



## Influence of phosphorus precipitation on permeability and soluble microbial product concentration in a membrane bioreactor

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### HIGHLIGHTS

- ▶ MBR pilot-plant with flat sheet membrane fed by raw municipal wastewater was monitored for 2 years.
- ▶ Impact of coagulant dosing on flux, nutrient removal, SMP and filtration cake was evaluated.
- ▶ Coagulant dosing resulted in a significant decline in carbohydrates and protein concentrations.
- ▶ High PO<sub>4</sub>-P, COD and NH<sub>4</sub>-N removal efficiency was achieved over periods with coagulant dosing.
- ▶ The main contributors to inorganic fouling were compounds of elements Ca, Si and Fe.

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### ABSTRACT

Many articles have been published on coagulant dosing in membrane bioreactors, though few have been long-term studies examining the treatment of real wastewater. This study summarises the results of a membrane bioreactor pilot-plant (flat sheet membrane, nominal pore size 0.03 μm) that treated real municipal wastewater for two-years. Both influence of phosphorus precipitation by ferric sulphate on membrane permeability (flux decrease) and soluble microbial product concentration (especially on carbohydrates and proteins) were monitored. Flux decrease over work cycles lasting several months without phosphorus precipitation were compared to two periods with precipitation. X-ray elemental diffractometry of the filtration cake showed differences in the main contributors to inorganic fouling, with decreases in Ca and Si during operation with coagulant addition, and an increase in Fe.

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### 1. Introduction

A membrane bioreactor (MBR) includes a membrane separation process into the standard activated sludge process. Inclusion of this

*Abbreviations:* C, carbohydrates; COD, chemical oxygen demand; EPS, extracellular polymeric substances; F/M, food to microorganisms ratio; HS, humic substances; IR, internal recycle;  $L_p$ , permeability; MLSS, mixed liquor suspended solids; MLVSS, mixed liquor volatile suspended solids; MBR, membrane bioreactor; NH<sub>4</sub>-N, ammonia nitrogen; NO<sub>3</sub>-N, nitrate nitrogen; P, proteins; PES, polyethersulphon; PFS, polymeric ferric sulphate; PFC, polymeric ferric chloride; PO<sub>4</sub>-P, phosphate phosphorus; SMP, soluble microbial products; SRT, sludge retention time;  $Y_{obs}$ , observed biomass yield;  $W_{org}$ , proportion of organic fraction; WWTP, wastewater treatment plant.

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process eliminates the weakest link in activated sludge wastewater treatment, making effluent quality independent of biomass settling characteristics. MBRs have several important advantages over conventional activated sludge systems, including high effluent quality, ease of operation and high bacteria removal efficiency.

MBR technology currently faces a number of research and development challenges, however, including membrane fouling, high membrane cost and the need for pretreatment. Membrane fouling increases operational costs and shortens membrane lifetime (Yang et al., 2006). Further, as the MBR mixed liquor includes both living organisms and their metabolites, the fouling is more complex than that of a simple membrane separation processes (Bae and Tak, 2005). Studies aimed at minimising membrane fouling can be divided into several groups: (i) those focused on the characteristics of the mixed liquor that affect membrane fouling, including its morphological characteristics (Lee et al., 2003; Gómez

et al., 2012); (ii) soluble microbial products – SMP and extracellular polymeric substances – EPS (Dvořák et al., 2011; Holba et al., 2012); and (iii) addition of flux enhancers, such as organic flocculants or inorganic coagulants (Dizge et al., 2011; Ngo and Guo, 2009).

