



Inorganic characteristics of cake layer in A/O MBR for anaerobically digested leachate from municipal solid waste incineration plant with MAP pretreatment

Lijie Zhou^{a,b,*}, Wei-Qin Zhuang^c, Biao Ye^d, Yashika Gregory De Costa^c, Xin Wang^e, Ke Yu^f, Shan Yi^g, Shufang Yang^h, Siqing Xia^{e,*}

^a College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China

^b Shenzhen Academy of Environmental Sciences, Shenzhen 518001, China

^c Department of Civil and Environmental Engineering, University of Auckland, Auckland 1142, New Zealand

^d Shanghai Pudong Architectural Design & Research Institute, Shanghai 201204, China

^e State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China

^f School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen 518055, China

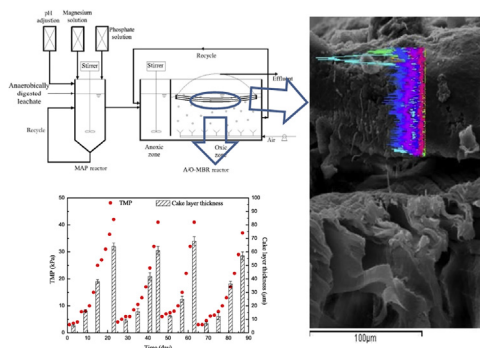
^g Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720-1710, USA

^h Shenzhen Municipal Design & Research Institute Co., Ltd, 3007 West Sungang Road, Shenzhen 518029, China

HIGHLIGHTS

- Inorganic insight into cake layer in MSWI leachate treatment system was studied.
- Anaerobically digested leachate with MAP pretreatment caused thicker cake layer.
- Residual Si and Al predominated the inorganic components in cake layer.
- Si-Al obviously accumulated at the end of cake layer due to high suction pressure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 April 2017

Received in revised form 14 June 2017

Accepted 15 June 2017

Available online 16 June 2017

Keywords:

Membrane fouling

Inorganic components

Anaerobically digested leachate from MSW incineration plant

Anoxic/oxic membrane bioreactor

ABSTRACT

Inorganic characteristics of cake layer in an anoxic/oxic membrane bioreactor (A/O MBR) for anaerobically digested leachate from a municipal solid waste incineration plant with MAP (magnesium ammonium phosphate precipitation) pretreatment was reported. During 90 days of operation, the A/O-MBR had formed a thick cake layer, causing severe fouling. BCR (European Community Bureau of Reference) results showed that Fe, Al, Ca, Mg, Si were the dominant inorganic components (especially residual Si and Al) in the cake layer. X-ray diffraction (XRD) analysis further presented that the cake layer contained complex inorganic substances with FeSiO_3 , CaAl_2O_3 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, CaCO_3 , CaPO_3OH , $\text{Mg}_2(\text{PO}_4)\text{OH}$, etc., while Si-Al crystal was the major inorganic component in the cake layer. Additionally, SEM-EDX showed a consistent distribution of inorganics along the front cross-section of the cake layer, indicating that the stable particles and metal ions led to the steady inorganic accumulation onto the membrane surface. However, it was revealed that high suction pressure aggravated the inorganic particle accumulation, especially for the Si-Al crystals, at the end of the cake layer.

© 2017 Elsevier B.V. All rights reserved.

* Corresponding authors at: College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China (L. Zhou).

E-mail addresses: pakerzhou@gmail.com (L. Zhou), siqingxia@gmail.com (S. Xia).

1. Introduction

Municipal solid waste (MSW) is a complex castoff consisting of food waste, building waste, paper, and plastic, that have been discarded by the public [1,2]. It has been reported that approximately 1.3 billion tons of MSW are generated per year, which is expected to increase to 2.2 billion tons per year by 2025 [3]. China makes up for around 13% of the world MSW production due to its rapid urbanization over the past three decades, which is becoming a major environmental concern for most Chinese cities [1,4]. Consequently, MSW treatment is a hot topic all over the world, especially in China. Although landfill is the traditional and principal MSW treatment technology that predominates over 65% of MSW treatment in China [1], incineration has been applied gradually and widely in the last decade due to its outstanding advantages (e.g. MSW reduction in volume, small footprint, etc.) [5–8]. In addition, large-scale incinerator plants are an attractive method to reduce the sharp increasing and non-classified MSW. About 31 million tons of MSW were treated with 109 MSW incineration plants in China (approximately 94,000 tons MSW/day) [9].

However, because of the high proportion of food wastes (with 45–65% of moisture) in the MSW of China, fresh MSW is needed to be stored in a waste bunker for a few days to leach the water for calorific value enhancement, leading to the generation of leachate (also known as “fresh leachate”) [4,10]. Compared with leachate from landfill, leachate generated in municipal solid waste incineration (MSWI) plants contains similar toxic pollutants, but at different levels, including high concentrations of organic compounds, ammonium content, and inorganic metal ions [4,11]. Additionally, each ton of MSW could produce over 200 L leachate [3], predicting that 94,000 tons of MSW will cause over 18,800 m³ leachate per day in China. Consequently, leachate from MSWI is a new environmental threat to the world, especially in China.

Currently, chemical precipitate, multi-parametric purification, adsorption techniques, and biological processes are widely applied for MSWI treatment [12–15]. Purification methods, such as micro-filtration, ultrafiltration, and reverse osmosis, are common methods carried out for treating MSWI [16]. Further treatment methods have also been researched targeting specific or hard to treat pollutants within MSWI. Xia et al. [17] indicated that Ca²⁺ in MSWI could be precipitated with CO₃²⁻, or SO₄²⁻. Kyriakopoulos et al. [18,19] reported that porous polymeric had a high adsorption for toxic pollutants, such as pesticides, which could be applied for special material removal in MSWI. Finally, it is widely accepted that biological processes perform well at high-strength organic loading with low operation costs, thus anaerobic digestion was considered as an effective and promising way for treating leachate from MSWI [2,4,15,20,21]. Lei et al. [22] and Ye et al. [14] reported that an anaerobic digestion reactor of up-flow anaerobic sludge bed (UASB) could effectively treat the leachate from MSWI. However, anaerobically digested leachate from MSWI still contains high concentrations of NH₄⁺-N, COD_{Cr}, and inorganic ions, and therefore, is an environmental threat which would require further consideration and treatment to be a viable and commercially used method.

Another area which has been rapidly gaining interest is the development of novel environmental options where waste can be utilized as a source of energy and feedstock [23–29]. Wu et al. [28] and Merino-Jimenez et al. [29] both used microbial fuel cells to utilize the electron transport during leachate biodegradation for renewable energy generation. Furthermore, studies have presented that MSWI leachate is an effective feedstock for methane production through anaerobic digestion [30–32]. In addition, due to high concentrations of ammonium and phosphate, MSWI leachate is widely used to recover MAP (magnesium ammonium

phosphate precipitation), which is an effective fertilizer for grass and trees [29,33].

