EVALUATION OF LANDFILL LEACHATE TREATMENT USING AEROBIC GRANULAR SLUDGE AND ACTIVATED SLUDGE PROCESSES

By

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Abstract

The treatment of synthetic landfill leachate and raw landfill leachate were investigated using two sets of 3 L aerobic sequencing batch reactors (SBR): activated sludge SBR (ASBR) and granular SBR (GSBR).

In synthetic young landfill leachate treatment, GSBR was more efficient in nitrogen and carbon removal than ASBR. During the steady period of the experiment, 99% total ammonium nitrogen (TAN) was removed through nitritation and nitrification in GSBR with an average influent TAN concentration of 498 mg/L. On the contrary, complete nitrification was not achieved in ASBR with a nitrification efficiency of 77±10%. GSBR also presented higher efficiency in denitrification and COD removal compared to ASBR. Phosphorus removal efficiency was almost identical in both reactors.

Synthetic old landfill leachate treatment using GSBR maintained the stable COD removal efficiency at 66%, when the ammonia nitrogen to the maximum of 465±46 mg/L. The ASBR required a start-up of at least 30 days and removed 59±9% of COD when an influent ammonia nitrogen concentration about 200 mg/L. The GSBR was also more efficient than the ASBR for nitrogen removal. The granular sludge reached a maximum ammonia removal of 95±7%, whereas 96±5% was achieved by ASBR. The phosphorus removal was likely affected by the free nitrous acid (FNA) and the low biodegradability of tannic acid.

In raw landfill leachate treatment, the total ammonia nitrogen (TAN) removal efficiency was in GSBR approximately 99.7%. However, the ASBR treatment did not show a consistent performance in TAN removal. TAN removal efficiency decreased with increasing ammonia concentration in the influent. Nitrification in GSBR was partially inhibited at FA concentrations

of 48 to 57 mg/L, which was two times more than the FA concentration that inhibited nitrification in ASBR. In terms of chemical oxygen demand (COD) removal, low removal efficiencies of 17% and 26% were observed in ASBR and GSBR, respectively. The low COD removal efficiencies were associated with the refractory organic content of the leachate used in this study, which resulted in a poor phosphorous removal performance as well.

Overall, aerobic granular sludge showed a better performance in removing nutrients and organic matter from young or old landfill leachate, being more efficient than the conventional suspended growth activated sludge. Therefore, the use of AGS for leachate treatment should be encouraged. Further investigations should also be addressed, especially with a focus on improving SND and phosphorus removal efficiencies.

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List of Abbrevations

AF	Anaerobic biofilter
AGS	Aerobic granular sludge
AOB	Ammonium oxidizing bacteria
AOPs	Advanced oxidation processes
AS	Activated sludge
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DO	Dissolved oxygen
EPS	Extracellular polymeric substances
FA	Free-ammonia
FNA	Free-nitrous acid
HRT	Hydraulic retention time
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
NOB	Nitrite oxidizing bacteria
OLR	Organic loading rate
PAO	Poly-phosphate accumulating organisms
PN	Protein
PS	Polysaccharide
RAS	Return activated sludge
rbCOD	Readily biodegradable COD
SBR	Sequencing batch reactors

NAR	Nitrite accumulation ratio
SRT	Sludge retention time
SVI	Sludge volum index
TAN	Total ammoniacal nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
UASBR	Upflow anaerobic sludge blanket reactor
VFA	Volatile fatty acid
XOCs	Xenobiotic organic compounds

Chapter 1 Introduction and objectives

The solid wastes are increasing with the development of city from population, industrial and commercial growth. Currently, the most common treatment of municipal and industrial solid wastes is deposit to the landfill. Dumping wastes to landfill is cheap and easy to operate compared with other methods (like incineration, anaerobic digestion) (Neczaj, Okoniewska and Kacprzak 2005). However, there are some environmental and health issues in landfill sites: the landfill site may attract vectors (like flies, birds) and they can carry the infectious disease from wastes; methane escape during the organism degradation could lead to potential explosive and methane is a kind of green gas; leachate generation and permeation could significantly influence the groundwater and soil environment.

The landfill leachate is one of the most important contamination problems in landfill sites. Leachate contains salts, heavy metals, organic matters, xenobiotic organic compounds (Renou et al. 2008), and it varies a lot from the different seasons and landfill cell operation years. Among xenobiotic organic compounds (XOCs), there are humic compounds, aromatic compounds, phenolic compounds, phthalic acid esters and so on, which have been commonly found in landfill leachate (Paxéus 2000, Sekman et al. 2011, Renou et al. 2008). XOCs are difficult to biodegrade in landfill leachate treatment because of their complex structures (Boonyaroj et al. 2016). Except so many pollutants inside leachate, the quantity of leachate generation is also huge. In 2015, the total volume of leachate removed was 46,000 kiloliters from the Brady Road Resource Management Facility, Winnipeg, MB, Canada (Heather, Nancy and Renée 2015). Therefore, both complicated components and huge volume of landfill leachate lead to the enormous challenge to find the optimal treatment technology.

The general treatment methods of landfill leachate are classified as physico-chemical and biological methods. The physico-chemical methods as the pretreatment or the final polish treatment are mainly used to remove color, suspended solids, COD, ammonia nitrogen and other pollutants. The processes include air stripping, advanced oxidation processes (AOPs), coagulation/ flocculation, membrane processes (Ferraz, Povinelli and Vieira 2013, Tatsi et al. 2003, Wiszniowski et al. 2006). However, the physico-chemical methods cost a lot and consume energy compared with biological methods. The biological methods are really efficient to remove organics and nutrients, especially the wastewater contain high level of biodegradable COD. The activated sludge is wildly used in leachate treatments. But the performance of activated sludge is easily influenced by its settleability, production of waste activated sludge, filamentous bulking. Recently, the aerobic granular sludge has been studied on the wastewater treatment and it can overcome the disadvantages of activated sludge. But only a few researches focused on the leachate treatments (Wei et al. 2012).

The goal of this research is to study the feasibility of aerobic granular sludge (AGS) treating landfill leachate at different stages. The objectives of this research are as follows:

- Compare the performance of processes based on AS and AGS on different landfill leachate. Assess granular sludge SBR (GSBR) and activated sludge SBR (ASBR) performance regarding organic matter and nutrient removal.
- Evaluate the processes used to treat synthetic landfill leachate and determine the best process to be used in a real treatment setting.

Chapter 2 Literature Review

2.1 Landfill Leachate

2.1.1 Landfill Leachate Characteristic

Landfill leachate is the liquid that has passed through the landfill waste, which includes rainwater through the waste, liquid produced by biochemical process in the landfill cells and the water in waste itself (Renou et al. 2008). Leachate production and components depend on various factors including the number of years the landfill has been in operation, waste types and some environmental factors. Usually, landfill leachate contains high concentrations of ammonia, heavy metals, biodegradable/refractory organic matter and xenobiotic compounds (Kjeldsen et al. 2002, Renou et al. 2008). According to the landfill operation time, landfill leachate is separated into "young" or "old" categories in the literature. In young landfills containing large amounts of biodegradable organic matter, a rapid anaerobic fermentation takes place, resulting in volatile fatty acids (VFA) as the main fermentation products (Welander, Henrysson and Welander 1997). The early phase of a landfill's lifetime is called the acidogenic phase, and leads to the release of large quantities of free VFA (Harmsen 1983). In a mature landfill, the methanogenic phase occurs. Methanogenic microorganisms develop in the waste, and the VFA are converted to biogas (CH_4, CO_2). The organic fraction in the leachate is degraded and changed into less biodegradable compounds (Anthonisen et al. 1976). The characteristics of different age landfill leachate are shown in Table 2.1.

Table 2.1. Characteristic of different age landfill leachate (Renou et al. 2008, Kurniawan, Lo and Chan 2006)

Parameters	Young	Old
Landfill operation years	<5	>10
pH	around 6.5	around 7.5
COD	4000-10000	<4000
BOD/COD	>0.3	<0.1
Organic compounds	80% VFA	Humic and fulvic acids
Biodegradability	High	Low

2.1.2 Treatment Methods

Conventional leachate treatments can be classified as chemical, physical, and biological treatments. However, in order to meet stringent quality standards for direct discharge of leachate into the surface water, an integrated method of treatment is commonly used (Wiszniowski et al. 2006).

2.1.2.1 Physico-chemical treatment

Physico-chemical treatments are mostly used for preliminary leachate treatment and final polishing treatment and also effective on removing organic matters, including reduction of suspended solids, colloidal particles, color, and toxic compounds.

a) Coagulation and flocculation

It is widely used as a pre-treatment, prior to the biological or reverse osmosis step, or as a final polishing treatment step in order to remove non-biodegradable organic matter. Aluminum sulfate, ferrous sulfate, ferric chloride and ferric chloro-sulfate are commonly used as coagulants (Amokrane, Comel and Veron 1997).

Several studies were reported on the examination of coagulation and flocculation for the treatment of landfill leachates. Those studies aimed at performance optimization, i.e. selection of the coagulant, determination of operational conditions, evaluation of the effect of pH, and investigation of flocculants addition (Tatsi et al. 2003). The COD removal rate is 20 to 90%, depending on the landfill age and type of coagulates.

b) Chemical oxidation

Chemical oxidation is used to treat leachate that contains soluble organic matter (which cannot be removed by physical separation), non-biodegradable matter and/or toxic substances that are not suitable for biological oxidation (Vogelpohl et al. 1997).

Growing interest has been recently focused on advanced oxidation processes (AOP). Most of them, except simple ozonation (O_3), use a combination of strong oxidants, e.g. O_3 and H_2O_2, irradiation, e.g. ultraviolet, ultrasound or electron beam, and catalysts, e.g. transition metal ions or photocatalyst (Renou et al. 2008). For instance, the efficiency of COD removal by using a Fenton reagent varied from 60% to 75% for mature and biologically pre-treated leachate, respectively (Lopez et al. 2004).

c) Air stripping

Air striping is the most commonly used method for eliminating a high concentration of NH_4^+-N in the wastewater. High levels of ammonium nitrogen are usually found in landfill leachate. In many applications, air stripping was used successfully in removing ammonium nitrogen that was present in leachate (Marttinen et al. 2002).

However, there are a few drawbacks to this technology. One drawback is the exhausted air which is mixed with NH_3 needs to be neutralized with either H_2SO_4 or HCl before it is released into the atmosphere. Otherwise, NH_3 emission will influence the air quality and human health. Other drawbacks are the calcium carbonate scaling of the stripping tower when lime is used for pH adjustment, and foaming when a large stripping tower is used (Li 1999).

d) Membrane filtration

Membrane filtration is the process that separates solid immiscible particles from the liquid stream primarily based on size difference. It includes: microfiltration, ultrafiltration, nano-filtration, and reverse osmosis. Membrane filtration cannot be used alone in leachate treatment, and usually is used as pre-treatment for other membrane process. Membrane filtration can achieve over 90% COD removal rate (Bohdziewicz, Bodzek and Górska 2001); however, cost is a concern. Membrane filtration requires high energy input. In addition, residue needs to be further treated and properly disposed of which increases the cost of the treatment.

2.1.2.2 Biological treatment

Biological processes are very effective in removing organic and nitrogen, especially from young landfill leachate when the BOD/COD ratio has a high value (>0.5). When the landfill operation time is longer than 10 years, the major presence of refractory compounds (mainly humic and fulvic acids) in leachate tends to limit the effectiveness of biological treatment.

a) Aerobic treatment

Aerobic treatment of leachate can be performed using suspended growth microorganisms activated sludge as well as with attached growth microorganisms. Both systems are commonly applied to municipal wastewater treatment and are adapted to treat leachate. This treatment method can produce a partial decrease in biodegradable organic compounds and achieve nitrification to transfer ammonia to nitrite and nitrate.

Both aerobic biological processes based on suspended-growth biomass, such as aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR), as well as other processes based on attached- growth biomass, such as membrane bioreactor and different biofilters, have been widely studied and adopted (Jokela et al. 2002).

b) Anaerobic treatment

Anaerobic digestion process involves the biological decomposition of organic and inorganic matter in the absence of molecular oxygen. As a result of conversion, a variety of end products including methane and carbon dioxide are produced. It is particularly suitable for treating leachate with high strength organic content, such as leachate streams from young landfills (Pokhrel and Viraraghavan 2004).

2.2 Aerobic Granular Sludge

Aerobic granular sludge technology has been a research topic of great interest in the wastewater treatment field. Aerobic granules are a type of sludge that can self-immobilize flocs and microorganisms into spherical and strong compact structures. One definition given by (Liu et al. 2009) "Granules making up aerobic granular activated sludge are to be understood as aggregates of microbial origin, which do not coagulate under reduced hydrodynamic shear, and which settle significantly faster than activated sludge flocs." The advantages of aerobic granular sludge are excellent settleability, high biomass retention, simultaneous nutrient removal and tolerance to toxicity (Adav et al. 2008). Due to these unique advantages, the aerobic granular sludge has been studied in different wastewater treatment methods (Ramos, Suárez-Ojeda and Carrera 2015, Moussavi, Barikbin and Mahmoudi 2010, Cassano et al. 2011, Lotito et al. 2012). Recent studies show that aerobic granular sludge treatment could be a potentially good method to treat high strength wastewaters with nutrients, toxic substances and xenobiotics.

2.2.1 Aerobic Granular Sludge Formation

2.2.1.1 Seed sludge

Usually activated sludge is used as seed to form the granules. Bacterial communities which constitute the activated sludge, play an important role in granulation because the more hydrophobic bacteria (easily attached with other flocs) live inside the sludge, the greater chance there is to achieve granulation (Wilén et al. 2008). When collecting a seed sludge sample, the temperature of the seed sludge is another crucial factor. In the cold weather, seed sludge could not be cultivated to granular sludge (Chen and Lee 2015). Recently, it was found that adding crushed granules in the seeding activated sludge was an efficient way to enhance the start-up granulation (Pijuan, Werner and Yuan 2011, Verawaty et al. 2012).

2.2.1.2 Aeration and famine period

Aeration is an important factor to influence the aerobic granulation, and superficial air velocity could influence the shear force (Tay, Liu and Liu 2004). The shear force could lead to microbial aggregation and produce denser, more compact granules, with higher extracellular polymeric substances (EPS) (Gao, Liu and Liang 2013). The DO level not only determines the granulation, but also the nitrification. There was no granular sludge formed when the air intensity was less than 1 L/min. At the high air intensity (2-3 L/min), stable granules were formed (Adav, Lee and Lai 2007).

The feast and famine periods that the periodic cycling between high and low substrate concentrations significantly influences granulation. It could select for accumulating bacteria in the reactor, like PAOs and GAOs. A famine period is the aerobic starvation phase where the organic substrate is unavailable. A long starvation phase is good for microbial granulation in the SBR (Tay, Liu and Liu 2001), but it has a negative effect on wastewater treatment and granule stability (Wang et al. 2006). Liu et al. (2007) indicate the starvation period is not a prerequisite for aerobic granulation. Zhou et al. (2013) used strong drag force and produced the aerobic granule sludge after 12 days of operation in a continuous flow airlift fluidized bed reactor without the feast-famine period.

2.2.1.3 Feed composition and organic loading rate

Aerobic granular sludge is cultivated in many different substrates. The structure of granules was highly dependent on the composition of substrate (Liu et al. 2009). The substrates used in granulation are shown in Table 1.2. Some substrates select for filamentous growth that indicates unstable granulation. The metal ions in the feed, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+} could influence the granulation (Adav et al. 2008). The negatively charged cell can be bound with Ca^{2+}, Mg^{2+} and precipitates form into the microbial nuclei, which can accelerate the granulation. However, Cu^{2+}, Fe^{2+}, and Zn^{2+} inhibit the attachment of granules at extremely low concentrations (Hao et al. 2016). The pH of a substrate greatly influences the microorganism's growth. At a low pH, fungi predominate the granulation and produce larger granules whereas bacteria control the granulation at high pH (Yang, Li and Yu 2008).

The organic loading rates (OLR) used for aerobic granulation are usually less than 15 kg $COD/m^3\ d^{-1}$ (Moy, Liu and Tay 2002). The highest OLR for the aerobic granulation is 22.5 kg $COD/m^3\ d^{-1}$ (Lopez-Palau, Dosta and Mata-Alvarez 2009). When the OLR is less than 15 kg $COD/m^3\ d^{-1}$, the aerobic granules can maintain their structure (Thanh, Visvanathan and Aim 2009). However, they will gradually disintegrate at higher values of OLR (18 kg $COD/m^3\ d^{-1}$)

(Long et al. 2015). The high OLR could result in the filamentous bacteria growth and protein of intracellular core as well as EPS hydrolysis, which influence the granular sludge stability.

Table 2.2. The substrates used in granulation (Liu et al. 2009)

Substrates	OLR (kg COD m^{-3} d^{-1})	Size mm	Filamentous growth
Glucose	6.0	2.4	Yes
Ethanol	2.5-7.5	3.2	Yes
Acetate	2.5	2.5	No
Phenol	3.6	0.5	No
Dairy wastewater	2.4	2	Yes
Domestic wastewater	1.0-1.6	0.5-2.0	Yes

2.2.1.4 Settling time

Settling time is a type of selection pressure. Short settling time can wash out the poor settle performance sludge and only the larger and settled granules are left in the reactors. The diversity of microorganisms is simpler at a settling time of 5 min than the seed sludge because of biomass washout (Adav, Lee and Lai 2009). Adav, Lee and Lai (2009) also indicated that the short settling time could determine the efficiency of following granulation processes at the initial stage.

2.2.2 Aerobic Granular Sludge Characteristics

2.2.2.1 Microbial characteristics

The microbial community of the aerobic granular sludge has been investigated by the several researches. According to the study of Winkler et al. (2013), the aerobic granular sludge has the similar functional groups of bacteria as the conventional activated sludge, although these two kinds of sludge are really different in structure and shape. Instead of the loose structure of the conventional activated sludge, the aerobic granular sludge has the compacted and layered structure, which formed into aerobic, anoxic, and anaerobic zones characterized by different redox potentials. The different redox potential zones allow the different functional bacteria for simultaneous nitrogen, phosphorus and COD removal (De Kreuk, Heijnen and Van Loosdrecht 2005b, Adav et al. 2008). Nitrification is performed by the autotrophic bacteria, while the heterotrophic bacteria are responsible for denitrification, carbon and phosphorous removal (Le 2014). As shown in Fig. 2.1., the outer layer of aerobic granular sludge is the aerobic zone. Autotrophic bacteria (ammonium-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB)) and some of the heterotrophic bacteria (glycogen accumulating organisms (GAOs), polyphosphate accumulating organisms (PAOs)) are presented in this zone. The inner layer is the anoxic/anaerobic zone. There are denitrifiers, anaerobic ammonium oxidizers (Anammox), denitrifying PAOs (DPAOs) and denitrifying GAOs (DGAOs). The core of aerobic granular sludge consists with the dead cells and precipitates (De Kreuk et al. 2005b, Xavier et al. 2007, Winkler et al. 2013).