The characteristics of activated sludge can be altered by dosing with organic flocculants, such as flux enhancers, or by addition of inorganic coagulants, such as aluminium or ferric salts (Le-Clech et al., 2006). While both aluminium and ferric coagulants are known to improve mixed liquor filterability (Wu et al., 2006), a decrease in oxygen uptake rate and inhibition of the activated sludge process have both been described by Surmacz-Gorska et al. (1996) following addition of aluminium salts. While the inhibiting effects of aluminium salts on release of phosphorus are characterised by chemical reactions, however, those affecting phosphorus uptake are influenced by biological effects (Liu et al., 2011). The influence of ferric salts on the nitrification process is negligible, with concentrations lower than  $40 \text{ mg L}^{-1}$  having no influence on simultaneous chemical precipitation of phosphorus (Liu et al., 2011).

Higher coagulation efficiency can be achieved using pre-polymerised coagulants such as polymeric ferric chloride – PFC (Jiang and Graham, 1998) or polymeric ferric sulphate – PFS; Wu et al. (2006) reporting PFS to be the most effective coagulant for membrane fouling control. Polymeric coagulants also have a positive effect on charge production and longer chain molecules, resulting in improved mixed liquor filterability; the optimal dose being defined Wu et al. (2006) as  $1.05 \text{ mM Fe}$ . Surplus polymeric coagulant, however, can lead to “colloidal restabilisation”.  $\text{Fe(III)}$  compounds are known to bridge negatively charged EPS functional groups, and also to promote an increase in floc size, density and shear force resistance (Li, 2005). In the Czech Republic, however, non-PFS is widely applied as a coagulant, hence the same form was chosen for this study.

In this study, the main aims of coagulant dosing were to minimise phosphorus concentrations in MBR effluent and to investigate the impact of precipitation products on flux decline; in part as detailed mechanisms of membrane fouling caused by  $\text{Fe(III)}$  compounds have yet to be classified. While many articles have been published about coagulant dosing in MBRs, most are based on laboratory-scale studies using synthetic wastewater (Zhang et al., 2008) or from short-term (few days) operation of a pilot-plant (e.g. Yang et al., 2011). This paper summarises results gained through two-years of MBR pilot-plant operation (four operational periods), during which actual municipal wastewater originating from a large agglomeration in central Bohemia was treated. In addition to coagulant dosing, impact on membrane fouling, nutrient removal efficiency, SMP concentration fluctuations and changes in filtration cake quality was also monitored.

## 2. Methods

### 2.1. Experimental set-up and operation

The MBR pilot-plant, which has a total volume of 510 L was operated for two years alongside a conventional municipal wastewater treatment plant – WWTP (central Bohemia, Czech Republic), allowing raw wastewater to be used as a feed. At the beginning of each operational period, activated sludge from the WWTP settling tank was used for inoculation of the MBR. Mechanical pre-treatment of the raw municipal wastewater consisted of filtration through fine 3 mm screens only. Main influent characteristics are summarised in Tables 1 and 2. The MBR was divided into two parts, i.e. anoxic and oxic sections (volume ratio 25% and 75%, respectively); the oxic section being equipped with fine bubble aeration (mean oxygen concentrations are provided in Tables 1 and 2).

The internal recirculation flow from aerobic to anoxic section was provided by airlift with average flow  $5 \text{ L min}^{-1}$ . Excess sludge was withdrawn periodically – according to the biomass concentration in the system. Separation of activated sludge was undertaken using a polyethersulphon (PES) flat sheet ultrafiltration membrane (nominal pore size  $0.03 \mu\text{m}$ ,  $6 \text{ m}^2$ ) immersed in the oxic MBR section. Filtration took place at a constant transmembrane pressure of 50 mbar, which resulted in a decrease in flux over time due to membrane fouling. The MBR was equipped with simultaneous phosphorus precipitation using a 41% solution of ferric sulphate; the solution being added to the mixed anoxic sections during the 3rd and the 4th operational periods. Basic pilot-plant operational characteristics are shown in Table 3.

### 2.2. Analytical methods

Both influent into and effluent from the MBR were tested for chemical oxygen demand (COD), ammonia nitrogen ( $\text{NH}_4\text{-N}$ ), nitrate nitrogen ( $\text{NO}_3\text{-N}$ ) and phosphate phosphorus ( $\text{PO}_4\text{-P}$ ). In addition, mixed liquor suspended solids (MLSS) were assessed gravimetrically. All parameters were measured in accordance with standard methods for water and wastewater examination (APHA, 2005).