Consequently, anaerobically digested leachate from MSWI is a promising tool to use as a method of MAP production [33] for the nutrient rich water for grass growth application, with advanced treatment. In addition, exchangeable fraction and reducible fraction of inorganic elements in MSWI, especially high concentrations of Ca²⁺, are recovery-capable for industrial raw material [34]. Parts of residual inorganic elements (such as struvite) are also considered to be recovered for industrial application [35]. Our previous work (Research fund of Tongji University: 20113083; Fig. S1) has built up a recovery system for MSWI, especially MAP production and nutrient irrigation for grass growth. The stream of the recovery system is pushed by gravity flow, and UASB is operated with anaerobic digestion to reduce system energy cost and improve methane production. Air supplement in the anoxic/oxic membrane bioreactor (A/O-MBR) is the major energy consumer in the system, comparatively, this recovery system for MSWI has a low-energy cost. In addition, the recovery system is a temperature-insensitivity process, whereby the system can be operated outdoors, despite temperature fluctuations. To ensure stability during operation, setting-up storage tanks between MAP and A/O-MBR was necessary for flux maintenance. Moreover, extra pumps are also needed for large-scale system operation to control high volume MSWI flux, and advanced treatment is also required for improvement in case of pollutant accumulation in soil. Ensuring that this recovery system (Fig. S1) is an effective reuse technology with low-energy cost and recoverable material production.

However, it was discovered that A/O-MBR had a severe fouling problem after MAP pretreatment, and the cake layer contained high concentrations of inorganic components. Furthermore, additional literatures [10,17,34] revealed that, compared with leachate from landfill, leachate from MSWI contained plenty of inorganic elements, such as calcium (Ca), silicon (Si), magnesium (Mg), iron (Fe), aluminum (Al) and sodium (Na). Therefore, inorganic components should potentially effect the fouling behavior, especially the inorganic structure of the cake layer, this requires further analysis.

This study aims to develop a fundamental inorganic insight into the cake layer of A/O-MBR for anaerobically digested leachate from MSWI after MAP pretreatment. A laboratory A/O-MBR was operated with anaerobically digested leachate, which was pretreated with MAP, for over 90 days to characterize the cake layer by various methods. The BCR (European Community Bureau of Reference) sequential extraction, XRD (X-ray diffraction), SEM-EDX (scanning electron microscopy-energy dispersive X-ray analyzer) were carried out to identify the inorganic structure of the cake layer.

2. Materials and methods

2.1. Set-up and operation

A laboratory-scale A/O-MBR (Fig. 1) with a working volume of 4.5 L (anoxic and oxic zone of 1.5 L and 3.0 L, respectively) was applied in this study after the MAP pretreatment. A polyvinylidene fluoride hollow fiber membrane module (total surface 0.02 m²; pore size 0.04 μm) (Litree Company, China) was installed at the middle of the oxic zone, while the constant flux was set at 1.5 mL/min with an intermittent suction mode (8 min ON/2 min OFF). Air was supplied continuously with a diffuser to maintain a dissolved oxygen (DO) range of 4–6 mg/L in the oxic zone, and a range of 0.15–0.3 mg/L DO in the anoxic zone. The recycle rate from the oxic to anoxic zone was kept at 400%. Trans-membrane pressure (TMP) was detected with a pressure gauge.

The anaerobically digested leachate applied in this study, was the effluent of UASB for fresh leachate from the MSWI in Changz-

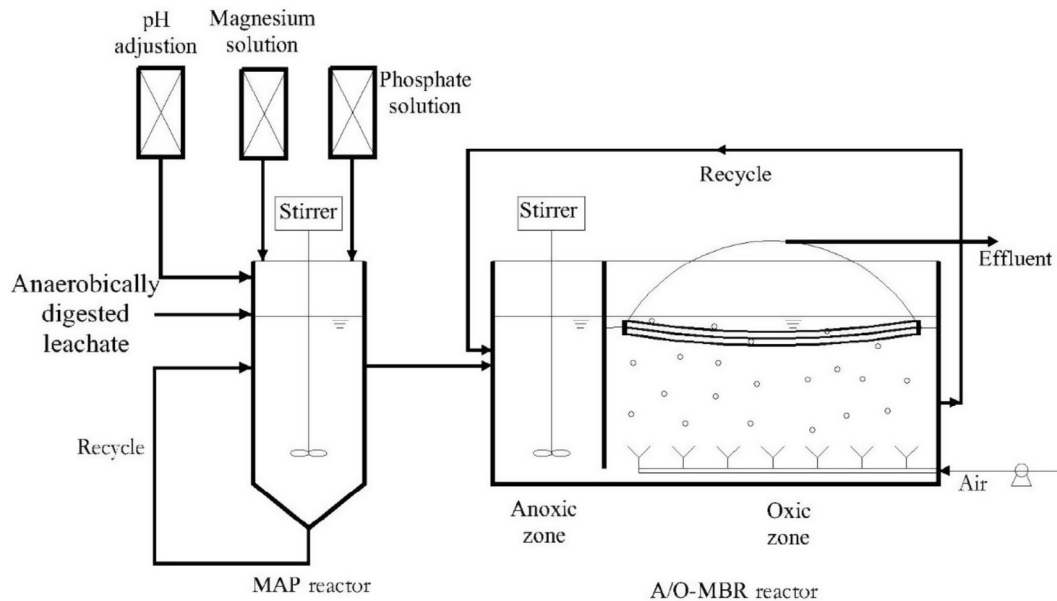


Fig. 1. A schematic of the A/O-MBR with MAP pretreatment used in this study. pH adjustment was applied to maintain MAP reactor in the range of pH 9–10 with NaOH solution.

Table 1
Reactor performance.

	Anaerobically digested leachate	Effluent of MAP reactor	Effluent of A/O-MBR reactor
NH ₄ -N (mg/L)	900–1400	130–240	15–20
TN (mg/L)	1000–1500	190–310	140–270
COD _{Cr} (mg/L)	1800–4100	1500–2400	400–600
TOC (mg/L)	240–800	210–770	60–110
TP (mg/L)	2.8–3.7	15–20	9–13
pH	7.8–8.7	7.5–8.4	7.4–8.0

MLSS 6.4 g/L; MLVSS 3.7 g/L; MLVSS/MLSS 57.8%.

hou (Jiangsu province, China). The leachate was first pretreated with a MAP reactor, then the effluent of the MAP reactor was applied as the influent of the anoxic zone of A/O-MBR. Characteristics of leachate and MAP reactor effluent are shown in Table 1. The inoculating biomass (5.0 g/L mixed liquor suspended solids (MLSS) and 4.2 g/L mixed liquor volatile suspended solids (MLVSS)) was withdrawn from the return activated sludge stream in Quyang WWTP (Shanghai, China). Newly inoculated A/O-MBR was initially operated with mixed influent of municipal wastewater and MAP reactor effluent, and then activated sludge was cultured with a gradual increase of MAP reactor effluent. When the A/O-MBR steadily treated the MAP reactor effluent, the membrane module was replaced with a new unit and A/O-MBR was operated for over 90 days during the experiments.