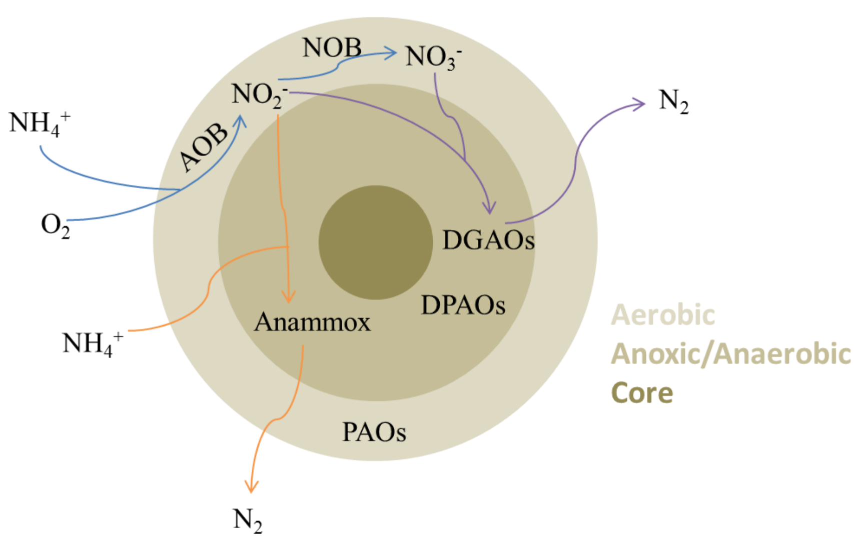


Figure 2.1. The structure and possible microbial distribution of the aerobic granular sludge

Microbial community in aerobic granular sludge could be various depending on the different factors, such as temperature, organic loading rate, seed sludge and so on. Ebrahimi et al. (2010) found at the lower temperature (20°C), *Rhodocyclaceae*-affiliating OTU 214 was present and biological phosphorous removal was observed, whereas there wasn't any phosphorus removal and same bacteria presented at the higher temperature (30°C, 35°C) . In the research of Li et al. (2008), it was shown that the higher organic loading in the reactor rate resulted in the lower species diversity of granular sludge, while the reactor with the lower organic loading rate had the higher species diversity. Compared with the seed sludge A from municipal wastewater treatment plant, the seed sludge B from beer wastewater treatment plant was much better to forming aerobic granular sludge (Song et al. 2010). Moreover, the dominant species in granules cultivated by seed sludge A were *Paracoccus* sp., *Devosia hwasunensi*, *Pseudoxanthomonas* sp., while the dominant species were *Lactococcus raffinolactis* and *Pseudomonas* sp. in granules cultivated by seed sludge B (Song et al. 2010). Except these factors, feast/famine periods and dissolved oxygen (DO) concentration could also influence the microbial community composition in granular sludge (Mulkerrins, Dobson and Colleran 2004, Xavier et al. 2007).

2.2.2.2 Physical, chemical and biological characteristics

Aerobic granular sludge characteristics include size, settleability, structure, SVI, EPS and so on. Usually, average aerobic granular sludge size is between 0.2-5mm in diameter and has a spherical surface. The structure characteristic and morphology of aerobic granules mainly depends on the substrate's composition (Han-Qing 2005). One of the important advantages of aerobic granular sludge is its fast settling performance. The sludge volume index (SVI) is the parameter to value the settling performance. The SVI of conventional activated sludge is between 100 to 200mL/g, while the aerobic granular sludge can be lower than 20mL/g (Su, Cui and Zhu 2012). The aerobic granular sludge settling velocity varied from 25 to 70mh^{-1}, which is almost 10 times higher than flocs (Liu et al. 2003). High settling velocity can enhance the biomass retention and organic degradation ability (Adav et al. 2008).

The surface hydrophobicity helps the cell self-immobilize and can be achieved by increasing shear force, which creates the stressful environmental condition. In order to adapt to the stressful condition, microorganisms increase their surface hydrophobicity and finally aggregate together (Liu and Tay 2002).

Extracellular polymeric substances (EPS) are produced by bacteria in the formation of a gel-like network and accumulate on the surface of cells, including polysaccharides (PS), proteins (PN), glycoproteins, nucleic acids and other compounds (Salama et al. 2016). EPS can keeps bacteria together in biofilms and have a significant influence on the physicochemical properties of microbial aggregates, including structure, surface charge, flocculation, settling properties, dewatering properties, and adsorption ability (Wingender, Neu and Flemming 1999). There are lots of extraction methods for EPS. Adav and Lee (2008) suggested one physico-chemical method: ultrasound followed by reaction with NaOH and formamide to extract EPS from aerobic granular sludge. The concentrations of protein and polysaccharides are the main parameters to analyze the EPS. Protein/Polysaccharides (PN/PS) ratios were > 3 for granules and a higher PN concentration could help granulation (McSwain et al. 2005).

2.2.3 Aerobic Granular Sludge Application

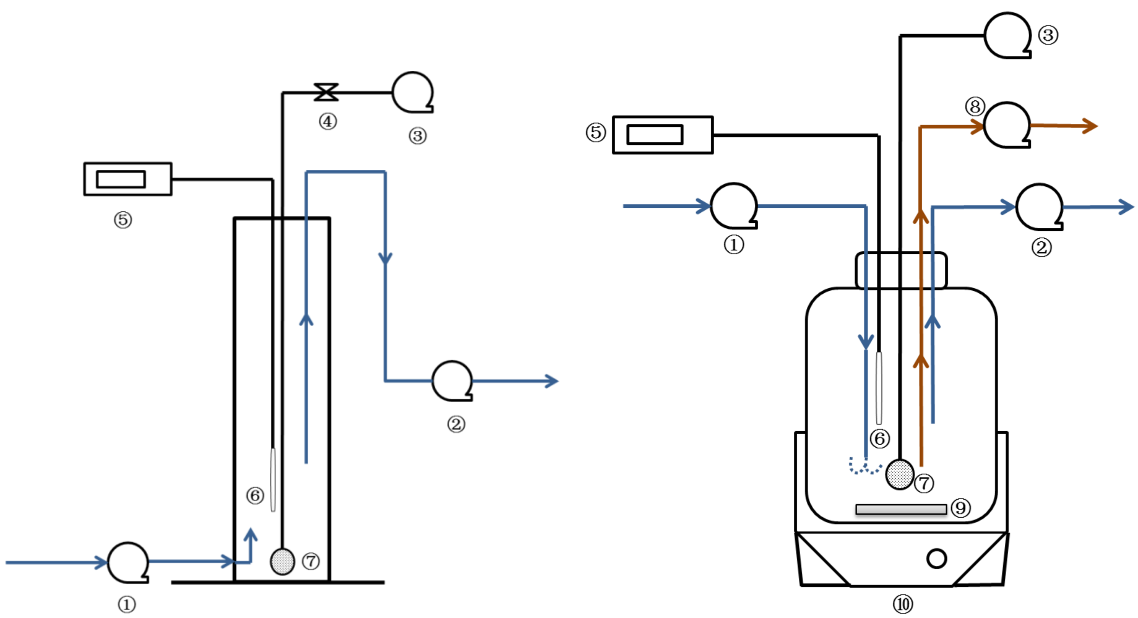
The aerobic granular sludge usually is cultivated in SBR and applied successfully as a wastewater treatment for high strength wastewater, toxic wastewater and domestic wastewater. Compared with conventional aerobic granular processes for COD removal, current research focuses more on simultaneous nutrient removal, particularly COD, phosphorus and nitrogen, under pressure conditions, such as high salinity or thermophilic conditions (Zhang, Hu and Lee 2016). Meanwhile, the removal of specific pollutants using aerobic granular processes is an interesting development for future studies.

Wei et al. (2012), used an SBR to develop aerobic granular sludge (AGS) for leachate treatment. The results were about 83% of COD removal and nitrogen removal varied from 44% to 92% depending on the different tested influent ammonia concentrations. Ramos et al. (2016a) used AGS to complete the phenolic compounds removal in the continuous air lifting reactor with a high concentration of salts (29 g mixed salts/L). A raw textile wastewater was treated by a sequencing batch biofilter granular reactor, which achieved 36% to 80% COD removal and more than 50% TSS reduction (Ramos et al. 2016a). A study on domestic wastewater treatment was accomplished in a micro-aerobic granular sludge reactor. The results showed more than 90% COD removal and 82% total nitrogen removal (Dash Wu, Liu and Dong 2011).

Chapter 3 Materials and Methods

3.1 Experiment Set-up

The return activated sludge (RAS) was collected from the Southend Water Pollution Control Centre in Winnipeg, MB, Canada. The aerobic granular sludge was gradually cultivated from the RAS in SBR. The GSBR consisted of a plastic column with a 45 cm height cm and a 12 cm internal diameter (Fig. 3.1.a). The ASBR consisted of a glass jar with a 30 cm height cm and a 15 cm diameter (Fig. 3.1.b). Total and working volumes of both reactors were the same: 5L and 3L, respectively. Both reactors were provided with an up-flow feeding. The air flow was kept between 2 and 3L/min during the aerobic phase. The mixed liquor pH was kept in the range of 6.5.



(a) (b)

Figure 3.1. The reactors set-up: ① feeding pump; ② decanting pump; ③ air compressor; ④ air flow meter; ⑤ pH controller; ⑥ pH meter; ⑦ air diffuser;⑧waste sludge pump; ⑨ stir bar; ⑩magnetic stir plate

3.2 Operation of Reactors

The ASBR and GSBR were operated at 3 cycles per day (8h each cycle), under a temperature of in the room 20±2℃. For the GSBR, each cycle consisted of a 30min feeding period, 1.5h of anoxic/anaerobic period, 5.5h of aerobic period, 5min of settling period and 12min of decanting period. For the ASBR, each cycle consisted of a 1.5h anoxic/anaerobic feeding period, 5.5h of aerobic period, 40min settling period and 12min of decanting period. Afterwards, while the mixed liquor was kept under mixing, there were 2min to waste the activated sludge from the ASBR. For both ASBR and GSBR, at each cycle, 1.5L of supernatant (treated effluent) were withdrawn from the reactors and 1.5L of feed was pumped into the reactors, keeping a working volume of 3L and an exchange ratio of 50%.

3.3 Raw Landfill Leachate and Synthetic Leachate

Raw leachate was collected from Brady Road Resource Management Facility (landfill) in Winnipeg. Due to the high concentration of ammonia nitrogen and COD, leachate was gradually loaded into the reactors as mixed with primary effluent at volumetric ratios varying from 10 to 100%. The primary effluent was collected from Southend Water Pollution Control Centre in Winnipeg. The characteristics of leachate and primary effluent are shown in Table 3.1.

The synthetic young leachate recipe was prepared according to Vangulck et al. (2004). As shown in Table 3.2, the components contained three kinds of volatile fatty acids (VFA), a small part of hardly biodegradable organic compounds, different salts and trace metals. The synthetic old landfill leachate was prepared with tannic acid (as the only organic carbon source), macro and micronutrients dissolved in tap water (Table 2.3). Every four days the feed was prepared in 20-L jars and stored at 4℃. The pH of the synthetic young leachate was 7.2 and the synthetic old leachate was 6.8.

Table 3.1. The characteristics of the raw leachate and municipal wastewater

Parameter	Leachate	Primary effluent
NH_4^+-N (mg/L)	700-1200	32-50
NO_2^--N (mg/L)	<1	<1
NO_3^--N (mg/L)	<1	<2
PO_4^{3-}-P (mg/L)	2-6	5-6
COD (mg/L)	1600-2850	363-521
BOD (mg/L)	140-480	180-210
pH	7.8	7.0

Table 3.2. Composition of the synthetic leachate

	Components	Per litre
Inorganic Compounds	NaCl	2000 mg
	$CaCl_2$	700 mg
	$NaHCO_3$	2000 mg
	NaOH	297 mg
	K_2HPO_4	32.5 mg
	NH_4Cl	120-496 mg
	Trace metal solution*	0.02 mL
Organic Compounds	Acetic acid	78.7 mg
	Propionic acid	74.2 mg
	Butyric acid	72 mg
	Acetone	41.5 mg
	Ethanol	41.4 mg
	Propanol	42.3 mg
	Phenol	21.4 mg

Table 3.3. Composition of the synthetic leachate containing tannic acid

Components	Per litre
Tannic acid	500 mg
NaCl	2000 mg
$CaCl_2$	700 mg
$NaHCO_3$	2000 mg
NaOH	297 mg
K_2HPO_4	32.5 mg
NH_4Cl	110-554 mg/L
Trace metal solution*	0.02 mL

***Table 3.4.** Composition of the trace metal solution

Components	Per litre
$FeSO_4$	2000 mg
H_3BO_4	50 mg
$ZnSO_4 \cdot 7H_2O$	50 mg
$CuSO_4 \cdot 5H_2O$	40 mg
$MnSO_4 \cdot 7H_2O$	500 mg
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	50 mg
$Al_2(SO_4)_3 \cdot 16H_2O$	30 mg
$CoSO_4 \cdot 7H_2O$	150 mg
$NiSO_4 \cdot 6H_2O$	500 mg
96% H_2SO_4	1 ml
Distilled water	1L

3.4 Sampling and analytical methods

Samples were taken from influent and effluent regularly. All samples were filtered (0.45µm) before the physico-chemical analysis. Dissolved phosphate, total ammonia nitrogen (TAN), nitrate and nitrite were measured by flow-injection analysis using a Lachat Instrument

QuikChem 8500. Soluble COD (SCOD) was measured by Hach kits. Mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), sludge volumetric index (SVI) at 5 and 30min, and phenols were measured according to APHA et al. (2005). To determine the percentage of phenols removed by volatilization rather than biodegradation, a kinetic test was performed as blank by aerating and mixing 3L of the synthetic wastewater in container free of any biomass, for the same period of the reactors operational cycle (8h).

The granular sludge and activated sludge biomass were characterized in terms of particle size, SVI and extracellular polymeric substances (EPS). Sludge particle size was determined by a Malvern Mastersize 2000 instrument. EPS were extracted from sludge by NaOH and formaldehyde method (Adav and Lee 2008). Protein and polysaccharides concentrations were measured by the modified Lowry assay kit and phenol-sulfuric acid colorimetric method (DuBois et al. 1956), respectively.

Free-ammonia (FA) and free-nitrous acid (FNA) were calculated according to Equation 1 and 2 (Anthonisen et al. 1976), while nitrite accumulation ratio (NAR) was determined by the Equation 3 (Sun et al. 2015). Simultaneous nitrification-denitrification was determined by the Equation 4 (Zeng et al. 2003) and Equation 5 (Shao 2008).

$$FA(mgN/L) = 17/14 * \frac{TAN \times 10^{pH}}{exp(^{6334}/_{273+T}) + 10^{pH}} \qquad \text{(Eq – 1)}$$

$$FNA(mgN/L) = 46/14 * \frac{NO_2^-}{Ka * 10^{pH}} \qquad \text{(Eq – 2)}$$

$$NAR\ (\%) = 100 * \frac{NO_2^-}{NO_2^- + NO_3^-} \qquad \text{(Eq – 3)}$$

$$SND\ (\%) = 100 * \frac{TN_O - TN_f}{TAN_{removed}} \qquad \text{(Eq - 4)}$$

$$Denitrification\ (\%) = 100 * \left(1 - \left(\frac{NO^-_{x\,f} - NO^-_{x\,0}}{TN_0 - TN_f}\right)\right) \qquad \text{(Eq – 5)}$$

$$Full\ Nitrification\ (\%) = 100 * \left(\frac{NO^-_{3\,effluent}}{TAN_{removed}}\right) \qquad \text{(Eq – 6)}$$

Chapter 4 Comparing Young Landfill Leachate Treatment Efficiency and Process Stability Using Aerobic Granular Sludge and Suspended Growth Activated Sludge

4.1 Introduction

In the last decade, waste management strategies have been directed to waste minimization (reduction, recover, reuse and recycling), encouraging final disposal alternatives to landfilling. The European Commission has proposed to Member States that a maximum of 10% of municipal solid wastes should be landfilled by 2030 (European Commssion 2015). Nonetheless, sanitary landfills still represent the most often used final disposal alternative for municipal solid waste in the world. Although landfilling comprises a well-established solution for waste management, it causes environmental impacts such as greenhouse gas and leachate production (Renou et al. 2008). Leachate is a wastewater with a diverse composition, including inorganic salts, heavy metals, high levels of total ammonium nitrogen (TAN), both biodegradable and refractory organic matter, and xenobiotic organic compounds. Based on its composition, leachate may be classified as young or old. Young leachate contains more volatile fatty acids (VFA) and has higher level of BOD (Biological oxygen demand)/COD ratio (>0.3) (Yuan, Jia and Poveda 2016, Renou et al. 2008). Old leachate is usually contains high TAN concentrations and low BOD/COD ratio (<0.3) as a result of organic matter stabilization under anaerobic conditions (Renou et al. 2008).

Leachate treatment strategies include on-site treatment plants (Zhao, Novak and Goldsmith 2012), transport to wastewater treatment plant and co-treatment with domestic wastewater (Ferraz et al. 2016) and reinjection or recycle to the landfill cell (Yuan et al. 2016). Physico-chemical, membrane and biological processes are among the successful methods reported for leachate treatment.