Total EPS concentration was calculated as the sum of concentrations for four EPS groups: carbohydrate, humic substances, protein and DNA. SMP were analysed in the supernatant obtained by gravitational sedimentation. EPS in activated sludge were quantified following thermal extraction according to Morgan et al. (1990). Carbohydrates content was analysed using the method of Dubois et al. (1956), with the exception that 5% phenol was applied instead of 80% (Raunkjær et al., 1994). Protein was measured spectrophotometrically using the method of Lowry et al. (1951); and HS were measured according to Sharma and Krishnan (1966). Revised values for protein and HS concentrations were obtained using the method of Frølund et al. (1995). DNA was analysed using the method of Burton (1956).

## 3. Results and discussion

### 3.1. Influence of ferric sulphate dosing on effluent quality

The primary objective of the MBR pilot-plant was to minimise nutrient concentration in the effluent and increase nutrient removal efficiency. The pilot-plant was initially operated over two periods of 165 and 175 days without ferric sulphate dosing. Chemical characteristics of the influent and effluent over these periods, including removal efficiencies, are shown in Table 1. Very high COD and  $\text{NH}_4\text{-N}$  removal efficiency was achieved over these two periods at 96.8% and 97.5%, respectively, for COD and 97.9% and 87.1%, respectively, for  $\text{NH}_4\text{-N}$ . On the other hand, removal of phosphorus (in the form of orthophosphate), e.g. by biomass incorporation was found to be inefficient, at 23.3% and 54.7%, respectively. This led to a decision to undertake coagulant dosing. Though aluminium salts are known to have a positive impact on decreasing filamentous bacteria (Tandoi et al., 2006), a ferric coagulant was chosen due to its higher optimal coagulation pH, as well as its wide application in the Czech Republic. A non-PFS was used, though this may have resulted in a lower impact on increase in activated sludge floc size and less improvement in filterability. The optimal dosage of ferric sulphate solution ( $12.4 \text{ mg Fe L}^{-1}$ ) was calculated based on the mean incoming concentration of  $\text{PO}_4\text{-P}$  and hydraulic retention times observed over the two previous periods. A similar optimal dosage was reported by Yang et al. (2011), based on several batch tests using different dosages of PFC (5, 10, 15 and  $20 \text{ mg L}^{-1}$  of Fe); the final optimal dosage concentration being

**Table 1**  
Influent and effluent characteristics without ferric sulphate dosing (mean value with minimum and maximum in parentheses).

Period	1st			2nd		
	Influent (mg L <sup>-1</sup> )	Effluent (mg L <sup>-1</sup> )	Average removal effic. (%)	Influent (mg L <sup>-1</sup> )	Effluent (mg L <sup>-1</sup> )	Average removal effic. (%)
COD	250 (100; 830)	8.0 (<2; 20)	96.8	480 (230; 1100)	12 (6; 33)	97.5
NO <sub>3</sub> -N	1.4 (0.2; 6.8)	23 (5.3; 47)	1.2 (0.2; 5.6)	11 (2.0; 29)		
NH <sub>4</sub> -N	49 (13; 87)	1.0 (<0.03; 5.9)	97.9	42 (26; 64)	5.5 (0.1; 31)	87.1
PO <sub>4</sub> -P	5.6 (1.4; 12)	4.3 (1.8; 9.3)	23.3	5.2 (1.7; 9.0)	2.3 (0.2; 4.9)	54.7
SS	130 (58; 650)	<2.0	100	520 (270; 1150)	<2.0	100
	Oxic part	Anoxic part		Oxic part	Anoxic part	
O <sub>2</sub> (mg L <sup>-1</sup> )	3.9 (2.2; 7.2)	0.20 (0.03; 0.74)		2.2 (0.08; 5.5)	0.26 (0.03; 1.5)	
pH	7.1 (6.6; 7.5)	7.1 (6.7; 7.5)		7.0 (6.3; 7.5)	7.1 (6.8; 7.7)	
T (°C)	19.7 (16.9; 22.5)			20.0 (19.6; 21.5)		