The hydraulic retention time (HRT) and solid retention time (SRT) remained at 50 days and 30 days, respectively. MLSS and MLVSS remained at 6.4 ± 0.8 g/L 3.7 ± 1.1 g/L during operation. When the transmembrane pressure (TMP) reached 40 kPa, the membrane module was removed for physical (washing with tap water) and chemical cleaning (1% NaOCl and 10% citric acid immersion for 6 h, respectively) to recover the membrane permeability.

2.2. Membrane resistance analysis

Membrane resistance, which is a major characteristic for membrane fouling, can be calculated with the following equation [36]:

$$R_{total} = R_{membrane} + R_{pore\ blocking} + R_{cake\ layer} \quad (1)$$

$$R_n = \frac{\Delta P}{\mu J} \quad (2)$$

$R_{membrane}$ is the resistance of the clean membrane, $R_{pore\ blocking}$ is the resistance due to pore blocking and $R_{cake\ layer}$ is the cake layer resistance. Resistance of concentration polarization was considered as the part of $R_{cake\ layer}$ in this study [37]. R_n is the total, membrane, pore blocking or cake layer. ΔP is TMP, J is permeate flux, μ is viscosity of the permeate water. R_{total} is the value summation of $R_{membrane}$, $R_{pore\ blocking}$ and $R_{cake\ layer}$.

2.3. BCR sequential extraction

Due to the complex inorganic components of the cake layer during the anaerobically digested leachate treatment, the modified BCR (the European Community Bureau of Reference) sequential extraction procedure [36,38,39] was carried out in this study. Inorganic components were classified into four fractions:

(F1) *Exchangeable fraction associated with carbonates*: metals are adsorbed on the sludge components and Fe and Mn hydroxides. This is the most mobile fraction and is potentially toxic for microorganisms.

(F2) *Reducible fraction associated with Fe and Mn oxides*: these oxides strongly bind the heavy metals, but these compounds are thermodynamically unstable in anoxic and acidic conditions.

(F3) *Organic matter-bound oxidizable fraction*: although metals in the F3 form are generally stable because of the recalcitrance of

typical humic organic matter, they can become soluble if the organic matter is biodegraded.

(F4) *Residual fraction*: F4 is the residual fraction that is generally considered to be inert, containing metals that are not extractable.

All freeze-dried cake layer samples of the cake layer and activated sludge were fractionated based on BCR sequential extraction as described previously [39,40]. Inorganic elements in each fraction were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES; Optima 2100 DV, Perkin Elmer, USA). Each experiment was conducted in triplicates and the results reported were the average values.

2.4. Other analysis

Determination of chemical oxygen demand (COD_{Cr}), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), total phosphorus (TP), total nitrogen (TN), MLSS and MLVSS were conducted in accordance with Standard Methods [41]. DO and pH were measured with a DO-and-pH meter (HQ4d, HACH, USA). Cake layer was scraped from the cake layer of the fouled membrane modules and freeze-dried for 48 h, before being applied for XRD (Bruker, Optik GmbH, Ettlingen, Germany) analysis. Before SEM (XL30, Philips, Netherlands)-EDX (Oxford Isis, UK) measurement, a piece of the membrane was cut from the middle section of the membrane module and frozen in liquid-nitrogen. Inorganic elements in the influent (anaerobically digested leachate, which was pretreated with MAP), effluent, sludge and cake layer were detected with an inductively coupled plasma-optical emission spectrometer according to the standard methods [41].

3. Results and discussion

3.1. Performance of reactor and membrane filtration

During the operation period, A/O-MBR presented a stable performance for treating the anaerobically digested leachate from MSWI with MAP pretreatment. A/O-MBR aimed to remove the biodegradable COD_{Cr} and most of $\text{NH}_4^+\text{-N}$ for further advanced treatment, before the wastewater can be recovered for agricultural application (Fig. S1). The effluent of COD_{Cr} and $\text{NH}_4^+\text{-N}$ in A/O-MBR remained at approximately 400–600 and 15–20 mg/L, respectively, meaning that A/O-MBR effectively removed parts of the pollutants, especially $\text{NH}_4^+\text{-N}$. However, MAP pretreatment led to plenty of phosphate flowing into the A/O-MBR reactor. Additionally, MLSS and MLVSS were 6.4 and 3.7 g/L, respectively, predicting an obvious inorganic accumulation in activated sludge compared with inoculating biomass.

Fig. 2 shows the variations of TMP and cake layer thickness during operation. As the significant index for evaluating membrane performance, the development rate of TMP directly reflects the extent of membrane fouling. During the 90 days of operation of the A/O-MBR, TMP variation was classified into 4 periods, and its development rate was around 1.9 kPa/d, indicating that the membrane module tolerated a steady-state fouling behavior during the experiment. In addition, Fig. 2 shows that cake layer thickness reached approximately 58–65 μm when TMP was 40 kPa, which was higher than that of A/O-MBR treated municipal wastewater [36], indicating that anaerobically digested leachate from MSWI caused the severe fouling behavior. Moreover, the average thickness growth rate of cake layer was around 3.4 $\mu\text{m}/\text{d}$, predicting that the membrane would be seriously fouled in approximately 20 days.

Membrane resistance analysis was also carried out in this study. Fig. 3 shows that $R_{\text{cake layer}}$ predominated over 80% of total mem-

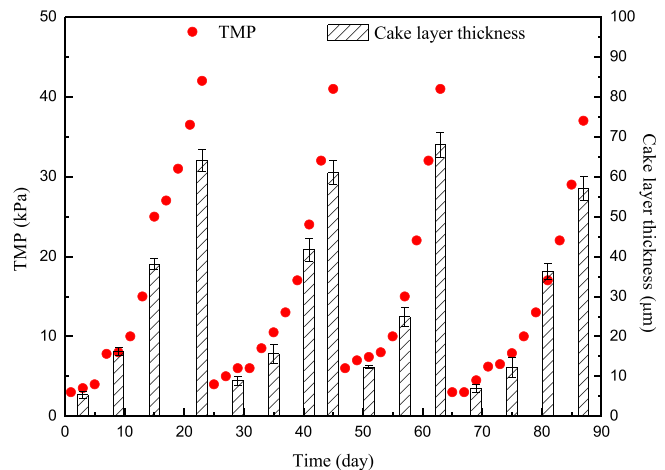


Fig. 2. TMP variation during reactor operation.