Air striping has been commonly used to reduce the TAN concentration in leachate. Ferraz et al. (2013) achieved 88% of TAN removal treating 12L of leachate for 72 hours using an aerated packed tower. Yuan et al. (2016) found that pH adjustment improved the air stripping efficiency as a pre-treatment prior to biological process. Alternatively, electrochemical process could remove 82% TAN and 87% COD from raw leachate at a high current level (200 mA/cm2) (Del Moro et al. 2016). Membranes are typically used at the final stage of leachate treatment, improving the quality of the pre-treated leachate in order to attend local discharge limits. A forward osmosis (FO) membrane system applied to a pre-treated leachate removed 98.6% of COD, 96.6% of total phosphorus (TP) and 76.9% of TAN (Dong et al. 2014).

Regarding biological treatment, the co-treatment of leachate with domestic wastewater has been extensively reported by the literature, presenting COD removal efficiencies up to 90% and satisfactory nutrients removal (Campos et al. 2014, Çeçen and Aktas 2004, Ferraz et al. 2016, Yuan et al. 2016). Despite the good results related to leachate co-treatment with domestic wastewater, there are important concerns about this alternative. As most existing wastewater treatment plants were not originally designed to treat leachate, is it unclear how they will perform at long-term receiving leachate. Another concern is the possibility of leachate to be simply diluted instead of effectively co-treated. In fact, it was reported that raw leachate was most probably partial biodegraded in SBR rather than diluted with domestic when co-treated at a volumetric ratio of 5% (Ferraz et al. 2016).

Alternatively, leachate can be treated on-site where facilities designed to attend its specific characteristics are used. Significant results have been reported from leachate treatment by biological systems that could be installed on-site, including: fungi, activated sludge and aerobic granular sludge (Wei et al. 2012, Yabroudi, Morita and Alem 2013, Ren and Yuan 2015). White rot fungi could remove 78% of color and 52% of COD after 4 days of immobilization (Saetang and Babel 2009). High removal efficiencies for COD (85%) and total nitrogen (90-95%) were obtained by full-scale sequencing batch reactor (SBR) plant treating leachate (Morling 2010). Promising results were also obtained when leachate was treated by aerobic granular sludge: COD removal was up to 83% and TAN removal was up to 44% (Wei et al. 2012).

Reactors based on the aerobic granular sludge present advantages over the conventional activated sludge process, such as: high settling velocity, compact structure, simultaneous nutrient removal, and ability to sustain high biomass concentration (Adav et al. 2008). In spite of those advantages over activated sludge, there is little literature testing the efficacy of granular sludge for leachate treatment, which has motivated the current research. This study aimed to compare the performances of activated sludge SBR (ASBR) and aerobic granular sludge SBR (GSBR) in treatment of a young leachate, focusing on organic matter and nutrients removal.

4.2 Results and Discussions

4.2.1 Biomass Characteristics

In GSBR, SRT was not controlled and calculated depending on the MLSS in reactor and effluent. At first 40 days, MLSS concentration fluctuated between 3500 mg/L and 5800 mg/L, whereas MLVSS was 55% of MLSS (Figure 4.1a). From day 43 to 122, biomass maintained the good settling performance and MLSS gradually increased to 9348±193 mg/L

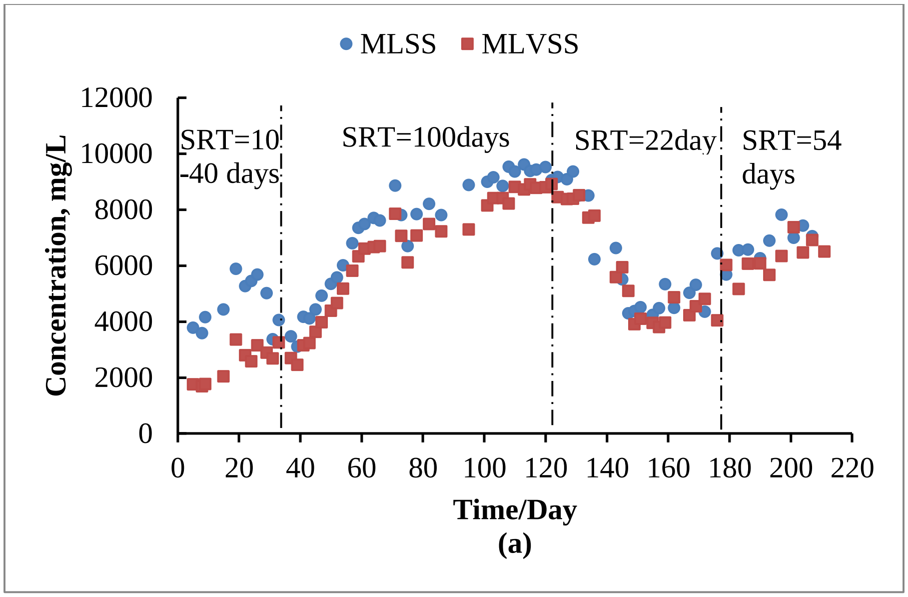
(MLVSS/MLSS=90%) at SRT 100 days, because biomass achieved granulation and size of AGS increased from 280 to 474μm. However, MLSS decreased sharply to 4230 mg/L as well as SRT (22 days) during day 130 to 176. The size of AGS also went down to 402 μm (Figure 4.2a). These observations indicated granules disintegration as a result of FA concentration increasing (5.5 to 7.0 mgN/L), which could affect AGS granulation and biomass washed out. Yang, Tay and Liu (2004) reported that granulation was inhibited when FA concentration increased, because the cell hydrophobicity reduced and it affected the sludge aggregation. At the end of experiment period, the AGS recovered and MLSS concentration went back to 6943±500 mg/L at SRT 54 days. AGS size was increased to 1100 μm. The average SVI_5 for the GSBR was 60 ml/g·VSS.

As shown in Figure 4.1b, the ASBR solid retention time (SRT) was controlled in ranges from 10 to 30 days. MLSS concentration was unstable at SRT of 10 days. MLSS concentration dropped from 5855±564 mg/L to 3413±250 mg/L during the first 50 days and MLSS only contained 50% of MLVSS. After 70 days, MLSS concentration kept decreasing and reached a minimum of 2246±10 mg/L. At the end period of 10 days SRT, MLSS concentration increased to 3580 mg/L. During the 20 and 30 days SRT period, MLSS concentration showed the stable rising trend and finally achieved 6830±476 mg/L. The average SVI_{30} for the AS was 42 ml/g·VSS, which indicated that good settling performances were obtained.

Based on the research of Adav and Lee (2008), the importance of EPS relies on their ability to act like the backbone of granules, providing stability. Regarding EPS composition, PN and PS were detected in this research. PN content was stable around 39.1 mg/g·VSS for GSBR and 40.0 mg/g·VSS for the ASBR (Table 4.1). However, the concentration of PS exceeded the concentration of PN in both reactors and PN/PS ratio was approximately 0.52 for the GSBR and 0.4 for the ASBR. This observation can be as a result of predominance of growing or "young" granules in the GSBR, whereas higher level of PN/PS ratio was associated to the predominance of mature granules (Yan et al. 2015, Zhu et al. 2012). As shown in Figure 4.2b, the AGS size increased with the PN/PS increased. This indicated that PN/PS ratio could influence the size of aerobic granular sludge, which was in agreement with the study of (Zhang et al. 2007): the higher PN/PS ratio could result in the higher surface hydrophobicity and help to aggregate the bigger granules.

Table 4.1. The characteristics of biomass in ASBR and GSBR

Reactor / **Parameter**	**GSBR**	**ASBR**
MLSS, mg/L	3105-9610	2125-7945
$SVI_{5/30}$, mL/g	59.9	42.3
Particle size, µm	466-1153	283
SRT, days	10-114	10- 30
PN, mg/g·VSS	39.1±7.6	40.0±5.6
PS, mg/g·VSS	84.5±31.5	108.4±31.2
PN/PS	0.52 ± 0.21	0.4 ± 0.15



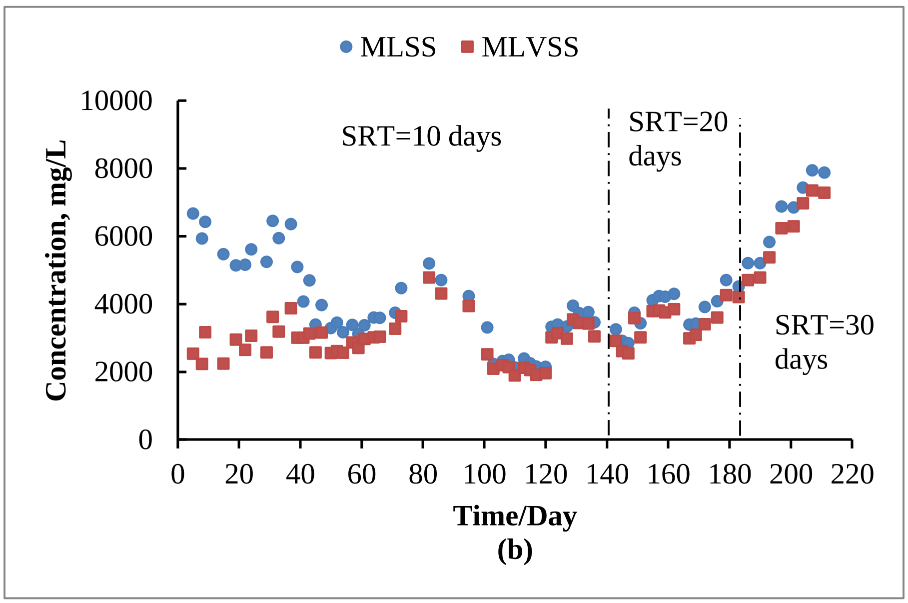


Figure 4.1. MLSS and MLVSS concentration profile along with time for (a) GSBR and (b) ASBR

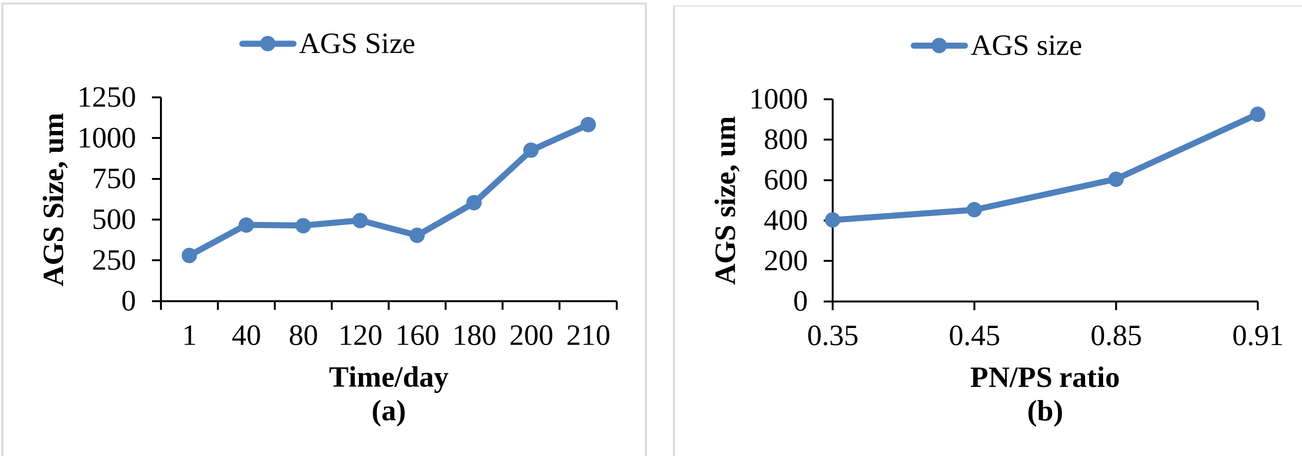


Figure 4.2. The AGS size distribution trend during the experiment (a) and the relationship between the AGS size and the PN/PS ratio in GSBR (b).

4.2.2 Nutrients Removal Performance

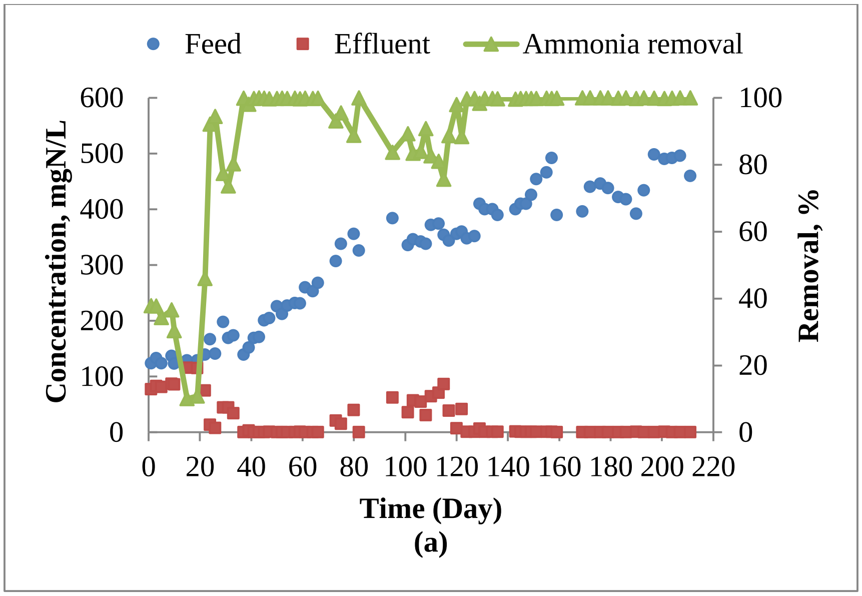
4.2.2.1 TAN removal

The total duration of the experiment was 211 days. The influent TAN concentration of GSBR was gradually increased from 128±5 mgN/L to 494±4 mgN/L (Figure 4.3a), imposing a nitrogen loading rate of 0.20±0.01 kgN/m^{3}d to 0.74±0.1kgN/m^{3}d. During the first 22 days, as biomass adapted to the synthetic young leachate, with only a small percentage (less than 40%) of the TAN was removed. When the influent TAN concentration was set at 300 mgN/L, from day 37, its removal efficiency was maintained at 99%. Afterwards, the influent TAN concentration continued increasing to 347±21 mgN/L, but the removal efficiency decreased to an average level of 87±6%. At this stage, FA concentration (pH=7.5) in the GSBR was 5.5 mgN/L, which was much higher than the reported toxic concentration, 4 mgN/L, for nitrifiers (Yang et al. 2004). Another factor could influence nitrification was dissolved oxygen. The outer layers of AGS consisted of heterotrophs and autotrophs. The heterotrophs were the major part in most layers, which competed with autotrophs (nitrifiers) for dissolved oxygen and space (De Kreuk et al.

2005b). Therefore, the lack of dissolved oxygen penetration through the layer of heterotrophs might be the reason for TAN removal efficiency decreasing. Nonetheless, the TAN removal efficiency recovered back to 99% after 50 days with high influent TAN concentration (between 400mgN/L and 498mgN/L).

As shown in Figure 4.3b, the nitrogen loads in ASBR increased with influent TAN concentration increasing, from 0.20±0.01 kgN/m^{3}d (131±5 mgN/L) to 0.68±0.02 kgN/m^{3}d (454±10 mgN/L). It was observed that the AS adapted more rapidly to the young leachate than the AGS, reaching 100% of TAN removal in 26 days. Similar to AGS, the AS removed 99% of the 300mgN/L TAN in the influent. As the influent TAN concentration exceeded 300 mgN/L from day 75, the TAN removal efficiency was unstable and it fluctuated between 76% and 99%. Furthermore, a sharp decreasing of TAN removal was observed and even down to a minimum of 27%, when the influent TAN concentration was over 400 mgN/L. During this period, FA concentration was up to 6.4 mgN/L and FNA concentration (pH=6.5) was 0.3 mgN/L, which could affect activity of nitrifiers (Yang et al. 2004, Zhou et al. 2011). As the experiment proceeded, the ASBR could gradually recover and TAN removal ranged between 60% and 80%.

These results showed that for both reactors TAN removal was intrinsically related to the influent TAN concentration, confirming the results obtained by Wei et al. (2012). The formation of FA and FNA had potential effects on the nitrification for both AGS and AS. Compared with AGS, AS need more time to recover and couldn't maintain good TAN removal (>90%), when higher TAN concentration (>400 mgN/L) was obtained. Thus, it was confirmed that the GSBR was more suitable for young leachate treatment with high TAN concentration (< 500 mgN/L).



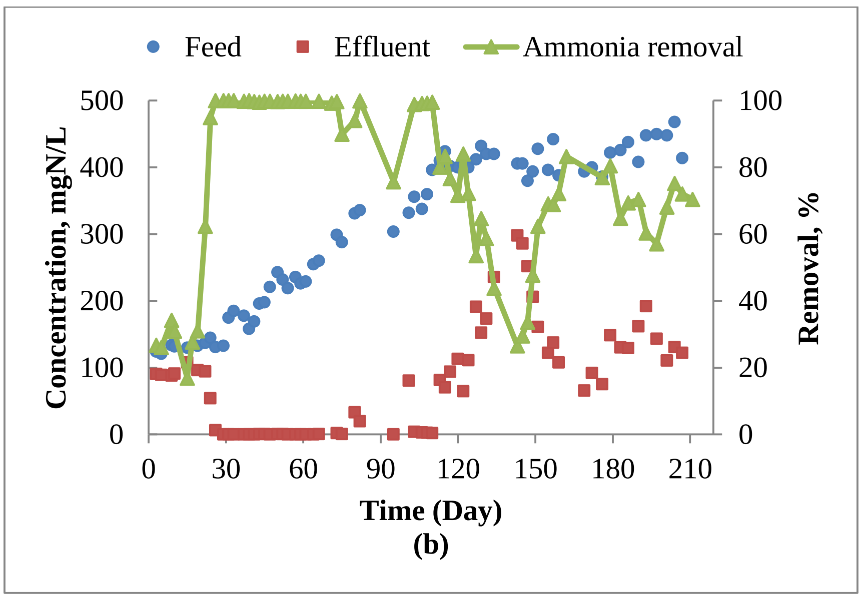


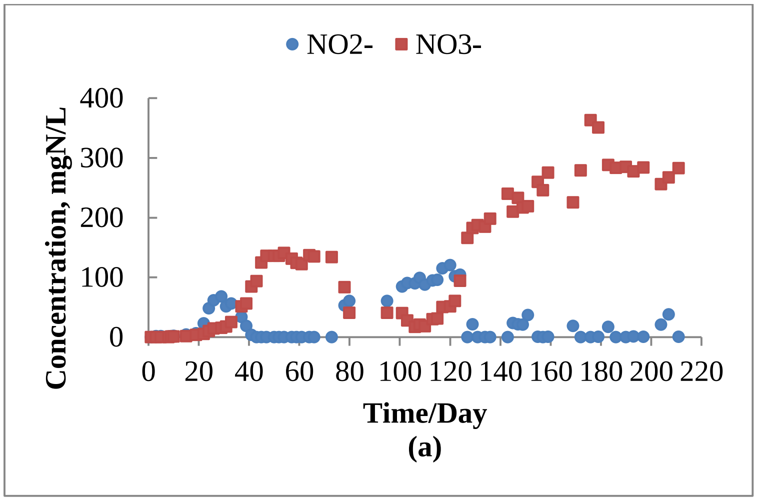
Figure 4.3. TAN concentration profile along with time for (a) the GSBR and (b) the ASBR

4.2.2.2 Nitrite and Nitrate Accumulation

According to Figure 4.4a, nitrite was the main component of NO_x^- (NO_2^-+NO_3^-) in the GSBR effluent during the first 33 days, indicating the occurrence of nitritation. Afterwards, as nitrite oxidizing bacteria (NOB) were being adapted to the leachate, nitrate was gradually increased in function of nitrite oxidation, resulting in an average full nitrification efficiency of 56±7% and average TN removal efficiency of 44±6%. From day 80, nitrite started accumulated again and nitrite accumulation rate (NAR) was 72%, meanwhile the TAN removal showed decreasing trend (Figure 4.3a). It indicated that nitrifiers (AOB+NOB) were inhibited. TN removal efficiency slightly increased to 48±6%, but full nitrification efficiency decreased sharply to 13±6%, whereas nitritation was the dominant process with an efficiency of 72±10%. The recent research found the FNA inhibition threshold to NOB was 0.02 mg/L (Zhou et al. 2011). During this period, FA (pH=7.5) concentration was 5.5 mg/L and FNA concentration (pH=6.5) gradually increased from 0 to 0.3 mg/L, which could potential influence AOB and NOB activity. However, as the AGS became adapted to influent TAN concentrations as high as 498 mgN/L, nitrite concentrations in the treated effluent were negligible and full nitrification efficiency was maintained at 56±12% until the end of the experiment.

