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Digestate application in landfill bioreactors: Nitrogen removal and digestate stabilization

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XXXI Ciclo

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Summary

Anaerobic digestion (AD) of organic fraction of municipal solid waste (OFMSW) or food waste has aroused attention increasingly as it can achieve both environment and economic benefits. The by-product from AD, the digestate, still rich in putrescible components and nutrients, is mainly considered for reutilization as a bio-fertilizer or a compost after its treatment. However, the limitations exist for digestate agricultural application because of nutrients surplus, fertilization seasons, high cost of long-distance transportation and low market acceptance. Besides, digestate from OFMSW and food waste needs to be disposed as "waste" when it does not comply with the regulation requirements.

The chapter 1 of the work is an overview on the digestate characterizations, regulations of agricultural use and application techniques. The concept of Back to Earths Alternatives (BEAs) introduced in the literature review involves that the residues, after appropriate treatment, "should be returned to their non-mobile state as they were before they were extracted from the ground to be used as raw materials ". The specific aim of BEA is to bring elements and materials back into the environment either as soil amendments or functional components for landfills. The novel concept can deal with the two dilemmas of digestate management and achieve the close of material loop.

Aim of the Chapter 2 was to develop an alternative option to use digestate to enhance nitrified leachate treatment through a digestate layer in landfill bioreactors. Two identical landfill columns (Ra and Rd) filled with the same solid digestate were set and nitrified leachate was used as influent. Nitrate nitrogen removal efficiency of 94.7% and 72.5% were achieved after 75 days and 132 days, respectively. These results suggest that those solid digestates could be used in landfill bioreactors to remove the nitrogen from old landfill leachate.

The study of Chapter 3 aims to evaluate the application of digestate in simulated landfill columns to enhance nitrogen conversion via short-cut nitrogen removal. Two identical simulated landfill reactors filled with solid digestate were setup and partial nitrified leachate was fed through the columns. After 109 days of operation, the average nitrite nitrogen and nitrate nitrogen removal efficiencies were 92.6% and 85.8%, respectively. The high concentrations of nitrite (1004 mg-N/L) did not significantly inhibit methane production during denitrification in the digestate-added landfill columns.

Aim of the Chapter 4 was to use a digestate layer in aged refuse bioreactors to enhance the denitrification capacity of aged refuse, stabilize digestate and mitigate the ammonia emission from digestate leaching with leachate recirculation. Six identical landfill columns filled with 0% (R0), 5% (R5), and 15% (R15) of solid digestate above aged refuse, were set and nitrified leachate was periodically fed and recirculated. Nitrate removal rate in R5 and R15 were 3.4 and 10.0 times higher than that of control (no digestate added). The results showed that instead of land use, solid fraction of digestate could be exploited as an inexpensive functional layer embedded in old landfill site to enhance denitrification capacity and achieve digestate stabilization with little ammonia leaching from digestate.

In conclusion, solid digestate was effective in reducing the oxidized nitrogen (nitrate or nitrite) content of nitrified leachate or partial nitrified leachate. Meanwhile, the organic matter content of the solid digestate was degraded under anaerobic conditions with low methane emission. Solid digestate with or without further treatment can be utilized as an engineered landfill biocover. Besides, solid digestate could be applied in external reactors to ex-situ treat nitrified leachate. At last, solid digestate can be used as functional layer embedded landfill to removal nitrogen in those old landfills with low denitrification capacities.

List of Publications

This Ph.D. thesis is based on the three published or accepted papers by peer-review journals and one submitted paper.

Published papers

Peng W, Pivato A (2017) Sustainable Management of Digestate from the Organic Fraction of Municipal Solid Waste and Food Waste Under the Concepts of Back to Earth Alternatives and Circular Economy. Waste and Biomass Valorization 1-14. doi: 10.1007/s12649-017-0071-2 (In press)

Peng W, Pivato A, Lavagnolo MC, Raga R (2018) Digestate Application in Landfill Bioreactors to Remove Nitrogen of Old Landfill Leachate. Waste Manag. 74:335-346. doi: 10.1016/j.wasman.2018.01.010

Peng W, Pivato A, Cerminara G, Raga R (2018) Denitrification of Mature Landfill Leachate with High Nitrite in Simulated Landfill Columns Packed with Solid Digestate from Organic Fraction of Municipal Solid Waste. Waste and Biomass Valorization 1-14. doi: 10.1007/s12649-018-0422-7 (In press)

Girotto F, **Peng W**, Rafieenia R, Cossu R (2018) Effect of Aeration Applied During Different Phases of Anaerobic Digestion. Waste and Biomass Valorization 9(2):161-174. doi: 10.1007/s12649-016-9785-9

Rafieenia R, Girotto F, **Peng W**, et al (2017) Effect of Aerobic Pre-Treatment on Hydrogen and Methane Production in a Two-Stage Anaerobic Digestion Process Using Food Waste with Different Compositions. Waste Manag 59:194–199. doi: 10.1016/j.wasman.2016.10.028

Submitted paper:

Peng W, Pivato A, Garbo F, Wang T.F (2018) Stabilization of Solid Digestate and Nitrogen Removal from Mature Landfill Leachate: a Combined Approach in Aged Refuse Landfill Simulation Bioreactors. (Submitted to Journal of Environmental Management, under review after 1st revision)

Prepared paper:

Effect of Biochar Application on Nitrogen Leaching and Waste Stabilization in Digestate-Based Facultative Landfill Reactors (Preparing)

Oral presentations:

Girotto F, **Peng W**, Rafieenia R, Cossu R (2016) Effects of Aeration on AD-a Review. VENICE 2016-6th International Symposium on Energy from Biomass and Waste, November 14th-17th, Venice, Italy.

Peng W, Pivato A (2016) Back to Earth Alternatives for Sustainable Management of Digestate from Organic Fraction of Municipal Solid Waste and Food Waste. VENICE 2016-6th International Symposium on Energy from Biomass and Waste, November 14th-17th, Venice, Italy.

Rafieenia R, Girotto F, **Peng W**, Cossu Raffaello (2016) Effect of Pre-Aeration in a Two-Stage AD Process. VENICE 2016-6th International Symposium on Energy from Biomass and Waste, November 14th-17th, Venice, Italy.

Poster presentations:

Peng W, Pivato A, Lavagnolo MC, Raga R (2017) Nitrogen Removal of Nitrified Leachate Through a Biofilter Column Packed with Solid Digestate. SARDINIA 2017-16th International Waste Management and Landfill Symposium-October 2nd-6th, 2017-Forte Village, S. Margherita di Pula, Italy.

Background and Aim of the Ph.D. activity

The biogas plants with OFMSW as substrate is increasingly installed to achieve the energy recovery and waste stabilization. After the recovery of the biogas, the biogas residual, digestate, needs to be well disposed as it still contains high content of undigested organic matter, nutrients, especially ammonia and other pollutants. Despite the agricultural use of digestate originated from agricultural biomass (manure, rice straw, etc.) can be legally applied, the digestate from OFMSW might be regarded as "waste". Consequently, agricultural use of digestate from OFMSW is not allowed. Therefore, innovative technologies of digestate management based on the concept of circular economy and Back to Earths Alternatives (BEAs) are indispensable for the sustainability of anaerobic digestion of OFMSW.

During the first Ph.D. year, much time was spent on the literature review of digestate management so that I have a general idea on the state of the art of the digestate management. The review paper entitled "Sustainable Management of Digestate from the Organic Fraction of Municipal Solid Waste and Food Waste Under the Concepts of Back to Earth Alternatives and Circular Economy" was published in *Waste and Biomass Valorization*. The three critical issues were addressed in the review paper.

- Considering to the complex composition of digestate from OFMSW, there is the lack of consensus on whether defines the digestate from OFMSW as "waste".
- Although the incineration and pyrolysis of dry solid digestate and dozens of techniques for liquid digestate treatment have been studied in recent years, there is still a lack of a systematic concept to guide digestate management.
- Beyond agricultural land use, landfills and other non-agricultural land utilizations could be other BEAs when digestate agricultural application is not feasible. There are limited studies on how to treat digestate prior to landfilling, how to apply digestate on a landfill (e.g., as a daily cover or mixing with MSW), and what effects digestate will have on landfill emissions and leachate quality.

Only if the source segregated OFMSW were virgin and uncontaminated, the digestate from OFMSW can be used as agricultural products. In practice, the OFMSW generally undergoes co-digestion with other substrates, like sewage sludge. Besides, the mechanically sorted OFMSW is contaminated in most cases. When the agricultural use was excluded from the BEAs, emerging sustainable landfill techniques could be adopted to achieve the final storage quality and close the material loops.

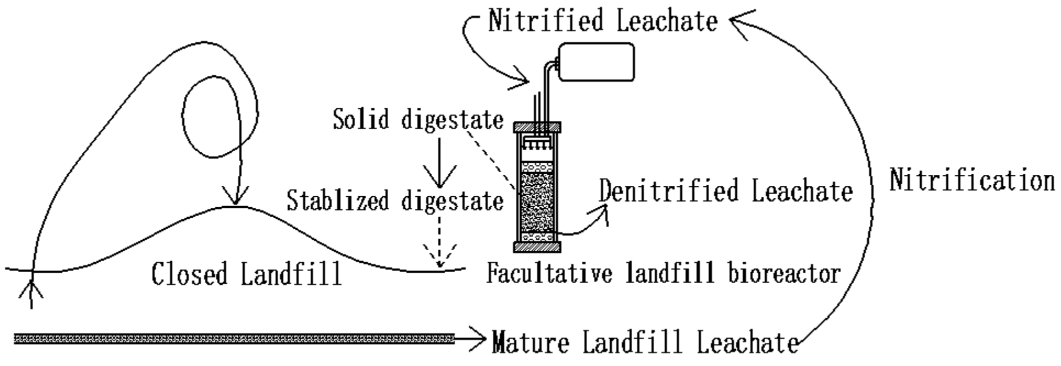

Figure 1. The digestate landfilling concept

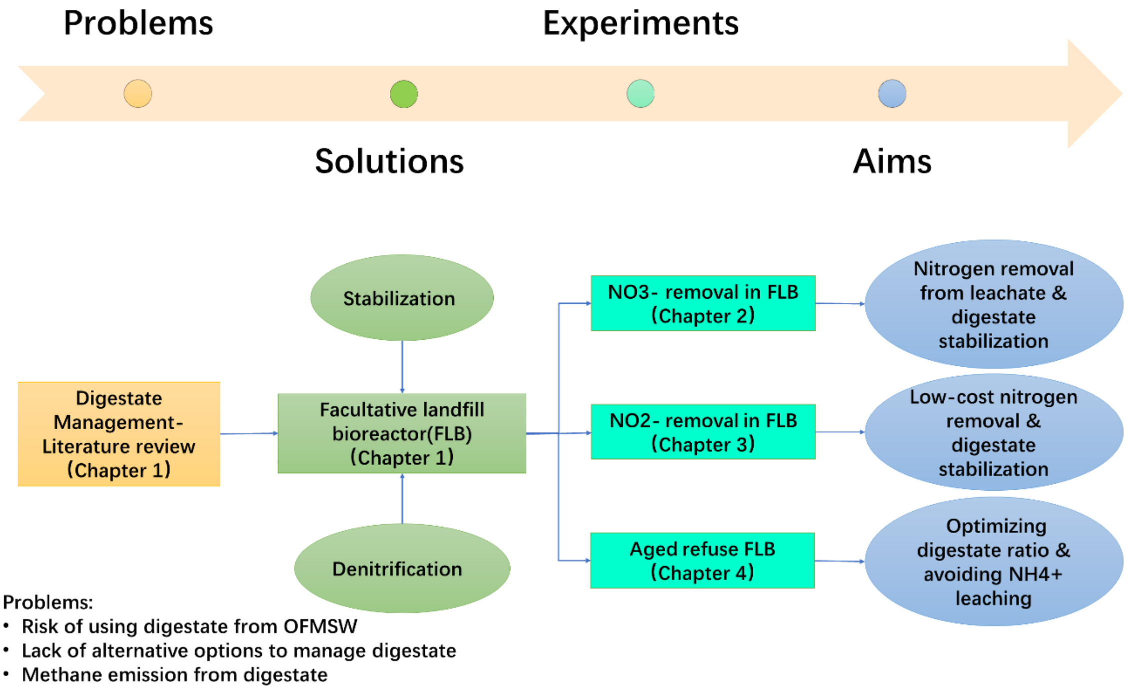

Figure 2. Sketch of the activities during the PhD

Chapter 1: Literature Review

1.1 Digestate management: State of the Art[1]

The organic fraction of municipal solid waste (OFMSW) is a heterogeneous material which has various characteristics depending on the origin and collection system (Alibardi and Cossu, 2015). Despite the heterogeneity, OFMSW, mostly comprised of food waste, is characterized by high moisture content and high biodegradability (Alibardi and Cossu, 2015, Lebersorger and Schneider, 2011, Zhang et al., 2007). Food waste is generally defined as "materials for human consumption that are subsequently discharged, lost, degraded, or contaminated" (Girotto et al., 2015) and is composed of organic waste and leftovers from residences, restaurants, cafeterias, canteens, and markets (Alibardi and Cossu, 2015). Anaerobic digestion (AD) of the OFMSW or food waste to recover energy by producing methane-rich biogas and stabilize wastes by degrading organic matter has been the subject of research from many decades (Mata-Alvarez et al., 1992; Peres et al., 1992). Meanwhile, digestate, the major byproduct of the process should be managed by composting and other biological conversion processes under the current economic and environmental policies (Möller and Müller, 2012; Teglia et al., 2010).

Digestate is a semi-stabilized material rich in organic matter and minerals (Tampio et al., 2016). During digestate management, this waste stream is commonly separated into solid and liquid fractions by using a solid-liquid separation unit on site (Fuchs and Drosg, 2013).

Agricultural wastes and energy crops digestate are almost exclusively land applied, while digestate generated from OFMSW and food waste needs to be further managed as waste. Some researchers believe that biowastes like OFMSW and food waste treated at AD plants are not considered a waste according to the definition of waste outlined in the European Waste Framework Directive 2008/98/EC. This directive states that "any

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[1] This work has been accepted for publication. Peng W, Pivato A (2017) Sustainable Management of Digestate from the Organic Fraction of Municipal Solid Waste and Food Waste Under the Concepts of Back to Earth Alternatives and Circular Economy. Waste and Biomass Valorization 1-14. doi: 10.1007/s12649-017-0071-2 (In press)

substance or object which the holder discards or intends or is required to discard"(European Parliament and Council, 2008; Fachverband Biogas et al., 2013). In the European Waste Catalogue (European Commission, 2000), there are two codes concerning digestate: “19 06 04 Digestate from anaerobic treatment of municipal waste” and “19 06 03 Liquor from anaerobic treatment of municipal waste”. This catalogue suggests that digestate from anaerobic treatment of OFMSW should be considered as a “waste”. Furthermore, digestate from OFMSW and food waste needs to be further treated according to Article 6 of the Waste Framework Directive (Fachverband Biogas et al., 2013). According to this article the ‘end-of-waste status’ states that certain specified wastes shall cease to be waste when they undergo some sort of recovery process. To date there is not specific criteria that has been set at the European level. It is up to member states to determine the final fate of digestate on a case-by-case basis (Fachverband Biogas et al., 2013). In Italy, digestate from AD plants treating OFMSW is considered a waste that needs to be further treated to comply with the national fertilizer regulations or disposal standards (Saveyn and Eder, 2014).

Recently, the end-of-waste criteria allows for the use of the digestate as a "product" under certain requirements. These requirements include product quality, input materials, treatment processes and techniques, provision of information, quality assurance procedures, etc. (Saveyn and Eder, 2014). Digestate which fails to comply with the quality protocol at the national or European level (end-of-waste criteria) is classified as waste that needs to undergo proper waste management control (WRAP, 2009).

All three forms of the digestate (i.e., whole, liquid and solid) can be land applied as the final disposal destination once it meets relevant regulatory standards and can be qualified as a “product” (Nkoa, 2014; Teglia et al., 2010). In Europe, some countries have their own digestate quality standards (e.g. PAS 110:2010 in UK (WRAP, 2010), RAL GZ245 and RAL GZ246 in Germany (Siebert, 2007), SPCR 120 in Sweden (Sverige, 2016), Italian Legislative Decree 217/06(Gazzetta Ufficiale, 2006), NFU44-051 French standards for organic amendments (AFNOR, 2006). These digestate quality standards have specifications for hygienic standards, impurities, degree of fermentation, odor, organic matter content, heavy mental content, and on parameters for declaration. The parameter for declaration outlines the essential characteristics and constituents of digestate products that help the end user determine the best practice of digestate land application (Siebert, 2007). However, high transportation costs have the potential to restrict the large-scale direct land application of the digestate (Delzeit and Kellner, 2013). The high nutrient content can also increase the potential of nitrogen pollution in aquatic ecosystems and could promote eutrophication of fresh water reservoirs (Lukehurst et al., 2010). Furthermore, the agriculture demand for nutrient supply can fluctuate during peak crop (e.g., beginning of spring) (Wellinger et al., 2013). In some areas, the land application of digestate is not an option due to potential to over saturate fields with phosphorus and nitrates (Neumann et al., 2016). Thus, alternative utilizations or destinations of digestate need to be developed besides direct land application.

Characterization of solid digestate from the AD of OFMSW and food waste

In this study, only the literature concerning the AD of OFMSW and food wastes was considered. Furthermore, this review separately outlined the treatment and management practices utilized for whole digestate, liquid digestate, and solid digestate. The characterization of the three forms of digestate are presented and discussed separately.

Basic characteristics

Digestate characteristics are outlined in **Table 1.1.1** and include pH, total solids (TS), volatile solids (VS), and total carbon (TC). These parameters are the declaration parameters used to assess the digestate quality when it is being used for agricultural applications (WRAP, 2010).

The digestate quality of OFMSW or food waste usually depends on the type of AD system (e.g., wet or dry, batch or continuous, single stage or multi-stage, co-digestion or mono-digestion). For example, the moisture content of the digestate is influenced by the choice between wet or dry AD process. Similarly, when the OFMSW undergoes a dry AD process, a digestate of nearly 35% solids content is produced (De Baere, 2008).

Therefore, the digestate from a dry AD process usually does not require a solid-liquid separation process. As observed in **Table 1.1.1**, the TS content of the whole digestate from OFMSW varied from 0.72-51.2% whereas TS contents of digestate from food waste was consistently under 10%. The latter observation could be explained by the preferential choice of wet AD process for this stream. Despite the significant variability in TS content, the VS content was relatively high for both types of OFMSW and food waste digestate, showing that high amounts of organic matter of the feedstock remained undigested. High organic matter content (61.7-80.4% TS), especially in the solid fraction of food waste digestate, can help to enhance soil physical properties (Rollett et al., 2015). The pH of both OFMSW (8.3-8.0) and food waste digestates (7.6-8.3) were above 7, which suggests that these materials are weakly alkaline. The alkaline pH of digestate has been regarded as a useful property in consideration of the global soil acidification problem (Makádi et al., 2012). Additionally, when digestate is used for heavy metal contaminated land remediation, its alkalinity can increase the pH level of soil and consequently enhance the immobility of heavy metals (Steele and Pichtel, 1998).