ranked between 10 and 15 mg L<sup>-1</sup>. In contrast, Zhang et al. (2008) tested several Fe(III) concentrations between 0 and 1.6 mM (0–89.4 mg L<sup>-1</sup>) and, based on zeta potential, they found 1.2 mM (66.9 mg L<sup>-1</sup>) to be the optimal Fe(III) concentration. At this level, the neutralised sludge floc and colloids were able to attract each other through charge neutralisation, producing larger floc and improved mixed liquor filterability. Such high Fe(III) concentrations, however, can lead to precipitation of all phosphorus present in the mixed liquor, resulting in a lack of phosphorus for microorganism metabolism although there is some phosphorus released from its precipitate due to the equilibrium. However, the dissolution kinetics of phosphorus precipitate is slower and the necessary phosphorus concentrations for non-limited biomass growth can be insufficient compared to the utilization by microorganisms. Furthermore, considering high biomass concentration (about 15 g L<sup>-1</sup>) under which the MBR pilot-plant was usually operated, this fact is more pronounced.

The pre-calculated optimal ferric sulphate dosage of 12.4 Fe mg L<sup>-1</sup> was used throughout the 3rd period. This had a positive impact on phosphorus removal efficiency (Tables 1 and 2), which increased to 84.7% compared with 23.3% (1st period) and 54.7% (2nd period). On the other hand, COD removal efficiency decreased to 90.6% compared with 96.8% (1st period) and 97.5% (2nd period). Similarly, NH<sub>4</sub>-N removal efficiency dropped to 84.7% compared to 97.9% (1st period) and 87.1% (2nd period). The higher COD and NH<sub>4</sub>-N effluent concentrations can be explained by a generally lower mixed liquor pH value and higher fluctuations (5.5–7.9; Tables 1 and 2). Different results were obtained by Yang et al. (2011), who observed no negative impact on COD removal efficiency (86.6% with and 82.7% without dosing) or NH<sub>4</sub>-N removal efficiency (98.8% with and 98.5% without dosing) using PFC, explainable through lower pH fluctuations (7.0–8.0) compared with those noted for the 3rd period above.

Based on these observations, the amount of ferric sulphate solution used was decreased during the 4th period, starting with a half-dose of ferric sulphate solution (Fe(III) 6.2 mg L<sup>-1</sup>) in order

**Table 3**

Basic pilot-plant operational characteristics (mean values; MLSS – mixed liquor suspended solids, MLVSS – mixed liquor volatile suspended solids,  $W_{org}$  – proportion of organic fraction, HRT – hydraulic retention time, SRT – sludge retention time).

Characteristic	Period			
	1st	2nd	3rd	4th
MLSS (g L <sup>-1</sup> )	14.9	14.4	18.0	15.7
MLVSS (g L <sup>-1</sup> )	11.7	11.4	12.1	11.2
$W_{org}$ (%)	79	79	67	71
HRT (h)	7.1	8.9	6.5	6.4
SRT (d)	80–90	60–70	70–80	60–70
F/M ratio $g_{COD} g_{MLVSS}^{-1} d^{-1}$	0.09	0.14	0.29	0.38
$Y_{obs} (g_{MLVSS} g_{removed}^{-1} COD)$	0.21	0.18	0.11	0.09

to obtain more information about impact on phosphorus precipitation efficiency, SMP concentration and decline in permeability ( $L_p$ ). This resulted in a slight decline in PO<sub>4</sub>-P removal efficiency, falling from a mean level of 85.6% in the 3rd period to 75.9% in the 4th.