Nitrite accumulated in the effluent of the ASBR throughout the whole experiment (Figure 4.4b). At beginning 66 days, NOB gradually had function as nitrite concentration reduced and nitrate concentration increased, which full nitrification efficiency achieved to the highest point 47% in this experiment. NAR was decreased from 100% to 8% and TN removal increased from 22±6% to 55±4%. However, full nitrification was not achieved and mostly performed via nitritation after day 80, in function of NOB inhibition by the high FA (6±0.7 mg/L) and FNA concentrations (0.4±0.07 mg/L). Although at the period of day 124 to 147, FNA decreased to minimum 0.09 mg/L, there was no significant nitrate concentration increasing over the nitrite. TN removal maintained at 38±5% at the end of operation days.

These results showed that the nitrifiers in the ASBR were much more sensitive to FA and FNA than those in the GSBR, highlighting the advantage of using granular sludge. In fact, the compact structure of granular sludge may prevent nitrifiers from having a direct contact with toxic compounds. On the other hand, microorganisms belonging to the activated sludge are mostly susceptible to be exposed to toxic compounds, such as FA and FNA (Liu et al. 2009).



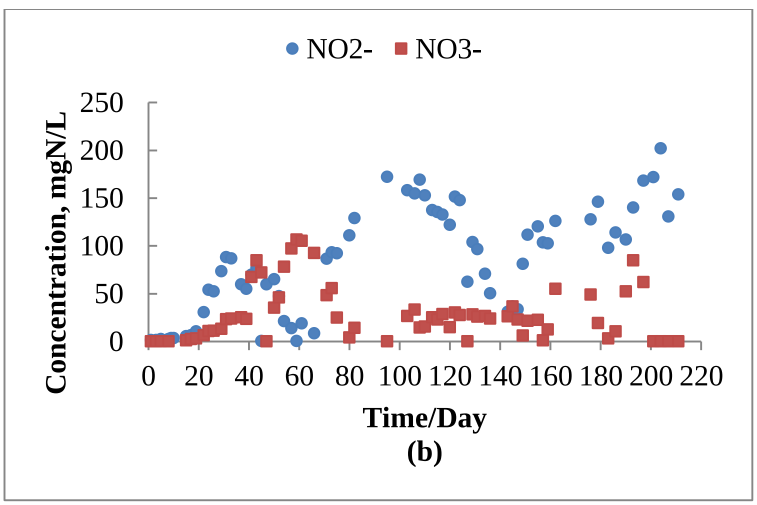
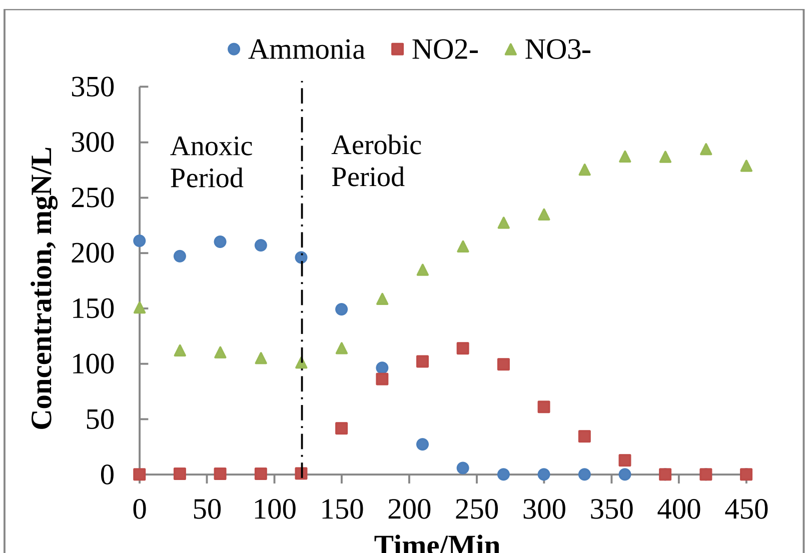


Figure 4.4. NO_2^- and NO_3^- accumulation in effluent of (a) the GSBR and (b) the ASBR

4.2.2.3 Denitrification

In order to assess nitrogen removal, a kinetic study was conducted on day 172. In Figure 4.5a, there was 49 mgN/L of NO_3^- removed via denitrification during the anoxic period and denitrification efficiency was 23% in GSBR. After 2.5 hours of aeration, TAN (196mgN/L) was completely removed through nitritation and nitrification and full nitrification efficiency was 64%. At the end of aeration, NO_x^- accumulated concentration in the effluent was 177 mgN/L. Therefore, 19 mgN/L of NO_x^- was removed as N_2 during the aerobic period. This observation confirmed the occurrence of SND with very low efficiency (only 10%). The low denitrification efficiency could be associated to the low level of available VFA as mainly was consumed by heterotrophic bacteria (like PAOs) As shown in Figure 4.5b, in ASBR the denitrification efficiency during anoxic period was close to 70% During aeration period, 97% TAN was removed through nitritation and nitrification after 5.5 hours' aeration and full nitrification efficiency was 11%.   Moreover, the nitrate concentration slightly increased by 30 mgN/L and nitrite gradually accumulated to 254 mgN/L at the end of cycle. The denitrification only happened in anoxic period and there is no SND in ASBR.



(a)

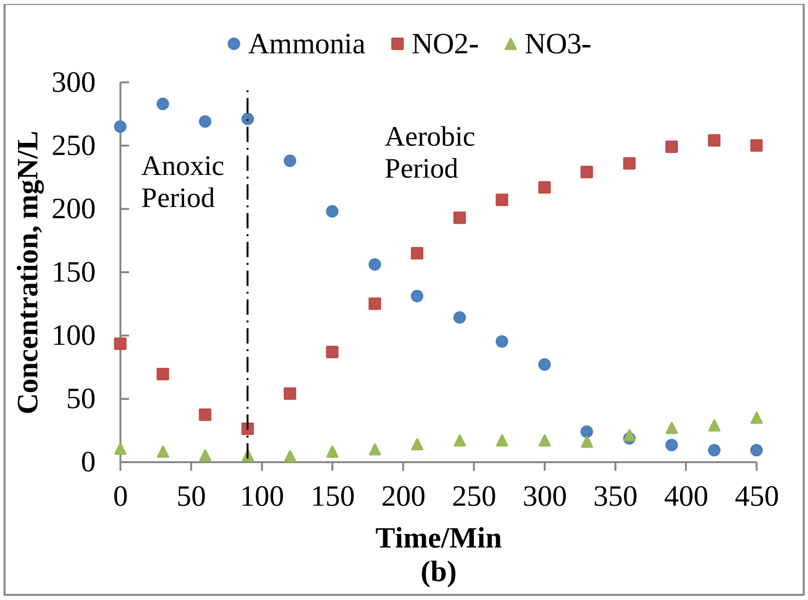
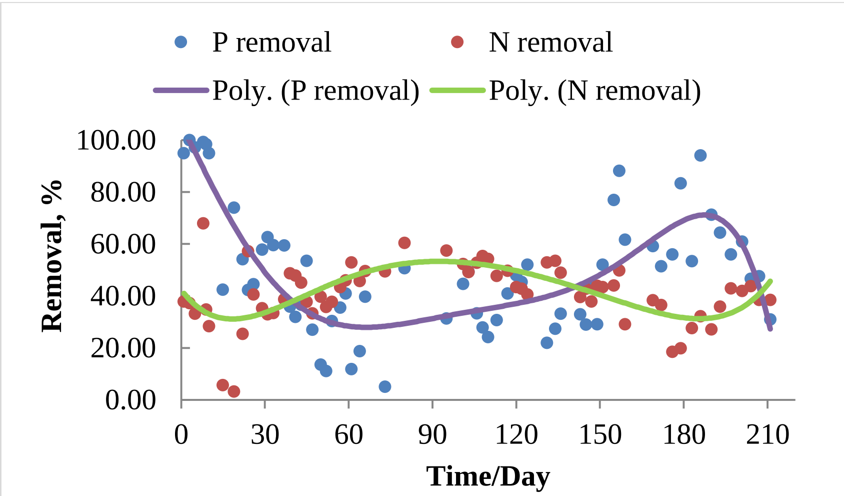


Figure 4.5. TAN and NO_x^- profiles along with time during kinetic test performed for (a) GSBR and (b) ASBR.

4.2.2.4 Phosphorus Removal

Phosphorus concentration in the influent of both reactors varied from 2 to 6 mg/L. Such variations could not be avoided due to possible precipitation of phosphate with other components of the synthetic leachate while it was kept under refrigeration. The phosphorus removals in GSBR and ASBR were shown in two stages during the whole experiment. At first stage (from day 1 to 73), the influent phosphorus concentration was 5±0.8 mg/L. High level of phosphorus removal (97±2%) was maintained during the first 10 days in GSBR, but it started to decrease gradually to less than 10%. The same trend was observed in ASBR. The phosphorus removal was 89±17% during the first 17 days and decreased to 13%. At the beginning of the first stage, phosphorus removals could be kept at a high level in both reactors, which probably resulted from the P storage by PAOs. At second stage (from day 78 to 211), the influent phosphorus concentration was 3±0.7 mg/L. Compared with the first stage, the phosphorus removal increased but it was fluctuant between 36±10% and 62±16% in GSBR, whereas phosphorus removal was almost stable in ASBR, 55±10%. As it is shown in Figure 4.6, that phosphorus removal trend during the operating cycles was opposite to nitrogen removal. This could have been caused by competition of heterotrophic denitrifiers and PAOs over VFA or readily-biodegradable COD (Guerrero, Guisasola and Baeza 2011).



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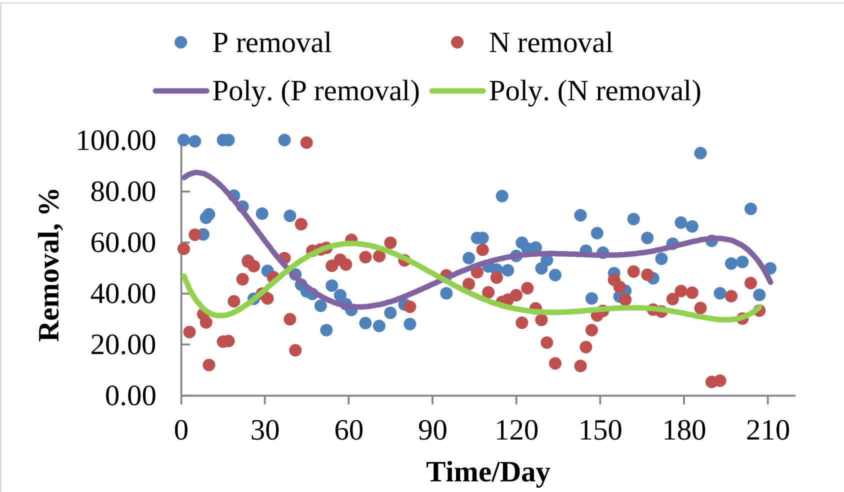
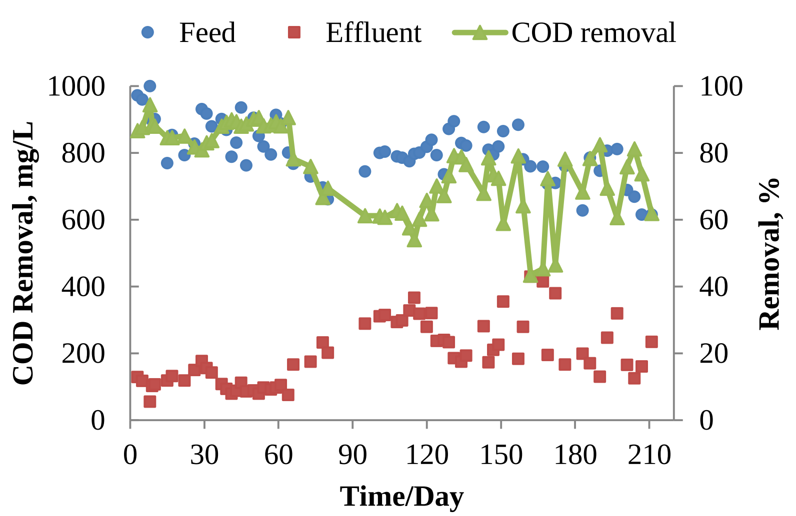


(b)

Figure 4.6 Phosphorus and nitrogen removals along with time for (a) the GSBR and (b) the ASBR

4.2.3 COD Removal

The average COD concentrations of synthetic leachate were 810±83 mg/L in GSBR and 811±75 mg/L in ASBR. In the GSBR (Figure 4.7a), the average COD removal during 73 days was high, around 87±4%. Then, COD removal began to decrease reaching an average of 67±11%. The same trend was observed for the ASBR (Figure 4.7b): during the first 73 days the average COD removal was 83±4%, decreasing to 52±11% throughout the rest of experiment. The COD removal decreasing in both reactors might be related to the influent COD/TAN ratio. A recent study reported the influent COD/TAN ratio could influence the dominant bacterial type in aerobic granules (Kocaturk and Erguder 2016). Kocaturk and Erguder (2016) found the higher COD/TAN ratio in the influent, it was the more suitable for COD removal. In current research, the average influent COD/TAN ratios was 5 before day 73 and decreased to 1.5 at the end of operation time in GSBR and ASBR, which could affect the COD removal based on the study of Kocaturk and Erguder (2016).



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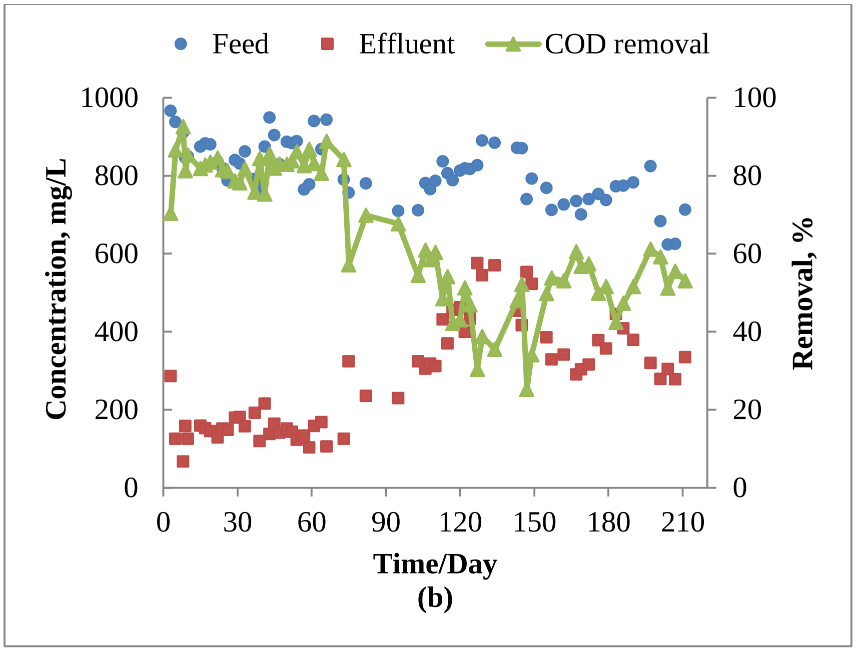


Figure 4.7. COD concentration in feed and effluent of (a) GSBR and (b) ASBR

4.3 Conclusion

Aerobic granular sludge achieved 99% of TAN removal with high level of influent TAN concentration and full nitrification efficiency (56±12%) was maintained without nitrite accumulation. Although for both reactors TAN removal was intrinsically related to the influent TAN concentrations. GSBR showed better performance compared to ASBR in leachate treatment, as it was able to recover in a short time from toxicity caused by high concentrations of FA (around 6 mgN/L) and FNA (0.3 mgN/L). COD removals ranged from 67 to 87% and phosphorus removal was approximately 49% in GSBR. According to the observations from this study, it can be concluded that the aerobic granular sludge presents a promising option to be applied as an on-site alternative for leachate treatment. Aerobic granular sludge showed a satisfactory level of performance in removing nutrients and organic matter from young landfill leachate, being more efficient than the conventional suspended growth activated sludge.