Nutrients

Digestate with high levels of ammonia nitrogen can be directly applied on agricultural land as a replacement for chemical fertilizer (Tampio et al., 2016). As shown in **Table 1.1.1**, digestate of OFMSW has a lower total Kjeldahl nitrogen (TKN=2.79-14 g/L) and ammonia content compared to food waste digestate (TKN=15.4 g/L) which is presumably due to the difference in the initial composition, especially the protein component, of these two feedstocks. After anaerobic digestion, the soluble ammonia concentration tends to increase with the degradation of protein present in the feedstock (Kayhanian, 1999). The ammonia content of the digestate accounts for approximately 60-80% of its total N content (Makádi et al., 2012). After solid-liquid separation of the digestate, the nutrients are distributed between the solid and liquid fractions. It is estimated that liquid digestate contains 70-80% of the total NH_4^+-N while the remaining 20-30% of the total NH_4^+-N are distributed in solid fraction (Fuchs and Drosg, 2013).

However, 55-65% of the total phosphorus remained in solid fraction after separation with the remaining total phosphorus (35%-45%) was found in the liquid (Fuchs and Drosg, 2013; Bauer et al., 2009). The P_2O_5/K_2O ratios of both OFMSW and food waste digestate (whole digestate) is around 1:3 **(Table 1.1.1)**. This ratio is ideal for grain and rape growth (Makádi et al., 2012). Therefore, digestates from OFMSW and food waste can be suitable to supplement of phosphorus and potassium in soils.

Table 1.1.1 Characterization of digestate from OFMSW and food waste

Types	OFMSW Whole	OFMSW Solid	Food Waste Whole	Food Waste Solid
Basic characteristics				
pH	8.30	8.80	7.60-8.30	7.97
TS (%)	0.72-51.2	7.23-27.0	1.99-7.88	9.00
VS (%TS)	62.1	68.0-71.0	61.7-73.6	80.4
TC (%TS)	34.6	12.8-22.7	32.8-39.5	-
Nutrients contents				
N-NH_4^+ (g/L)	1.7-27.5	-	3.37	5.7
TKN (%TS)	2.79-14	-	15.4	-
C/N	1.3-29.8	12.1-20.9	2.63	-
TN (%TS)	1.3-12.4	1.09	4.15	3.97
P_2O_5 (%TS)	0.2-0.9	1.49	0.93	0.9
K_2O (%TS)	0.6-1.0	0.78	2.33	2.33
Biological stability				
TOC	27.5-45.9 (%TS)	52.9 (%VS)	34.6 (%TS)	-
COD (g/g-VS)	1.62	-	1.50	1.90
VFA (g/kg FM^a)	0.3	-	0.18	-
OUR^b (gO_2/(kgVS h))	2.82-3.78	-	0.68-0.91	-
RBP^c (L/gVS)	0.346	-	0.061-0.311	0.185-0.418

Heavy metals				
Cd (mg/kg)	0	-	<0.4	-
Pb (mg/kg)	15	-	9.8-36	-
Cu (mg/kg)	55	-	14-80	-
Hg (mg/kg)	-	-	<0.23	-
Ni (mg/kg)	50	-	11-20	-
Zn (mg/kg)	78	-	56-300	-
Cr (mg/kg)	188	-	6-40	-
Reference	(Tampio et al., 2016; Michele et al., 2015; Quina et al., 2015; Teglia et al., 2011a; Antoine et al., 2011; Zeng et al., 2012; Zhang et al., 2012)	(Bustamante et al., 2012; Eliyan, 2007; Rao and Singh, 2004; Tambone et al., 2010; Zeshan, 2012)	(Boni et al., 2016; Tampio et al., 2016; Drennan and DiStefano, 2010; Phil Wallace et al., 2011; Opatokun et al., 2017; Buss et al., 2016; Govasmark et al., 2011)	(Phil Wallace et al., 2011; Tampio et al., 2016)

[a] FM: Fresh Matter

[b] OUR: Oxygen Uptake Rate

[c] RBP: Residual Biogas Potential

Digestate stability

Biological stability is an important indicator for the utilization and final disposal of digestate, such as agricultural use, compost and landfill mining (Teglia et al., 2011b; Pivato et al., 2016; Lü et al., 2017). Unstable digestate are inclined to produce high level of leachate and odors (Lü et al., 2017). The chemical oxygen demands (COD) of digestate originated from food waste are 1.5 and 1.9 g/g VS, as shown in **Table 1.1.1**, which exceeds the limit of 0.43 g/g-VS set by PAS110-2010 (**Table 1.1.2**). The oxygen uptake rate (OUR) represents the aerobic stability indicator while residual methane potential (RMP) represents the anaerobic stability of the digestate (PAS, 2013; Gómez et al., 2006). Drennan et al. (2010) reported the OUR of food waste digestate around 0.68-0.91 g O_2 /kg-VS/h. As a majority of the organic matter remains in the solid fraction of digestate, solid digestate might be less stable with respect to the liquid and whole digestate (Drennan and DiStefano, 2010). Phil Wallace (2011) reported that each of the solid and liquid fractions of food waste digestate had different residual biogas potential (RBP) (Phil Wallace, et al., 2011). The whole digestate and separated liquid fractions were reported to be well below the RBP limit value of 0.25 liters biogas/g VS while the solid fraction of digestate showed an even higher RBP (Phil Wallace et al., 2011). These data suggest that the solid fraction of the digestate might need further stabilization to meet the RBP stability limit because the methane (main component of residual biogas) emissions will exert a negative impact on global warming when digestate is used as a bio-fertilizer.

Heavy metals

Comparing heavy metal content of the digestate from food waste (**Table 1.1.1**) with the compliance criteria (**Table 1.1.2**), it is observed that all the heavy metals were below the regulatory limits, suggesting that the digestate from food waste could be less of a risk to agricultural use. However, Cr content of digestate from OFMSW, 188 mg/kg-TS, was above the compliance criteria (Trzcinski and Stuckey, 2011). When the digestate failed to meet the criteria, it should be defined as "waste" and it can be used as a component in artificial soils or on land not utilized for food production or fodder crops (Trzcinski and Stuckey, 2011; European Commission, 2001).

Required digestate quality

Soil utilization

Despite presenting numerous reuse potentials, final utilization of digestate (classified both as “waste” or as a “product”) needs to meet specific quality and functional requirements. These requirements are mainly aimed at avoiding risk to human health and the environment (Saveyn and Eder, 2014). In Europe, several countries, including Germany, United Kingdom (UK), and Italy have digestate standards that mainly define limits of specific parameters for agricultural applications only (WRAP, 2010; Siebert, 2007; Gazzetta Ufficiale, 2006). In addition to the digestate, agricultural use as a biofertilizer, contaminated soil remediation by digestate, and digestate-derived biochar were also discussed.

The existing standards of regulation for heavy metals vary slightly among different countries (**Table 1.1.2**). In practice, the anaerobic co-digestion of food waste with sewage sludge is conducted in AD plants to improve the overall process performance. The digestate originating from these sources have the potential to get contaminated by heavy metals found in the sewage sludge (Dai et al., 2013; Kim et al., 2003).

Organic pollutants could be another threat to digestate quality (**Table 1.1.2**). Organic pollutants appearing in the digestate could be attributed to the co-digestion substrates, especially sewage sludge and manure (Dai et al., 2013; Kim et al., 2003; Kupper et al., 2008). Except for potential risk from PAHs, other organic pollutants contaminated digestate were not identified (Kupper et al., 2008). PAH concentration in one fourth of the samples were above the Swiss guide value for compost (4 mg/kg-TS) (Brändli et al., 2007).

As for biological and ecotoxicological parameters, digestate used as a fertilizer must ensure that the quality of the product has limited pathogens, viruses, and weed seeds (Seadi et al., 2012). These unwanted biological contaminants can be reduced by the proper control of the AD process or by applying specific post-treatment processes that target specific biological contaminant (Seadi et al., 2012). Specific measures include distinguishing "dirty area" and "clean area" at each AD plant, controlling the source of feedstock, conducting hygiene measures to avoid cross-contamination between raw feedstock and digestate (Seadi et al., 2012). Therefore, digestate quality regulations not only provide limit values for specific contaminants but they also provide guidance on how to control these parameters during the AD process (**Table 1.1.2**).

As shown in **Table 1.1.2**, the concentration of organic acids (RAL-GZ 245), volatile fatty acids (VFAs) (PAS 110:2010) and the RBP (PAS 110:2010) of the digestate can be used as indicators of the degree of fermentation which are measures of the stability of digestate.

The composition of the digestate should be described and declared before it is utilized as a fertilizer or soil amendment (Seadi et al., 2012). Declaration of pH, nutrients, dry matter content, organic matter are all part of the assurance schemes for digestate quality in some European countries (Seadi et al., 2012). Indigestible materials and large particles could remain in the digestate as physical impurities which include stone, glass, sands, and plastics.

Landfill

Digestate of unacceptable quality should be regarded as “biowaste”, which cannot be used on agricultural land for food and fodder crop production (EuropeanCommission, 2001; Antoine P Trzcinski and Stuckey, 2011). The possible pathways to use this stabilized biowaste is as a daily, temporary or final landfill cover. According to European Union (EU) landfill directive, the amount of biodegradable waste that can be disposed of in landfills should be reduced progressively (Council, 1999). Despite this directive, the landfill might be an important destination for the biowaste to close the material loop (EuropeanCommission, 2001).

Council Directive 1999/31/EC offers several key points for a landfill site (Council, 1999):

- Landfill sites can be divided into three categories: hazardous waste, non-hazardous waste, and inert waste landfills.

- Landfill sites will not accept liquid waste.
- Only treated waste may be landfilled.

Thus, only the solid fraction of digestate with post treatment could be sent to non-hazardous waste landfill sites. Specific limit values for wastes acceptable for disposed in a landfill are comprehensively described in Directive 2003/33/EC (Council, 2003).

Table 1.1.2 Regulations for applying digestate as biofertilizer for soil

Parameters	Unit	Upper limit value	Reference
Heavy metal			(Siebert, 2007; WRAP, 2010; AFNOR, 2006; Gazzetta Ufficiale, 2006; Sverige, 2016)
Cd	mg/kg-TS	1.0 -3.0	
Pb	mg/kg-TS	100 -180	
Cu	mg/kg-TS	100-600	
Hg	mg/kg-TS	1-2	
Ni	mg/kg-TS	50-100	
Zn	mg/kg-TS	400-800	
Cr	mg/kg-TS	100-120	
Cr^{6+}	mg/kg-TS	0.5	(Gazzetta Ufficiale, 2006)
Organics			
PAHs Polycyclic aromatic hydrocarbons	mg/kg-TS	6	(Republik Österreich (BGBl.), 1994)
PCDD/F Dioxins and furans	ng TE/kg TS	20	(Republik Österreich (BGBl.), 1994)
HCH, DDT, DDE etc. (Chlorinated pesticides)	mg/kg Products	0.5	(Republik Österreich (BGBl.), 1994)
PCB (Polychlorinated biphenyls)	mg/kg TS	0.2	(Republik Österreich (BGBl.), 1994)
AOX (Absorbale organic halogens)	mg/kg TS	500	(Republik Österreich (BGBl.), 1994)
LAS (Linear alkylbenzenesulphonates)	mg/kg TS	1300	(Miljøministeriet, 2006)
NPE (Nonylphenol and nonylphenolethoxylates)	mg/kg TS	10	(Miljøministeriet, 2006)
DEPH Di (2-ethylhexyl) phthalate	mg/kg TS	50	(Miljøministeriet, 2006)
Impurities			
Weight of impurities	%TS	0.5	(Siebert, 2007; WRAP, 2010)
Area sum of the selected impurities	cm^2/L fresh matter	25	(Siebert, 2007)
Biological contaminants			
Germinable weeds and sprouting	number/liter	2	(Siebert, 2007)
Salmonella	Absent in g fresh matter	25-50	(Siebert, 2007; WRAP, 2010)

Stability and odor			
Organic acids (total)	g/L	4	(Siebert, 2007)
Volatile fatty acids	g COD / g VS	0.43	(WRAP, 2010)
Residual biogas potential	L / g VS	0.25	(WRAP, 2010)
Organic matter	%TS	≥30	(Siebert, 2007)
Parameters for declaration			
Basic information	Product type (digestate product liquid or solid); Name and detail of producer; Name and detail of customer; Date of dispatch		(Siebert, 2007; WRAP, 2010) (Fuchs, et al., 2001)
Physical Characteristic	Dry matter content; Organic matter; pH-value; Weight or volume; Density; Salt content		(Siebert, 2007; WRAP, 2010) (Fuchs, et al., 2001)
Nutrient Parameters	Plant nutrients (total) (N, P, K, Mg, S); Nitrogen soluble (NH_4^+-N, NO_2^{-}N); Micro-nutrients; C/N ration		(Siebert, 2007; WRAP, 2010) (Fuchs, et al., 2001)
Harmful elements	Water soluble chloride (Cl-); Water soluble sodium (Na); Heavy metals if the thresholds have been exceeded		(Siebert, 2007; WRAP, 2010) (Fuchs, et al., 2001)
Others	Alkaline effective matter (CaO); Reference for good practical use		(Siebert, 2007; WRAP, 2010) (Fuchs, et al., 2001)

Other land applications

As a kind of biowaste, other land applications of digestate include landscape restoration in discarded quarries and mines, anti-noise barriers, road construction, golf courses, ski slopes and football pitches (EuropeanCommission, 2001). The stabilized biowaste should meet the requirements of **Table 1.1.3** (EuropeanCommission, 2001). Comparing to the quality criteria for digestate products (Table 1.1.2), the limit values of stabilized digestate are much higher. Furthermore, stabilized biowastes should also fulfil the sanitation regulations if they are spread on land likely accessible to the public (EuropeanCommission, 2001).

Table 1.1.3 Regulations for applying stabilized biowaste as land use

Parameters	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PCBs	PAHs	Impurities > 2 mm
Limit value [a]	5	600	600	5	150	500	1500	0.4	3	< 3%

[a] Normalized to an organic matter content of 30%

Enhancement techniques for management of solid digestate

Composting & thermal drying

Compared to the whole digestate, the separated solid fraction of digestate is more suitable for agricultural use based on both logistical and agro-technical reasons. Nonetheless, solid digestate could be further post-treated through composting to harvest high-quality compost (Torres-Climent et al., 2015). However, composting the digestate can reduce the fertilizer’s nutrient value and has the potential to cause the emission of greenhouse gases (e.g. nitrous oxide) (Möller and Müller, 2012). A new alternative digestate valorization route could be a thermal conversion technique (Monlau et al., 2015). Thermal drying of the digestate could reduce transportation costs due to the volume reduction and could handle the surplus of nutrients in areas vulnerable to excess nutrient load (Maurer and Müller, 2012). Cheap sources of energies like Combined Heat and Power (CHP) and solar represents a means to accomplish thermal drying of the digestate (Fuchs and Drosg, 2013; Maurer and Müller, 2012). However, the potential for ammonia emissions is a drawback to the drying process (Maurer and Müller, 2012). During the drying process the pH needs to be kept constant to avoid ammonia loss through volatilization (Pantelopoulos et al., 2016).

Incineration

Incinerating the digestate can reduce a significant fraction of the volume and organic matter. Additionally, fertilizer elements such as phosphorous, potassium and calcium present in the bottom ash could be recycled (Kratzeisen et al., 2010). Dried solid digestate could also be used as a solid fuel for combustion (Kratzeisen et al., 2010). Properties of digestate fuel pellets depends on the type of substrates used in an AD plant (Kratzeisen et al., 2010). The digestate in the study by Kratzeisen (2010) originated from agricultural biomass including maize silage, grass, grass silage, sugar sorghum, poultry manure, and corn cob which were mainly lignocellulosic material and combustible (Kratzeisen et al., 2010). The combustion quality of digestate from OFMSW and food waste combustion still needs to be investigated further.

Pyrolysis

Pyrolysis of digestate can produce biochar, bio-oil, and syngas (Monlau et al., 2015; Neumann et al., 2016, 2015; Opatokun et al., 2015). Bio-oil obtained from digestate pyrolysis can be used as an engine fuel (Hossain et al., 2016). Biochar and syngas can be utilized as a fuel but more importantly these products could be applied to AD to improve the overall performance (Ellen MacArthur Foundation, 2013; Monlau et al., 2015). Biochar has been reported to enhance the stability of the AD process and methane yield (Luo et al., 2015; Mumme et al., 2014; Lü et al., 2016). The syngas, which is enriched in hydrogen (H_2) and carbon dioxide (CO_2), could be an important substrate for hydrogenotrophic methanogens (Ellen MacArthur Foundation, 2013).

Pyrolysis of the digestate from food waste can produce bio-oil with calorific value as high as 13.5 MJ/kg, syngas consisting of CH_4, H_2, CO_2, and CO, and biochar (Opatokun et al., 2015).

When digestate is classified as a "waste", post treatments are often required (**Figure 1.1.1**). Pyrolysis is an emerging option for digestate management (Fabbri and Torri, 2016) and converts the organic matter into char, bio-oil, and syngas in an oxygen free atmosphere (Neumann et al., 2015). The char can be used as a soil amendment or as a source of energy while the syngas and bio-oil are fuels with high calorific values and can be used as a form of renewable energy (Monlau et al., 2015). Another option for digestate is the use as material for daily, temporary, and final cover at a sanitary Landfill. The digestate would need to be dewatered and stabilized prior to disposal to ensure the material meets the stringent standards for landfills.