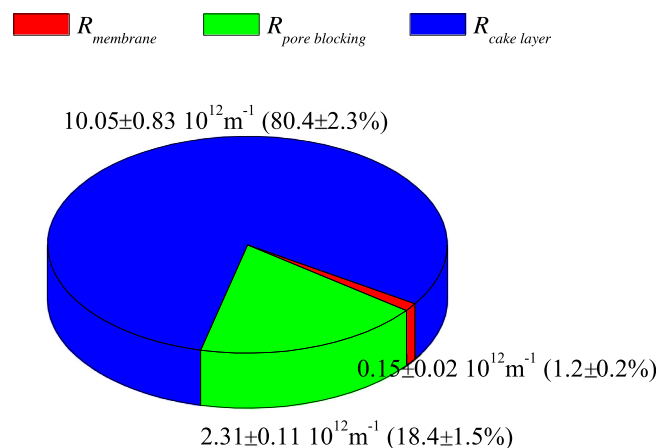


Fig. 3. Membrane resistance during operation.

brane resistance, indicating that cake layer fouling was the dominant fouling behavior in leachate treatment. Additionally, $R_{\text{pore blocking}}$ reached approximately $18.4 \pm 1.5\%$, which was similar as results of other MBR treated leachate systems [42], but higher than treated municipal wastewater [36,43], predicting a severe pore blocking process for leachate treatment.

3.2. BCR analysis

As previous literature [36,38,39] reported, inorganic components are classified into 4 fractions according to the BCR sequential extraction procedure. Table 1 presents the results of exchangeable (F1), reducible (F2), oxidizable (F3) and residual (F4) fractions for each inorganic element. The major inorganic elements of the cake layer were Fe, Mg, Ca, Al and Si (due to their form of ions K and Na were not considered in this study). Table 1 also shows that Si and Al predominated in the inorganic components of the cake layer, especially residual Si ($240 \pm 20 \text{ mg/dry cake layer g}$) and residual Al ($93 \pm 8 \text{ mg/dry cake layer g}$), which was similar to the results from Zhou et al. [36]. Si was considered as one of the most significant inorganic elements during cake layer formation [37,44,45]. Even though leachate had MAP pretreatment to remove most of the $\text{NH}_4^+\text{-N}$ with crystallization, the pretreated anaerobically digested leachate still contained plenty of Si and Al, which resulted in the inorganic accumulation of activated sludge (Section 3.1).

Consequently, predominance of residual Si and Al in the cake layer was mainly due to most of the Si and Al in the influent, especially non-soluble parts, being obstructed in the reactor (Table 2). Previous studies [46,47] on MBR for leachate treatment mainly studied components of Ca and Mg, especially CaCO_3 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, $\text{Mg}_2(\text{PO}_4)_2\text{OH}$, etc. In addition, the comparison of Si between cake layer and sludge indicates that the majority of the Si was retained in the cake layer in the form of residual insoluble fraction, which can also be seen in Table 2, thus XRD analysis was carried out to identify the chemical structure. Fig. S2 shows that inorganic components contained FeSiO_3 , CaAl_2O_3 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, CaCO_3 , CaPO_3OH , $\text{Mg}_2(\text{PO}_4)_2\text{OH}$, CaSiO_3 , CaSi_2O_5 , SiO_2 , Al_2O_3 , CaSO_4 , FePO_4 , etc, predicting that cake layer contained different forms of Si. Zhou et al. [36] also reported that Si and Al was accumulated in the cake layer in the form of $\text{SiO}_2\text{-Al}_2\text{O}_3$ crystal particles. Consequently, it was clear that the residual Si and Al played a dominant role in the cake layer.

In addition, Fe, Mg and Ca were identified as the second dominant inorganic elements in the cake layer. As Table 2 shows, Fe was mainly in the fraction of the organic matter-bond oxidizable (F3) (1.1 ± 0.8 mg/dry cake layer g) and the residual (F4) (5.4 ± 2.2 mg/dry cake layer g). Organic matter-bond oxidizable Fe was mainly because Fe is involved in plenty of bacterial metabolisms [48], also the low solubility product (K_{sp}) for most of the Fe components (e.g. FePO_4 K_{sp} 9.91×10^{-16}) resulted in the high residual Fe in the cake layer. Fig. S2 also shows that parts of residual Fe were in the form of FeSiO_3 and FePO_4 , which was due to high concentrations of soluble Si and phosphate in the influent.

The influent of A/O-MBR contained high concentrations of Mg, due to excess Mg^{2+} addition for MAP pretreatment (Table 2). Although a high concentration of Mg was in the influent, only 13 mg/dry cake layer g residual Mg was found in the cake layer, while parts of the soluble Mg outflowed through the membrane, indicating that Mg does not easily accumulate in the cake layer. In addition, comparisons between the cake layer and sludge indicated that exchangeable fraction of Mg was prior to accumulation in the sludge, and residual Mg was prior to attribution onto the membrane surface. This was because Mg^{2+} easily combined with carbonates in mixed liquid and was removed as precipitate in the reactor bottom. Fig. S2 shows that Mg might be in the form of $\text{Mg}_2(\text{PO}_4)_2\text{OH}$ in the cake layer, because of the excess dosage of MAP pretreatment.

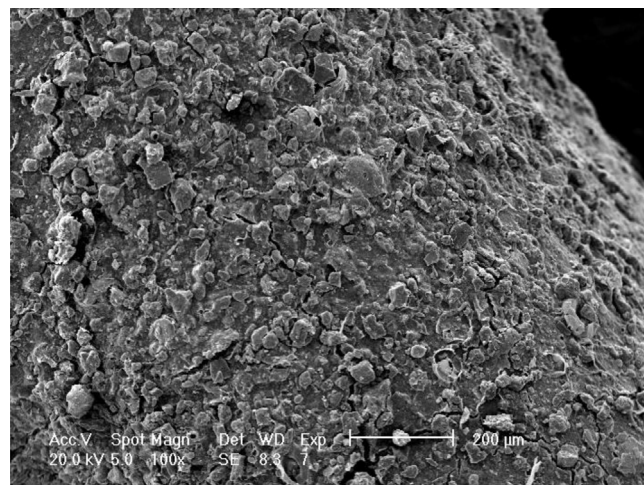


Fig. 4. SEM image of cake layer surface.