This decrease, however, was not as low as could be expected. During the 4th period, the lowest dose of ferric sulphate utilized could potentially react with PO<sub>4</sub>-P preferentially. In contrast, an increase in the number of side-reactions could occur, especially with the hydroxyl and carboxyl SMP groups, owing to higher dose of coagulant (3rd period). This could also explain the decline in EPS concentration detected during the 3rd period. According to Galarneau and Gehr (1997), Fe(III) reacts rapidly not only with orthophosphates but also with hydroxyl ions. The decline in Fe(III) dosage led to an increase in mean pH from 6.92 and 6.98 (oxic and anoxic sections, 3rd period) to 7.37 and 7.48 (4th period). As a result, a slight increase in COD removal efficiency was also observed. On the other hand, NH<sub>4</sub>-N removal efficiency declined significantly (Table 2) due to low temperature in the MBR pilot plant during the winter months (minimum winter temperature reaching just 12 °C). This mean temperature was significantly lower in comparison with previous operational periods when temperature

**Table 2**  
Influent and effluent characteristics with ferric sulphate dosing (mean value with minimum and maximum in parentheses).

Period	3rd			4th		
	Influent (mg L <sup>-1</sup> )	Effluent (mg L <sup>-1</sup> )	Average removal effic. (%)	Influent (mg L <sup>-1</sup> )	Effluent (mg L <sup>-1</sup> )	Average removal effic. (%)
COD	640 (190; 1260)	60 (10; 130)	90.6	810 (430; 1340)	64 (25; 91)	92.1
NO <sub>3</sub> -N	0.9 (<0.1; 2.7)	4.5 (<0.1; 18)	0.6 (<0.1; 1.5)	5.5 (<0.1; 11)	0.9 (<0.1; 2.7)	4.5 (<0.1; 18)
NH <sub>4</sub> -N	46 (11; 73)	7.1 (0.1; 47)	84.7	42 (10; 67)	16 (1.3; 38)	61.9
PO <sub>4</sub> -P	4.9 (1.6; 8.2)	0.7 (<0.002; 2.4)	85.6	3.6 (1.5; 6.2)	0.9 (0.5; 1.4)	75.9
SS	1420 (280; 9600)	<2.0	100	880 (400; 1730)	<2.0	100
	Oxic part	Anoxic part		Oxic part	Anoxic part	
O <sub>2</sub> (mg L <sup>-1</sup> )	3.4 (0.30; 7.5)	0.13 (0.06; 0.40)		2.1 (0.20; 4.2)	0.18 (0.04; 0.80)	
pH	6.9 (5.5; 7.9)	7.0 (6.4; 7.6)		7.4 (7.0; 7.8)	7.5 (7.0; 7.8)	
T (°C)	20.0 (16.7; 21.1)			14.2 (12.1; 16.3)		

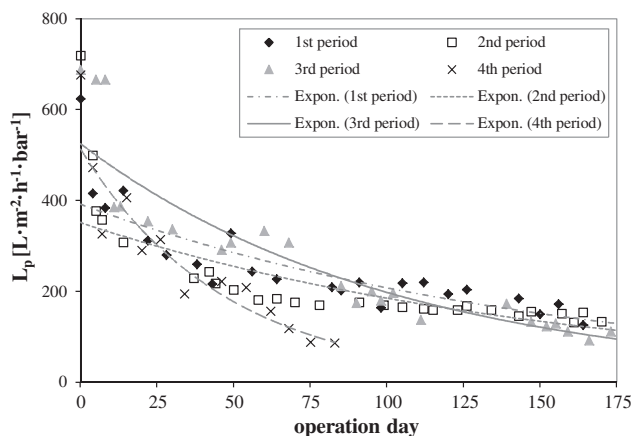


Fig. 1. Evolution of permeability decline over four operational periods.

fluctuated around 20 °C (Tables 1 and 2). The low temperatures result in lower nitrification rates because of strong negative relationship between nitrification rate and temperature (Henze et al., 2008).