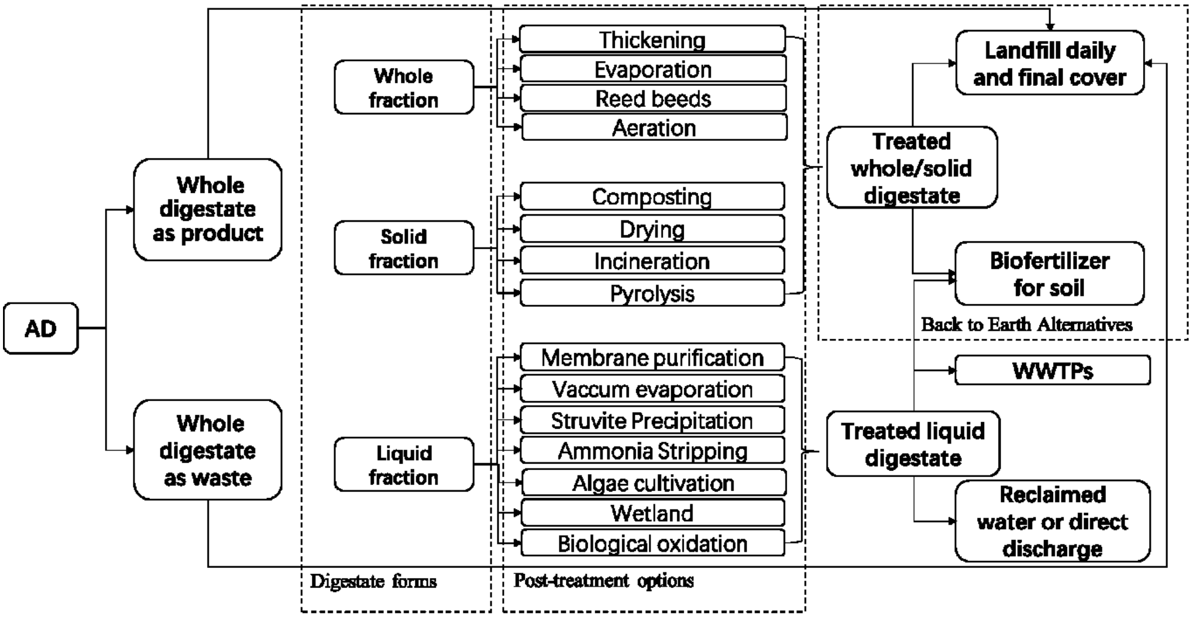

Figure 1.1.1. General process of digestate management: from Anaerobic Digestion (AD) to Back to Earth Alternatives

The circular economy concept could be a systematic strategy to address the challenges of digestate management, limitations of land application (as a products), and of the need for post-treatment (as a waste). A well-designed waste management strategy along with the concept of circular economy presents a restorative and regenerative option for sustainable digestate management (Gregson et al., 2015; Ellen MacArthur Foundation, 2012). This concept can also fully exploit the nutrient value of the digestate, ensure maximum water reuse and/or enable a more efficient conversion to energy (Dahlin et al., 2016; Monlau et al., 2016; Riding et al., 2015). Nonetheless, circular economy cannot achieve ambitious goals such as closing the materials loop without addressing the issue of management of residues from production and recycling processes (Cossu, 2016). To put circular economy concept into practice for digestate management, an integrative approach could be the Back to Earth Alternatives (BEAs). The concept of BEAs involves that the residues, after appropriate treatment, "should be returned to their non-mobile state as they were before they were extracted from the ground to be used as raw materials, which would provide for the actual closing of material cycles" (Cossu, 2016). Based on the BEAs, digestates with or without appropriate treatment are brought back into the environment either as a soil amendment or as functional component for a landfill (e.g., cover material). Generally, digestate of acceptable quality can be applied on agricultural land, while dewatered digestate of unacceptable quality can be used for the landfill cover system. This approach could facilitate the closing of the digestate material cycle in the environment

Digestate management with circular economy concept and BEA

Solutions for handling digestate from OFMSW and food waste and recovering nutrients without additional risks to environment and human health could be achieved by integrating AD into digestate management (**Figure 1.1.2**). Generally, AD and digestate management are separate units in AD plants even though a portion of the digestate can be recirculated back to anaerobic digesters as inoculum (Pognani Michele et al., 2015; Wu et al., 2017). However, AD can be integrated with digestate management under circular economy concepts. Progressive integrations ("industrial symbiosis") of AD and liquid digestate land use, AD and digestate pyrolysis, AD and digestate incineration, will establish functional connections and links across these different processes according to the system view of circular economy concept (Monlau et al., 2016).

OFMSW and food waste can be the feedstocks of AD and the control of AD substrates and performance of AD mainly determine the quality of digestate (Al Seadi and Lukehurst, 2012). Besides, energy crops cultivated from the marginal land with digestate as biofertilizer (Nabel et al., 2014), can be used as AD co-substrate with OFMSW and food waste (Nordberg and Edström, 2005). Nabel et al. (2014) found that the application of 40 tons of digestate per hectarea showed obvious fertilization effect on *Side hermaphrodita* (an energy crop), cultivating on a marginal sandy soil. Anaerobic co-digestion of energy crops and OFMSW achieved a methane yield of 0.33-0.38 L g/VS and the good performance can be attributed to a better nutritional composition (Nordberg and Edström, 2005). At last, pyrolyzed digestate (biochar) can also serve as a supplement for AD and the biochar can work as a supporting material to enrich methanogens and to relieve ammonia inhibition (Mumme et al., 2014). In these ways, both high-efficiency AD and complete digestate utilization can be fulfilled.

When solid digestate is qualified as a biofertilizer for soil, “food to waste to food” concept includes the AD of food waste and sequent digestate used as a biofertilizer for vegetable production in a greenhouse (Stoknes et al., 2016). This concept could be used at a small-scale anaerobic digester, as small amounts of digestate can easily be utilized on the nearby land without long-distance transportation which is costly. Except for using digestate as a biofertilizer for agricultural production, a small quantity of solid digestate is also sent to a landfill either for disposal or used as component in the cover system (Mouat et al., 2010).

When digestate is classified as a “waste” or large amounts of surplus digestate is produced, one possible solution is the integration of pyrolysis into AD (**Figure 1.1.2**), which could improve the efficiency of resource utilization (Monlau et al., 2016). A well-designed dual system (i.e., AD and pyrolysis) can produce several biofuels such as biomethane from AD, and bio-oil, biochar, and syngas from pyrolysis (Fabbri and Torri, 2016; Monlau et al., 2015; Monlau et al., 2016; Opatokun et al., 2015). Biochar can improve the overall soil fertility and can be used as an additive for anaerobic digestion to improve the overall methane yield (Lü et al., 2016; Luo et al., 2015; Monlau et al., 2016; Mumme et al., 2014). The amounts of surplus digestate can be significantly reduced by incineration even though incineration does not make best value use of this resource due to the nitrogen loss (Baddeley, 2014). It was found that the electricity generated by combusting solid digestate from co-digestion OFMSW, food waste and energy crops, could cover 13-18% of total electricity consumption (Li et al., 2013). When integrating digestate combustion with AD, the digestion period should be optimized as it will not only determine the biogas yield but also affect heating value of the solid digestate (Li et al., 2013). Besides, it is still lack of in-depth knowledge on the phosphorus recovery from ashes of digestate combustion. Liquid digestate identified as a product or waste can be used as a medium for microalgae cultivation and can be integrated with AD under the concept of biorefinery (Uggetti et al., 2014). The biorefinery aims to maximize the value derived from microalgae to produce added-value chemicals, products (feeds and energy crops), and biofuels (biodiesel, bioethanol and biogas) (Uggetti et al., 2014). Harvest microalgae could be co-substrate that can be fed into anaerobic digesters (Xia and Murphy, 2016). Microalgal biomass produced in reactors with liquid digestate as a nutrient medium, can be further extracted for biochemicals, biofuels, feeds, and soil conditioners (Xia and Murphy, 2016). WWTPs, reclaimed water utilization, or direct discharge could be the destinations for surplus liquid digestate.

The concept of circular economy holds that waste does not exist as the delicate design of materials, products, and system can eliminate waste (Ellen MacArthur Foundation, 2013). Although waste can be reused as much as possible, the aim of closing the material loop cannot be achieved without confronting the management of residues from production and recycling process (Cossu, 2016). As for digestate management, the residues could be surplus digestate, ashes from digestate incineration, and biochar from digestate pyrolysis. Under the concept of BEAs, the destinations of these residues may include utilization of compost/digestate in agriculture, production of landscape restoration materials, and disposal in a permanent waste deposit site (Cossu, 2016).

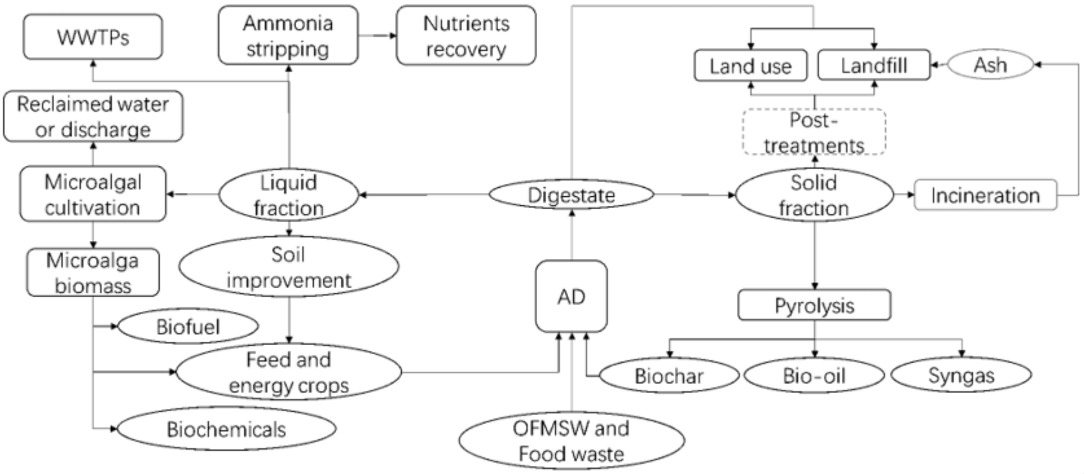

Figure 1.1.2. Digestate management with circular economy concepts: integrating AD and digestate disposal (Monlau et al., 2015; Xia and Murphy, 2016)

Conclusions

Digestate needs to be well disposed of and treated in AD plants with OFMSW and food waste as feedstocks. The three different forms of digestate, whole digestate, solid digestate, and liquid digestate, have various qualities, which dictate their utilizations and treatment techniques. Digestate quality depends mainly on the feed types and operating conditions of a specific anaerobic digester while gaps between solid digestate and liquid digestate were determined by solid-liquid separation units.

Although the incineration and pyrolysis of dry solid digestate and dozens of techniques for liquid digestate treatment have been studied in recent years, there is still a lack of a systematic concept to guide digestate management. For example, the integration of AD and pyrolysis of digestate could make full use of all materials and produced energy, which will be in accordance with the concept of circular economy. Introducing the circular economy concept into digestate management could help to close the material loop. However, the best practice of digestate management with circular economy concept are still under development.

BEA, as core value chain links of the circular economy concept, can be introduced into digestate management. Beyond agricultural land use, landfills and other non-agricultural land utilizations could be other BEAs when digestate agricultural application is not feasible. There are limited studies on how to treat digestate prior to landfilling, how to apply digestate on a landfill (e.g., as a daily cover or mixing with MSW), and what effects digestate will have on landfill emissions and leachate quality

1.2 An alternative option to manage solid digestate: Facultative Bioreactor Landfill

Introduction of facultative bioreactor landfill

Unlike a conventional landfill, bioreactor landfill can accelerate the stabilization and degradation municipal solid waste because of the enhancement of microbial activity by input of air and liquid (US, EPA). Four types of bioreactor landfill were described as **Table 1.2.1**. Facultative landfill bioreactor aims at combining the degradation of waste with the in-situ removal of nitrogen from leachate. It can be operated with an on-situ leachate nitrification followed by in-situ leachate denitrification by leachate recirculation (Berge, 2005). Nitrate, present in high concentrations in the nitrified leachate, can be removed by facultative microorganisms which use it for their respiration (Berge, 2005). This process is applied to anaerobic landfills since denitrification process occurs in anoxic conditions. The in-situ treatment of leachate can also reduce the costs related to the construction and management of a denitrification plant.

Waste types of facultative bioreactor landfill

As shown in **Table 1.2.2**, municipal solid waste (MSW) with different ages have been used in facultative landfill bioreactors (Jokela et al., 2002, Price et al., 2003, Fu et al., 2009, Zhong et al., 2009, Chen et al., 2009). 1-year-old refuse rich in biodegradable organic carbon shows much higher denitrification capacity compared to 11-year-old refuse (Chen et al., 2009). However, autotrophic denitrification (anammox) was found in aged refuse bioreactor landfill, which also contributed to the nitrogen removal (Wei et al., 2017, Xie et al., 2013). Nonetheless, there is less knowledge on the behavior of facultative landfill bioreactors filled with digestate from anaerobic digestion of MSW.

Table 1.2.1 Four types of bioreactor landfills (Summarized from Berge, et al., (2005))

Aerobic	Operation	• Adding air; Leachate recirculation
	Advantages	✓ Increased settlement; Decreased metal mobility; Reduced leachate; Reduced cost for methane control
	Disadvantages	✧ Landfill fires; High cost for aeration
Anaerobic	Operation	• Moisture addition
	Advantages	✓ Increased methane production; Lower operation cost
	Disadvantages	✧ Lower degradation rate; Ammonia accumulation; Physical instability of waste mass
Hybrid	Operation	• Sequential aerobic-anaerobic
	Advantages	✓ Removal of nitrogen; More biologically stable leachate
	Disadvantages	✧ No full-scale operation experience
Facultative	Operation	• Ex-situ nitrified leachate recirculation
	Advantages	✓ Simultaneously removing nitrogen and stabilizing waste
	Disadvantages	✧ Extra nitrification

Table 1.2.2 Facultative bioreactor landfill used to remove nitrogen from landfill leachate

Waste type	Nitrification	Nitrate (mg-N/L)	Pathways	ANRR[a] (mg N/kg TS/d)	Ref.
9-year-old MSW 45-year-old MSW	Aerobic filter reactor	50-150	Heterotrophic	3.8	(Jokela et al., 2002)
Composed and fresh MSW	Add nitrate	400	Heterotrophic	140	(Price et al., 2003)
Fresh MSW	Add nitrate	4000	Heterotrophic	1625	(Fu et al., 2009)
15-year-old MSW	CSTR	200-2200	Heterotrophic	28.6	(Zhong et al., 2009)
1-year-old MSW 6-year-old MSW 11-year-old MSW	Add nitrate	1000	Heterotrophic & Autotrophic	163.2 72 26.4	(Chen et al., 2009)

[a] ANRR: Average Nitrogen Removal Rate

Nitrification and Denitrification pathways

Landfill leachate generally rich in ammonia-nitrogen/ammonium because of the degradation of organic nitrogen and solubilization of ammonia-nitrogen/ammonium. The ammonia will accumulate in landfill leachate and the nitrification (Reactions (1) and (2)) are unlikely to occur as no extra oxygen addition or air infiltration in conventional landfill sites. As shown in Reaction (1) and (2), the typical nitrification is a two-step process. Nitrifying bacteria include ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). The reaction (1) is regarded as the limiting step as the AOB grows more slowly than NOB (Grady et al., 1999). However, the growth rates of AOB are faster than that of NOB under low dissolved oxygen (Ma et al., 2015). Thus, the nitrite will accumulate under low dissolved oxygen. As shown in Reaction (1), the generated hydrogen ion will consume the alkalinity. As the rate of heterotrophic nitrification are very low (Barraclough and Puri, 1995), autotrophic nitrification is generally a major pathway, which suggest that no extra carbon source is required for the nitrification of landfill leachate. Extra nitrification is compulsory for facultative bioreactor landfill. The common nitrification reactions were summarized in **Figure 1.2.1**.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

Biological heterotrophic denitrification is an anoxic process, which NO_3^- will be reduced to NO_2^-, NO, N_2O and finally molecular N_2, as shown in Reaction (3)(4)(5)(6). Denitrifying bacteria (denitrifier) includes heterotrophic and facultative microorganisms. Under anoxic conditions, nitrate is reduced to N_2 and carbon sources are oxidized to CO_2 by the Gram-negative aerobic heterotrophs, which abundantly exist in water and soil (Gómez et al., 2000). Thus, young municipal solid waste rich in organic matter has better denitrification capacity than that of aged municipal solid waste (Chen et al., 2009). The biological heterotrophic denitrification will not only convert NO_3^- to N_2 gas but also stabilize the waste as the consumption of organic carbon.

$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$ (3)

$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$ (4)

$2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O$ (5)

$N_2O + 2e^- + 2H^+ \rightarrow N_2(g) + H_2O$ (6)

Recently, the anaerobic ammonium oxidation (Anammox) was considered to have contributed to the nitrogen removal in bioreactor landfill simulators (Valencia et al., 2011, Wei et al., 2017, Xie et al., 2013). However, possible of ammonia oxidation via anammox might be excluded in solid digestate bioreactor, as the solid digestate is fresh and containing high concentrations of COD, as well as high nitrite in the feed and effluent, which is all unbeneficial for anammox growth.

Autotrophic denitrification (Anammox):

$NH_4^+ + 1.32NO_2^- \rightarrow N_2 + 0.26NO_3^-$ (7)

Autotrophic denitrification via Reaction (8) might occur in the solid digestate facultative bioreactor landfill. The solid digestate could be rich in sulfide as the reduction of sulfate in anaerobic digestion (Möller and Müller, 2012).

Autotrophic denitrification (sulfide):

$8NO_3^- + 5HS^- + 3H^+ \rightarrow 4N_2 + 5SO_4^{2-} + 4H_2O$ (8)

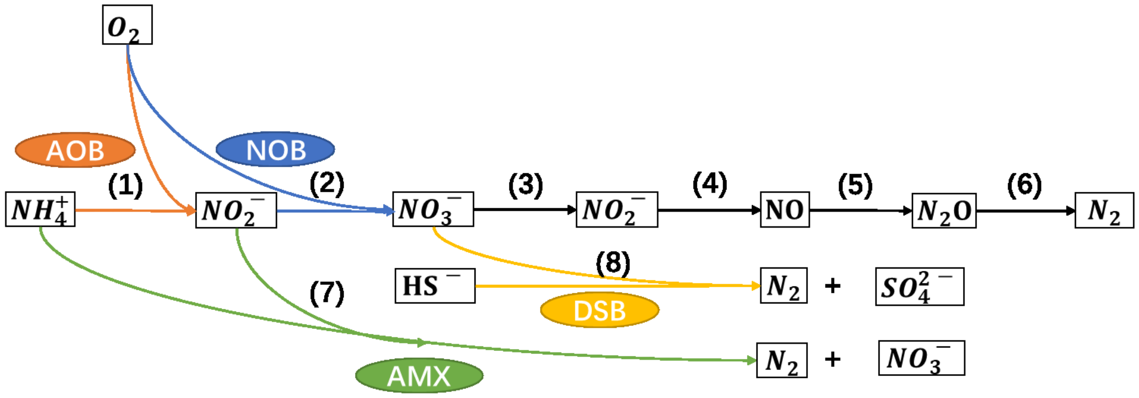

Figure 1.2.1 Nitrification and denitrification pathways in facultative bioreactor landfills (Modified from Ma et al., (2015))

Nitrogen removal via facultative bioreactor landfill

Facultative bioreactor landfills filled with fresh MSW or treated MSW have been used for nitrogen removal from landfill leachate (Jokela et al., 2002, Price et al., 2003, Fu et al., 2009, Zhong et al., 2009, Chen et al., 2009). As presented in **Table 1.2.2**, fresh MSW shows high denitrification capacity while aged MSW has less denitrification potential compared to the fresh MSW (Chen, et al., 2009). Besides, the mature landfill leachate is usually generated from old landfill site. Therefore, it could be a challenge to in-situ treat mature landfill leachate. Based the concept of circular economy and BEAs, solid digestate might be applied in the old landfill site to simultaneously achieve nitrogen removal of mature landfill leachate and digestate stabilization.

Chapter 2: Digestate application in landfill bioreactors to remove nitrogen of old landfill leachate-Nitrate pathway[2]

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Abstract

Anaerobic digestion of organics is one of the most used solution to gain renewable energy from waste and the final product, the digestate, still rich in putrescible components and nutrients, is mainly considered for reutilization (in land use) as a bio-fertilizer or a compost after its treatment. Alternative approaches are recommended in situations where conventional digestate management practices are not suitable. Aim of this study was to develop an alternative option to use digestate to enhance nitrified leachate treatment through a digestate layer in a landfill bioreactor. Two identical landfill columns (Ra and Rb) filled with the same solid digestate were set and nitrified leachate was used as influent. Ra ceased after 75 day's operation to get solid samples and calculate the C/N mass balance while Rb was operated for 132 days. Every two or three days, effluent from the columns were discarded and the columns were refilled with nitrified leachate (average N-NO_3^- concentration=1,438 mg-N/L). N-NO_3^- removal efficiency of 94.7% and N-NO_3^- removal capacity of 19.2 mg N-NO_3^-/gTS-digestate were achieved after 75 days operation in Ra. Prolonging the operation to 132 days in Rb, N-NO_3^- removal efficiency and N-NO_3^- removal capacity was 72.5% and 33.1 mg N-NO_3^-/gTS-digestate, respectively. The experimental analysis of the process

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[2] This work has been published on *Waste Management*. **Peng W**, Pivato A, Lavagnolo MC, Raga R (2018) Digestate application in landfill bioreactors to remove nitrogen of old landfill leachate. Waste Manag. 74:335-346. doi: 10.1016/j.wasman.2018.01.010

suggested that 85.4% of nitrate removal could be attributed to denitrification while the contribution percentage of adsorption was 14.6%. These results suggest that those solid digestates not for agricultural or land use, could be used in landfill bioreactors to remove the nitrogen from old landfill leachate.

