0.1	7.1 ± 0.03	6.8 ± 0.01	6.85±0.05	6.82 ± 0.06	6.74 ± 0.06

Conductivity, temperature and pH were measured automatically at a frequency of each hour, $n > 20$ for each experiment, biopolymer concentration was analyzed once every operating day. n.a.: not analyzed due to the lack of OND detector during that period.

[a] Dose [mmolMe^{3+}/L].

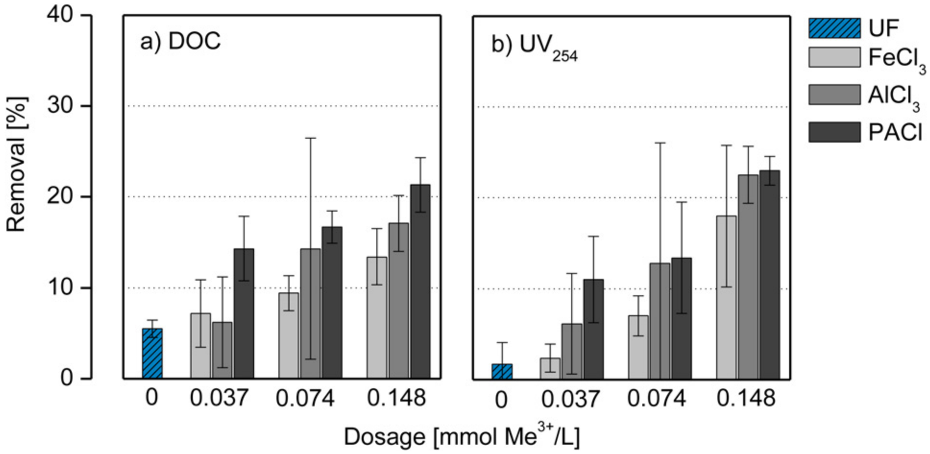

Fig. 6. Pilot results of the removal of DOC and UV_{254}-containing substances with and without in-line coagulation by UF ($n = 2–5$ under each dosage condition).

membrane fouling. The most significant difference in permeability recovery by using NaOH/NaClO and H_2SO_4 appeared in cleaning the membranes fouled in filtering PACl coagulated water. Using base and oxidant the permeability can only be regained to 60% of its original value, while acid cleaning increased the overall recovery to above 90%. Under a higher coagulant dosing level, more significant cleaning effect using acid can also be achieved. This result indicates that inorganic materials are important components in the fouling layer.

The contribution of the coagulant hydrolysis products or precipitates to fouling was investigated using multi-cycle membrane filtration test. The results show that all of these coagulants in salt solution lead to irreversible attachment to the membrane (Fig. 10). At a similar dosage (0.037 mmol Me^{3+}/L), PACl led to the most significant flux decline. The correspondingly formed fouling was also mostly irreversible (Fig. 10).

Noting that the experiments were conducted in neutral pH range, the flux decline and irreversible attachment caused by different coagulants can be related to the substances formed in coagulation under this condition. With respect to the monomeric coagulants, it is evident that both Fe and Al salt form precipitates at neutral pH, in which amorphous metal hydroxides are the major components [27,28]. These material present relatively low fractal dimension (the shape of the flocs is of lower complexity) [29], porous structure, large size [27] and close to zero charge at neutral pH range [28]. Although their accumulation on membrane surface leads to flux decline, the formed fouling is readily removable because of the comparatively loose cake structure and low interaction strength with the membrane (low static electronic attraction). In the present experiment, $AlCl_3$ related precipitates showed higher fouling effect than that of $FeCl_3$. This can be attributed to the specific character of the partly pre-hydrolyzed Al products (basicity 30%, Table 2). As reported, pre-hydrolyzation can form certain Al species such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, namely Al_{13} [30], which are of high density and charge intensity. They form a dense cake layer with low reversibility during membrane filtration [14]. With respect to PACl, it is a highly pre-hydrolyzed coagulant (basicity 80%, Table 2). A larger amount of Al_{13} polymers and clusters are expected to form in water than by using the partly pre-hydrolyzed $AlCl_3$ [31]. The correspondingly formed fouling is reasonably of decreased reversibility.