Throughout the MBR pilot-plant operation, any significant influence of Fe(III) salt dosing on changes or occurrence of foaming in the system was not observed.

### 3.2. Interaction of SMPs and metal ions

Flux declined rapidly over the initial phase, especially over the first 10 operational days (Fig. 1). When the flux reached  $5 \text{ L m}^{-2} \text{ h}^{-1}$  (corresponding to an  $L_p$  of  $100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ), the membrane module was replaced. Dosing with ferric sulphate resulted in neither a clear positive nor negative impact. This may have been a result of higher MLSS concentrations (Table 3) compared with Yang et al. (2011), who operated an MBR pilot-plant with MLSS concentrations in the range of  $6.22\text{--}6.99 \text{ g L}^{-1}$ . Due to these higher MLSS concentrations, morphologic sludge characteristics had a stronger impact on mixed liquor filterability than coagulant presence. The decrease in membrane fouling frequency caused by coagulant addition was observed by Mishima and Nakajima (2009). They reported the positive effect of Fe(III) addition on the reduction of membrane fouling potential. However, Mishima and Nakajima (2009) used in their study synthetic wastewater mainly consisting of glucose and sodium glutamate, which can explain the difference in their observation and this study done with real wastewater.

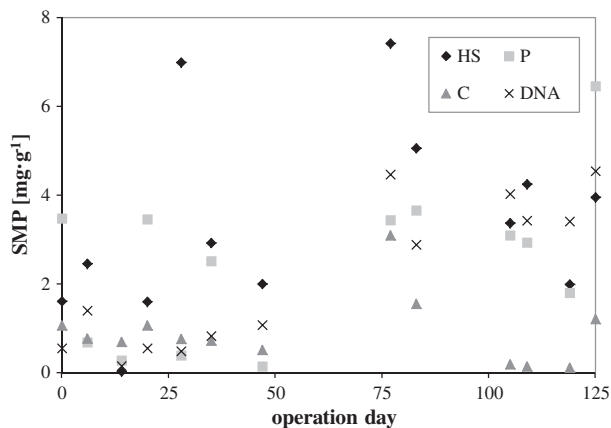


Fig. 2. Evolution of soluble microbial product concentration without Fe(III) dosing (1st period; HS – humic substances, P – proteins, C – carbohydrates).

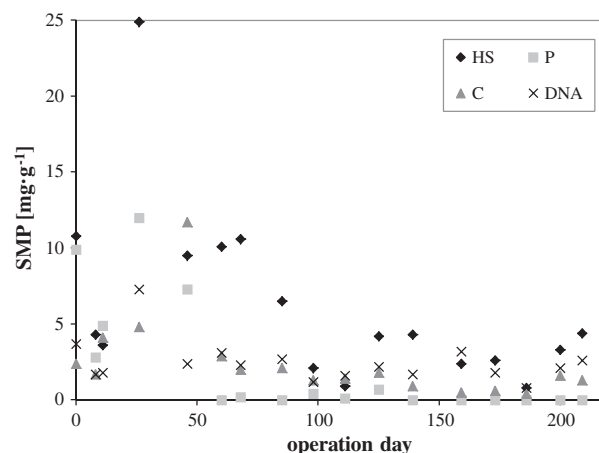


Fig. 3. Evolution of soluble microbial product concentration with Fe(III) dosing at  $12.4 \text{ mg L}^{-1}$  (3rd period; HS – humic substances, P – proteins, C – carbohydrates).