Chapter 5 Assessment of Old Landfill Leachate Treatment by Aerobic Granular Sludge and Activated Sludge Processes

5.1 Introduction

Landfilling is used worldwide as a strategy for municipal solid waste (MSW) disposal. Modern landfills offer a safe final disposal of MSW; however, when the liquids (e.g. precipitation, water content of the waste) seep through the waste, it generates a wastewater pollutant called leachate. Among its constituents, there are heavy metals, dissolved solids, ammonia, biodegradable, and refractory organic matter. To prevent impact on the environment and human health, leachate that must be accumulated from the landfills and treated. According to the biodegradation stage of MSW, the concentrations of these compounds may vary and leachate can be classified as old or young. The latter refers to leachates containing a high amount of volatile fatty acids (VFAs), whereas old leachates are mostly constituted by refractory organic matter (as humic substances) and high ammonia nitrogen concentrations (Renou et al. 2008).

The most commonly used methods for leachate treatment; especially, old landfill leachate is physico-chemical and biological processes. Deng et al. (2011) tested the application of sulfate radical-advanced oxidation process (SR-AOP) to simultaneously remove refractory organics and ammonia nitrogen from old leachate. The results of laboratory tests showed that AOP and coagulation processes could reduce the refractory organic content of old leachate. Moravia et al. (2013) reported removal of 50% for humic substances and 76% for true color when old leachate was treated by AOP/Fenton. With a focus on reuse of water, the treated leachate was further submitted to microfiltration and ultrafiltration, which removed almost all the remaining organics. Despite the good results, physico-chemical methods typically need to be combined to produce a treated effluent in accordance with restricted discharge limits. Consequently, its application may be limited by the high operational costs related to energy and chemicals consumption (Renou et al. 2008).

Biological processes have been also used worldwide to treat leachate. They are particularly effective to treat young leachate containing easily biodegradable organic matter (Renou et al. 2008). In the research of Zhu et al. (2013), the biological processes that combined ASBR with SBR could improve the COD and total nitrogen (TN) removal from the young landfill leachate. When the influent COD of the system was 7000–10000 mg/L and TN reached 1200–1500 mg/L, the high COD and TN removal rate were maintained above 89% and 97%, respectively. Other research by Brennan et al. (2017) studied co-treatment of leachate in wastewater treatment plants (WWTP) and found that young leachates, loaded at volumetric ratios greater than 2%, could significantly influence the nitrification in WWTP, whereas intermediate leachates, loaded at volumetric ratios of up to 4%, did not inhibit nitrification.

There are several concerns about the application of biological processes for the treatment of old leachate, which contains high concentrations of ammonia and refractory organic matter (Renou et al. 2008). Nonetheless, certain strategies may be adopted to enhance the biological treatment of the old leachate, including the pre-treatment and co-treatment with domestic wastewater.

Chemlal et al. (2014) found that the advanced oxidation process (AOP) as pre-treatment could enhance the performance of an aerated bioreactor in sequence, which increased the biodegradability of the refractory fractions. Finally, the AOP-bioreactor allowed an abatement of 90% of BOD and 87% of COD from the old leachate. According to research conducted by Yuan et al. (2016), the old leachate after air stripping as a pre-treatment was used to merge with varying volumes of municipal wastewater ($V_{leachate}/V_{wastewater}$ = 2.5%, 5%, 10%) followed by co-treated using SBR. At the favorable leachate ratio of 2.5%, 87% and 100% of COD and phosphorus were removed from the pre-treated leachate through the SBR process, respectively. Similar results have been reported in other research works (Ferraz et al. 2016, Campos et al. 2014). Moreover, EI-Gohary and Kamel (2016) increased the leachate volume ratio to 50% with a similar treatment process (air stripping + aerobic and anaerobic biological batch-scale processes). The results were showed that the COD removal rate of aerobic treatment was 64%, which was higher than anaerobic treatment at 41%. Increasing the leachate volume ratio could influence biological nutrient removal performance in the co-treatment.

Recent studies have discussed the treatment of domestic and industrial wastewaters by aerobic granular sludge (AGS), which reported their higher tolerance to toxic substances and adverse conditions compared to the activated sludge process (Pronk et al. 2015, Lotito et al. 2012). Wei et al. (2012) treated old leachate using AGS and reported removals of 83% for COD and up to 92% for ammonia nitrogen. This is the only paper about leachate treatment by AGS; however, this topic must be further investigated.

Considering that the literature is lacking information regarding leachate treatment by AGS, this study aimed to assess old leachate treatment by AGS in comparison with the activated sludge process. The study was performed using two sequencing batch reactors (SBR), an activated sludge SBR (ASBR) and an aerobic granular sludge SBR (GSBR). The reactors were evaluated based on the organic matter and nutrient removal efficiencies.

5.2 Results and Discussions

5.2.1 Biomass Characteristics

The GSBR and ASBR were operated for 200 days. The ASBR was inoculated with 3430 mg/L of MLSS, but this value decreased to 1550 mg/L during a start-up period of 30 days. The activated sludge presented good settling properties: the values of SVI_5 and SVI_{30} were 45±1.8mL/gVSS and 42 ± 8 ml/gVSS, respectively. According to Metcalf and Eddy (2003), good settleability is observed when the sludge presented SVI_{30} values smaller than 150 ml/gVSS.

The GSBR was inoculated with activated sludge at an MLSS concentration of 4030 mg/L. As granulation was developed, the MLSS concentration in the GSBR was gradually increased, reaching an average of 8070±615 mg/L after 100 days. This value was maintained along over time, whereas the MLVSS represented about 86% of the MLSS concentration. The average size of the seed sludge was 118 µm and it increased up to 307 µm in approximately three weeks as the AGS was developed. Great settling properties were observed as the AGS was formed: the SVI_5 decreased from the initial value of 45±1.8 mL/gVSS to 25±3.5 mL/gVSS.

Regarding EPS analysis, protein concentration (PN) in both reactors was quite similar: 30.75 mg/gVSS for the GSBR and 33.59 mg/gVSS for the ASBR (Table 5.2). However, the difference between the two types of sludge was highlighted by the polysaccharide (PS) concentration. Due to the intrinsic characteristics of granulation, i.e., granules' backbone being constituted by PS (Adav and Lee 2008), the PS concentration was higher in the GSBR than in the ASBR. The ratio PN/PS was on average 0.60 for the GSBR and 0.75 for the ASBR. The preponderance of PS over PN is associated with the hydrophilic properties of microbial aggregates (Sheng, Yu and Li 2010).

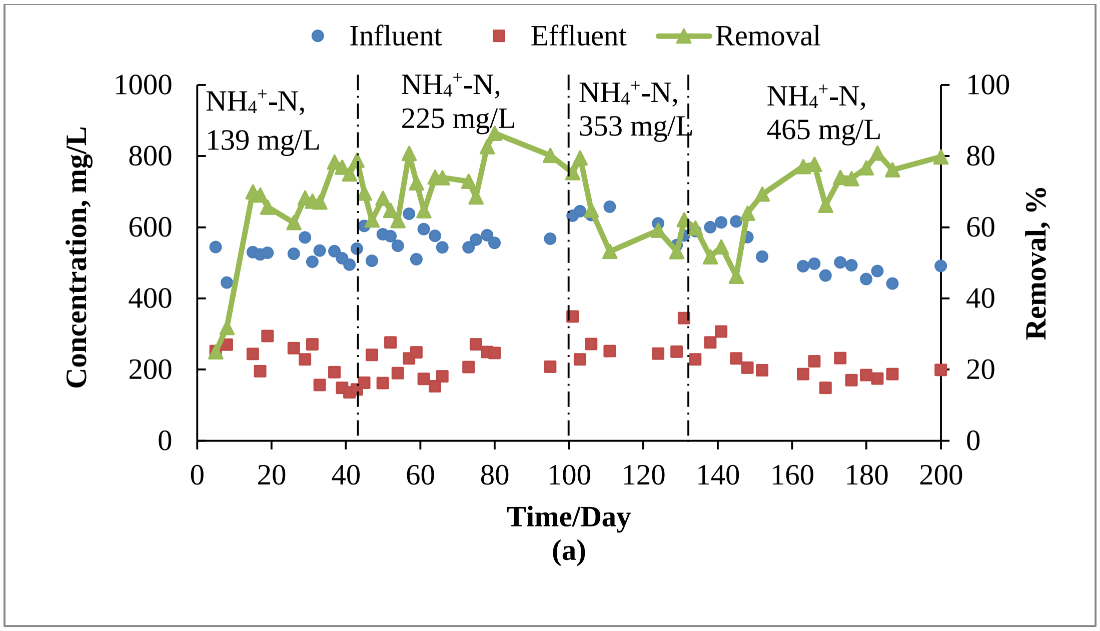
Table 5.1. The average PN, PS concentration and PN/PS ratio in GSBR and ASBR

Biomass	PN mg/L	PS mg/L	PN/PS
Aerobic granular sludge	30.75	70.13	0.60
Activated sludge	33.59	49.55	0.75

5.2.2 COD Removal

The influent COD concentrations were similar in both reactors, ranging from 448 to 654 mg/L. As shown in Figure 5.1, the GSBR was much more efficient in removing the COD than the ASBR. In other words, the granular sludge could tolerate higher concentrations of influent COD and ammonia nitrogen than those applied to the ASBR. As shown in Figure 5.1a, after 15 days the GSBR was already removing 70% of COD, maintaining the stable removal efficiency in 73±8% while the influent ammonia nitrogen was up to 225±21 mg/L. When the influent ammonia nitrogen concentration was increased to 450 mg/L, COD removal decreased to 55±8%. However, the granular sludge recovered its performance in maintaining a COD removal efficiency of 66±12%. It was clear that the GSBR could tolerate a high ammonia nitrogen concentration of 465±46 mg/L.

In contrast to the GSBR, the ASBR did not present a stable COD removal during the first 30 days of the start-up where the efficiencies varied from 38 to 70% (Figure 5.1b). While the influent ammonia nitrogen concentration was 136 mg/L, COD removal was 59±12%. As the ammonia nitrogen was slightly increased to 168 mg/L, the biomass could tolerate such concentration and COD removal was slightly increased to 62±8%. At the last stage of the experiment, where ammonia nitrogen was increased to 217 mg/L, COD removal slightly decreased to 59±9%.



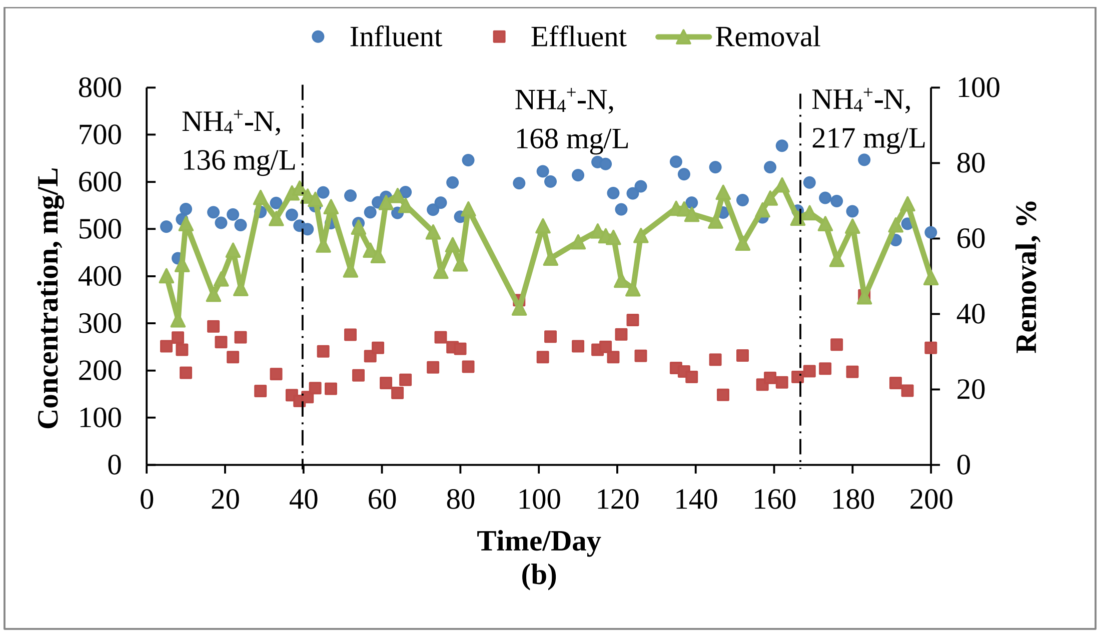


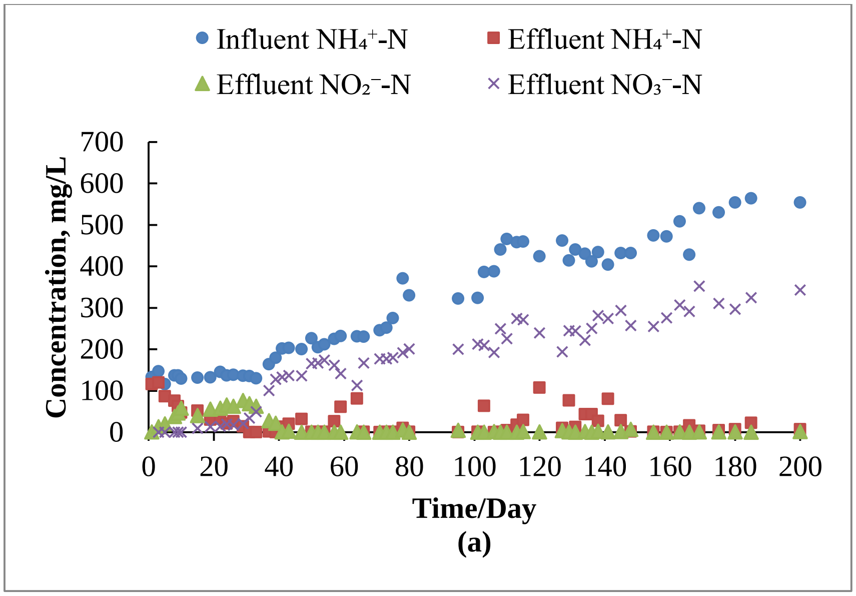
Figure 5.1. COD removal profiles along with time: (a) GSBR and (b) ASBR.

5.2.3 Nutrients Removal

5.2.3.1 Nitrogen removal

The ammonia nitrogen concentration in the influents was gradually increased in accordance with the increasing dosages of NH_4Cl in the feed of both reactors. The nitrogen loads varied from 0.28±0.03 kgN/m^{3}d (139±14 mg/L) to 1.02±0.08 kgN/m^{3}d (465±46 mg/L) for the GSBR and from 0.27±0.02 kgN/m^{3}d (136±9 mg/L) to 0.43±0.05 kgN/m^{3}d (217±26 mg/L) for the ASBR.

After 15 days, ammonia nitrogen removal (nitritation+ nitrification) (Eq. 7) by the GSBR was already 61% (Figure 5.2a). As the biomass became adapted to the increasing influent concentrations of ammonia nitrogen, the removal efficiencies were also increased. A maximum average of ammonia removal of 95±7% was obtained when the GSBR was loaded with 1.02±0.08 kgN/m^{3}d (465±46 mg/L). The same trend was observed for TN, whereas the maximum removal efficiency of 39±7% was observed when the maximum nitrogen load was applied. Accordingly, SND efficiency (Eq.6) at the last stage of the experiment was 40±7%, indicating that SND was most likely the primary mechanism of TN removal, which was further assessed by kinetic tests. Figure 3a shows that production of nitrate increased with time and its concentrations were much higher than nitrite. At the last stage of the experiment, the full nitrification efficiency was 62±9% (Eq. 3), suggesting that nitrifiers in the GSBR were not significantly inhibited by the lower influent FA concentration of 2.7 mgN/L at pH of 7. This result was in agreement with the previous study that nitrifiers from activated sludge were inhibited at FA concentrations of 4 mgN/L (Yang et al. 2004). However, denitrification or SND do not seem to have been fully achieved, which was further assessed during a kinetic test (Figure 5.3a).



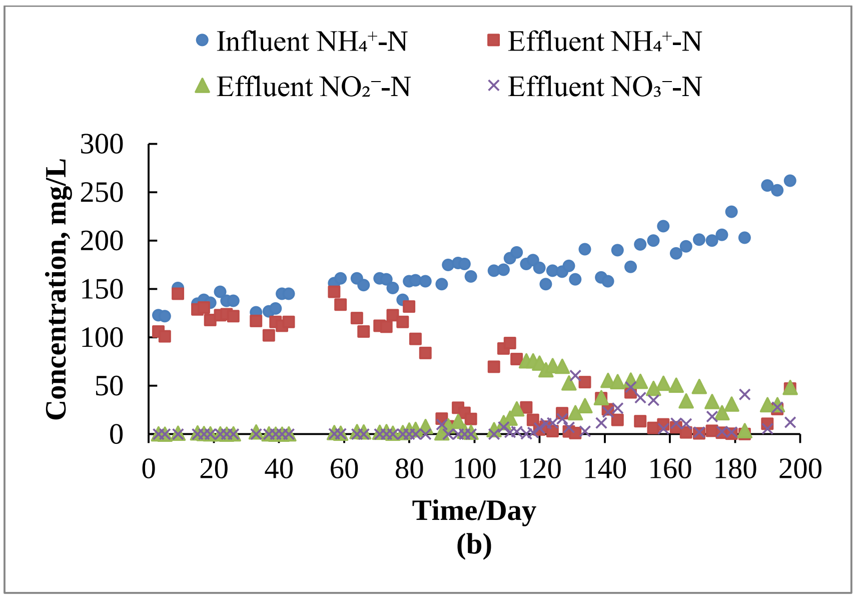
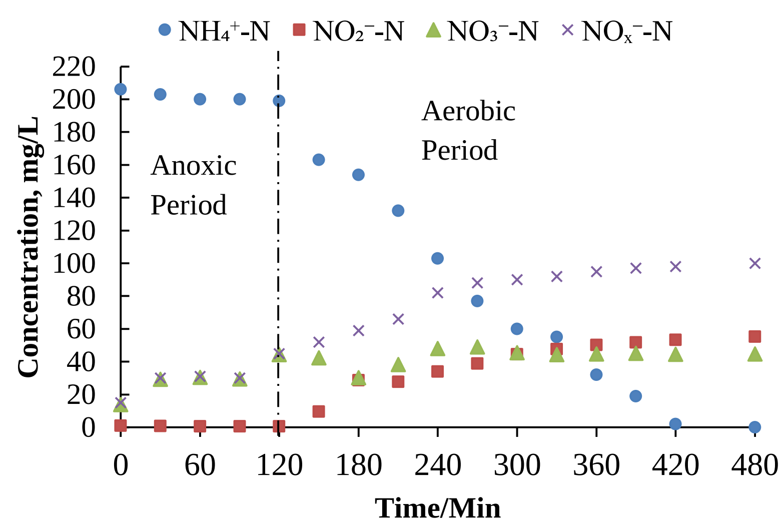


Figure 5.2. Ammonia nitrogen, nitrite nitrogen and nitrate nitrogen profile along with time: (a) GSBR and (b) ASBR.