Ca is a widely researched element in the cake layer analysis. Previous studies [36,37] reported that Ca in cake layer was mainly in the form of CaSO_4 and CaCO_3 . Trzcinski et al. [46] also reported that cake layer in MBR for leachate treatment contained $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. In this study, F1 (7.2 ± 2.5 mg/dry cake layer g) and F4 (21 ± 4 mg/dry cake layer g) of Ca predominated the calcium components of cake layer. Fig. S2 shows a complex structure of Ca with CaAl_2O_3 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, CaCO_3 , CaPO_3OH , CaSiO_3 , CaSi_2O_5 , CaSO_4 , which were the calcium components with low K_{sp} . Xia et al. [17] also reported that CaSiO_3 and CaSO_4 existed in the MSWI residual of the fresh leachate. Therefore, compared with other elements, Ca had the most complex chemical structure in the cake layer of A/O-MBR treated leachate from MSWI with MAP pretreatment.

3.3. SEM-EDX analysis

Fig. 4 shows the SEM image (100 \times) of the cake layer surface. The cake layer surface was obviously covered with plenty of particles. However, the section of the cake layer surface involved in treating synthetic or municipal wastewater contained less particles [37,49]. The particle difference of the cake layer surface was mainly

Table 2

Inorganic compounds identified by the BCR sequential extraction procedure within each fraction of cake layer,^a sludge (mg/dry sample g)^b and average concentrations of inorganic compounds in the reactor influent and effluent (mg/L).^c

	Fe	Mg	Ca	Al	Si
<i>Cake layer</i>					
F1	0.04 ± 0.01	1.0 ± 0.4	7.2 ± 2.5	0.00 ± 0.00	1.1 ± 0.7
F2	0.02 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.02 ± 0.01	1.5 ± 0.3
F3	1.1 ± 0.8	0.4 ± 0.1	1.2 ± 0.7	0.8 ± 0.3	2.0 ± 0.5
F4	5.4 ± 2.2	13 ± 3	21 ± 4	93 ± 8	240 ± 20
<i>Sludge</i>					
F1	0.06 ± 0.01	6.4 ± 1.2	8.3 ± 1.3	0.02 ± 0.01	0.9 ± 0.2
F2	0.05 ± 0.03	0.7 ± 0.5	4.0 ± 0.5	1.1 ± 0.5	0.8 ± 0.3
F3	2.2 ± 0.9	0.3 ± 0.1	0.8 ± 0.4	1.3 ± 0.3	1.2 ± 0.2
F4	3.6 ± 1.0	2.6 ± 0.3	17 ± 3	48 ± 10	160 ± 40
<i>Influent</i> ^d					
Total	23 ± 6	40 ± 8	70 ± 8	180 ± 25	420 ± 30
Soluble	20 ± 3	34 ± 7	45 ± 3	30 ± 7	40 ± 8
<i>Affluent</i> ^e	5 ± 1	20 ± 3	28 ± 3	20 ± 5	18 ± 4

^a The BCR sequential extraction procedure of cake layer was carried out in triplicate when the operation of the membrane stopped (TMP 40 kPa): n 12.

^b The BCR sequential extraction procedure of sludge was performed in triplicate every 15 days: n 18.

^c Average concentrations of inorganic components of A/O-MBR in influent and effluent were detected every 3 days: n 30.

^d Influent was the influent of A/O-MBR, which was the effluent of MAP reactor.

^e Due to the separation performed by the membrane, all reported elements in the effluent were in the soluble fraction.

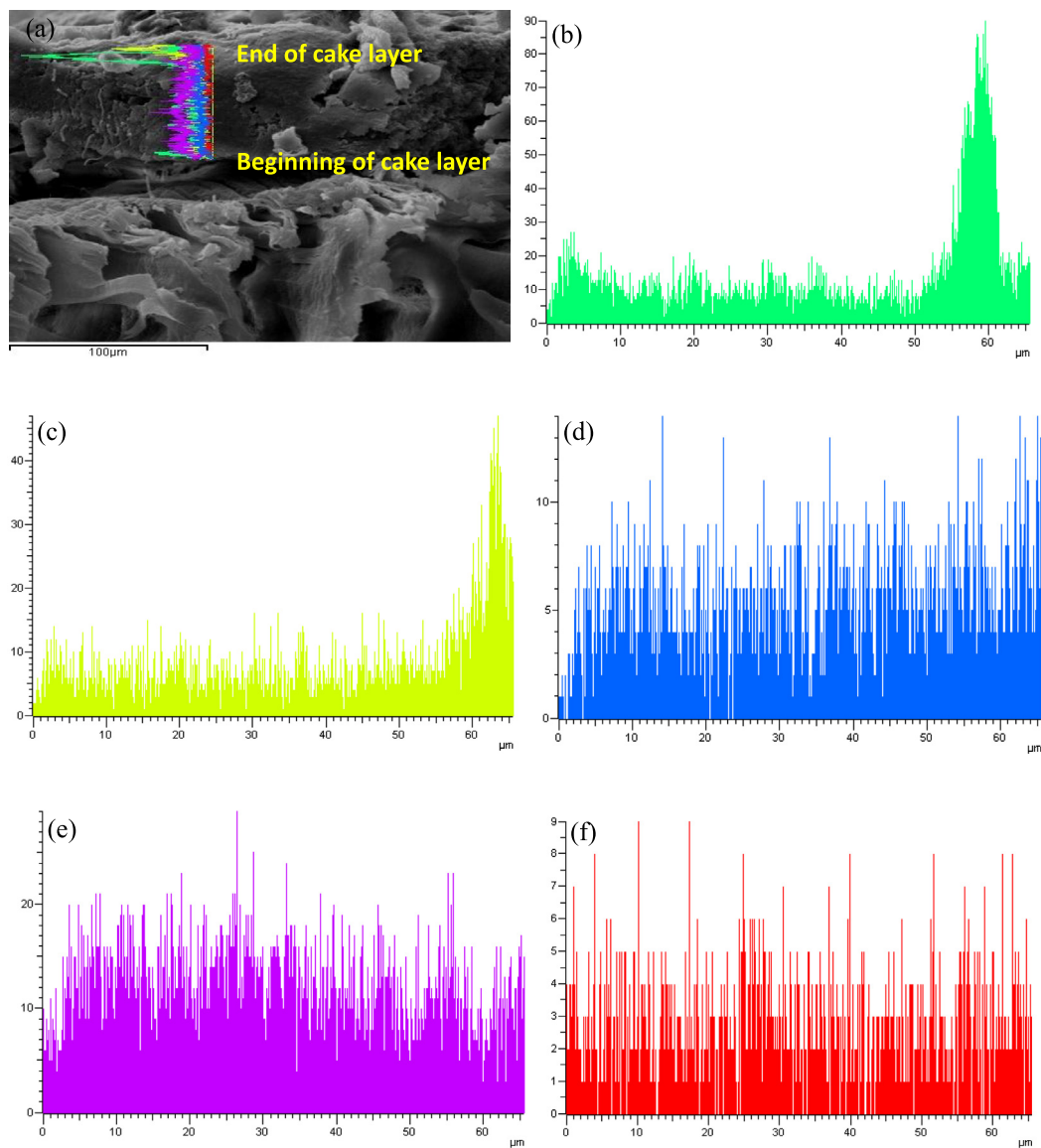
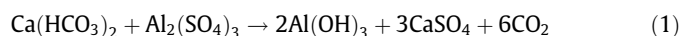