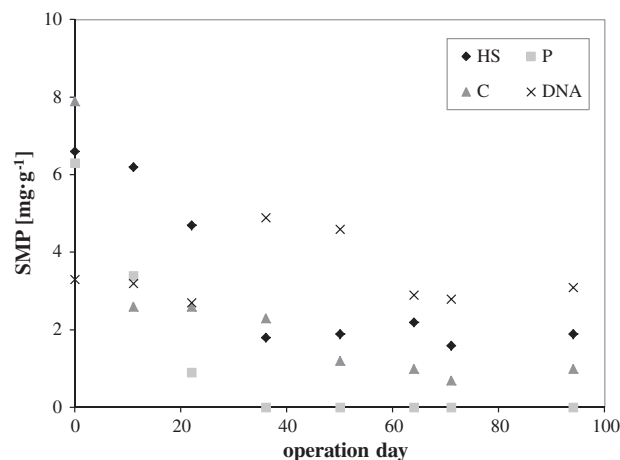


Fig. 4. Evolution of soluble microbial product concentration with Fe(III) dosing at  $6.2 \text{ mg L}^{-1}$  (4th period; HS – humic substances, P – proteins, C – carbohydrates).

The evolution of SMP concentrations in the mixed liquor supernatant during the 1st, 3rd and 4th operational periods are summarised in Figs. 2–4. Significant concentration fluctuations in all four SMP groups monitored (humic substances, carbohydrates, proteins and DNA) were observed over the period without ferric sulphate addition (1st period). Dosing with Fe(III) at  $12.4 \text{ mg L}^{-1}$ , which was initiated at the start of the 3rd period, resulted in a significant decline in carbohydrates and protein concentrations (Fig. 3). Mishima and Nakajima (2009) observed direct dependence of Fe(III) addition on protein concentration decrease. These authors explained observed decrease in permeate protein concentrations by coagulation and flocculation effect of Fe(III). The biopolymers contain large amounts of anion groups such as  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  (Razska et al., 2006; Meng et al., 2007). The Fe(III) was easily precipitated and was able to bridge the deposit biopolymers, resulting in a dense cake layer (Yang et al., 2011). A similar situation was reported by You et al. (2006), who reported problems with inorganic fouling caused by  $\text{Ca}^{2+}$ . He et al. (2011) also noted Mg, Al, Ca and Fe as being major contributors to inorganic fouling. The possibility of a reaction between Fe(III) and SMPs, and their probable retention on the membrane, was confirmed by analysis of EPS in the filtration cake. This analysis was performed after termination of the 1st and 3rd periods, the results of which are summarised in Table 4. By the 3rd period, content of total EPS was almost double at  $116.0 \text{ mg g}^{-1}$  (compared to  $68.3 \text{ mg g}^{-1}$  in

**Table 4**  
Extracellular polymeric substance content in filtration cake ( $\text{mg g}^{-1}$ ) following operation with and without Fe(III) dosing.

EPS group	Without Fe(III)		Without Fe(III)	
	Loosely bound	Tightly bound	Loosely bound	Tightly bound
Carbohydrates	3.46	6.68	8.26	27.3
Humic substances	4.10	13.9	9.06	20.0
Proteins	7.59	14.3	3.41	31.9
DNA	6.53	11.8	7.10	8.96
SUM	21.7	46.6	27.8	88.2

**Table 5**  
Overview of elements in the filtration cake (%), analysed using X-ray elemental diffractometry.

Element	Ca	Si	Fe	P	Al	S	K	Ti	Mg	Other
After 1st period	25.9	21.8	17.5	9.2	8.7	5.6	3.4	1.9	1.3	4.6
After 3rd period	18.6	19.7	26.9	5.4	9.5	10.8	3.0	1.4	1.1	3.4

the 1st period), and carbohydrate levels were almost three times higher at  $35.5 \text{ mg g}^{-1}$  (compared to  $10.1 \text{ mg g}^{-1}$ ). Reaction of the SMP with Fe(III) increased its contribution in the filtration cake layer (Table 5), with content increasing from 17.5% to 26.9% by the 3rd period. The effect of Fe(III) on SMP was confirmed by observation of the mixed liquor during the 4th period. At the beginning of this period, and after the drop in Fe(III) dosage to  $6.2 \text{ mg L}^{-1}$ , a slight increase in SMP concentration and an increase in carbohydrates was observed (Fig. 4). The influence of ferric salts on SMP removal was also investigated by Mishima and Nakajima (2009), who found that the quantity of SMP removed increased due to a positive charge in the Fe(III).