According to a kinetic test performed on day 95 (Figure 5.3a), the GSBR cycle started with 221 mg/L of TN and 121 mg/L were removed at the end of it (i.e, TN removal of 55%). The denitrification was not observed during the anoxic period. It is worth noting that despite the availability of carbon source during the anoxic period due to feeding, the incoming influent could not have been properly mixed with all the settled biomass, which resulted in the absence of significant denitrification activity. Additionally, tannic acid could have been less susceptible to biodegradation under anaerobic/anoxic conditions rather than under aerobic conditions, which was also observed by (Ramos, Suárez-Ojeda and Carrera 2016b). In contrast, during the aerobic period, 121 mg/L of TN were removed via SND at an efficiency of 59%. Our results were in agreement with other studies in the literature related to the treatment of ammonium-rich wastewaters (Wei et al. 2012, Yan et al. 2015).

During the first 40 days, ammonia nitrogen removal (Eq.7) by the ASBR was extremely low, 13±6% (Figure 5.2b), i.e., it was almost 7 times lower than the efficiency presented by the GSBR for the same influent ammonia concentration. As the biomass became adapted to the increasing influent concentrations of ammonia nitrogen, the removal efficiencies were also increased. A maximum average of ammonia removal, 96±5%, was obtained when the ASBR was loaded with 0.4±0.05 kgN/m3d (217±26 mg/L). The TN removal efficiencies (Eq.7) also increased with time, reaching a maximum of 72±10% when the maximum nitrogen load was applied. Nitrate was detected at concentrations as low as 10 mg/L only after 100 days, whereas during most of the experimental duration NAR (Eq.4) ranged from 70 to 85% (Figure 5.2b). A kinetic test was performed to better investigate the mechanisms for TN removal. In contrast to the GSBR, the influent FA concentrations (pH=7.0) applied to the ASBR ranged from 0.8 to1.2 mgN/L (half of the FA applied to the GSBR), which interfered with the performance of nitrite oxidizing bacteria (NOB) because inhibition of NOB occurred at FA of 0.1 to 1 mgN/L (Yun and Kim 2003). Therefore, the influent FA concentration was a possible factor of nitrite accumulation in ASBR, conforming to the previous study (Cydzik-Kwiatkowska et al. 2013).

The kinetic test for the ASBR was performed on day 135 (Figure 5.3b), when the cycle started with 145 mg/L of TN and 83 mg/L were removed at the end of it (i.e., TN removal of 57%). The denitrification efficiency during the anoxic period was 18%, which was likely associated to the low biodegradability of tannic acid under anaerobic/anoxic conditions, whereas the ASBR was provided with mixing in the absence of aeration. Nonetheless, during the aerobic period, 68 mg/L of TN were removed via SND at an efficiency of 63%. Although this result was similar to the SND presented by the GSBR, the latter was loaded with an influent ammonia nitrogen concentration that was 1.5 times higher than GSBR.



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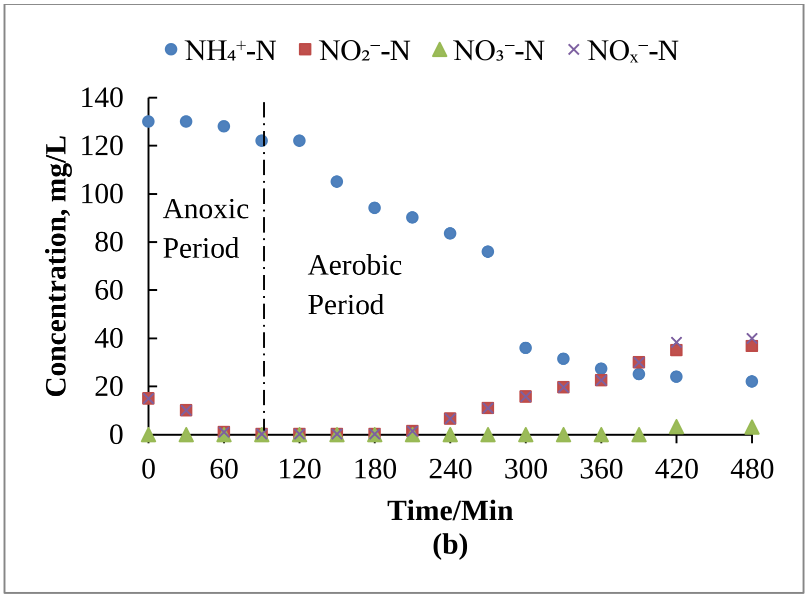
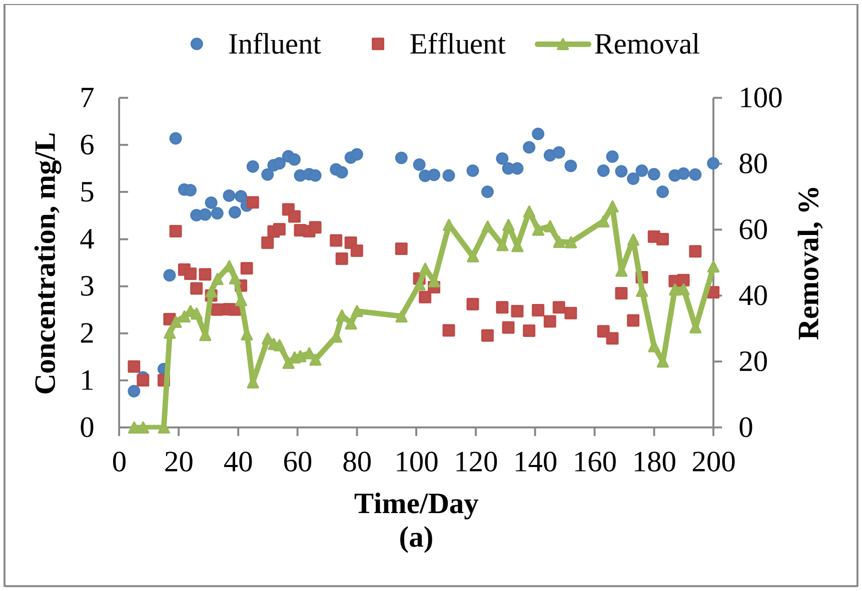


Figure 5.3. Nitrogen removal during a typical cycle by (a) the GSBR and (b) the ASBR.

5.2.3.2 Phosphorus removal (PR)

The influent phosphorus concentration of approximately 6 mg/L was found in both reactors (Figure 5.4). However, phosphorus removal (PR) by the GSBR was gradually increased with time and reached a maximum efficiency of 54±7% (Figure 5.4a). The same trend was observed for the ASBR, which presented a maximum PR of 49±14% (Figure 5.4b). Despite these similar average efficiencies, it was clear that the ASBR presented considerable fluctuations in comparison with the GSBR, which were much more stable.

These moderate PR efficiencies could have been caused by the low biodegradability of tannic acid. A previous study (Muszyński and Miłobędzka 2015) reported that polyphosphate accumulating organisms (PAO) accounted for 70% of all bacteria from AGS when the ratio COD/P was 15:1, which was associated with a high phosphorus release/dissolved organic carbon uptake ratio (0.4). The opposite trend was observed when the COD/P ratio was 100:1, favoring the glycogen accumulating organisms (GAO), which compete with PAO for carbon source. In the current research, the ratio COD/P throughout the experiment varied from 75:1 to 100:1, probably favoring the GAO activity. Additionally, phosphorus removal could have been affected by FNA. It was recently reported (Jabari et al. 2016) that at an FNA concentration of 1.2 μgN/L inhibited 88% of PAO activity. In our study, FNA (pH=6.5) varied from 1 to 5 μgN/L for the GSBR, whereas it was extremely high for the ASBR, ranging from 13 to 97 μgN/L.



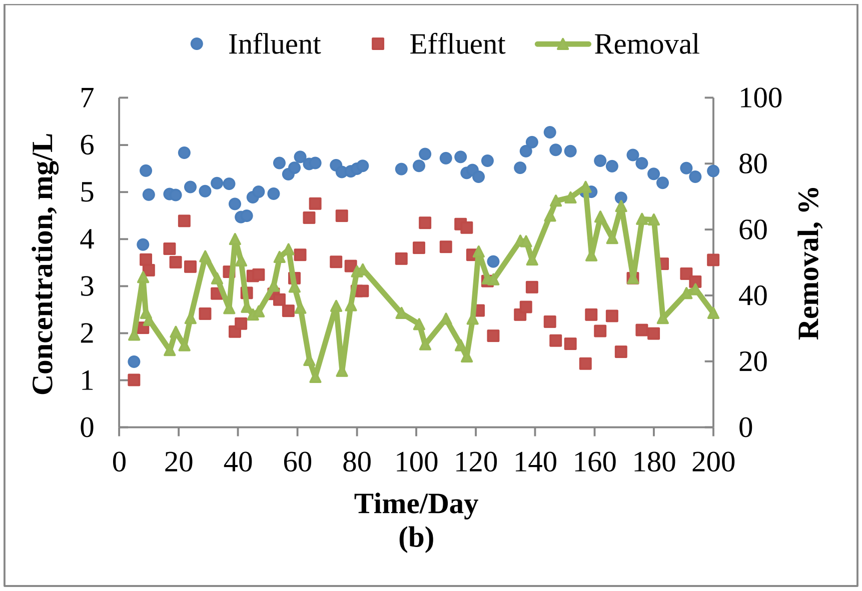


Figure 5.4. Phosphorus removal (PR) along with time for (a) the GSBR and (b) the ASBR

5.3 Conclusions

This study compared the performances of a GSBR and an ASBR in the treatment of old leachate. From our results, it was concluded that the GSBR was much more efficient than the ASBR regarding the organic matter and nitrogen removal. The PR was similar for both reactors. The granular biomass was able to tolerate influent ammonia concentrations 1.5 times higher than those applied to the ASBR. Although the GSBR was exposed to higher FA concentrations, no nitrite accumulation was observed. In contrast, NAR was up to 85% for the ASBR. Further investigations should be addressed, especially with a focus on improving SND and PR efficiencies; however, the use of AGS should be encouraged for a high-strength wastewater such as old landfill leachate.

Chapter 6 Biological leachate treatment: suspended growth activated sludge vs aerobic granular sludge

6.1 Introduction

Leachate is a collection of wastewater generated in landfills due to the precipitation through municipal solid wastes, the liquid produced by biochemical processes in landfill cells, and the water constituent of the wastes (Renou et al. 2008). The composition of leachate is dependent on several factors, including temperature, precipitation, the composition of landfill waste, and the age of landfills. However, the main constituents of leachate include heavy metals, xenobiotic compounds, high concentrations of total ammonia nitrogen (TAN), and biodegradable and refractory organic matter (Renou et al. 2008, Kjeldsen et al. 2002).The terms “young” and “old” have been extensively used in literature to classify leachate regarding its composition: young leachates are characterized by acidic pH and the majority of its organic content is easily biodegradable (volatile fatty acid); whereas old leachates are characterized by alkaline pH with high concentrations of TAN and refractory organic matter, such as humic substances (Renou et al. 2008).

Several alternative methods have been considered to treat leachate. Numerous physico-chemical processes such as coagulation/flocculation, air stripping, oxidation, adsorption, and filtration have been applied to remove nitrogen and organic matter (Ferraz et al. 2013, Liu et al. 2015, Renou et al. 2008, Wu et al. 2010). However, restricted discharge limits may require the association of two or more processes, which would also increase the operational costs of physico-chemical treatment of the leachate (Renou et al. 2008).

Biological processes have been extensively applied to treat raw leachate or combination of leachate and domestic wastewater (Renou et al. 2008). High removal efficiencies of COD at 89% and TN at 97% were observed in young leachate treatment (Zhu et al. 2013). However, treatment of old leachates containing refractory organic matter and high concentrations of ammonia nitrogen has been shown to be more difficult (Contrera et al. 2013, Gabarró et al. 2012). It should be noted that biomass can be adapted to the composition of old leachates depending on biomass acclimation and start-up strategy. Successful treatment of old leachate was reported using an anaerobic sequencing batch biofilm reactor after biomass acclimation to leachate contained 4500 mgN/L of ammonia and 600 mgN/L of free ammonia (FA) (Contrera et al. 2013).

Leachate co-treatment with domestic wastewater is considered as an alternative to overcome the limitations of old leachate treatment by biological processes. The co-treatment has been reported as a feasible option and can be applied to the existing wastewater treatment plants (Renou et al. 2008).

In a recent study by Yuan et al. (2016), a pre-treated leachate using air stripping was mixed with domestic wastewater at different volumetric ratios (2.5%, 5%, and 10%) and was treated in an SBR thereafter. For a volumetric ratio of 2.5% of leachate, COD removal ranged from 63 to 87% and almost 100% phosphorus removal was reported. These results were in agreement with Campos et al. (2014) where bench-scale activated sludge (AS) reactors were operated in batches. The authors treated domestic wastewater and pre-treated leachate by air stripping at a volumetric ratio of 2% and obtained 87% of COD removal. The COD removal efficiencies were comparable to those obtained by exclusive domestic wastewater treatment (Ferraz et al. 2016). It was also reported that up to a volumetric ratio of 2%, the organic matter of old leachates was mostly biodegraded rather than being diluted into domestic wastewater (Campos et al. 2014, Ferraz et al. 2014, Ferraz et al. 2016).

Conventional suspended growth activated sludge has been extensively applied to treat leachate or mixtures of leachate and domestic wastewater. Aerobic granular sludge (AGS) can be considered as a valuable alternative to biological treatment of leachate due to its peculiar characteristics. Cultivated in SBR in late 1990, AGS presents unique characteristics, including high settling velocity, compact structure, simultaneous nutrient removal capability, and ability to sustain high biomass concentration (Adav et al. 2008). Current applications of AGSR comprise the treatment of industrial wastewater (Lotito et al. 2012, Ramos et al. 2016a), saline wastewater (Moussavi et al. 2010), and domestic wastewater (Ni et al. 2009). However, the literature is currently lacking papers about leachate treatment by AGSR. An important contribution was provided by Wei et al. (2012), who used an SBR to develop AGS for leachate treatment. Their results indicated close to 83% of COD removal and nitrogen removal varied from 44% to 92% depending on the influent ammonia concentrations.

Considering the advantages of AGS presented above and the lack of studies supporting AGS application in leachate treatment, this study aimed to compare the performance of AS and AGS in biological leachate treatment.

6.2 Results and Discussions

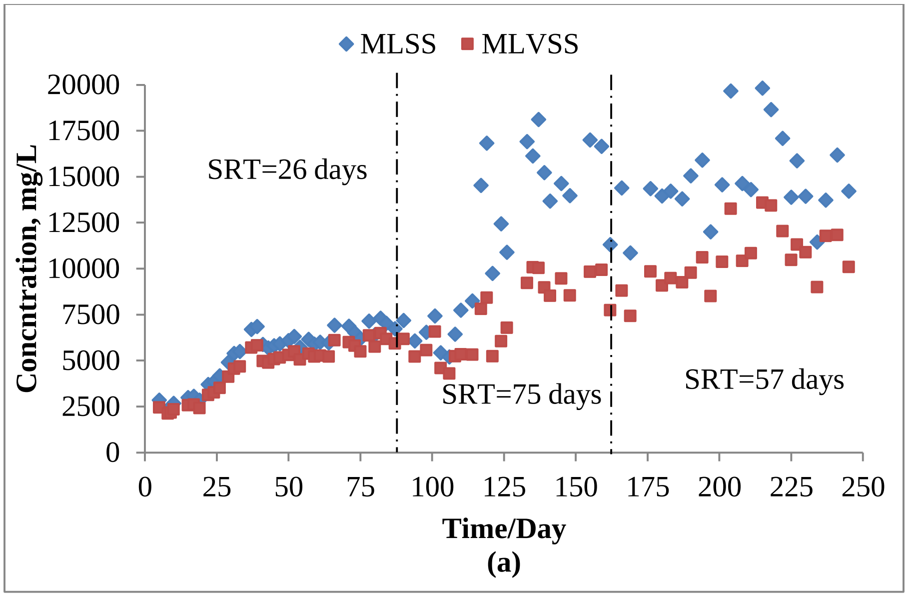
6.2.1 Aerobic sludge characteristic

The GSBR and ASBR were operated for 245 days each. In GSBR, biomass gradually grew and MLSS increased from 2591±222 mg/L to 6476±522 mg/L during the first 40 days (Figure 6.1a), when MLVSS was close to 87% of MLSS concentration. After 90 days, MLSS increased up to

14533±2526 mg/L and SRT increased up to 75±15 days, but MLVSS/MLSS ratio was dropped to 0.59. From day 162 to the end of the experiment, MLSS stayed stable at a concentration of approximately 12707±2273 mg/L and MLVSS ratio increased to 71% of MLSS. At the beginning of the experiment, the increase in MLSS concurred with granulation. Particle size increased from the initial value of 180 to 260 µm after 15 days. After 70 days, the biomass was mostly granular (90%) and average particle size varied from 210 to 480 µm.

As shown in Figure 6.1b, SRT was controlled from 10 to 40 days in ASBR. At SRT of 10 days, MLSS was slightly increased from 2092±220 mg/L to 3000±505 mg/L and MLVSS/MLSS ratio was approximately 0.88. After 113 days from the reactors' inoculation, SRT increased up to 20 days. By increasing the SRT, MLSS was significantly increased to approximately 20000 mg/L. However, MLSS concentration decreased as SRT increased to 30 and 40 days. At the end of the experiment, MLSS stayed at 7010±689 mg/L and MLVSS/MLSS increased from 0.47 to 0.62.