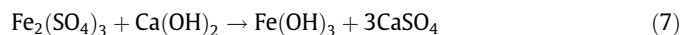
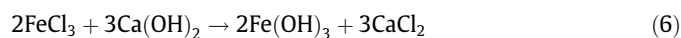
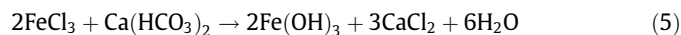
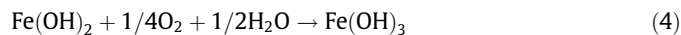
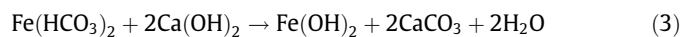
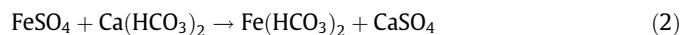
Fig. 5. Elements distribution along the cross-sectional cake layer: (a) SEM of the cross-sectional cake layer; (b) Si; (c) Al; (d) Mg; (e) Ca; (f) Fe. (x-axis (μm) presents thickness of cake layer, and $0 \rightarrow 67 \mu\text{m}$ means the beginning of cake layer \rightarrow the end of cake layer; y-axis (no unit) presents the intensity of element).

because of high concentrations of inorganic components in the influent. However, due to the cake layer surface being covered by plenty of particles, it led the SEM to not effectively detect the mass distribution of the inorganics in the cake layer, therefore the mass distribution had to be analyzed with BCR data (Table 2). The weight percentage rate between Fe, Mg, Ca, Al, Si in the cake layer was 1.7:3.7:7.6:24.1:62.9, indicating that inorganic Al and Si was the inorganic majority of the cake layer. Previous study [36] and Fig. S2 predicted that Si-Al was in the form of $\text{SiO}_2\text{-Al}_2\text{O}_3$ crystal particles. Fig. S2 also shows that Si existed in the form of FeSiO_3 , CaSiO_3 , CaSi_2O_5 , etc., inducing a higher weight percentage of Si than that of Al in the cake layer.

To identify the inorganic distribution in the cake layer, line scan SEM-EDX, which is a semi-quantitative method, was carried out in this study. Fig. 5 shows Si, Al, Mg, Ca and Fe distributions along the $67 \mu\text{m}$ cross-sectional cake layer. The different intensity of each element along the cake layer revealed that Si and Al predominated in the cake layer, which was consistent with the BCR results. Si, Al, Mg, Ca, and Fe were uniformly distributed along the front ($0\text{--}50 \mu\text{m}$) cross-section of the cake layer, indicating that Si, Al, Mg,

Ca and Fe accumulated into the cake layer under the steady-state fouling behavior. Furthermore, a precipitate of aluminum hydroxide formed in the leachate, containing high concentrations of calcium [10,50] (Eq. (1)). Fe ions also presented an active precipitate capacity in the leachate treatment (Eqs. (2)–(7)). Moreover, low K_{sp} of CaSiO_3 (2.5×10^{-8}), CaSO_4 (4.9×10^{-5}), CaCO_3 (2.8×10^{-9}), MgCO_3 (6.8×10^{-6}), $\text{Mg}(\text{OH})_2$ (5.6×10^{-12}), $\text{Mg}_3(\text{PO}_4)_2$ (1.0×10^{-24}), MgNH_4PO_4 (2.5×10^{-13}) means Ca^{2+} and Mg^{2+} would easily precipitate in activated sludge. Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+} also have a strong flocculation capacity to bridge and combine with inorganic crystals (like MgNH_4PO_4 , $\text{SiO}_2\text{-Al}_2\text{O}_3$). Metal anions were also well distributed along the cross-sectional cake layer due to their ion form [51,52]. Therefore, the stable particles and metal ions in the activated sludge of A/O-MBR for leachate treatment led to the steady inorganic accumulation on the membrane surface, observed as the well-inorganic-distribution along the cross-sectional cake layer.





However, at the end of the cake layer, Si and Al had an obvious increase of their intensity, indicating that Si and Al components fast accumulated in the cake layer. This might be due to the cake layer structure and suction pressure. As previous work [51] showed, flocculated anions (Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) varied the cake layer structure into porous and loosened with sweeping and bridging, thereby providing the cake layer with a stable inorganic accumulation and a steady formation with a low suction pressure. By the end of the fouling process, the thickness of the cake layer had increased significantly, requiring a higher suction pressure to maintain the flux. However the high suction pressure enhanced the inorganic particle accumulation into the cake layer, especially the dominating inorganic components of Si-Al crystals.

4. Conclusions

Inorganic characteristics of cake layer in A/O MBR for anaerobically digested leachate from MSWI plant with MAP pretreatment was studied. During 90 days of operation, A/O-MBR had a thicker cake layer, leading to severe fouling behavior. BCR analysis predicted that the cake layer had elements of Fe, Al, Ca, Mg, Si as dominant inorganic components (especially residual Si and Al). XRD results further showed that cake layer contained a complex inorganic substance with FeSiO_3 , CaAl_2O_3 , $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, CaCO_3 , $\text{CaPO}_3\text{-OH}$, $\text{Mg}_2(\text{PO}_4)\text{OH}$, etc. Si-Al crystals were the major inorganic components in the cake layer. In addition, SEM-EDX showed a consistent distribution of inorganics along the front cross-sectional cake layer, indicating that the stable particles and metal ions led to the steady inorganic accumulation onto the membrane surface. High suction pressure promoted the inorganic particle accumulation, especially Si-Al crystals, at the end of the cake layer.

Acknowledgments

This work was supported by the National Key Research and Development Plan of China (2017YFC0403400), Natural Science Foundation of China (NSFC 51678422), Foundation of State Key Laboratory of Pollution Control and Resource Reuse (Tongji University) (PCRRT16003), and “the 111 Project”. In addition, W.-Q.Z. thanks the Catalyst: Leaders funding (CHN-UOA1601) provided by the New Zealand Ministry of Business, Innovation and Employment, and administered by the Royal Society Te Apārangi. Y.G.De C. is supported by the Faculty of Engineering PhD Scholarship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.06.073>.