Keywords: Solid digestate; Leachate; Nitrate; Adsorption; Denitrification; Landfill

2.1 Introduction

Solid digestate from the anaerobic digestion of organic waste is a semi-stable material that is rich in organic matter and minerals. With or without further treatment, this type of solid digestate is often used as a bio-fertilizer or soil conditioner applied to agricultural fields. In Italy, the digestates from agricultural residues (manure and energy crops) are almost exclusively spread to the land while digestates from organic fraction of municipal solid waste (OFMSW) is classified as wastes, which cannot be directly used in agriculture but need to be further treated. Besides, high transportation costs (Delzeit & Kellner, 2013), the potential for eutrophication (Lukehurst et al., 2010), low agriculture demand during some seasons (Wellinger et al., 2013) and strict regulations in nitrate sensitive zone (Neumann et al., 2016) could also restrict land use of digestate.

When digestate is not qualified for land use or land use is not possible, alternative options for digestate disposal could be based on the concept of Back to Earth Alternatives (BEA), which considers a landfill as a necessary sink to close the material loop (Cossu, 2016; Peng & Pivato, 2017). When solid digestate is applied to a landfill site, it might be possible to combine solid digestate disposal with leachate treatment.

It is generally known that leachate from old landfill sites is usually rich in ammonia, but its low content of biodegradable organics make denitrification the rate limiting step for a good nitrogen removal (Kozub & Liehr, 1999). Leachate treatment options to remove nitrogen include conventional denitrification through wastewater treatment technologies (Renou et al., 2008), phytotreatment (Garbo et al., 2017; Lavagnolo et al., 2016) and on-site denitrification by recirculation of nitrified leachate (Berge et al., 2006; Bolyard & Reinhart, 2016; Shao et al., 2008; Shou-liang et al., 2008). Either strategy for nitrogen removal includes nitrification and denitrification.

A functional layer of digestate in the temporary top cover of a landfill might facilitate nitrate biological conversion and physical/chemical removal, when nitrified leachate is recirculated on the top. Several studies tested nitrified leachate denitrification in landfill reactors filled with old waste because of its low cost (Jokela et al., 2002; Zhong et al., 2009; Sun et al., 2014). However, limited organic carbon in old waste could decrease the nitrate reduction rate (Wu et al, 2009). On one hand, digestate rich in organic matter could offer a partial external carbon source for nitrate denitrification as digestate contains an amount of total organic carbon (TOC) in the range of 27.5-45.9%-total solid (TS) (Michele et al., 2015; Quina et al., 2015; Zhang et al., 2012). Unlike the high nitrogen content in digestate from agricultural biogas production using manure and energy crops, digestate from OFMSW with less nitrogen content is preferred to be used as carbon source because less ammonia will be transferred into the leachate with leaching. In addition to the heterotrophic denitrification potential by using digestate as an external carbon source, nitrogen in both leachate and digestate might also be removed through autotrophic metabolic pathways (Valencia et al., 2011; Xie et al., 2013). On the other hand, solid digestate might have a nitrate adsorption capacity, as it happened with the municipal solid waste (MSW) in a landfill bioreactor experiment (Fu et al., 2009). Activated carbon, sepiolite, surfactant-modified zeolite and zeolite clinoptilolite has been used as absorbents for nitrate removal (Malekian et al., 2011; Öztürk & Bektaş, 2004), however they might not be suitable in case of leachate because of the high cost (Della Rocca et al., 2007).

In this study nitrate removal from nitrified leachate was investigated, using a digestate layer in two reactor columns. The nitrate removal pathway and the effect of solid digestate on nitrate adsorption were evaluated.

2.2 Materials and methods

Solid digestate and leachate

The solid digestate was obtained from a full scale thermophilic two-stage wet anaerobic digestion facility (Camposampiero, Padua, Italy) for the treatment of sewage sludge and source-segregated biodegradable waste. This plant has a total reactor volume of 3300 m^3 and operates at a hydraulic retention time of 22 days. After the end of anaerobic digestion, the digestate was separated by centrifugation. The solid digestate was composted to stabilize the material prior to land use whereas the liquid was treated internally at the wastewater treatment plant. The average characteristics of the solid digestate samples were: Total Solids (TS) = 25.6%, Volatile Solids (VS) = 64.1% TS, TOC = 314 g-C/kg-TS, Total Kjeldahl Nitrogen (TKN) = 48.5 g-N/kg-TS.

Raw leachate was collected from a MSW landfill located in Northern Italy where untreated MSW were disposed of during the 1980s. The physical-chemical characteristics of the raw leachate and nitrified leachate are reported in **Table 2.2.1**. The raw leachate was nitrified in a nitrification tank described below.

Table 2.2.1. Raw and nitrified leachate characteristics

Parameters	Raw Leachate		Nitrified leachate [a]	
	Average	Range	Average	Range
pH	8.95	8.85-9.05	7.08	5.69-8.30
TOC (mg-C/L)	264	252-276	415	273-565
TC (mg-C/L)	1600	1580-1620	553	366-725
BOD	60	58-62	30	15-45
COD	1014	987-1041	952	814-1090

TKN (mg-N/L)	1723	1698-1748	90	35-236
N-NH_4^+ (mg-N/L)	1703	1665-1741	71	7-208
N-NO_2^-(mg-N/L)	1.9	1.6-2.2	1.8	0.0-62.3
N-NO_3^-(mg-N/L)	0	0	1438	605-1791
SO_4^{2-} (mg-N/L)	206	201-211	188	184-192

[a]. Unlike the stable characteristics of raw leachate, the characteristics of nitrified leachate depend on the performance of the nitrification reactor, which slightly changed over time.

Experimental setup

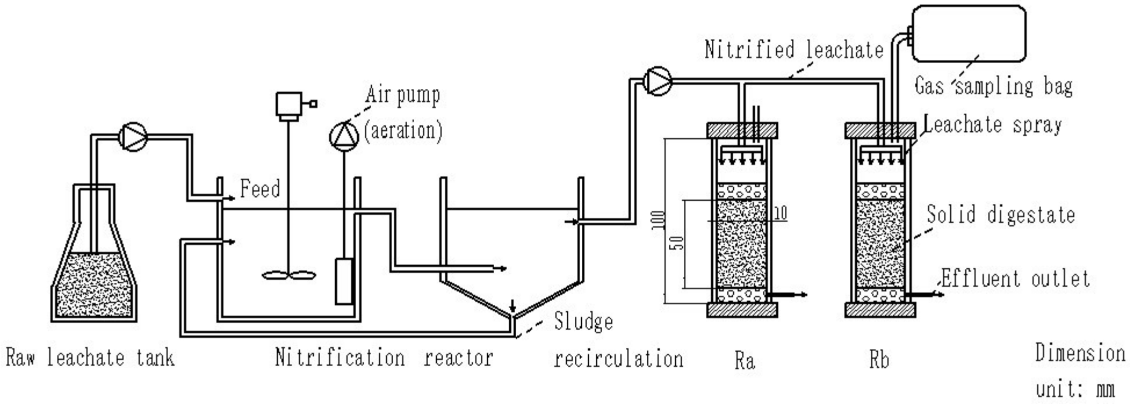

Figure 2.2.1. Reactor setup and experimental sketch

The experimental setup includes two parts: leachate nitrification reactors and landfill simulation columns. The experiment schematic is shown in **Figure 2.2.1**. For complete nitrification, the dissolved oxygen in the aeration tank was kept around 4 mg O_2/L. For every liter of raw leachate, 2 grams of sodium bicarbonate was added to provide alkalinity and to buffer the pH. Temperature for nitrification was maintained at 25±2 °C. The landfill simulation reactors were operated using two identical reactors (Ra and Rb) by using polymethyl methacrylate columns (height 100 cm and inner diameter 10 cm). A gravel layer (10-cm thickness) was placed at the bottom and at the top of each column for leachate drainage. 3.0 kg of raw solid digestate was added to each reactor, resulting an average density of 764 kg/m^3. Before the start-up of the two columns, pure nitrogen gas was used to flush the columns to maintain anaerobic conditions. Every two or three days, 0.50 L or 0.75 L of nitrified leachate (equivalent to 0.76 g-N/kg-VS day) produced from the leachate nitrification reactor were added to the landfill bioreactors and the effluent collected from columns was sampled and discharged at the same time. Every day effluent from the landfill bioreactors were recirculated to the digestate body three times. The nitrified leachate volume was set according to Xie et al., 2013 and based on preliminary experiments, which indicate that a loading rate around 0.73 g-N/kg-VS/day was necessary to maintain a stable nitrate removal.

Landfill reactor Ra’s operation ceased after 25 feeding cycles (approximately 75 days) to get solid samples and calculate the C/N mass balance while the operation of reactor Rb was extended until 48 feeding cycles (132 days). Each feeding cycle lasted 2-3 days. . At the end of the experiments, the total liquid-to-solid ratios (L/S) were equivalent to 17 ml/g and to 32 ml/g, respectively, for Ra and Rb.

Nitrate removal efficiency was calculated by equation (1) and was used to evaluate the denitrification performance of the landfill columns:

$$\text{Nitrate removal efficiency} = \sum_{i=1}^{n} \frac{C_{inf,i}V_{inf,i} - C_{eff,i}V_{eff,i}}{C_{inf,i}V_{inf,i}} \times 100\% \qquad (1)$$

where:

$C_{inf,i}$ and $C_{eff,i}$ = influent and effluent concentrations of nitrate in the landfill columns at feeding cycle *i*;

$V_{inf,\,i}$ and $V_{eff,\,i}$ = influent and effluent volumes at *i* feeding cycle;

n = total feeding cycles; *n* equal to 25 and 48, for Ra and Rb, respectively.

Analytical method

All liquid samples were analyzed according to the CNR-IRSA Italian standard methods. Leachate samples were analyzed periodically for pH, Total Carbon (TC), TOC, TKN, N-NO_3^-, N-NO_2^-, N-NH_4^+ and SO_4^{2-}. TC and TOC were measured by a TOC-VCSN Shimadzu Analyzer. N-NO_3^-, N-NO_2^-, N-NH_4^+ and SO_4^{2-} were determined using a UV-vis spectrophotometer (Shimadzu UV-1601). TKN was measured by a distillation titration procedure after acid digestion.

Solid digestate samples were characterized before filling the reactors (referred to as SD) and at the end of both the tests after 75 days and 132 days of treatment (referred to as SD-T, SD-M, SD-B according to their positions, top-T, middle-M and bottom-B, in the columns). TS, VS, TKN, TOC, N-NO_3^-, Respiration Index (RI_4 and RI_7) were determined for all solid samples. TS, VS were measured according to Standard Methods (APHA, 2005). Solid samples were dried in an oven at 105 °C for 24 hours prior to analysis using a TOC-VCSN Shimadzu analyzer. TKN was determined by the Kjeldahl method. RI_4 and RI_7 were analyzed by a Sapromat apparatus (H+P Labortechnik, Germany). N-NO_3^- in the solid digestate was calculated from the results of analyzing the eluate from the leaching test. The biochemical methane potential (BMP) test of the initial solid digestate referred to those described in (Girotto et al., 2017). All tests on the solid samples were performed in duplicate.

Leaching tests were conducted according to the standard EN-12457-2 and the eluates obtained were analyzed for pH, TC, TOC, N-NO_3^-, N-NO_2^-, N-NH_4^+, SO_4^{2-}, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) following the aforementioned methods for liquid samples.

Gas emissions were monitored in the two reactors and samples were collected periodically for characterization. Gas compositions (CO_2, CH_4, N_2 and O_2) was analyzed by a micro-gas chromatograph (Varian 490-GC) equipped with a 10 m MS5A column, 10 m PPU column, and a thermal conductivity detector. The carrier gas was argon. The water displacement method was used to measure the volume of biogas collected from the landfill simulation columns (Berge et al., 2006).

All statistical analyses were carried out using Statgraphics Centurion XVII (version 17.1.08).

Adsorption tests

Adsorption of nitrate ions onto solid digestate was studied using batch tests (Öztürk & Bektaş, 2004). Solid digestate was oven-dried at 105 °C for 2 h before being used (Öztürk & Bektaş, 2004). Batch experiments were conducted using different adsorbent doses (0.2 g, 0.5 g, 1.0 g, 5.0 g, and 10 g of dry solid digestate) and 50 ml nitrified leachate (1438 mg $N\text{-}NO_3^-$/L) added to a capped bottle (60 ml) and rotated at 20 rpm. The corresponding L/S were 250 ml/g, 100 ml/g, 50 ml/g, 10 ml/g, and 5 ml/g, respectively. The room temperature (20±2°C) was maintained for all adsorption test. After 24 hours, the nitrate concentration in the supernatant was determined. This time was considered sufficient to reach the equilibrium as suggested by other authors (Öztürk & Bektaş, 2004; Wang et al., 2007) and by the standard adsorption test (OECD, 2000). During this period, any biological activity (denitrification) was assumed to be negligible.

For comparison, adsorption tests were also conducted by applying potassium nitrate (KNO_3) solution (100 mg/L) instead of nitrified leachate. KNO_3 solution (100 mg/L) was chosen as a standard nitrate source for nitrate adsorption assessment, as reported by other researchers (Krayzelova et al., 2014; Song et al., 2016).

Nitrate removal efficiency (R) was calculated following equation (2):

$$\mathrm{R} = \frac{C_I - C_E}{C_I} \times 100\% \quad (2)$$

The adsorption capacity of adsorbent (Q_E, mg-N/g-TS) was calculated following equation (3):

$$Q_E = (C_I - C_E) \times \frac{V/1000}{M} \quad (3)$$

where:

C_I = initial concentrations of nitrate in solution (mg-N/L),

C_E = equilibrium concentrations of nitrate in solution between solid and liquid phases (mg-N/L)

V = solution volume (ml),

M = dry mass of adsorbent (g-TS).

Mass balance

At the end of the experiment, the carbon and nitrogen balance for each column was calculated, based on the following equation (4):

$$W_{initial.s} + W_{input.l} = W_{final.s} + W_{output.l} + W_{output.g} + W_{unaccounted} \quad (4)$$

where:

$W_{initial.s}$=Total mass of carbon or nitrogen in initial solid digestate, g/kg-TS of SD;

$W_{input.l}$= Total mass of carbon or nitrogen input from nitrified leachate, g/kg-TS of SD;

$W_{final.s}$= Total mass of carbon or nitrogen in solid digestate at the end of experiment, g/kg-TS of SD;

$W_{output.l}$= Total mass of carbon or nitrogen loss through liquid effluent, g/kg-TS of SD;

$W_{output.g}$= Total mass of carbon or nitrogen loss through gas emission, g/kg-TS of SD

$W_{unaccounted}$=Total mass of unaccounted carbon or nitrogen, g/kg-TS of SD

2.3 Results and discussion

Effluent characteristics variation in the columns

$N\text{-}NO_2^-$ and $N\text{-}NO_3^-$ concentrations

The influent and effluent concentrations of $N\text{-}NO_2^-$ and $N\text{-}NO_3^-$ for each column are shown in **Figure 2.3.1**.

In Ra, the effluent $N\text{-}NO_3^-$ concentrations were close to zero until day 54. When Ra operation ceased after 75 days, the $N\text{-}NO_3^-$ content was 482 mg-N/L and the average $N\text{-}NO_3^-$ removal efficiency was 94.7%. In Rb, the effluent $N\text{-}NO_3^-$ concentrations were almost zero until day 33 and then fluctuated around 120 mg $N\text{-}NO_3^-$/L until day 49. Afterwards, the $N\text{-}NO_3^-$ concentration in Rb gradually increased to 791 mg/L at day 77 because of the elevated $N\text{-}NO_3^-$ loading rate in Rb. Ra operation ceased and Rb continued to run until $N\text{-}NO_3^-$ concentration in the effluent were stable and around 937 mg/L.

Meanwhile, effluent $N\text{-}NO_2^-$concentrations in both Ra and Rb exhibited similar trends to $N\text{-}NO_3^-$ variation. The correlation coefficients between $N\text{-}NO_3^-$ and $N\text{-}NO_2^-$ variation over time, calculated by Statgraphics Centurion XVII, were 0.831 and 0.723, respectively for Ra and Rb. $N\text{-}NO_2^-$started to accumulate from 40 days with corresponding nitrate removal efficiency deteriorating, which suggested that $N\text{-}NO_2^-$ accumulation is a marker of over loading of denitrification process. Extracellular nitrite would accumulate when nitrate respiring bacteria grow more rapidly than denitrifiers (Glass & Silverstein, 1998).

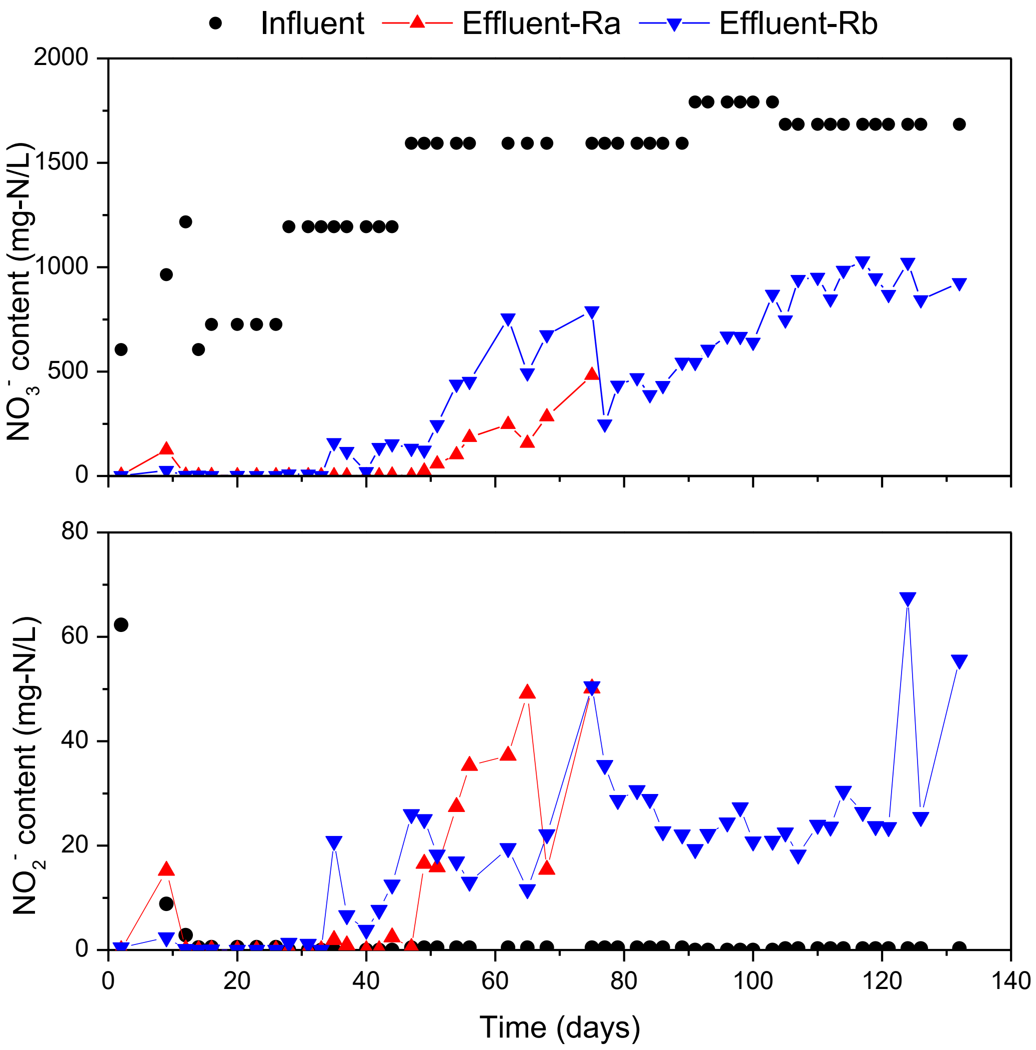

Figure 2.3.1. Dynamics of N-NO_3^- and N-NO_2^- influent and effluent concentrations in landfill simulation columns

N-NH_4^+ and TKN concentrations

As presented in **Figure 2.3.2.**, concentrations of TKN for Ra and Rb had similar trends. A high TKN level (average 2,133 mg-N/L) was maintained during the initial period (0-12 days), which were consistent with the variation of TOC. TKN eventually dropped rapidly to 1,085 mg-N/L since day 14. After this period, there was a gradual decrease to 51 mg-N/L. The N-NH_4^+/TKN ratio of the treated leachate varied between 0.41 and 1.0 and the average percentage of N-NH_4^+/TKN was 0.77. It was found that ammonia originating from the solid digestate could be solubilized and released into the effluents.