Both reactors showed good settleability. The average value of SVI_{30} in ASBR was approximately 20 mg/L on the 198th day, which increased to 54 mL/g after 245 days. Although the average value of SVI_5 in GSBR was approximately 19 mL/g during the whole experiment, it was much lower than SVI_{30} in ASBR. This confirmed the higher settling velocity of AGS over suspended growth activated sludge.



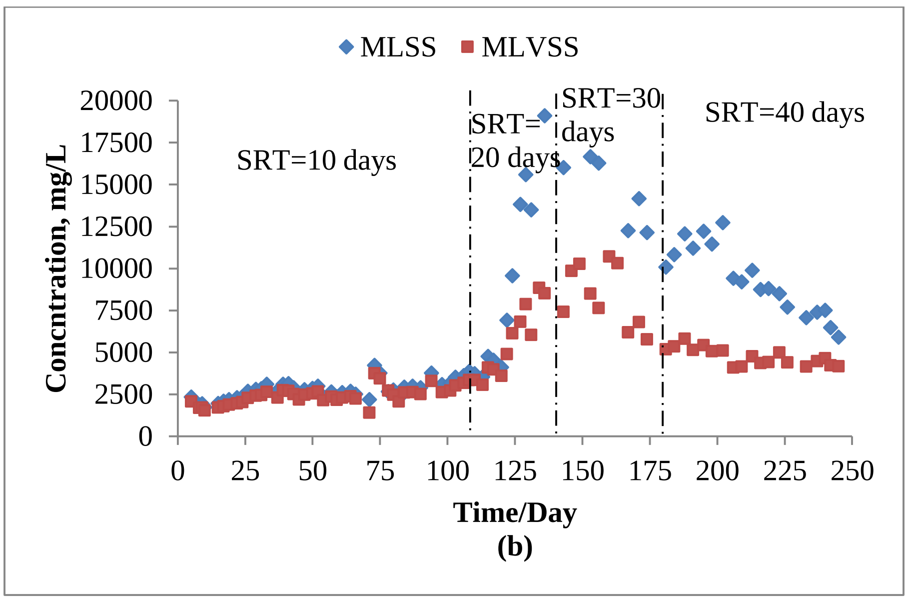


Figure 6.1. MLSS and MLVSS concentrations over the course of the study: (a) GSBR and (b) ASBR

6.2.2 EPS production

Extracellular polymeric substances (EPS) are produced by bacteria and form a gel-like network and accumulate on the surface of cells. EPS includes polysaccharides (PS), proteins (PN), glycoproteins, nucleic acids, and other compounds (Salama et al. 2016). The concentrations of protein and polysaccharides are the main parameters to analyze the EPS. Therefore, PN and PS production was monitored in GSBR to track their changes associated with increasing volumetric ratios of leachate in the influent. According to Figure 6.2a, PS was predominantly higher than PN for the evaluated volumetric ratios of leachate (60% to 100%), and the average PN/PS ratio varied from 0.28 to 0.42. The PN/PS ratio showed a decreasing trend by increasing the influent leachate volume. This indicates that leachate affected PN and PS production and subsequently influenced the stability of aerobic granular sludge. Because of hydrophobic and hydrophilic characteristics of PN and PS, respectively, higher PN/PS ratio results in higher surface hydrophobicity and helps granules formation and their stability (Zhang et al. 2007). However, the results from this study contradict some previous studies on EPS composition in aerobic granular sludge (Yan et al. 2015, Zhu et al. 2012). In the aforementioned studies, the content of PN was predominant over PS, especially when mature granules dominated the system. In ASBR, PN concentration was higher than PS (Figure 6.2b) and the average PN/PS ratio was between 0.77 and 2.35. The PN/PS ratio showed increasing trend as the influent leachate ratio increased (50-65%). This could result from increasing the free ammonia concentration by the increased influent leachate ratio could inhibited the PS production (Yang et al., 2004).

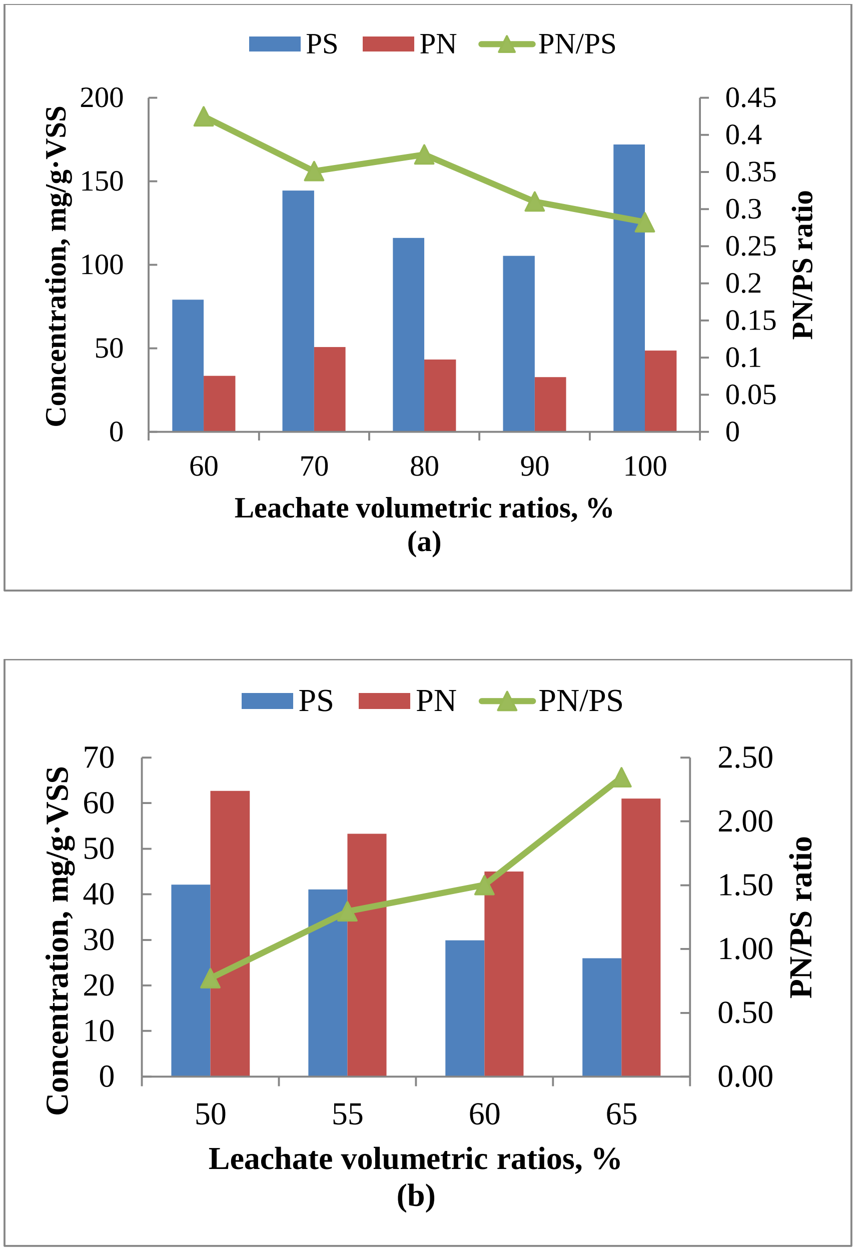


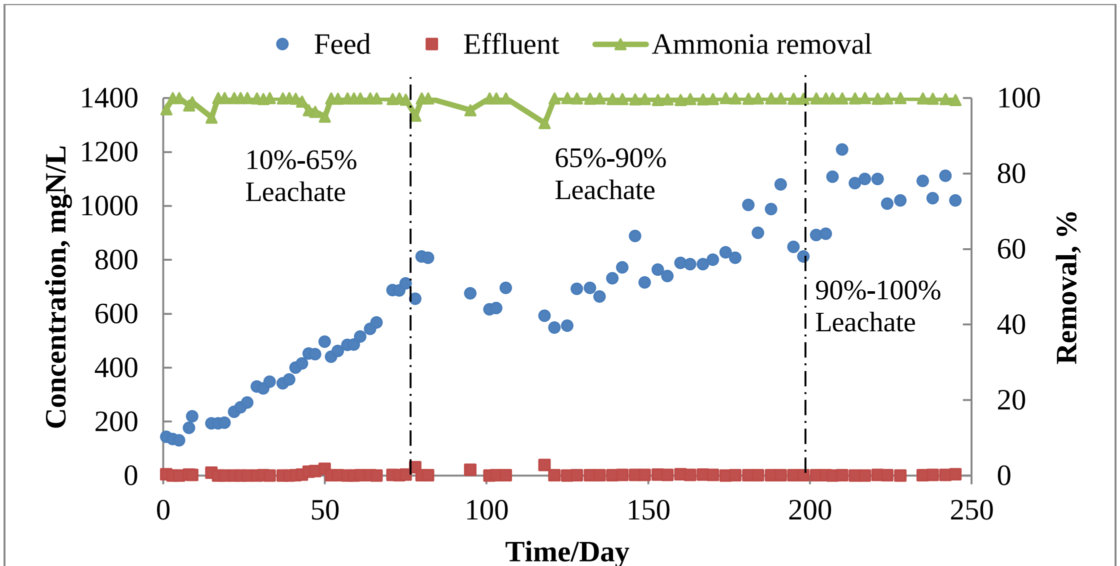
Figure 6.2. PN, PS concentration and PN/PS ratio at different influent volumetric ratios of leachate for (a) GSBR and (b) ASBR.

6.2.3 Nitrogen Removal Performance

6.2.3.1 Ammonia nitrogen removal

The TAN removal efficiency of GSBR and ASBR are shown in Figure 6.3. The TAN concentration in GSBR influent was gradually increased from 130 to 1209 mgN/L. This was done by increasing leachate volumetric ratio in the influent from 10% to 100%. As shown in Figure 6.3a, high TAN removal efficiencies were observed in GSBR. During the entire experimental period (over 245 days), ammonia removal efficiency in GSBR was stable and close to 99%. Despite the high TAN concentration in the influent as the ratio of leachate eventually increased to 100%, TAN removal efficiency was kept at approximately 99.7±0.2%. For ASBR (Figure 6.3b), TAN concentration in the influent was in the range of 81 to 712 mgN/L when the leachate mixing ratio was 10-65%. During the first 78 days of operation, TAN removal remained steady at 98% when leachate was diluted with primary effluent at volumetric ratios below 45% (TAN concentration in the influent was less than 580 mgN/L). However, when the volumetric ratio of leachate increased up to 65% and TAN concentration was in the range of 400-700 mgN/L, significant fluctuations in TAN removal efficiency were observed. TAN removal rate decreased to 25% on day 202. Due to the poor TAN removal performance, TAN concentration in the influent was decreased in the range of 380-500 mg/L from day 216 (by decreasing leachate mixing ratio to 30-50%) with the goal to recover high TAN removal efficiency. However, only a maximum of 57% TAN removal efficiency was observed.

In a previous study, Wei et al. (2012) found that TAN removal was significantly inhibited in a GSBR when influent ammonia concentrations were as high as 934–1169 mgN/L. The results presented herein showed that although the GSBR influent ammonia concentration was up to 1209 mg/L, it did not significantly influence ammonia removal efficiency. The granular sludge was able to adapt to the increased TAN concentration; whereas, the suspended growth activated sludge was more sensitive to the high level of TAN concentration (Figure 6.3b). It is well recognized that nitrifiers in activated sludge are very sensitive to the growth media. The resilience of the nitrifiers in the aerobic granular sludge could be due to the unique structure of the granular sludge. In other words, the outer layers of biomass in granules can protect nitrifiers that are located in the inner layers from the harsh conditions in the environment.



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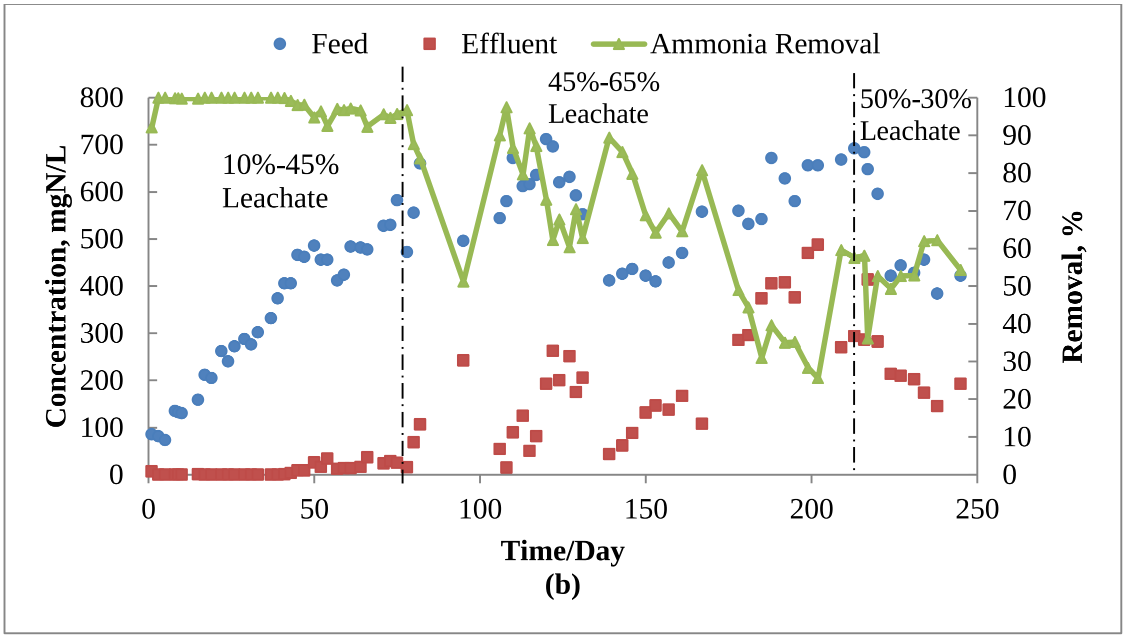


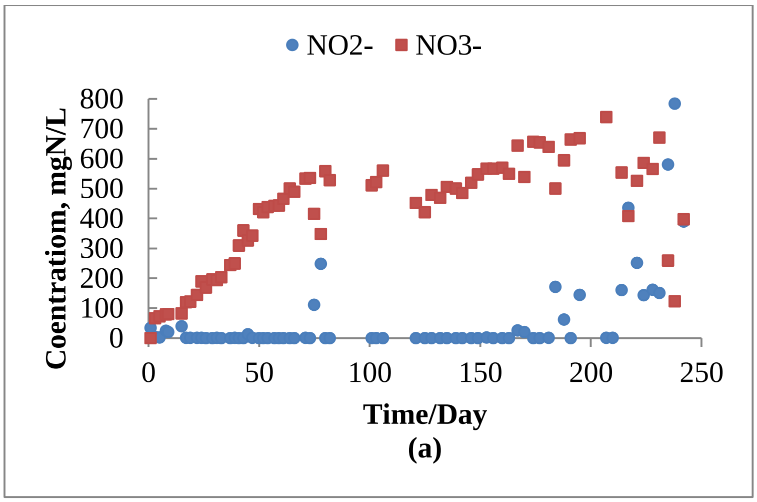
Figure 6.3. Ammonia nitrogen concentration in feed and effluent, (a) GSBR, (b) ASBR

6.2.3.2 NO_2^- and NO_3^- accumulation

As shown in Figure 6.4a, the NO_2^- concentration in the treated effluent was less than 1 mgN/L from day 15 to 181 as the GSBR influent TAN concentration was less than 900 mgN/L (leachate volumetric ratio <90%); however, there were a few data higher than 20mgN/L. During this period, full nitrification efficiency (nitritation+nitrification) was increased from 46±7% to 78±9% and TN removal efficiency was decreased from 40±7% to 24±7%. As influent ammonia concentration further increased (900–1209mgN/L), NO_2^- accumulation was observed and NAR varied from 18.4% to 86.4%, indicating that nitrification was partially inhibited. It was reported that FA up to 4 mgN/L could inhibit nitrite oxidizing bacteria (NOB) in aerobic granules (Yang et al. 2004). When nitrification was partially inhibited, FA concentration varied from 40 to 59 mgN/L, which was 12 times higher than the limit value determined by Yang et al. (2004). From day 184 to 210, it was shown that accumulated NO_2^- could be gradually oxidized to NO_3^-, indicating a possible adaptation of NOB to the high FA level (45 mgN/L) in GSBR, which is in agreement with Wei et al. (2012). At the end of the experiment, the nitrification efficiency was decreased to 36% and TN removal efficiency was almost the same as before, around 23±7%.

Similar observation was also obtained from ASBR (Figure 6.4b). During the first 15 days, the NO_2^- was the main component in the effluent. As NOBs were being adapted to the leachate, the concentration of NO_3^- was gradually increased. Under the low influent TAN (less than 450 mgN/L) condition, only nitrate was detected in the effluent at the TN removal efficiency of 37±5%. However, NO_2^- further accumulated when influent TAN concentration surpassed 450mgN/L from day 50, whereas FA concentration was 21–31 mgN/L, the full nitrification was inhibited significantly. The NO_2^- accumulation occurred rapidly (NAR>80%) and NO_3^- decreased sharply to 0 mgN/L in the effluent. This also accompanied with a decrease in TAN removal and full nitrification efficiency was decreased from 66±9% to almost 0. Although NOBs recovered functionality from the 113th day when the FA concentration around 30 mgN/L, NOBs were inhibited again after day 157 and NO_2^- predominated in the effluent. TN removal efficiency was kept at 21±6% during the latter end of the operational days.

In a previous study (Ferraz et al. 2016), NOB of a pilot-scale activated sludge reactor was partially inhibited by FA at the concentration of 3 mgN/L during the co-treatment of domestic wastewater and old leachate at a volumetric ratio of 5%. The concentration of FA in the current study was up to 10 times higher, indicating the importance of sludge acclimatization. Furthermore, FNA also partially inhibited the ammonia oxidizing bacteria (AOB). A previous study found that free nitrous acid (FNA) concentration ranging from 0.42-1.72 mgN/L could cause 50% reduction in AOB activity (Zhou et al. 2011). However, FNA was too low to affect AOB activity, whose activity may have been also partially inhibited by FA. Another possible factor could be inorganic carbon source. AOB and NOB are chemoautotrophs, the low availability of CO_2 from the slow degradation of the rdBOD, which could be part of the problem with the nitrogen cycle in both reactors. Comparing GSBR and ASBR, the latter was more susceptible to the toxic effects of FA, while GSBR seemed to have a higher tolerance to toxic substances.