References

- [1] J.L. Hong, Y.L. Chen, M. Wang, L.P. Ye, C.C. Qi, H.R. Yuan, T. Zheng, X.Z. Li, Intensification of municipal solid waste disposal in China, *Renew. Sustain. Energy Rev.* 69 (2017) 168–176.

- [2] A. Cesaro, V. Belgiorno, Pretreatment methods to improve anaerobic biodegradability of organic municipal solid waste fractions, *Chem. Eng. J.* 240 (2014) 24–37.
- [3] Y. Dang, Y.Q. Lei, Z. Liu, Y.T. Xue, D.Z. Sun, L.Y. Wang, D.E. Holmes, Impact of fulvic acids on bio-methanogenic treatment of municipal solid waste incineration leachate, *Water Res.* 106 (2016) 71–78.
- [4] Z.L. Ye, X.Q. Xie, L.H. Dai, Z.W. Wang, W.H. Wu, F.Y. Zhao, X.M. Xie, S.Q. Huang, M.L. Liu, S.H. Chen, Full-scale blending treatment of fresh MSWI leachate with municipal wastewater in a wastewater treatment plant, *Waste Manage.* 34 (2014) 2305–2311.
- [5] D.A. Zou, Y. Chi, J. Dong, C. Fu, M.J. Ni, Supercritical water oxidation of MSW leachate: factor analysis and behavior of heavy metals, *Environ. Progr. Sustain. Energy* 33 (2014) 1117–1124.
- [6] S.L. Feng, X.M. Wang, G.J. Wei, P.G. Peng, Y. Yang, Z.H. Cao, Leachates of municipal solid waste incineration bottom ash from Macao: heavy metal concentrations and genotoxicity, *Chemosphere* 67 (2007) 1133–1137.
- [7] Y.Q. Peng, J.H. Chen, S.Y. Lu, J.X. Huang, M.M. Zhang, A. Buekens, X.D. Li, J.H. Yan, Chlorophenols in municipal solid waste incineration: a review, *Chem. Eng. J.* 292 (2016) 398–414.
- [8] G. McKay, Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review, *Chem. Eng. J.* 86 (2002) 343–368.
- [9] Z.Y. Lou, B. Bilitewski, N.W. Zhu, X.L. Chai, B. Li, Y.C. Zhao, Environmental impacts of a large-scale incinerator with mixed MSW of high water content from a LCA perspective, *J. Environ. Sci.* 30 (2015) 173–179.
- [10] Y. Dang, R. Zhang, S.J. Wu, Z. Liu, B. Qiu, Y.L. Fang, D.Z. Sun, Calcium effect on anaerobic biological treatment of fresh leachate with extreme high calcium concentration, *Int. Biodeterior. Biodegrad.* 95 (2014) 76–83.
- [11] Z. Liu, Y. Dang, C.H. Li, D.Z. Sun, Inhibitory effect of high $\text{NH}_4\text{-N}$ concentration on anaerobic biotreatment of fresh leachate from a municipal solid waste incineration plant, *Waste Manage.* 43 (2015) 188–195.
- [12] G.L. Kyriakopoulos, D. Doulia, A. Hourdakos, Effect of ionic strength and pH on the adsorption of selected herbicides on Amberlite, *Int. J. Environ. Anal. Chem.* 86 (2006) 207–214.
- [13] G.L. Kyriakopoulos, D. Doulia, Adsorption of pesticides on carbonaceous and polymeric materials from aqueous solutions: a review, *Sep. Purif. Rev.* 35 (2006) 97–191.
- [14] J.X. Ye, Y.J. Mu, X. Cheng, D.Z. Sun, Treatment of fresh leachate with high-strength organics and calcium from municipal solid waste incineration plant using UASB reactor, *Bioresour. Technol.* 102 (2011) 5498–5503.
- [15] F. Fang, A.A. Abbas, Y.P. Chen, Z.P. Liu, X. Gao, J.S. Guo, Anaerobic/aerobic/coagulation treatment of leachate from a municipal solid wastes incineration plant, *Environ. Technol.* 33 (2012) 927–935.
- [16] J. Hashisho, M. El-Fadel, Membrane bioreactor technology for leachate treatment at solid waste landfills, *Rev. Environ. Sci Bio-technol.* 15 (2016) 441–463.
- [17] Y. Xia, H. Zhang, K. Phoungthong, D.X. Shi, W.H. Shen, L.M. Shao, P.J. He, Leaching characteristics of calcium-based compounds in MSWI Residues: from the viewpoint of clogging risk, *Waste Manage.* 42 (2015) 93–100.
- [18] G.L. Kyriakopoulos, D. Doulia, E. Anagnostopoulos, Adsorption of pesticides on porous polymeric adsorbents, *Chem. Eng. Sci.* 60 (2005) 1177–1186.
- [19] G.L. Kyriakopoulos, D. Doulia, Morphology of polymeric resins in adsorption of organic pesticides, *Fresenius Environ. Bull.* 16 (2007) 731–734.
- [20] L.A. Fdez-Guelfo, C. Alvarez-Gallego, D.S. Marquez, L.I.R. Garcia, Biological pretreatment applied to industrial organic fraction of municipal solid wastes (OFMSW): effect on anaerobic digestion, *Chem. Eng. J.* 172 (2011) 321–325.
- [21] W.L. Zhang, L. Zhang, A.M. Li, Anaerobic co-digestion of food waste with MSW incineration plant fresh leachate: process performance and synergistic effects, *Chem. Eng. J.* 259 (2015) 795–805.
- [22] Y.Q. Lei, D.Z. Sun, Y. Dang, H.M. Chen, Z.Q. Zhao, Y.B. Zhang, D.E. Holmes, Stimulation of methanogenesis in anaerobic digesters treating leachate from a municipal solid waste incineration plant with carbon cloth, *Bioresour. Technol.* 222 (2016) 270–276.
- [23] J.R. Nair, F. Bella, N. Angulakshmi, A.M. Stephan, C. Gerbaldi, Nanocellulose-laden composite polymer electrolytes for high performing lithium–sulphur batteries, *Energy Storage Mater.* 3 (2016) 69–76.
- [24] L. Zolin, J.R. Nair, D. Beneventi, F. Bella, M. Destro, P. Jagdale, I. Cannavaro, A. Tagliaferro, D. Chaussy, F. Geobaldo, C. Gerbaldi, A simple route toward next-generation energy storage concept by nanofibres-based self-supporting electrodes and a solid polymeric design, *Carbon* 107 (2016) 811–822.
- [25] F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Gratzel, C. Gerbaldi, Approaching truly sustainable solar cells by the use of water and cellulose derivatives, *Green Chem.* 19 (2017) 1043–1051.
- [26] F. Bella, D. Pugliese, L. Zolin, C. Gerbaldi, Paper-based quasi-solid dye-sensitized solar cells, *Electrochim. Acta* 237 (2017) 87–93.
- [27] A.K. Mondal, K. Kretschmer, Y. Zhao, H. Liu, H. Fan, G. Wang, Naturally nitrogen doped porous carbon derived from waste shrimp shells for high-performance lithium ion batteries and supercapacitors, *Microporous Mesoporous Mater.* 246 (2017) 72–80.
- [28] D. Wu, T. Wang, X.H. Huang, J. Doling, B. Xie, Perspective of harnessing energy from landfill leachate via microbial fuel cells: novel biofuels and electrogenic physiologies, *Appl. Microbiol. Biotechnol.* 99 (2015) 7827–7836.
- [29] I. Merino-Jimenez, V. Celorrio, D.J. Fermin, J. Greenman, I. Ieropoulos, Enhanced MFC power production and struvite recovery by the addition of sea salts to urine, *Water Res.* 109 (2017) 46–53.