However, the ammonia releases gradually subsided and ceased after 75 days of operations as the ammonia concentrations in both the influent and effluent were almost equal after 75 days.

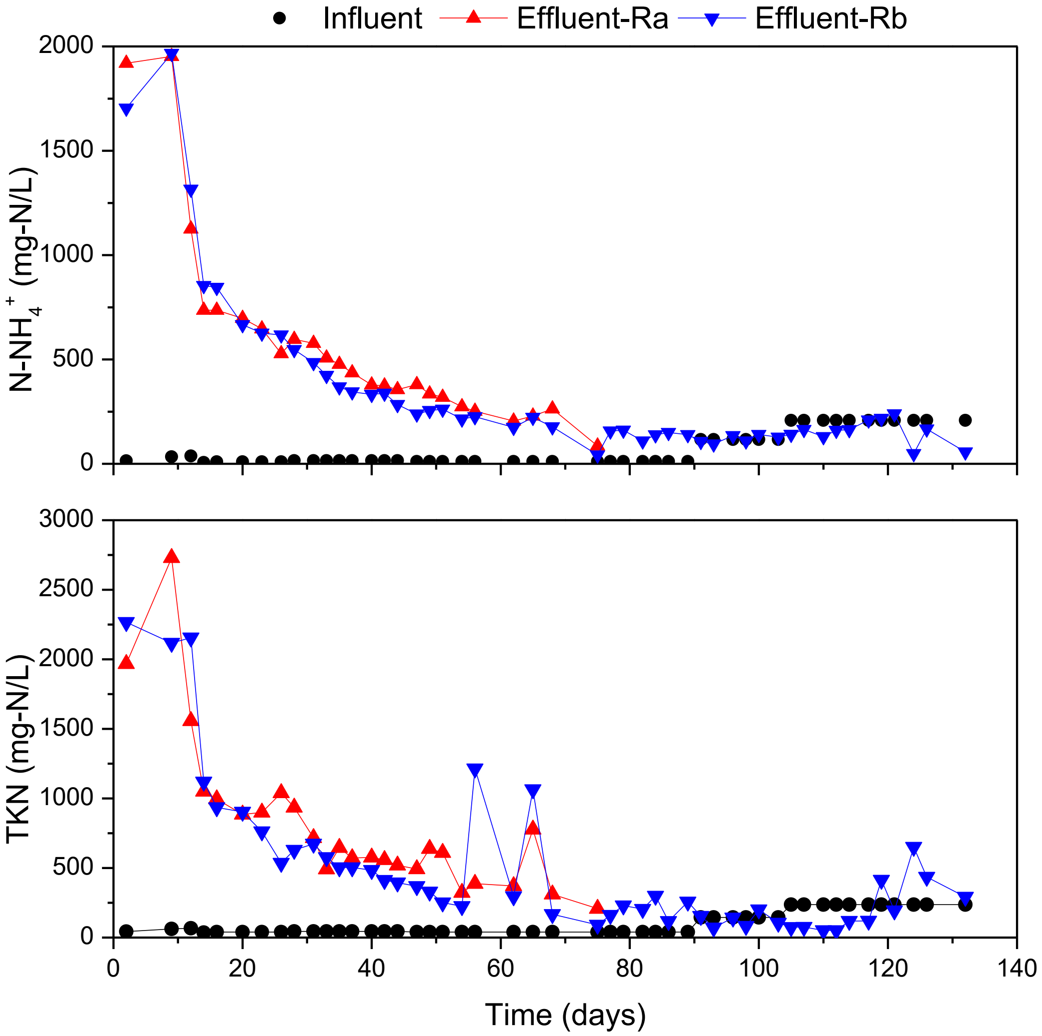

Figure 2.3.2. Dynamics of N-NH$_4^+$ and TKN of influent and effluent concentrations in landfill simulation columns

pH and sulfate

The pH of the effluent in Ra varied between 7.55 and 9.48 while in Rb it ranged from 7.62 to 9.81, as shown in **Figure 2.3.3 (a)**. The pH decreased in the beginning can be attributed to the digestate hydrolysis and then fermentation as BMP and RI$_4$ of the digestate were around 0.032 L/g-VS and 31.1 mg O$_2$/g-TS, respectively. The pH increased and fluctuated around 9.0, presumably due to the consumption of H^+ ions caused by denitrification (Glass & Silverstein, 1998). The decrease in pH during 98-121 days could also be due to the low pH of the influent. The pH mean square deviations of the influent, effluent-Ra and effluent-Rb were 0.87, 0.42, 0.50, respectively. These values suggest that there is a potential for high pH buffering of the digestate added landfill bioreactors.

Figure 2.3.3 (b). shows that average sulfate effluent concentrations during operation in the two columns, Ra and Rb. In the first 20 days of operation, average sulfate concentrations for Ra and Rb decreased from 1,644 mg SO_4^{2-} /L to 1,053 mg SO_4^{2-} /L, which could be attributed to the leaching of solid digestate as its eluate contain high sulfate concentration (**Table 2.3.1**). Sulfate in the effluent of both Ra and Rb increased gradually after 33 days, suggesting that the sulfur-based autotrophic denitrification presumably occurs in the columns (Berge et al., 2006; Sahinkaya et al., 2011). Three inorganic sulfur forms, hydrogen sulfide ion (HS^-), sulfur (S) and thiosulfate were reported to work as electron donors for nitrate denitrification (Berge et al., 2006; Mora et al., 2014; Sahinkaya et al., 2011). As digestate contains hydrogen sulfide and reduced sulfur compound formed from the reaction between sulfate and protons under anaerobic conditions (Möller & Müller, 2012), the following reaction (1) may have happened.

$$1/5\mathrm{NO_3^-} + 1/8\mathrm{HS^-} + 3/40\mathrm{H^+} \rightarrow 1/10\mathrm{N_2} + 1/8\mathrm{SO_4^{2-}} + 1/10\mathrm{H_2O} \quad (5)$$

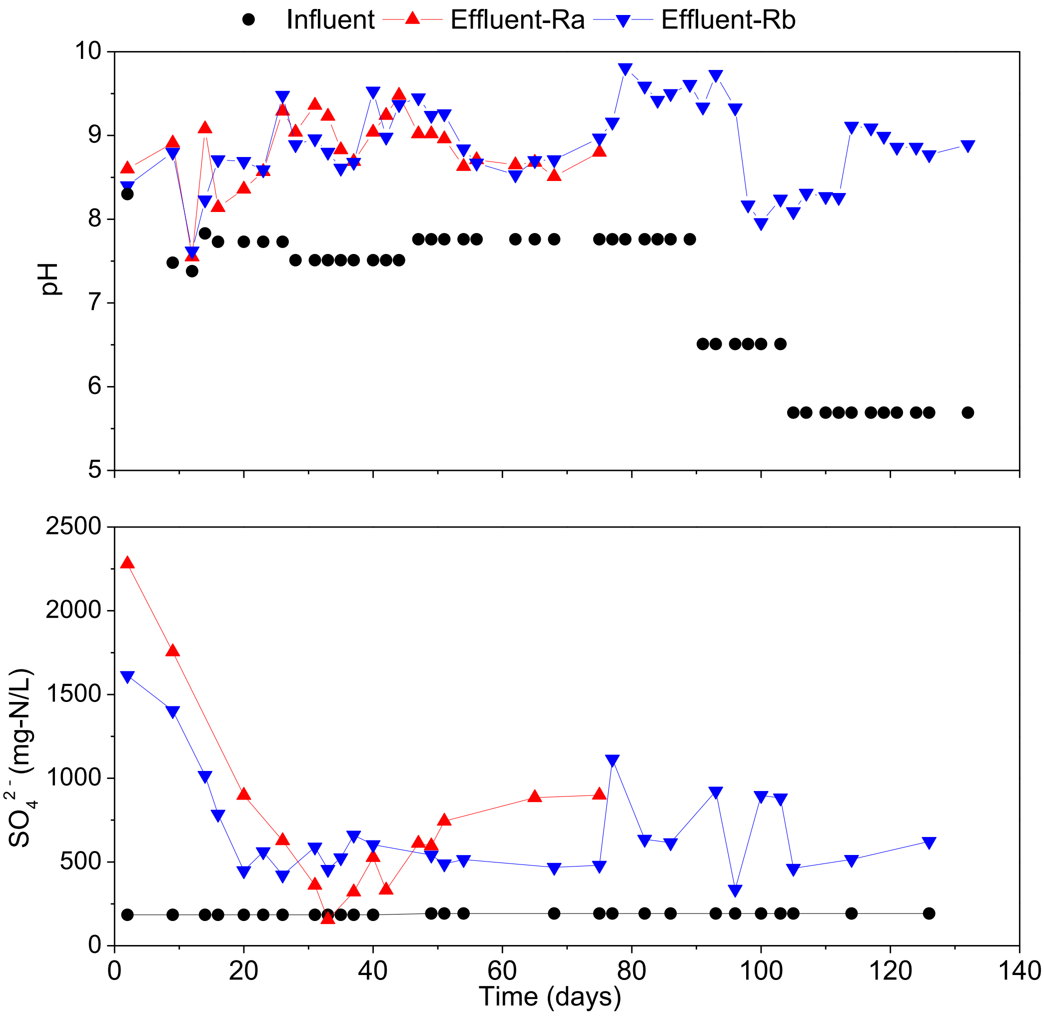

Figure 2.3.3. Dynamics of pH (a) and sulfate (b) of influent and effluent concentrations in landfill simulation columns

TOC and TC concentrations

As illustrated in **Figure 2.3.4.**, the evolution of TOC was similar to that of TC. The average effluent TOC concentrations were between 1,607 and 1,775 mg-C/L during the initial period between days 0 and 12. The high level of TOC in this period is due to the leaching of organic matter from the solid digestate, which might add the burden for leachate treatment. In the following 120 days, TOC kept stable which suggested TOC might be mainly consisted of refractory organic substances. The estimation of organic matter transferring from digestate to leachate during the early stage should be better investigated in a further development. As the TOC will gradually be washed away along leaching, it is necessary to define the limiting time of digestate to support denitrification. It depends on the substrate, on the quality of leachate and on the environmental conditions. For full-scale application, lab tests as the one performed are necessary to estimate the limiting time. In this study, the results show a time of 75 days in which the nitrate removal efficiency was high (**Figure 2.3.1**).

Compared to the low inorganic carbon content (137±24 mg-C/L) in the influent, the high inorganic carbon (ranged from 608-1,710 mg-C/L) in the effluent suggests that the mineralization of solid digestate in the columns occurred.

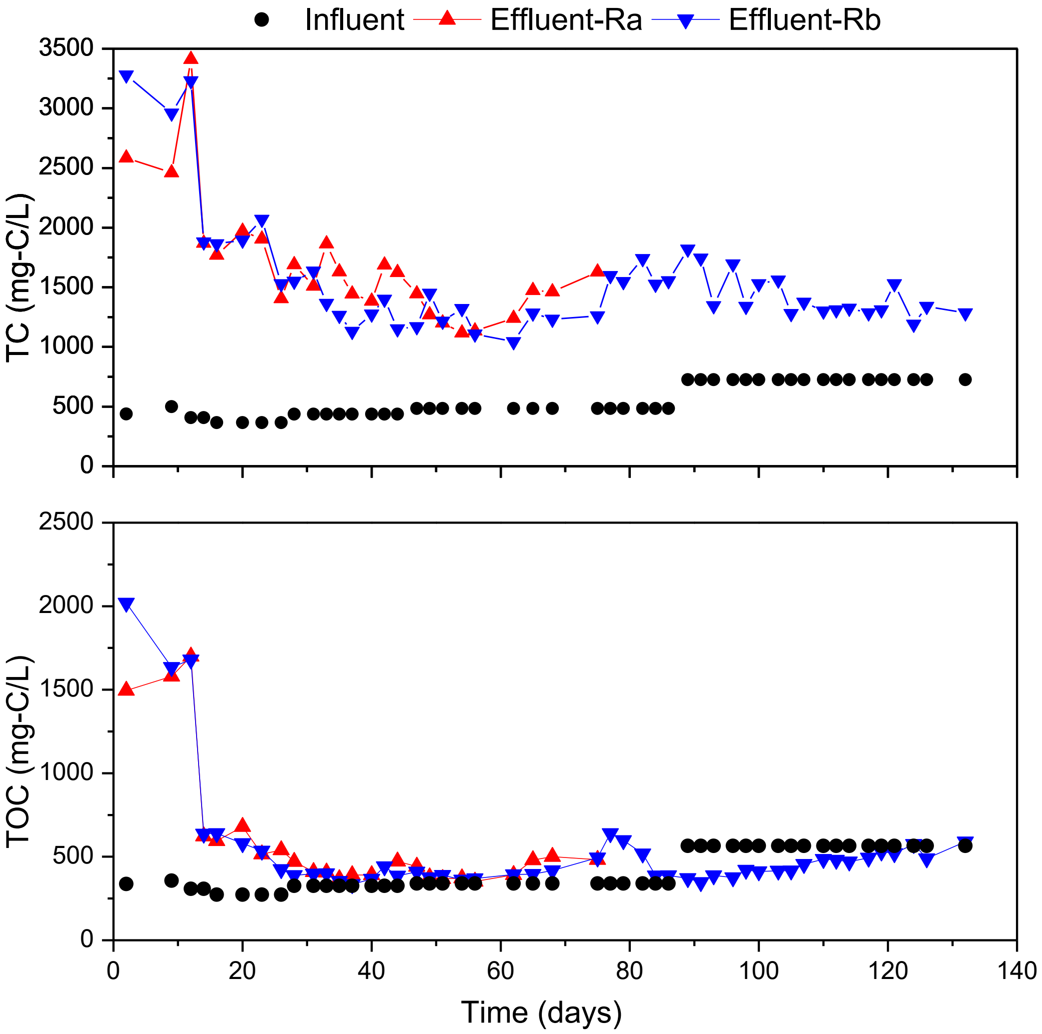

Figure 2.3.4. Dynamics of TC and TOC concentrations in landfill columns

Table 2.3.1 Quality parameters of digestate sample at the beginning, middle-phase, and the end of the test: characterization of solid samples and the eluate from a standard leaching test

		SD	Ra (Middle-phase)				Rb (End-phase)			
		(Initial)	SD-T	SD-M	SD-B	Mean	SD-T	SD-M	SD-B	Mean
Solid phase	TS (%)	25.6	21.0	21.5	21.0	21.2±0.2	19.6	20.2	20.8	20.2±0.5
	VS (%TS)	64.0	60.3	60.8	59.4	60.2±0.6	57.9	56.7	56.9	57.2±0.5
	RI_4 (mg O_2/g-TS)	31.1	7.5	7.2	8.9	7.9±0.7	2.9	5.2	10.0	6.0±3.0
	RI_7 (mg O_2/g-TS)	53.5	12.1	12.6	13.6	12.8±0.6	8.0	10.7	18.6	12.4±4.5
	TKN (g N/kg-TS)	48.6	36.2	36.0	38.9	37.0±1.3	35.8	36.2	35.9	36.0±0.2
	N-NO_3^- (mg N/kg-TS) [a]	10	5040	3890	490	3140±1930	6230	5000	1620	4280±1950
	TOC (g C/kg-TS) [b]	314	291	288	283	287±3	286	293	299	293±5
	BMP (L/g-VS)	0.032	-	-	-	-	-	-	-	-

Eluate from leaching test	pH	7.72	8.25	8.20	8.11	8.19±0.06	7.93	8.40	8.09	8.14±0.19
	TOC (mg C/L)	283	123	71	83	92±22	166	161	100	142±30
	COD (mg O_2/L)	896	370	398	460	409±38	486	458	458	467±13
	N-NH_4^+ (mg N/L)	348	13	15	38	22±12	82	116	177	125±39
	N-NO_3^- (mg N/L)	1	320	250	32	200±123	469	387	129	328±145
	N-NO_2^- (mg N/L)	0.3	34.1	72.5	118.0	74.9±34.3	63.5	14.5	22.5	33.5±21.5
	SO_4^{2-} (mg/L)	1327	171	228	692	364±233	185	165	431	260±121

[a] N-NO_3^- in solid digestate was calculated from the results of analyzing eluate from leaching test.

[b] TOC can also be regarded as TC in the solid digestate because inorganic carbon is lower than the detective limit

Mass balance

Carbon and nitrogen mass balances were estimated considering the TC and total nitrogen (TN) content in the solid, liquid and biogas samples at the beginning, middle (Ra) and at the end (Rb) of the anaerobic landfill process (**Table 2.3.2**) (**Figure 2.3.5**). Carbon mass balance showed differences among the analyzed and the calculated content of TC. TOC in solid samples represented TC as inorganic carbon accounted for less than 5%. The losses or unaccounted quantity in the system for Ra and Rb were 15.1 g C/kg-TS (4.7% of TC in column) and 7.7 g C/kg-TS (2.3% of TC in column). The TC in the column was calculated by taking the sum of TC in initial solid digestate and nitrified leachate. A significant gap between the analyzed and calculated final content can be explained by waste heterogeneity (Cossu et al., 2016). In this study, only 4.7% and 2.3% of the TC was unaccounted which suggests that the solid digestate was homogenous. Despite of the low loss of TOC in Ra and Rb (**Figure 2.3.5**), the degradability of TOC decreased greatly as the RI_4 of the initial solid digestate decreased from 31.1 mg O_2/g-TS to 7.9 mg O_2/g-TS (Ra) and 6.0 mg O_2/g-TS (Rb) (**Table 2.3.1**). Liquid output for Ra and Rb were 5.9% and 9.2% of the initial carbon content in the solid digestate respectively, which is comparable to previous research (Cossu et al., 2016). Methane emissions were negligible in this study and were most likely a result of nitrate and nitrite inhibition on methanogenesis (Percheron et al., 1999). Besides, the organic carbon in solid digestate is not easily degradable for anaerobic digestion.