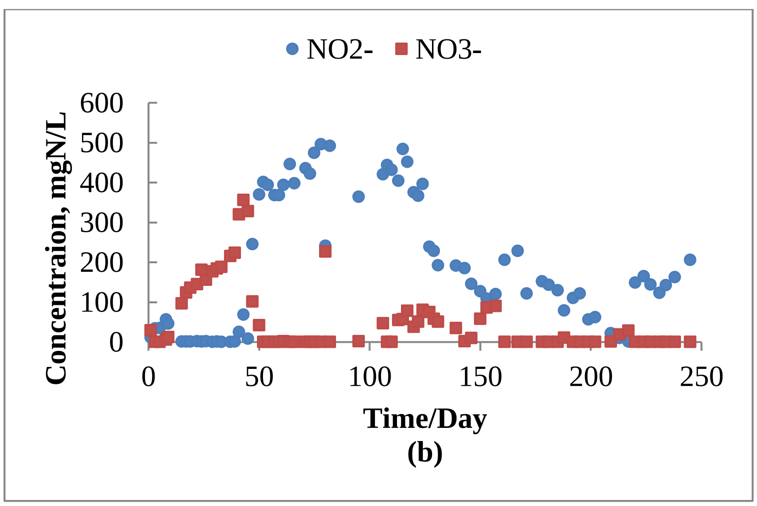
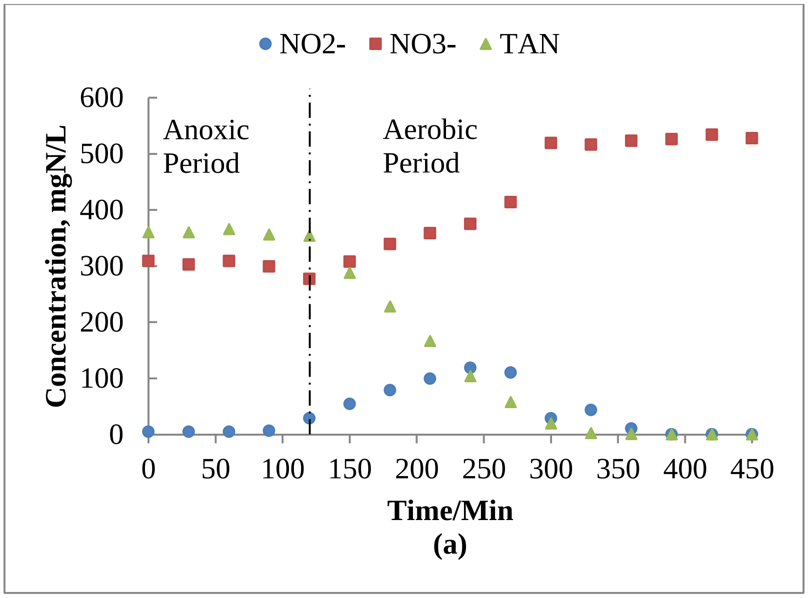


Figure 6.4. NO_2^- and NO_3^- accumulation in the effluents of (a) GSBR and (b) ASBR

6.2.3.3 Denitrification

High nitrogen removal efficiency was not satisfactorily achieved in both reactors: 26% in GSBR and 23% in ASBR. To have a better understanding of nitrogen removal, a kinetic batch test was conducted on day 82. According to Figure 6.5a, there was only 8 mgN/L NO_3^- removed in GSBR through denitrification during the anoxic period. During the aerobic period, 100% TAN removal was recorded (354 mgN/L) after 4 hours of aeration and TAN was completely oxidized to NO_3^-. At the end of the aeration period, 250 mgN/L of NO_x^- was accumulated in the effluent. Therefore, there was 104 mgN/L of NO_x^- removed during the aerobic period. This observation confirmed the occurrence of SND with a low efficiency of 29% in the reactor. In Figure 6.5b, NO_2^- was accumulated throughout a kinetic test and NO_3^- concentration in ASBR kept at 0 mgN/L. It was observed that 20 and 10 mgN/L of nitrogen were removed during the anoxic and aerobic period, respectively. A low denitrification efficiency of 13% was observed in ASBR. Meanwhile, TAN was not completely removed during the cycle. The relatively low total nitrogen removal efficiency from both reactors might be related to the low biodegradable COD available in the old leachate, which resulted in low level of carbon sources available to the denitrifiers. Moreover, other heterotrophic bacteria (like PAO) can compete for biodegradable COD with denitrifiers, which might have influenced the efficiency of denitrification and SND.



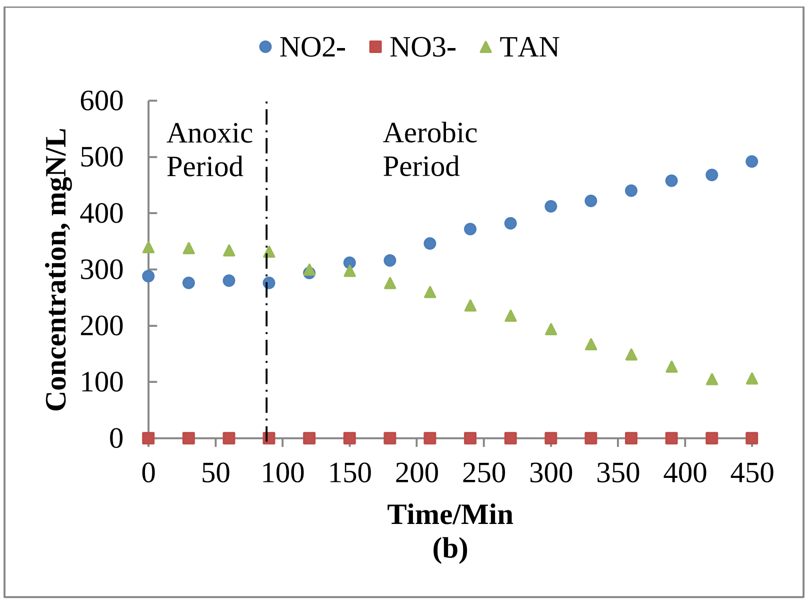
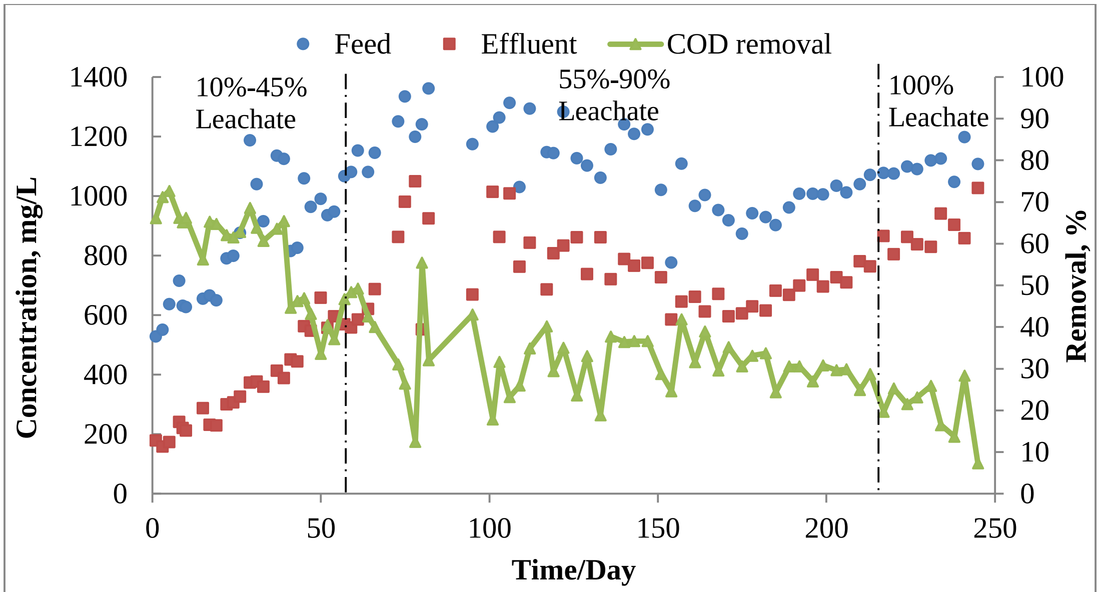


Figure 6.5. TAN, NO2- and NO3- concentration in (a) GSBR and (b) ASBR during a kinetic test

6.2.4 COD and Phosphorus Removal

The average COD removal efficiency of GSBR was around 65% for the first 40 days (Figure 6.6a). Afterward, the decrease in COD removal was observed as the leachate volume ratio increased. When the leachate volume ratio was less than 45%, the COD removal efficiency was around 43±5%. As influent leachate ratio was further increased to 90%, COD removal efficiency decreased again to 31%. At the end of the experiment, there was only 7% COD removed in GSBR. In figure 6.6b, the same trend of COD removal was shown in ASBR. When the leachate ratio was less than 35%, COD removal was as high as 63%. However, with the addition of more leachate as influent, a lower level of COD removal was achieved. The COD removal subsequently dropped to 14% at 65% leachate in the influent. When leachate ratio decreased to 30%, COD removal recovered to 34% on day 228. The performances of the two reactors suggested that most of the COD in leachate was poorly biodegradable. However, granular sludge showed a better removal performance compared to activated sludge, especially at the higher ratios of leachate in influent.



(a)

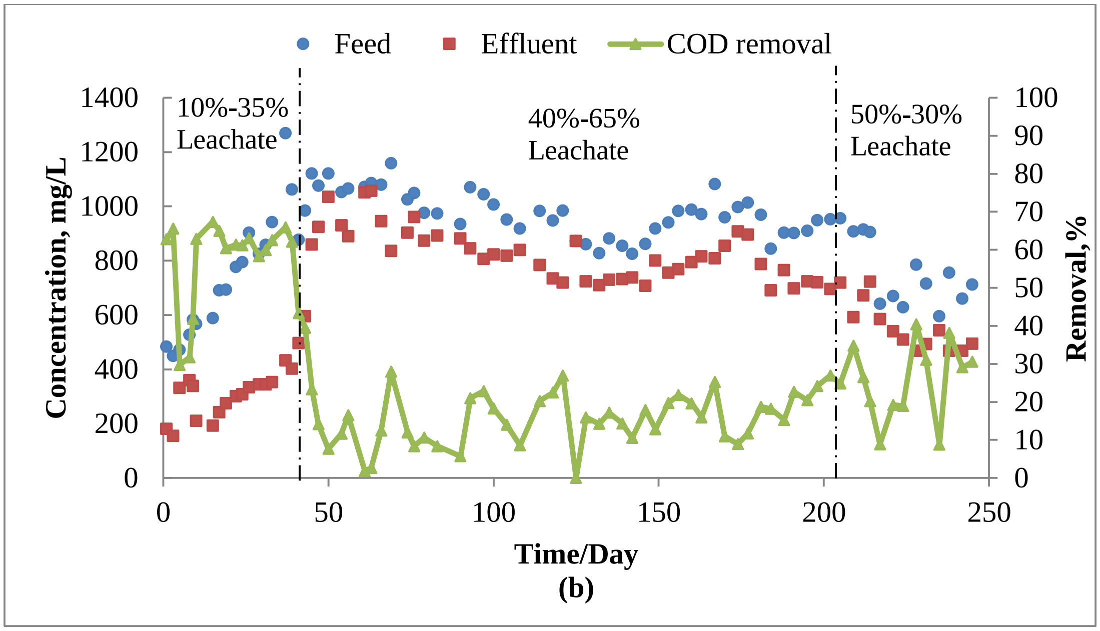


Figure 6.4. COD concentration in feed and effluent of (a) GSBR and (b) ASBR

Phosphorus concentration in the feed was between 3 to 6 mg/L. No phosphorus removal was observed in either reactors. Poor phosphorus removal efficiencies were assumed to be associated with low levels of readily biodegradable COD (rbCOD) in the leachate. In addition to the low level of rbCOD in leachate, FNA was presumed to have an inhibitory impact on polyphosphate accumulating organisms (PAO). It is reported that FNA can have an inhibitory impact on PAOs at concentrations as low as 0.5×10^{-3} mgN/L (Saito, Brdjanovic and van Loosdrecht 2004). The average FNA concentrations were 0.006 mgN/L and 0.013 mgN/L in GSBR and ASBR, respectively. These FNA concentrations were higher than the reported FNA toxicity threshold for PAOs.

6.3 Conclusion

Landfill leachate treatment was investigated using two aerobic SBRs; namely, ASBR and GSBR. The best results for ammonia removal were obtained in GSBR where TAN removal was stable and close to 99.7±0.2% throughout the experimental duration while increasing leachate volumetric ratio up to 100% in influent. ASBR was not consistent in removing TAN, providing removal efficiencies of 99±2% 30% leachate, and 56±6% at 90% leachate in influent. The biomass in GSBR was more resistant to FA toxicity as nitrification was partially inhibited at 40 to 59 mgN/L of FA, which was two times more than FA concentration at which ASBR biomass was inhibited. However, a nitrogen mass balance indicated that both reactors behaved similarly. The total nitrogen removal for GSBR and ASBR were approximately 26.0 and 23.0%, respectively. Regarding COD removal, GSBR removed up to 31% of COD when leachate ratio increased from 50 to 90%, while COD removal in ASBR was close to 14% as leachate ratio increased from 40 to 65%. Such low efficiencies were associated with the refractory organic content of the leachate used in this study, which also caused a poor phosphorous removal.

Chapter 7 Conclusions

- Total ammonia nitrogen removal:

Compare with activated sludge (AS), aerobic granular sludge (AGS) had better TAN removal performances with three different wastewaters: synthetic landfill leachates and raw leachate. TAN removal could be maintained over 95% in GSBR, along with increasing volumetric ratios of raw leachate up to 100% and high influent TAN concentration in synthetic feed (see section 4.2.2, 5.2.3 and 6.2.3), whereas, TAN removal efficiency was decreased in ASBR (see Figure 4.3, 5.2 and 6.1). AS also need time to adapt to the synthetic old leachate (see Figure 5.2) at the beginning of experiment.

AGS achieved 56±12% of nitrification efficiency, 62±9% in synthetic old landfill leachate without the nitrite accumulation (see section 4.2.2 and 5.2.3). In raw leachate, the nitrification efficiency was varied from 36% to 78% and the nitrite accumulation only happened when leachate ratio was up to 90% (see section 6.2.3). However, ASBR did not present a stable nitrification with lower TAN removal among these three treatments due to the toxicity from FA and FNA. GSBR showed better performance compared to ASBR in three leachate treatments, as it was more resistant to the toxicity caused by high concentrations of FA and FNA and was able to recover (see section 4.2.2.2, 5.2.3.1 and 6.2.3.1).

- Denitrification and TN removal:

From the kinetic batch tests, AGS in GSBR were observed and showed that denitrification took place in both anoxic and aerobic periods with three different leachates. The denitrification and SND efficiencies were really low. The highest efficiencies of denitrification and SND were 55%, 59% performed by AGS with synthetic old leachate. AS had denitrification during the anaerobic period in ASBR. AS treated synthetic young leachate that achieved denitrification (70%) only during anoxic period. Meanwhile, the activated sludge had denitrification during the aerobic period when it was treated with synthetic old landfill leachate and raw leachate (see section4.2.2.3, 5.2.3.1 and 6.2.3.3).

TN removal efficiency was low in this research. The similar results were obtained in the young leachate and raw leachate treatments: GSBR had better TN removal than ASBR. However, in the synthetic old leachate treatment, ASBR showed higher TN removal.

- COD and phosphorus reduction:

Regarding COD removal of raw landfill leachate, AGS removed up to 31% of COD when leachate ratio increased from 50 to 90%, while COD removal in ASBR was close to 14% as leachate ratio increased from 40 to 65%. Such low efficiencies were associated to the refractory organic content of the leachate used in this study, which also caused a poor phosphorous removal (see section 6.2.4).

COD removal of synthetic young landfill leachate decreased from 87 to 67% as time passed in GSBR. The same trend was observed for the ASBR: the average COD removal was 83%, and decreased to 52% (see section 4.2.3). For both reactors, phosphorus removal not stable during the whole period and efficiencies were fluctuated (see section 4.2.2.4)

AS and AGS performed similarly for organic matter removal of synthetic old leachate, which COD removal was 66% in the GSBR and 59% in the ASBR (see section 5.2.2). Phosphorus removal (PR) by the GSBR was gradually increased with time and reached a maximum efficiency of 54% (see Figure 5.4a). The same trend was observed for the ASBR, which presented a maximum PR of 49% (see Figure 5.4b).

In conclusion, according to the observations from this experiment set, the aerobic granular sludge presents a promising option to be applied as an on-site alternative for leachate treatment. Aerobic granular sludge showed a better performance in removing nutrients and organic matter from young or old landfill leachate, being more efficient than the conventional suspended growth activated sludge. Further investigations should also be addressed, especially with a focus on improving SND and phosphorus removal efficiencies.

Chapter 8 Engineering Significance of the Present Research

According to this experiment set, the aerobic granular sludge (AGS) shows the better treatment performance on landfill leachate than activated sludge. Consider the economic benefits, a leachate treatment plant with AGS can save both money and working space: the cost could be reduce at least 20% and space requirements can be reduced by as much as 75% (De Kreuk, De Bruin and Van Loosdrecht 2005a). Currently, the full scale aerobic granular sludge are adapted for industrial applications and domestic sewage treatment (Pronk et al. 2015). Portugal built the first full-scale wastewater treatment plant with aerobic granular sludge in 2010 in Europe. The Netherlands also treats wastewater (35% from industry) in full-scale AGS wastewater treatment plant (Giesen et al. 2013).

If AGS are implemented full-scale in onsite leachate treatment plant in the future, based on the conclusion of this research, the improvements can be done through the following suggestions: the additional VFA should be added into the old leachate/wastewater to improve the phosphorous removal and denitrification; co-treat with domestic wastewater at the optimal ratio to diluted toxicity of leachate and increase its biodegradability; aerobic granular sludge stability should be evaluated in different influent conditions before the large-scale application, and the equalization tank can help to keep the influent in same condition to avoid leachate and wastewater seasonal differences (Goel, Flora and Chen 2005).

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