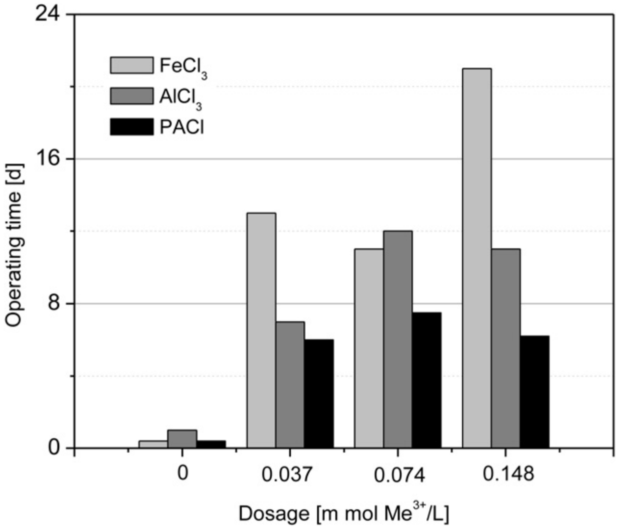

Fig. 7. Operating time of the UF pilot plant under different coagulation conditions (operating time refers to the duration from starting the operation of the UF pilot plant until the TMP reached 600 mbar).

Fortunately after these tests, the lost permeability of the membrane can be completely recovered using acid (HCl, pH 2, data not shown). This confirms that dissolving metal related precipitates using acid results in decomposition of the irreversible attachment caused by these substances (e.g., Al_{13} [32]).

In relation to the results presented above, it appears that fouling phenomenon in UF of coagulated SE is a co-effect of different fouling-causing/control mechanisms. The improvement of the performance of UF by in-line coagulation is a result of: (i) removal of critical foulants (biopolymers, Fig. 3), and (ii) modification of size distribution of foulants to larger particles and subsequent formation of loose fouling layer (Fig. 5). However, fouling is inevitable because: (a) residual foulants interact with membrane and (b) hydrolysis products or precipitates formed during coagulation (Figs. 9 and 10) lead to irreversible accumulation on membrane. TMP control effect under different coagulation conditions (coagulant type and dose) can be interpreted considering these items (Table 4).

For instance, the superior effect of dosing $FeCl_3$ on TMP control over using $AlCl_3$ and PACl can be understood with respect to foulant removal and character of flocs formed. At low dosage (0.037 mmol Me^{3+}/L), $FeCl_3$ removed more foulants (Figs. 2 and 3) than the other two coagulants through complexation and/or adsorption [33], possibly due to higher hydrolysis and precipitation rate than that of