- [30] N. Sanphoti, S. Towprayoon, P. Chairprasert, A. Noparatana, The effects of leachate recirculation with supplemental water addition on methane production and waste decomposition in a simulated tropical landfill, *J. Environ. Manage.* 81 (2006) 27–35.
- [31] N. Sanphoti, S. Towprayoon, P. Chairprasert, A. Noparatana, Enhancing waste decomposition and methane production in simulated landfill using combined anaerobic reactors, *Water Sci. Technol.* 53 (2006) 243–251.
- [32] J.H. Luo, G.R. Qian, J.Y. Liu, Z.P. Xu, Anaerobic methanogenesis of fresh leachate from municipal solid waste: a brief review on current progress, *Renew. Sustain. Energy Rev.* 49 (2015) 21–28.
- [33] H.M. Huang, J.H. Liu, C.L. Xu, F.M. Gao, Recycling struvite pyrolysate obtained at negative pressure for ammonia nitrogen removal from landfill leachate, *Chem. Eng. J.* 284 (2016) 1204–1211.
- [34] Y. Xia, P.J. He, H.X. Pu, F. Lu, L.M. Shao, H. Zhang, Inhibition effects of high calcium concentration on anaerobic biological treatment of MSW leachate, *Environ. Sci. Pollut. Res.* 23 (2016) 7942–7948.
- [35] H. Zhang, P.J. He, L.M. Shao, X.J. Li, Leaching behavior of heavy metals from municipal solid waste incineration bottom ash and its geochemical modeling, *J. Mater. Cycles Waste Manage.* 10 (2008) 7–13.
- [36] L. Zhou, S. Xia, L. Alvarez-Cohen, Structure and distribution of inorganic components in the cake layer of a membrane bioreactor treating municipal wastewater, *Bioresour. Technol.* 196 (2015) 586–591.
- [37] F.G. Meng, H.M. Zhang, F.L. Yang, L.F. Liu, Characterization of cake layer in submerged membrane bioreactor, *Environ. Sci. Technol.* 41 (2007) 4065–4070.
- [38] E. Peruzzi, G. Masciandro, C. Macci, S. Doni, S.G.M. Ravelo, P. Peruzzi, B. Ceccanti, Heavy metal fractionation and organic matter stabilization in sewage sludge treatment wetlands, *Ecol. Eng.* 37 (2011) 771–778.
- [39] G. Rauret, J. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, *J. Environ. Monit.* 1 (1999) 57–61.
- [40] H.M. Li, X. Qian, W. Hu, Y.L. Wang, H.L. Gao, Chemical speciation and human health risk of trace metals in urban street dusts from a metropolitan city, Nanjing, SE China, *Sci. Total Environ.* 456 (2013) 212–221.
- [41] China-NEPA, *Water and Wastewater Monitoring Methods*, Chinese Environmental Science Publishing House, Beijing, China, 2002.
- [42] S. Sanguanpak, C. Chiemchaisri, W. Chiemchaisri, K. Yamamoto, Influence of operating pH on biodegradation performance and fouling propensity in membrane bioreactors for landfill leachate treatment, *Int. Biodeterior. Biodegrad.* 102 (2015) 64–72.
- [43] C. Qi, J. Wang, Y. Lin, New insight into influence of mechanical stirring on membrane fouling of membrane bioreactor: mixed liquor properties and hydrodynamic conditions, *Bioresour. Technol.* 211 (2016) 654–663.
- [44] X.L. Yang, H.L. Song, M. Chen, B. Cheng, Characterizing membrane foulants in MBR with addition of polyferric chloride to enhance phosphorus removal, *Bioresour. Technol.* 102 (2011) 9490–9496.
- [45] W. Guo, H.-H. Ngo, J. Li, A mini-review on membrane fouling, *Bioresour. Technol.* 122 (2012) 27–34.
- [46] A.P. Trzcinski, D.C. Stuckey, Inorganic fouling of an anaerobic membrane bioreactor treating leachate from the organic fraction of municipal solid waste (OFMSW) and a polishing aerobic membrane bioreactor, *Bioresour. Technol.* 204 (2016) 17–25.
- [47] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard. Mater.* 150 (2008) 468–493.
- [48] B. Blanc, C. Gerez, S.A. de Choudens, Assembly of Fe/S proteins in bacterial systems biochemistry of the bacterial ISC system, *Biochim. Biophys. Acta Mol. Cell Res.* 2015 (1853) 1436–1447.
- [49] Y.S. Hu, X.C.C. Wang, Z.Z. Yu, H.H. Ngo, Q.Y. Sun, Q.H. Zhang, New insight into fouling behavior and foulants accumulation property of cake sludge in a full-scale membrane bioreactor, *J. Membr. Sci.* 510 (2016) 10–17.
- [50] Eddy, Metcalf, F.L. Burton, H.D. Stensel, G. Tchobanoglous, *Wastewater Engineering: Treatment and Reuse*, fourth ed., McGraw Hill, 2003.
- [51] L. Zhou, Z. Zhang, X. Meng, J. Fan, S. Xia, New insight into the effects of Ca(II) on cake layer structure in submerged membrane bioreactors, *Biofouling* 30 (2014) 571–578.
- [52] L. Zhou, Z. Zhang, W. Jiang, W. Guo, H.-H. Ngo, X. Meng, J. Fan, J. Zhao, S. Xia, Effects of low-concentration Cr(VI) on the performance and the membrane fouling of a submerged membrane bioreactor in the treatment of municipal wastewater, *Biofouling* 30 (2014) 105–114.