Despite many previous authors reporting a positive effect of coagulant presence on membrane  $L_p$  (e.g. Song et al., 2008; Ji et al., 2010), there was no clearly confirmed effect in this study. This was probably a result of the significantly lower optimum dose for Fe(III) used in this study compared to previous studies (i.e. 200 and  $500 \text{ mg L}^{-1}$ , respectively), as well as the relatively high activated sludge concentrations ( $13.4\text{--}16.9 \text{ g L}^{-1}$ ). Dosing with high concentrations of ferric salt is known to result in a significant decrease in pH and total precipitation of phosphorus. A lack of phosphorus would result in serious problems for the metabolism of microorganisms and, therefore, for the whole wastewater treatment process; emphasising the need to maintain sufficiently high phosphorus concentrations in the system at all times.

While not undertaken in this study, a further convenient step might include testing of PFS and comparing the results presented in this study with data obtained following a change in coagulant type. The results could indicate the influence of polymeric chains on the various monitored parameters.

### 3.3. Role of inorganic components in the fouling process

The results of X-ray elemental diffractometry (Table 5) indicate that dosing with Fe(III), and inorganic matter in general, plays an important role in the membrane fouling process. As X-ray elemental diffractometry cannot detect elements with an atomic number lower than 9, elements such as C, O, N are not included in these results. A comparison of the results obtained during analysis of the filtration cake layer after the 1st and 3rd operational periods indicates a significant increase in Fe(III) content (17.5% and 26.9%, respectively) caused by both dosing with ferric sulphate and its reaction with EPS, as described in earlier. In addition to the high Fe(III) content, compounds including such elements as Ca, Si, P, Al, S, K, Ti and Mg were also identified as main contributors to inorganic fouling. Very similar results were published by Meng et al. (2007), who identified P, Si, Ca, S, K, Fe, Al and Mg as major

inorganic components of the filtration cake layer. Phosphorus was quantified as the main contributor to fouling in the study by Meng et al. (2007) due to the absence of Fe(III) dosing; though aside from this, the results are comparable. In contrast, Zhu et al. (2011) analysed membrane foulants in a full-scale MBR being used for treatment of supermarket wastewater. They identified Mg, Ca, Na, Al, K and Si as the main contributors to formation of fouling layers. In the study of Zhu et al. (2011), Mg was identified as the main contributor, being found at concentrations higher than those in both this study and that of Meng et al. (2007). One of the explanations for this may lie in the differing source of wastewater, i.e. supermarket wastewater in the case of Zhu et al. (2011) and municipal wastewater in both this study and that of Meng et al. (2007). Incoming municipal wastewater is highly likely to contain higher concentrations of Fe(III) and Si(IV), probably released from old water supply pipes and the sewage system, respectively. Yang et al. (2011) found increased Fe(III) content in membrane cake layer. They dosed  $10\text{--}15 \text{ mg L}^{-1}$  Fe(III) as PFC into the MBR pilot-plant (of a similar configuration used in this study) treating real municipal wastewater. The findings by Yang et al. (2011) are in agreement with the results of this study (Table 5).

## 4. Conclusions

Impact of coagulant dosing on SMP decrease, especially on carbohydrates and proteins, was observed.

Without Fe(III) dosing were achieved minimum  $L_p$  values after 175 days. Similar results were obtained during dosage with Fe(III) at concentration  $12.4 \text{ mg L}^{-1}$ . Dosage at  $6.2 \text{ mg L}^{-1}$  Fe(III) during the 4th operational period resulted in minimum  $L_p$  being achieved twice as quickly.

Following coagulant dosing, EPS concentrations in the filtration cake layer were twice as high as those found during periods without phosphorus precipitation (i.e. with no coagulant dosing).

The main contributors to inorganic fouling were compounds containing the elements Ca, Si and Fe.

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