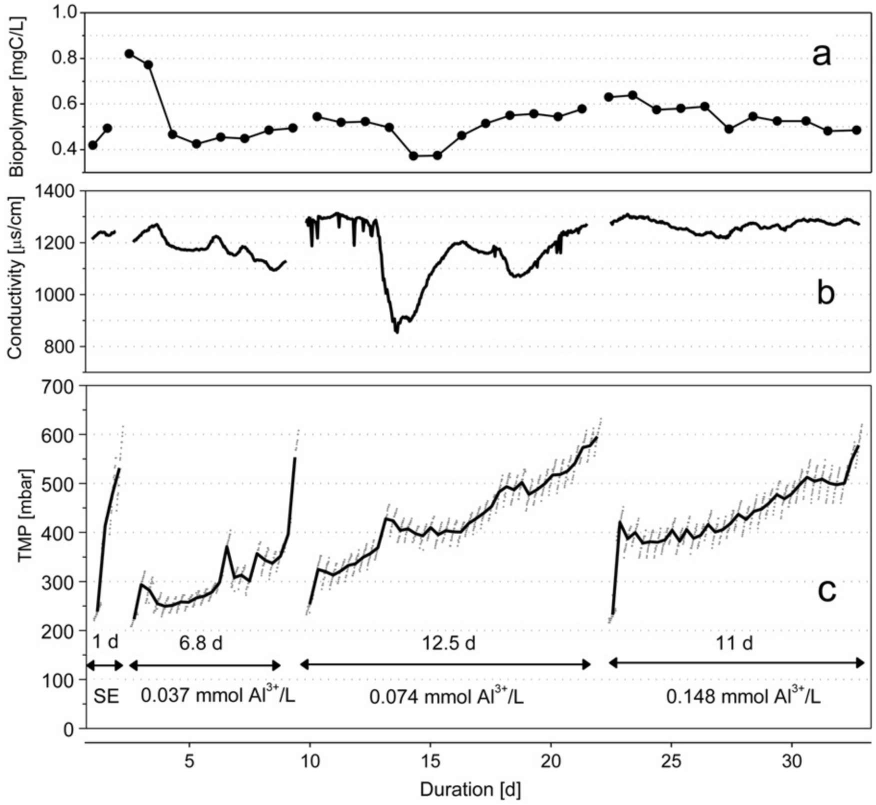

Fig. 8. Variation of (a) biopolymer concentration, (b) conductivity, and (c) TMP development of the UF pilot plant by in-line dosing $AlCl_3$.

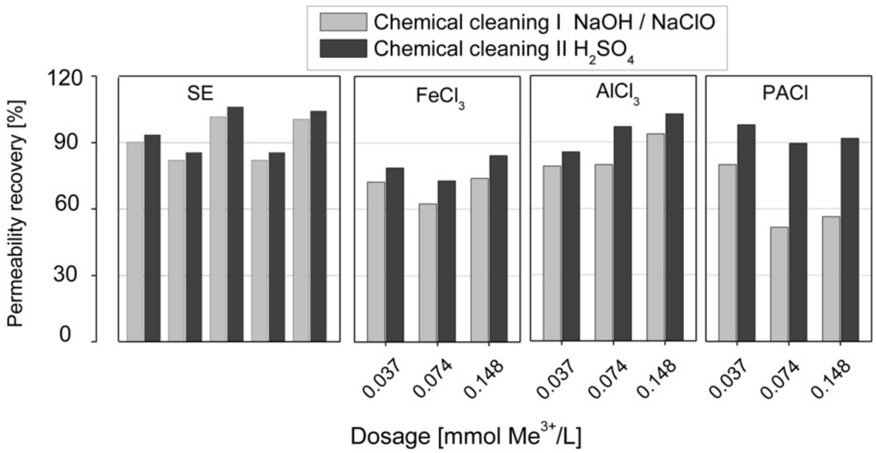

Fig. 9. Permeability recovery of UF membranes after chemical cleaning.

alum ones [28]. The interaction between $FeCl_3$ related flocs (contain adsorbed/complexed organics and metal-based precipitates, mainly metal hydroxides [31]) and membrane is weaker than that of Al-based species (Fig. 10).

Possibly due to increased formation of hydrolysis products/precipitates and their unselective reaction with organic molecular functional groups [34], increasing dosage resulted in similar foulant removal using these three reagents (Fig. 2).

Table 4
Attribution of different items to fouling phenomena by in-line coagulation with UF.

	On the removal of organics				On filterability of water	On the interaction with membrane	On TMP control as a co-effect	Role of acid in chemical cleaning
	BP	C/N in BP	DOC	UV_{254}				
$FeCl_3$ ↑	+	0	+	+	+	−−	++	+
$AlCl_3$ ↑	++	+	+	++	+	−	+	+
PACl ↑	++	+++	+	++	++	++	−	+++

↑: increase of dosage (from 0.037–0.148 mmol Me^{3+}/L); 0: no effect; + to +++: degree of effect increases from ‘have effect’ to ‘have very significant effect’; − to −−: degree of effect decreases from ‘some decrease’ to ‘significant decrease’; BP: biopolymers.