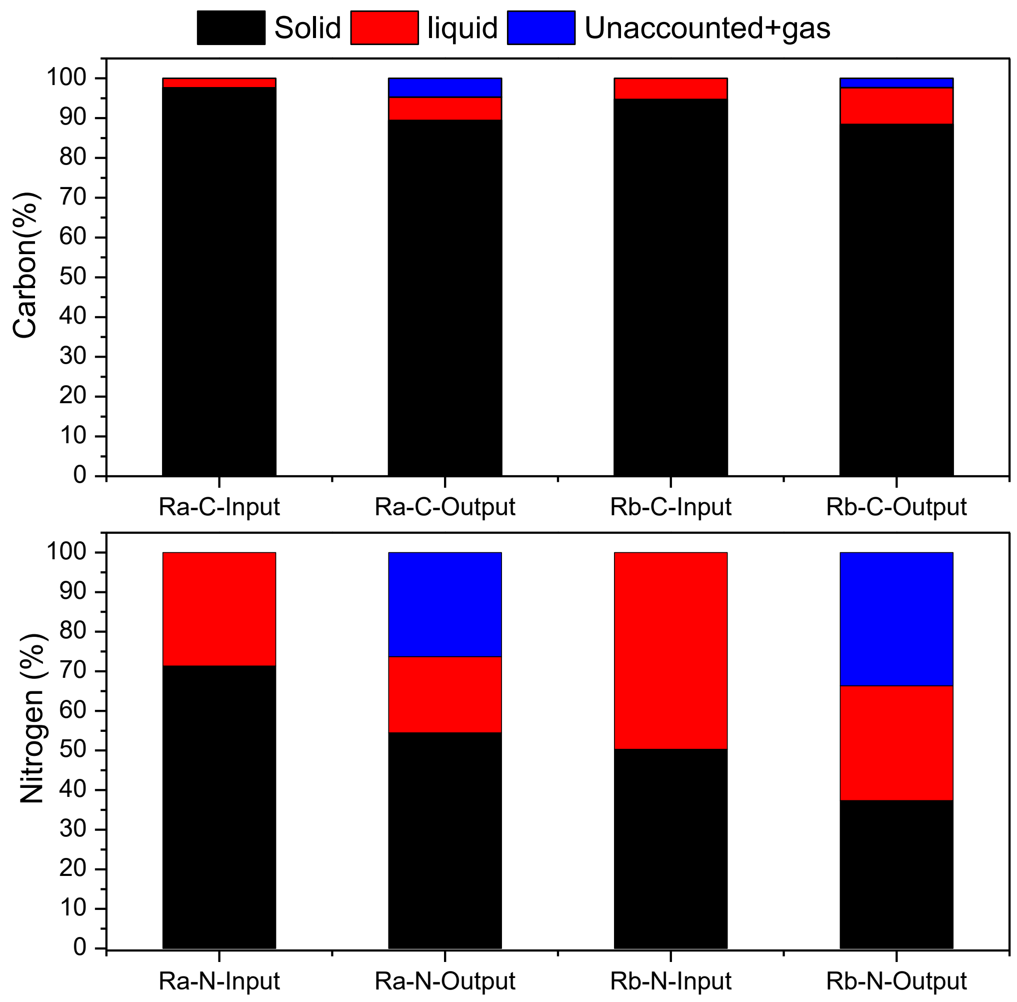

Figure 2.3.5. Carbon and nitrogen distribution in Ra and Rb

TN emissions were associated with TKN and NO_x^- in the effluent. Approximately, 26.3% and 33.6% of the total nitrogen in Ra and Rb, respectively, were unaccounted (**Table 2.3.2**) (**Figure 2.3.5**), which could be due to denitrification although nitrogen gas was not well measured in Ra and Rb. The difficulty of monitoring nitrogen gas, recognized by other authors (Berge et al., 2006), is a limit of the current research. Although a high nitrate removal was achieved in both Ra and Rb **(Figure 2.3.2)**, nitrogen outputs from the effluents for Ra and Rb were as high as 13.1 g N/kg TS and 28.0 N/kg TS, respectively (**Table 2.3.2**). These results can be explained by a significant fraction of ammonia or TKN leaching from solid digestate, especially in the initial phase (**Fig 2.3.2**). The TN removals included those of liquid fraction (nitrified leachate) and solid fraction (digestate), as shown in **Figure 2.3.5**. The TN removals (TN input minus TN output in the columns) were 17.9 g N/kg TS-SD (Ra) and 32.5g N/kg TS-SD (Rb), which accounted for 26.3% (Ra) and 33.6% (Rb) of TN input, as shown in **Table 2.3.2**. Considering the operation time, the average specific rates of TN removal were 0.239 g N/day/kg TS-SD (0.373 g N/day/kg VS-SD) for Ra and 0.256 g N/day/kg TS-SD (0.384 g N/day/kg VS-SD) for Rb. These values are higher than 0.117 and 0.196 g N/day/kg TS found in the experiment developed by Berge et al. (2006), but lower than 0.666 g N/day/kg VS found in the experiment of Xie et al. (2013). Thus, it is also intriguing to develop various nitrogen removal pathways in the digestate-added bioreactor. Beyond nitrogen removal in the nitrified leachate, the TN of solid digestate, mainly TKN, decreased to 76.3% (Ra) and 74.3% (Rb) of the initial solid digestate in the two columns.

Table 2.3.2 Mass balance in the digestate landfill columns

	Ra		Rb	
Carbon	g C/kgTS	%	g C/kgTS	%
$C_{initial.s}$ (Initial carbon in solid digestate)	313.7	97.6	313.7	4.7
$C_{input.l}$ (Carbon input from leachate)	7.6	2.4	17.6	5.3
$C_{final.s}$ (Final carbon in solid digestate)	287.6	89.5	293	88.4
Coutput.l (Carbon output from leachate)	18.9	5.9	30.6	9.2
$C_{output.g}$ (Carbon output from CO_2 and CH_4 emission)	0.0	0.0	0.0	0.0
$C_{unaccounted}$ (Unaccounted)	15.1	4.7	7.7	2.3
Nitrogen	g N/kgTS	%	g N/kgTS	%
$N_{initial.s}$ (Initial nitrogen in solid digestate)	48.6	71.4	48.6	50.3
$N_{input.l}$ (Nitrogen input from leachate)	19.5	28.6	48.0	49.7
$N_{final.s}$ (Final nitrogen in solid digestate)	37.1	54.5	36.1	37.4
$N_{output.l}$ (Nitrogen output from leachate)	13.1	19.2	28.0	29.0
$N_{output.g}$ (Nitrogen output from N_2 emission)	Undetected	-	Undetected	-
$N_{unaccounted}$ (Unaccounted)	17.9	26.3	32.5	33.6

Effects of adsorption on nitrate removal

Figure 2.3.6 shows the removal efficiency of nitrate as a function of the solid digestate as the adsorbent dosage in two different nitrate sources (i.e., KNO_3 and nitrified leachate). Using 100 mg/L of KNO_3 as a nitrate source, the removal efficiency of nitrate increased with the increased weight of solid digestate. Theoretically, the experimental values expressed that a maximum adsorption rate is reached at 5 g/50 ml according to the Langmuir adsorption isotherm. Increasing the dosage did not improve the removal efficiency. The nitrate removal efficiency of 1 g of solid digestate per 50 ml of KNO_3 solution was 24%, while 1.0 g activated carbon per 50 ml of KNO_3 solution could achieve around 71% removal efficiency (Öztürk & Bektaş, 2004). When nitrified leachate was used as a nitrate source, the optimum removal efficiency was around 11%, which is significantly lower compared to using KNO_3 as a nitrate source. This behavior can be attributed to the different initial nitrate concentrations in nitrified leachate (1,438 mg $N\text{-}NO_3^-$/L) and KNO_3 solution (100 mg/L) because the initial nitrate concentrations greatly influence the removal efficiency according to equation (2). The results mentioned above revealed that nitrate concentrations for a given source can influence the mass of nitrate adsorption at equilibrium (Wang et al., 2007). The equilibrium adsorbent mass decreased from 5 g to 1.0 g with an increase in the initial concentration from 14 mg $N\text{-} NO_3^-$/L (equivalent to 100 mg/L KNO_3) to 1438 mg $N\text{-}NO_3^-$/L, respectively. This behavior suggests that a much higher availability of nitrate anions at a higher initial concentration can increase the adsorption process. **Figure 2.3.6(a)** shows that the slope of curve in the KNO_3 solution was higher than that of nitrified leachate and a significant portion of the available nitrate anions in the nitrified leachate could explain the slope of flattening curve (Mohsenipour et al., 2015). It is worth mentioning that less knowledge was available on the adsorption of leachate dissolved organic nitrogen (DON) with hydrophobic and hydrophilic chemical properties while DON of leachate may significantly contribute to nitrogen discharge (Bolyard & Reinhart, 2017).

Based on the L/S ratios, adsorption capacity of the dry solid digestate, with nitrified leachate as nitrate source was plotted in **Figure 2.3.7**. When the L/S was equal to 16 (L/S of Ra) and 28 (L/S of Rb), the predicted adsorption capacities for Ra and Rb were 3.78 mg-N/g-TS and 7.21 mg-N/g-TS, respectively. These two predicted values were comparable with N-NO_3^- concentration of solid digestate at the end of the experiments, 3.14±1.93 mg-N/g-TS for Ra and 4.28±1.95 mg-N/g-TS for Rb (**Table 2.3.1**). Furthermore, it can be estimated that the nitrate removal from adsorption in Ra (765 g-TS of digestate) and Rb (765 g-TS of digestate) were around 2,402 mg N-NO_3^- and 3,274 mg N-NO_3^-, respectively. These nitrate removal in Ra and Rb accounted for 15.5% and 9.38% of total nitrate input.

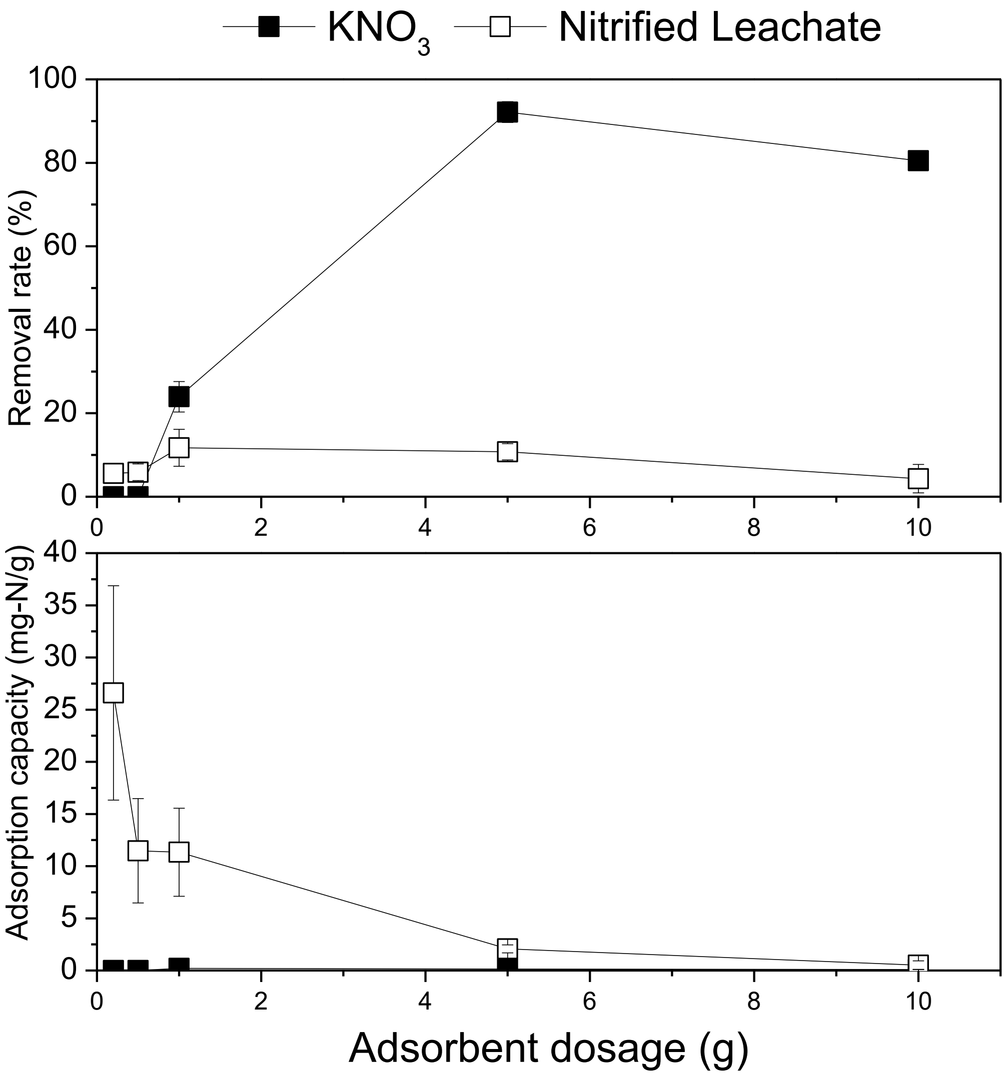

Figure 2.3.6. Nitrate removal efficiency (a) and adsorption capacity (b) with 100 mg/L

KNO_3 or nitrified leachate as the nitrate source

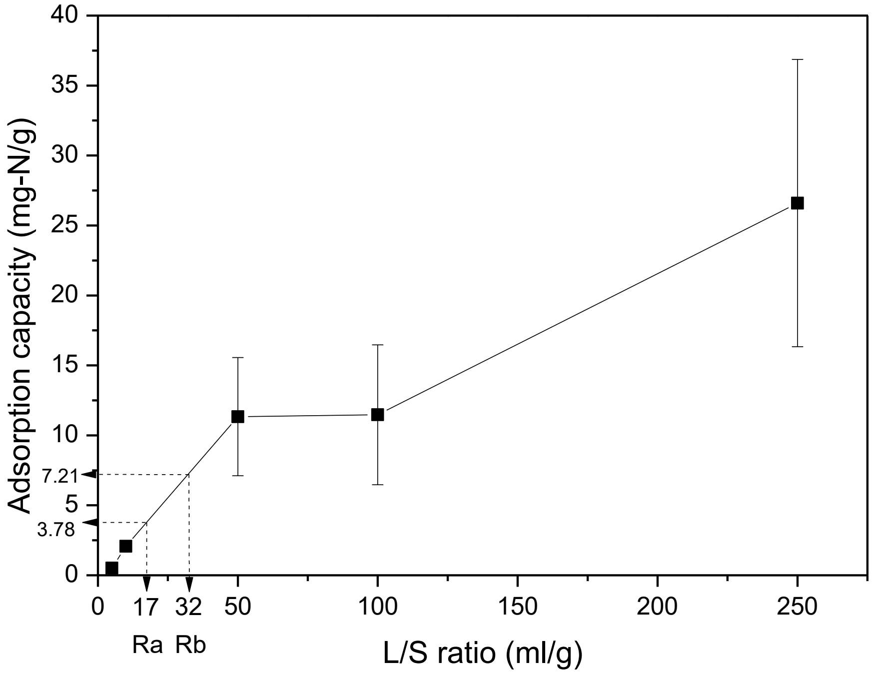

Figure 2.3.7. Adsorption capacity of solid digestate with increasing L/S ratio

Effect of autotrophic denitrification on nitrate removal

As shown in **Table 2.3.1**, TOC in the solid digestate decreased by 8.6% in Ra. Interestingly, the TOC in Ra and Rb at the end indicated no significant differences while the partial nitrate removal (38.8%-84.4% calculated by **Figure 2.3.2**) still occurred in Rb, which suggests that autotrophic denitrification might appear in the digestate-added landfill bioreactor after a prolonged operation.

Nitrate removal in both Ra and Rb was coupled with production of sulfate concentration (**Figure 2.3.3(b)**), which suggested partial nitrate removal might be due to autotrophic denitrification. Presumably the sulfate in the effluents was produced by the reaction (1) instead of leaching from 33 days of operation, which is based on the gradual increase in sulfate concentrations. It is estimated that the cumulative sulfate productions in Ra and Rb were 2,808 mg and 5,168 mg, respectively. Based on reaction (1), it is calculated that 655 mg of $N\text{-}NO_3^-$ in Ra and 1,538 mg of $N\text{-}NO_3^-$ in Rb were removed through autotrophic denitrification, which accounted for approximately 4.3% and 4.4% of the total nitrate input in Ra and Rb, respectively. Berge et al (2006) found that 10-15% of the nitrate removal was via autotrophic denitrification in MSW landfill reactors in the laboratory (Berge et al., 2006). Comparatively, the percentage of nitrate removal through autotrophic pathway was relatively low in the digestate-added system. However, the autotrophic denitrification potential of the treated solid digestate was still significant as the sulfate concentration in Rb remained around 623 mg/L after 126 days of operation.

Besides, sulfate concentration from leaching test on SD-B sample was much higher than those of SD-T and SD-M, which may suggest that the strong activity of autotrophic denitrification occurred in the bottom of the columns.

Effect of heterotrophic denitrification on nitrate removal

Beyond nitrate removal through adsorption and autotrophic denitrification, nitrate removals in Ra and Rb were also assumed to be converted into nitrogen gas via heterotrophic denitrification.

For every 1 g of $N\text{-}NO_3^-$ removal, denitrification consumes approximately 3.7 g of biodegradable COD and produces 3.93 g of CO_2 and 1 g N_2 which can be calculated from reaction (2) (Chiu & Chung, 2003; Matějů et al., 1992).

$$5C_6H_{12}O_6 + 24NO_3^- + H^+ \rightarrow 12N_2 + 30CO_2 + 42H_2O \quad (2)$$

The biodegradable organic matter in both Ra and Rb were degraded given the decrease in the RI_4 of both Ra and Rb by 74.6% and 80.6% of initial values, respectively. Meanwhile, the reduction in biodegradable organic matter in Ra and Rb could not be attributed to effluent loss as the TOC concentration was stable in the effluent after the initial 0-12 days, which suggested that the TOC residual of the effluent was recalcitrant. It was obvious that the inorganic carbon was continuously produced in the effluent of both Ra and Rb by comparing the TC and TOC (**Figure 2.3.4**). This trend supports the occurrence of heterotrophic denitrification with undigested organic matter in solid digestate as carbon source. However, quantification of the denitrification processes is complicated as due to periodic nitrogen diffusion to the atmosphere as nitrogen gas (Berge et al., 2006).

Besides, transfer of nitrified leachate in the landfill simulation columns may also affect the heterotrophic denitrification. As shown in **Table 2.3.1**, the nitrate concentrations from top of the columns to the bottom decreased significantly. Meanwhile, leaching TOC also decreased from SD-T, SD-M to SD-B, similar to nitrate, which might be an indicator for heterotrophic denitrification. The low-speed nitrified leachate transfer observed in the two columns may have caused a longer nitrate retention time in the bottom of the bottom of column relative to that of the top, which may explain the concentration gradient phenomenon in the columns. After considering the balance of hydraulic pattern and biological process, accelerating leachate recirculation rate could help improve the low-speed nitrate transfer observed. Besides, no relevant settlement was observed during the experiments.