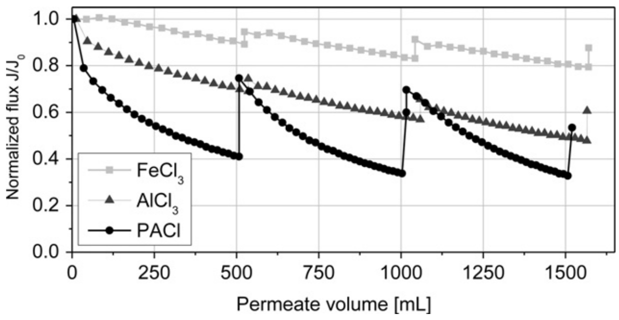

Fig. 10. Fouling effects of the tested coagulants in UF (dosage of 0.037 mmol Me^{3+}/L in salt solution at controlled neutral pH range).

Thus, TMP control depends mainly on the character of the flocs.

For monomeric metal salts at close to neutral pH, the presence of porous metal hydroxides (e.g., $Al(OH)_3$ [30]) in flocs leads to a looser and more readily removable fouling layer compared to polymeric coagulants (reflected by lower specific resistance [14]). At an increased dosage, Fe-related flocs present larger mean floc size and decreased fractal dimension while that of Al-formed flocs can only be slightly changed [15,29]. This may lead to the difference of deposition layer formed by different flocs, and thus the reversibility of the fouling layer. Although the fractal dimension of the flocs decreases at increased PACl dosage [32], the reason that this had little effect on improving TMP control might be due to the formation of dense cake layer and high residual charge effect of PACl-related flocs. These factors offset the positive effect on foulant removal and lead to more severe irreversible attachment.

4. Phosphorus removal

Lab-scale results of total phosphorus and ortho-phosphate removal are shown in Fig. 11. It can be seen that the UF membrane alone can remove some phosphorus because part of them are in colloidal form. A dosage of any kind of coagulants improved the removal. At each dosage level the most significant removal was achieved by using $FeCl_3$, while the lowest by using PACl. Dosing

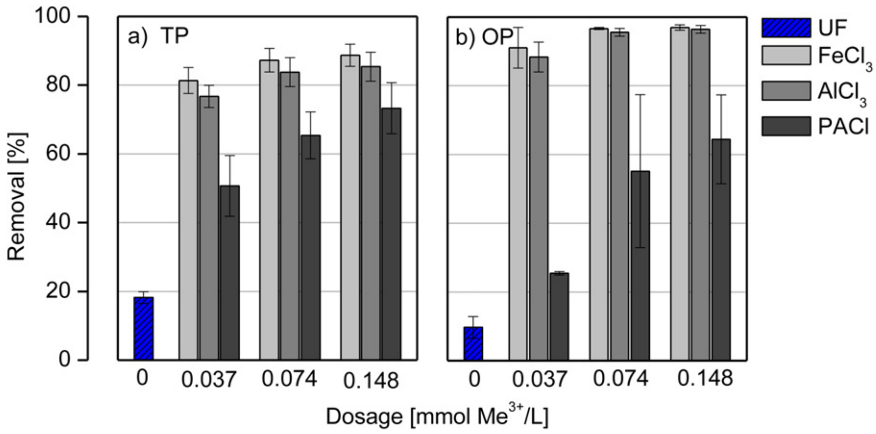

Fig. 11. Lab-scale results of the removal of: (a) TP and (b) OP under different coagulation conditions (n = 3–11 under each coagulation condition). TP: total phosphorus; OP: ortho-phosphate.

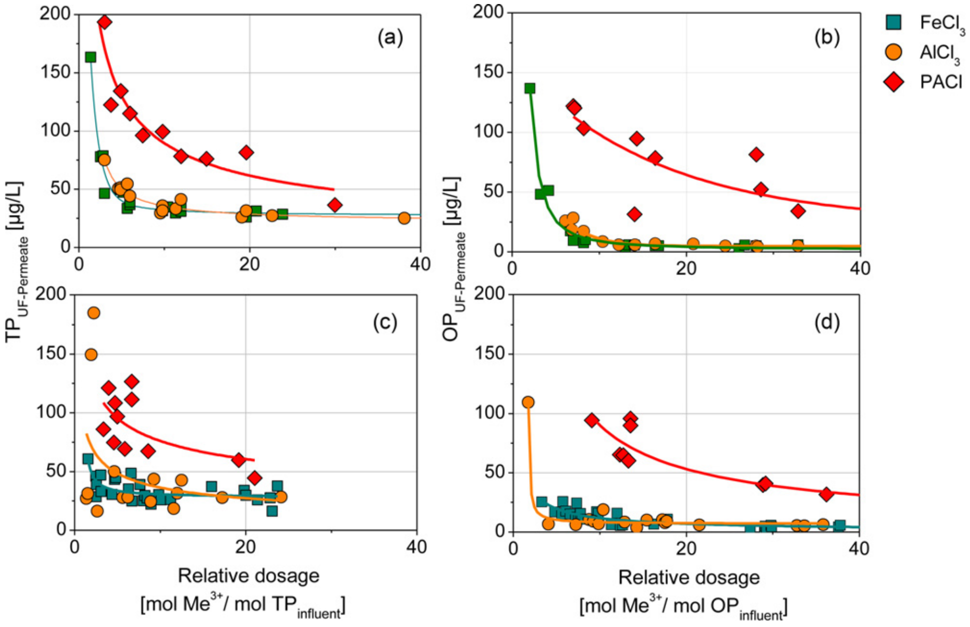

Fig. 12. Relationship between relative dosage of coagulant to P content and residual P concentration in UF permeate: lab-scale results in terms of: (a) TP and (b) OP, pilot-scale result in terms of (c) TP and (d) OP.

PACl from 0.037 to 0.148 mmol Me^{3+}/L is obviously not a suitable option to remove phosphorus from treated wastewater.

The relationship of relative coagulant dosage (mol Me^{3+} to mol TP or OP in feedwater) and phosphorus concentration in permeate was investigated in lab-scale UF filtration tests. Fig. 12a and b shows that when the relative dosage (using $FeCl_3$ and $AlCl_3$) is higher than 4, TP concentration in the permeate can be kept below 50 μg/L. The relative dosage obtained from lab-scale tests were partly confirmed by pilot experiments (Fig. 12c and d). The calculation based on long-term monitoring shows that a relative dosage of 2.5 mol/mol (for $FeCl_3$ and $AlCl_3$ to TP in feedwater) is enough to keep TP concentration lower than 50 μg/L in permeate. This value is lower than that obtained from the lab tests. One of the possible reasons might be the different MWCO of the membranes applied in lab- and pilot-scale experiments (Sections 2.3.1 and 2.3.2). Moreover in lab tests, each membrane was new for each experiment. The UF pilot plant was operated for at least several days. The accumulated fouling layer may also contribute to the removal of phosphorus.

5. Conclusions

The present work investigated fouling control effects and phosphorus removal by applying in-line coagulation prior to UF using $FeCl_3$, $AlCl_3$ and PACl. According to both lab- and pilot-scale results, the following conclusions can be made:

1. In-line coagulation using $FeCl_3$, $AlCl_3$ and PACl can remove biopolymers from treated wastewater and improve the filterability of the water sample effectively. Generally, an increase in dosage from 0.037 to 0.148 mmol Me^{3+}/L leads to higher biopolymer removal effect. Compared to the other two coagulants, PACl prefers to remove protein-like material than other fractions in biopolymers.
2. In-line coagulation slows down TMP development significantly in UF of treated wastewater. By using monomeric $FeCl_3$ and $AlCl_3$ at neutral pH, an increase of the dosage generally leads to a better performance of UF (0.037 to 0.148 mmol Me^{3+}/L). For PACl, an increasing dosage in this range has no obvious influence on TMP control effect.
3. Fouling control is determined by organic foulants removal, property of fouling layer structure and the adherence of hydrolysis products/precipitates to the membranes using in-line coagulation combined with UF process. Using $FeCl_3$ can achieve better fouling control effect than dosing $AlCl_3$ and PACl in the present working conditions.
4. Phosphorus removal effects obtained through lab-scale experiments can reflect the performance of coagulation in pilot-scale tests. $FeCl_3$ is considered a suitable coagulant for fouling control and simultaneous phosphorus removal during in-line coagulation with UF.

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