Comparison with bioreactors filled with refuse

As shown in **Table 2.3.3**, the denitrification rates of Ra and Rb were 254 mg N/kg TS/d and 249 mg N/kg TS/d, respectively. The denitrification capacities achieved in this study show significantly higher efficiency compared with the bioreactor filled with fresh or old municipal solid waste (Price et al., 2003; Chen et al., 2009; Zhong et al., 2009). Nonetheless, drainage clogging occurred at the late phase of the two columns in this study. The low hydraulic conductivity of the digestate might limit the leachate recirculation (Jokela et al., 2002). Besides, ammonia and TOC leaching loss from solid digestate at the beginning stage should be considered in the real application.

Table 2.3.3 Denitrification capacity of bioreactors filled with waste or digestate

Nitrate (mg-N/L)	Waste type	ANRR mg N/kg TS/d	Reference
400	Composed refuse	140	(Price et al., 2003)
200-2200	Landfill refuse	28.6	(Zhong et al., 2009)
1000	1-year-old refuse	163.2*	(Chen et al., 2009)
	6-year-old refuse	72.0*	
	11-year-old refuse	26.4*	
1438	Solid digestate	256	This study

*the data were calculated by the authors.

2.4 Conclusions

Solid digestate was effective in reducing the nitrate content of nitrified leachate. Meanwhile, the organic matter content of the solid digestate was degraded under anaerobic conditions without producing methane. Approximately 94.7% of the nitrate removal efficiency was achieved after 75 days of operation in Ra, which means that the capacity of nitrate removal was 19.2 mg N-NO_3^-/g TS-digestate. Extending the operation to 132 days in Rb resulted in an average N-NO_3^- removal efficiency and N-NO_3^- removal capacity of 72.5% and 33.1 mg N-NO_3^-/g TS-digestate of nitrate removal, respectively. Adsorption to solid digestate contributed to 16.4% and 12.9 % of nitrate removal in Ra and Rb, respectively. The remaining portion of the nitrate removal in both Ra and Rb could be attributed to the heterotrophic and autotrophic denitrification. Beyond the high nitrate removal, the average specific rates of TN removal were 0.239 g N/day/kg TS-SD (Ra) and 0.256 g N/day/kg TS-SD (Rb). These results suggest that the solid digestate could be applied in external reactors to ex-situ treat nitrified leachate. Besides, solid digestate can be used as functional layer embedded landfill to removal nitrogen in those old landfills with low denitrification capacities. At last, solid digestate with or without further treatment can be utilized as an engineered landfill biocover.

Chapter 3: Digestate application in landfill bioreactors to remove nitrogen of old landfill leachate-Nitrite pathway[3]

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Abstract:

The management of solid digestate from organic fraction of municipal solid waste is essential component of sustainable biogas plants. Beyond land use, this study aims to evaluate the application of digestate in simulated landfill columns to enhance nitrogen conversion of partially nitrified landfill leachate (PNL). Two identical simulated landfill reactors filled with solid digestate were setup and PNL was fed through the columns. The PNL characteristics were 1004 mg N-NO_2^-/L, 428 mg N-NO_3^-/L, and 434 mg N-NH_4^+/L. After 109 days of operation, the average N-$NO_2^-$and N-NO_3^- removal efficiencies were 92.6% and 85.8%, respectively. The high concentrations of nitrite did not significantly inhibit methane production during denitrification in the digestate-added landfill columns as the average specific methane production yield was 20.1 L CH_4/kg VS. These results suggest that the novelty of applying solid digestate in a landfill can achieve denitrification in a carbon limited environment observed in mature landfill leachate and stabilization of the digestate.

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Keywords: Digestate, OFMSW, Mature Landfill Leachate, Partial Nitrification, Denitrification, Bioreactor Landfill, Circular Economy

3.1 Introduction

Solid digestate (SD) from the organic fraction of municipal solid waste (OFMSW) and sewage sludge is an anaerobically decomposed waste produced in biogas plants. In Italy, digestates from the OFMSW needs to be further treated while digestates from agricultural substrates (e.g., manure and energy crops) are exclusively land applied (Saveyn and Eder, 2014). Beyond the land application and a fraction of the liquid or solid digestate recirculated back to anaerobic digesters as inoculum (Peng et al., 2015; Wu et al., 2017), digestate that does not meet regulatory standards or surplus solid digestate could be treated in landfill under the concept of Back to Earth Alternatives (Peng and Pivato, 2017). Peng et al. (2018) applied solid digestate in a landfill bioreactor column and demonstrated that the digestate was a suitable denitrification layer to remove nitrogen from old nitrified landfill leachate.

Old landfill leachate is generally characterized by a high concentration of ammonia nitrogen and recalcitrant organic matter such as humic and fulvic-like compounds (Kulikowska and Klimiuk, 2008; Zhang et al., 2009). Low concentration of biodegradable organic matter generally limits the biological denitrification as there is a shortage of organic carbon source (Zhang et al., 2007). The remaining organic matter in the digestate could provide an additional source of carbon for heterotrophic denitrification in partially nitrified landfill (PNL) leachate rich in nitrite and bio-refractory organics (Wu et al., 2016, Chung et al., 2015).

In a facultative landfill bioreactor with in situ nitrogen removal, where leachate is on-site nitrified and recirculated (DeAbreu, 2003), nitrate can be converted to nitrogen gas through denitrification as several microorganisms can use nitrate as an electron acceptor for respiration (Berge et al., 2005; DeAbreu, 2003; Kristanto et al., 2017; Price et al., 2003). The facultative bioreactor landfills showed a much higher nitrate removal rate than conventional landfills and a bioreactor landfill with raw leachate recirculation (DeAbreu, 2003).

Compared to the traditional process for biological nitrogen removal via nitrate, nitrogen removal via nitrite as a shortcut biological nitrogen removal process could reduce the oxygen consumption by 25% and a reduction in the carbon source by 40% (Hellinga et al., 1998; Wu et al., 2009a). Therefore, recirculating PNL in a digestate-added bioreactor landfill would be a cost-effective way to remove ammonia.

Moreover, in a facultative landfill reactor filled with digestate, it is possible to facilitate the anaerobic ammonium-oxidizing process, known as Anammox, as anammox bacteria has been proven to be present in the digestate from agricultural wastes (Di Domenico et al., 2015). Anammox was considered to have, to a large extent, contributed to the nitrogen removal in bioreactor landfill simulators (Valencia et al., 2011, Wei et al., 2017). Furthermore, Xie et al (2013) identified the microbial community structure and demonstrated that 10% of the total nitrogen removal was attributed to Anammox in an aged refuse bioreactor.

Based on the understanding from the aforementioned studies, the aim of this study was to assess the performance of nitrogen removal in PNL added to landfill bioreactor columns filled by digestate.

3.2 Materials and methods

Raw Leachate and Digestate

Solid digestate was obtained from a full-scale biogas plant (Camposampiero, Padua, Italy). The digester was fed with the OFMSW and sewage sludge. The characteristics of the raw solid digestate samples were: Total Solids (TS)=19.4±0.1%, Volatile Solids (VS)=62.0±0.3%TS, Total Organic Carbon (TOC)=285±1.2 g-C/kg-TS, Total Kjeldahal Nitrogen (TKN)=51.0±0.2 g-N/kg-TS. Raw leachate was collected from a closed municipal solid waste landfill located in Northern Italy. Untreated municipal solid wastes were disposed during the 1980s. The raw leachate was partially nitrified in a laboratory-scale nitrification reactor (**Figure 3.2.1**). The physical-chemical characteristics of raw leachate and PNL are given in **Table 3.2.1**.

Table 3.2.1. Characteristics of raw and partially nitrified leachate

Parameters	Raw leachate	PNL
pH	8.68	6.67
TOC (mg-C/L)	466	565
TC (mg-C/L)	3030	955
BOD_5	21.5	6.11
COD	1998	1526
TKN (mg-N/L)	1723	550
$N\text{-}NH_4^+$ (mg-N/L)	1660	434
$N\text{-}NO_2^-$(mg-N/L)	0.8	1004

N-NO_3^-(mg-N/L)	3.6	428
TON (mg-N/L)	4.4	1432
SO_4^{2-} (mg-N/L)	42	72

Experimental Setup

The partial nitrification of leachate was performed in a 10 L laboratory-scale aeration tank. The schematic of the aeration tank is shown in **Figure 3.2.1**. Intermittent aeration, ran for 30 seconds and stopped for 15 seconds, was applied to the aeration tank. The dissolved oxygen (DO) in the reactor was maintained in the range of 0.3-0.5 mg O_2/L (Chen et al., 2016). Alkalinity was not added during the partial nitrification process. The temperature was kept at room temperature 25±2 °C by an air conditioner. All the PNL generated was collected and stored in the PNL collection tank (**Figure 3.2.1**) for future use in the simulated landfill reactor columns.

The simulated landfill reactors were operated using two identical columns (Rc and Rd) as shown in **Figure 3.2.1**. The height of the two polymethyl methacrylate columns was100 cm while their inner diameter was 10 cm. A 10 cm thick gravel layer was set at the bottom and at the top of each column to promote adequate leachate drainage. Three kg of raw solid digestate was added to each column, resulting in an average density of 764 kg/m^3. Periodically, well mixed PNL was fed through the two columns using a peristaltic pump. At the same time, effluent collected from the bottom of the columns was sampled and stored at 4 °C. The loading rate in terms of oxidized nitrogen (i.e., nitrite and nitrate) was 0.79 g total oxidized nitrogen (TON)/ (kg-VS digestate·day) up until 31 days of operation. The first period (0-31 days) can be considered as a high loading rate stage. The TON loading rate was set according to Peng et al. (2018) and based on preliminary experiments. After the nitrogen reduction through denitrification, the total nitrogen (TN) loading rate was adjusted to 0.23 g TON/ (kg-VS digestate·day) since day 31 to day 109 to achieve a high nitrogen removal percentage. The second period (32-109 days) was considered a low loading rate stage. The two simulated landfill reactor columns, Rc and Rd, were operated until 109 days.

Nitrogen removal efficiency and average nitrogen removal rate (ANRR, mg N/kg TS/d) were calculated by equation (1) and equation (2), respectively, which were used to evaluate the denitrification performance of the simulated landfill reactor columns:

$$\text{Nitrogen removal efficiency} = \frac{\sum_1^n (C_{inf,i}V_{inf,i} - C_{eff,i}V_{eff,i})}{\sum_1^n (C_{inf,i}V_{inf,i})} \times 100\% \qquad (1)$$

$$\text{ANRR} = \frac{\sum_{i=1}^n (C_{inf,i}V_{inf,i} - C_{eff,i}V_{eff,i})}{M \cdot t} \qquad (2)$$

where:

- $C_{inf,i}$ and $C_{eff,i}$ = influent and effluent concentrations of nitrogen species, TN, TON, $N\text{-}NO_3^-$ or $N\text{-}NO_2^-$, in the landfill columns at feeding cycle i;
- $V_{inf,\,i}$ and $V_{eff,\,i}$ = influent and effluent volumes at i feeding cycle;
- n = total feeding cycles; n equal to 25 for Rc and Rd;
- M=total solid (TS) of total digestate, kg;
- t=operation time, days.

Physical and Chemical Analysis

The test parameters for gas samples included gas composition and volume. Gas compositions (CO_2, CH_4 and N_2) were analyzed by a micro-gas chromatograph (Varian 490-GC) equipped with a 10 m MS5A column, 10 m PPU column, and a thermal conductivity detector. The carrier gas was argon. Volume of the produced biogas was determined using the water displacement method. Leachate samples were characterized for pH, Total Carbon (TC), TOC, TKN, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, $N\text{-}NH_4^+$, SO_4^{2-}, Chemical Oxygen Demand (COD), and five-day Biochemical Oxygen Demand (BOD_5) according to the CNR-IRSA Italian standard methods (CNR-IRSA, 2003). pH was determined by a pH meter (Titromatic, Crison). TC and TOC was measured by a TOC analyzer (Shimadzu TOC-V CSN) according to the standard Italian method IRSA-CNR

29/2003 vol. 2 n. 504. TKN was determined by a distillation titration (VELP® Scientifica UDK 127 Distillation Unit and HACH® Crison TitroMatic 2S) procedure after acid digestion. N-NO_3^-, N-NO_2^-, N-NH_4^+ and SO_4^{2-} were measured by a UV-Vis spectrophotometer (Shimadzu UV-1601). COD was measured according to the standard Italian method IRSA-CNR 29/2003 vol. 2 n.5130 (digestion with $K_2Cr_2O_7$ in an acid solution). BOD_5 was determined according to the standard Italian method IRSA-CNR 29/2003 vol. 2 n. 5120 B2. The 5-day dissolved oxygen concentration was measured with a dissolved oxygen probe.

Solid digestate samples were taken for characterization prior to filling the reactors and after treatment with PNL addition. TS, VS, TKN, TOC, Biochemical Methane Potential (BMP) and respiration index (RI_4 and RI_7) were measured for all samples. TS and VS were determined on approximately 30 g samples according to the standard Italian gravimetric method IRSA-CNR Q 64/84 vol.2 n.2. TKN was measured by the Kjeldahl method. Prior to analyzing the TOC content using a TOC analyzer (Shimadzu TOC-V CSN), the solid samples were dried in a 105°C oven for 24 hours.

The equipment and procedure used to run the BMP tests as described in Girotto et al. (2017) with granular sludge as the inoculum. Blank BMP tests were conducted using only inoculum were carried out to quantify the methane produced by the granular sludge. The RI_4 and RI_7 were measured by a Sapromat apparatus (H+P Labortechnik, Germany).

Leaching tests were conducted conforming to the standard EN-12457-2 (BSI, 2002) and the eluates were analyzed for the following parameters, pH, TC, TOC, N-NO_3^-, N-NO_2^-, N-NH_4^+, SO_4^{2-}, COD and BOD_5 which were determined following the same methods for liquid samples.

3.3 Results and discussion

Effluent Characteristics Variation in the Columns

$N\text{-}NO_2^{-}$ and $N\text{-}NO_3^{-}$ Concentrations

Figure 3.3.1 illustrates the evolution of influent $N\text{-}NO_2^{-}$, $N\text{-}NO_3^{-}$, TON and TN and the corresponding characteristics of the effluent. The loading rate was 0.79 g TON/ (kg-VS digestate·day) for 31 days after which the loading rate decreased to 0.23 g TON/ (kg-VS digestate·day). After the start-up phase (0-4 days), 15-30% of TON remained in the effluents while TON content of the effluent was kept low in the following days of the first phase (0-31 days). The average TON removal efficiency of Rc and Rd was 95.2 ± 0.01 % during the first phase (0-31 days) while it decreased to 79.9 ± 0.09 % during the second phase (32-109 days). The TON removal efficiency decrease in the second phase can be attributed to the reduction in the biodegradable organic carbon with operation time since heterotrophic denitrification depends on the availability of biodegradable carbon.

In this study, the TN removal depended on both nitrogen reduction from $N\text{-}NO_2^{-}$ or $N\text{-}NO_3^{-}$denitrification and nitrogen augment from ammonia release. TN removal efficiencies during the first phase were around 22% while they gradually increased to 50% with the decrease of ammonia released from the digestate. At the second phase (32-109 days), 49%-63% of TN removal efficiencies were achieved when considering the ammonia release.

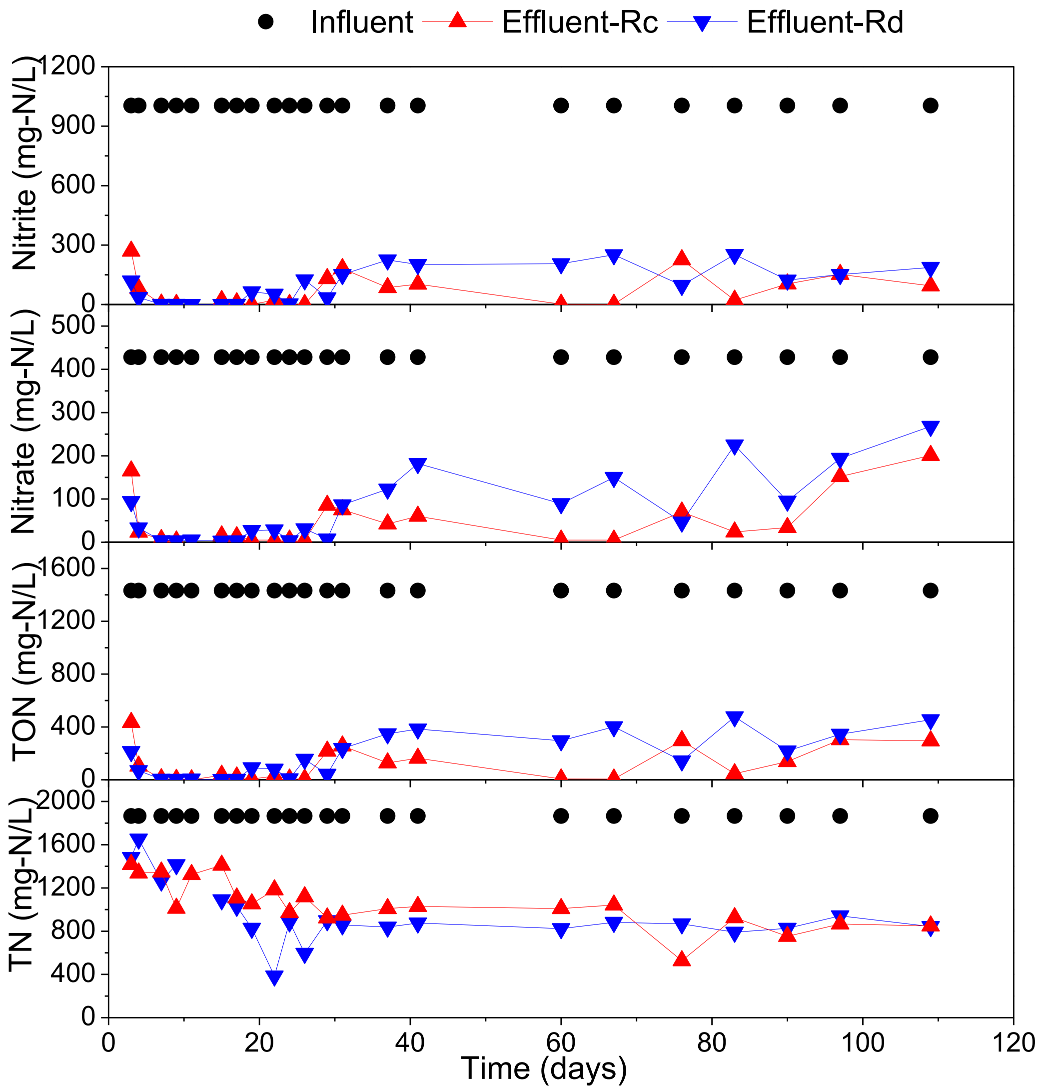

Figure 3.3.1. Dynamics of N-NO_2^- (a), N-NO_3^-(b), TON (c) and TN(d) influent and effluent concentrations in simulated landfill bioreactor columns

N-NH_4^+ and TKN Concentrations

During this study the average N-NH_4^+/TKN ratio of the effluent leachate varied between 90.0% and 91.7% during the first and second phases, respectively (**Figure 3.3.2**). The amount of ammonia in the effluent was relatively high at the beginning because of leaching and degradation of the digestate. However, the decrease of ammonia with time was due to two mechanisms (1) the decrease in the solubility of ammonia and release from digestate and (2) the possibility of nitrite removal via ammonia oxidation cannot be excluded especially when the BOD_5 in the effluents dropped below 1 mg-O_2/L (Valencia et al., 2011, Xie et al., 2013).

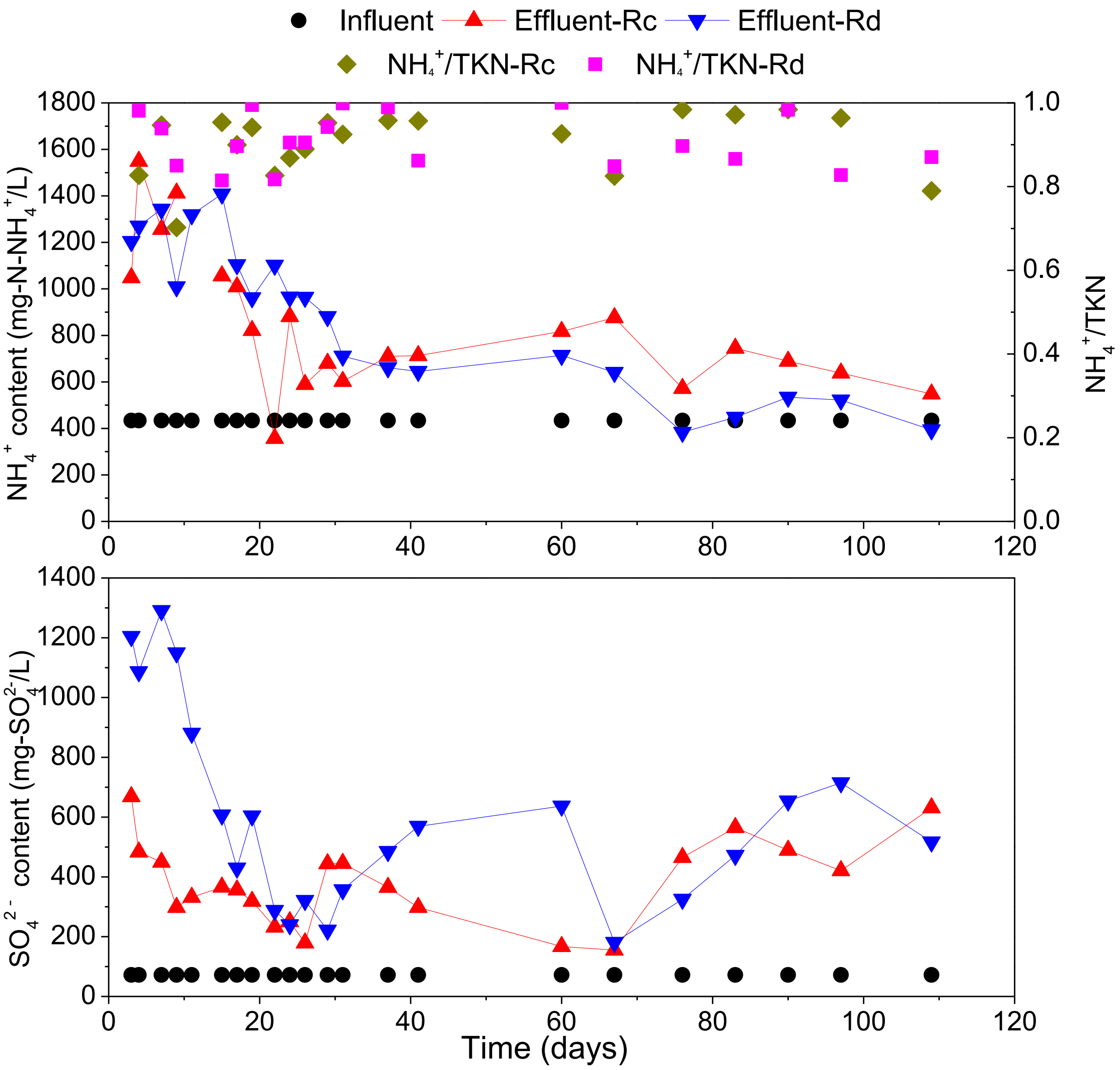

Figure 3.3.2. Dynamics of N-NH_4^+, N-NH_4^+/TKN and sulfate influent and effluent concentrations in simulated landfill bioreactor columns

Sulfate

Figure 3.3.2 illustrates the sulfate concentrations of the denitrified effluents during operation in the two columns (Rc and Rd). In the first phase, the average sulfate concentrations for Rc and Rd decreased from 936±268 mg SO_4^{2-} /L to 401±44 mg SO_4^{2-} /L, which could presumably be due to the sulfate leaching from the solid digestate as the eluate contain 1117 mg SO_4^{2-} /L (**Table 3.3.1**). Sulfate in the effluents of columns Rc and Rd increased gradually after 24 days, suggesting the possible occurrence sulfur-based autotrophic denitrification (Berge et al., 2006; Sahinkaya et al., 2011).

Table 3.3.1. Quality parameters of the digestate samples at the beginning and the end of the test period: characterization of solid samples and the eluate from a standard leaching test

		Initial	End of the test	
			Rc	Rd
Solid phase	TS (%)	19.4±0.1	17.2±0.1	17.8±0.1
	VS (%TS)	62.0±0.3	60.0±0.5	59.5±0.1
	RI_4 (mg O_2/g-TS)	13.8±0.40	14.2±0.59	11.6±0.04
	RI_7 (mg O_2/g-TS)	22.4±0.98	22.5±0.53	18.6±0.07
	TKN (g N/kg-TS)	51.0±0.2	41.8±0.5	38.8±0.7
	TOC (g C/kg-TS)	285±1.2	279±3.6	281±2.5
	BMP (L/kg-VS)	27.0±0.3	6.8±0.5	9.0±0.2
Eluate from leaching test	pH	8.73	8.68	8.49
	TOC (mg C/L)	725	392	394
	COD (mg O_2/L)	964	978	768
	BOD (mg O_2/L)	452	305	222
	$N\text{-}NH_4^+$ (mg N/L)	801	610	512
	$N\text{-}NO_2^-$ (mg N/L)	≤0.2	≤0.2	≤0.2
	SO_4^{2-} (mg/L)	1117	250	273

TOC, TC, COD and BOD_5/COD

The measured TOC was high at start up, as observed in **Figure 3.3.3**, which could be due to a high rate of TOC leaching from the digestate. The measured TOC decreased until day 40 due to the reduction of its release. After day 40, a reduction in the fluctuation of TOC was observed as the balance between TOC production and consumption was achieved.

The variations of COD concentrations were similar to those of TOC, which showed a slight decrease at the beginning and then a reduction in fluctuation. However, the COD at the end increased slightly which could be attributed to the transfer of the refractory organic matter from the solid phase (digestate) to the liquid phase (leachate).

The BOD_5/COD during the first phase increased at the beginning then gradually decreased close to zero. The augment of BOD_5/COD can be due to both leaching of soluble organic matter and partial hydrolysis of the digestate while the observed decline of BOD_5/COD resulted from the consumption of carbon from both denitrification and biogas production.

As illustrated in **Figure 3.3.3**, TOC in the effluent from the simulated landfill reactors columns did not show an obvious decrease during the biogas production (Valencia et al., 2011), which can be attributed to the additional TOC added to the system from the PNL. The TOC of the effluent from the simulated landfill reactor was lower than that of the influent and remained stable, which may suggest that the effluent TOC was recalcitrant (Berge et al., 2006). The lower biodegradability of the denitrified effluents was also supported by the low BOD_5/COD that ranged from 0 to 0.146 (**Figure 3.3.3**) and falls within the typical BOD_5/COD ratio (0.02 and 0.13) that is generally accepted as low biodegradable (Ağdağ and Sponza, 2005). Inorganic carbon was continuously produced in the effluent, which suggests the occurrence of heterotrophic denitrification (Nascimento et al., 1997).

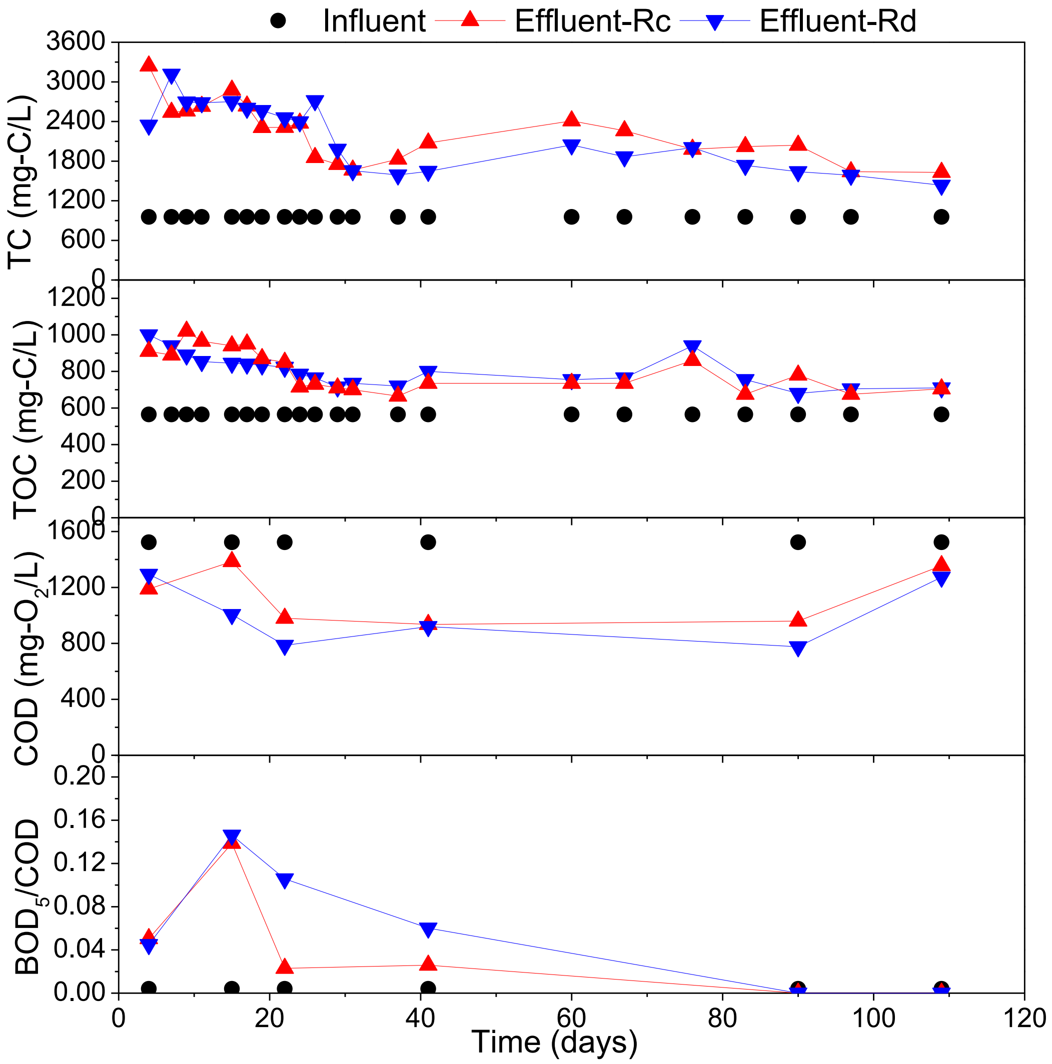

Figure 3.3.3. Dynamics of TC, TOC and COD and BOD_5/COD influent and effluent concentrations in simulated landfill bioreactor columns

Biogas Production

Both columns produced biogas before starting the addition of PNL. After the addition of PNL, the average concentrations of CH_4 and CO_2 in the biogas was 36.6% and 8.69 %, respectively. The methane percentage in the biogas accounts for a specific methane production yield of 20.1 NL CH_4/kg VS. The continuous methane production suggests that anaerobic digestion of the digestate occurred in the columns, which further indicated that intermediate chemicals (such as volatile fatty acids and hydrogen) of anaerobic digestion which can work as electron donors for the denitrification of

$N\text{-}NO_2^-$ and $N\text{-}NO_3^-$(Chung et al., 2015).

$N\text{-}NO_2^-$ and $N\text{-}NO_3^-$ can inhibit methanogenesis by recirculating nitrified leachate (Chung et al., 2015, Jokela et al., 2002, Zhong et al., 2009, Sun et al., 2017). A TON loading greater than 0.0114 g N/ (kg TS·d) could result in the decrease of CH_4 in a landfill column filled with municipal solid waste (Sun et al., 2017). In the present study, 0.492 and 0.141 g N/ (kg TS·day) of TON loading did not show significant delay in methane production.

Carbon and Nitrogen Mass Balance

Carbon and nitrogen mass balances were conducted at the beginning and at the end of the operation of the simulated landfill reactors columns (**Table 3.3.2 and Figure 3.3.4**). The TC in the column was calculated by taking the sum of TC in initial solid digestate, PNL, and biogas emissions. The TC in the liquid output for Rc and Rd were 9.7% and 11.0% of the total carbon content (solid digestate and accumulative input from PNL), respectively, which is comparable to previous research (Peng et al., 2018). Methane production yields were 19.8 NL/kg VS (Rc) and 20.4 NL/kg VS (Rd), respectively. The unaccounted carbon in Rc and Rd was approximately 13.9 g C/kg TS (4.7% of total carbon in column) and -1.3 g C/kg TS (-0.5% of total carbon in column), respectively.

TN emissions were consisted of TKN and TON in the effluent. Approximately 1.5 % and 0.2% of the TN in Rc and Rd, respectively, was unaccounted in the mass balance calculations (**Table 3.3.2** and **Figure 3.3.4)**. TON removal efficiencies of 88.5% and 71.3% were achieved in Rc and Rd, respectively, while nitrogen emission from the denitrified effluents for Rc and Rd were as high as 12.5 g N/kg TS and 15.8 g N/kg TS, respectively (**Table 3.3.2**). These results can be due to a significant ammonia or TKN leaching from the solid digestate which was observed to be significant in the initial phase (**Figure 3.3.2**). The TN removals were 22.5 g N/kg TS-SD (Rc) and 24.4 g N/kg TS-SD (Rd), which accounted for 29.1% (Rc) and 31.6 % (Rd) of TN input, as shown in **Table 3.3.2**. Considering the operation time, the average specific rates of TN removal were 0.111 g N/day/kg TS-SD (0.179 g N/day/kg VS-SD). Compared to the TN concentration in the influent, the TN concentration in the effluent was reduced with a clear N_2 gas production (**Figure 3.3.1** and **Figure 3.3.5**), which suggests denitrification occurred. Additionally, the contribution of digestate adsorption on TN removal could be negligible since N-NO_2^- and N-NO_3^- concentrations of the leaching eluate of the final digestates were less than 0.2 and 5.0, respectively (**Table 3.3.1**).

Table 3.3.2 Mass balance of the simulated landfill reactors columns

	Rc		Rd	
Carbon	g C/kg-TS	%	g C/kg -TS	%
$C_{initial.s}$ (Initial carbon in solid digestate)	285.0	95.2	285.0	95.2
$C_{input.l}$ (Carbon input from leachate)	14.3	4.8	14.3	4.8
$C_{final.s}$ (Final carbon in solid digestate)	247.4	82.7	257.8	86.2
$C_{output.l}$ (Carbon output from leachate)	29.0	9.7	33.0	11.0
$C_{output.g}$ (Carbon output from CO_2 and CH_4 emission)	8.9	3.0	9.8	3.3
$C_{unaccounted}$ (Unaccounted)	13.9	4.7	-1.3	-0.5
Nitrogen	g N/kg-TS	%	g N/kg-TS	%
$N_{initial.s}$ (Initial nitrogen in solid digestate)	51.0	66.0	51.0	66.0
$N_{input.l}$ (Nitrogen input from leachate)	26.3	34.0	26.3	34.0
$N_{final.s}$ (Final nitrogen in solid digestate)	41.8	54.1	38.8	50.2
$N_{output.l}$ (Nitrogen output from leachate)	12.5	16.2	15.8	20.4

$N_{output.g}$ (Nitrogen output from N_2 emission)	21.8	28.2	22.5	29.1
$N_{unaccounted}$ (Unaccounted)	1.12	1.5	0.17	0.2

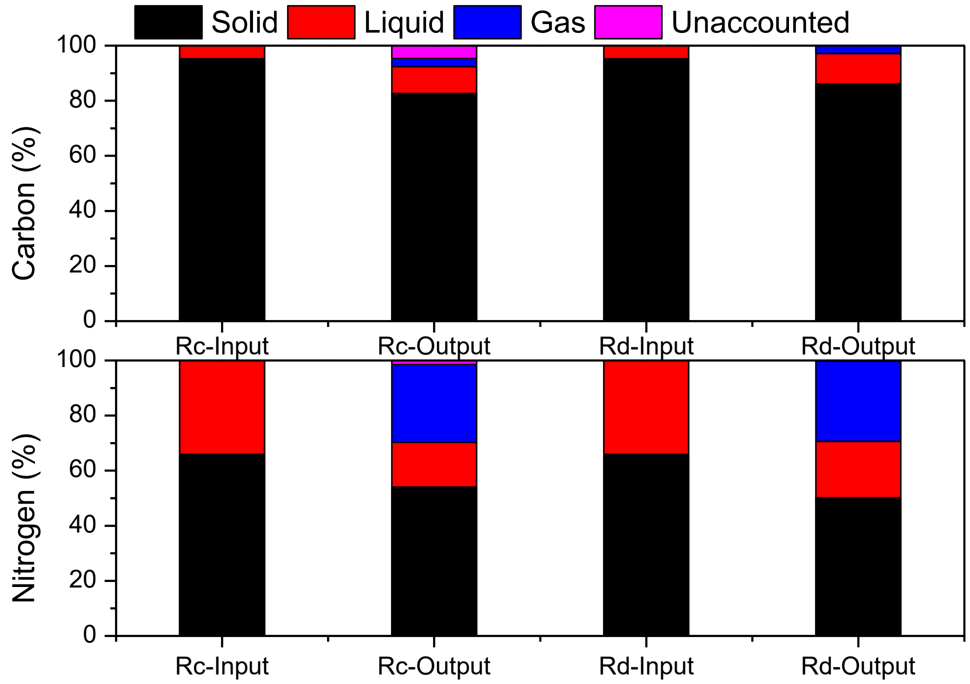

Figure 3.3.4. Carbon and nitrogen distribution in Rc and Rd

Biodegradability of Digestate

To evaluate the biodegradability of the digestate, the respiration index and BMP of the digestate were analyzed before and after the PNL addition. The losses of TOC in Rc and Rd were almost negligible (**Table 3.3.1**). Meanwhile, the aerobic degradability of treated digestate in Rc and Rd did not change significantly given the RI$_4$ of the initial solid digestate was 13.8±0.4 mg O_2/g-TS, which is comparable with the RI$_4$ (14.2 mg O_2/g-TS (Rc) and 11.6 mg O_2/g-TS (Rd)) at the completion of this study (**Table 3.3.1**). The slight difference in the aerobic degradability between the raw and the treated digestate could be due to the contribution of the carbon adsorbed on the digestate given the COD and TOC were equal to 1526 mg O_2/L and 565 mg C/L, respectively, as shown in **Table 3.3.1**. The leaching of the PNL through the solid digestate could have favored the organic matter adsorption and therefore the RI_4 of the digestate did not decrease significantly. On the other hand, the BMP decrease (**Table 3.3.1**) was supported by the biogas production shown in **Figure 3.3.5**. No decrease in RI but a decrease in BMP might suggest that there was a removal of anaerobically degradable components but not the aerobic components.

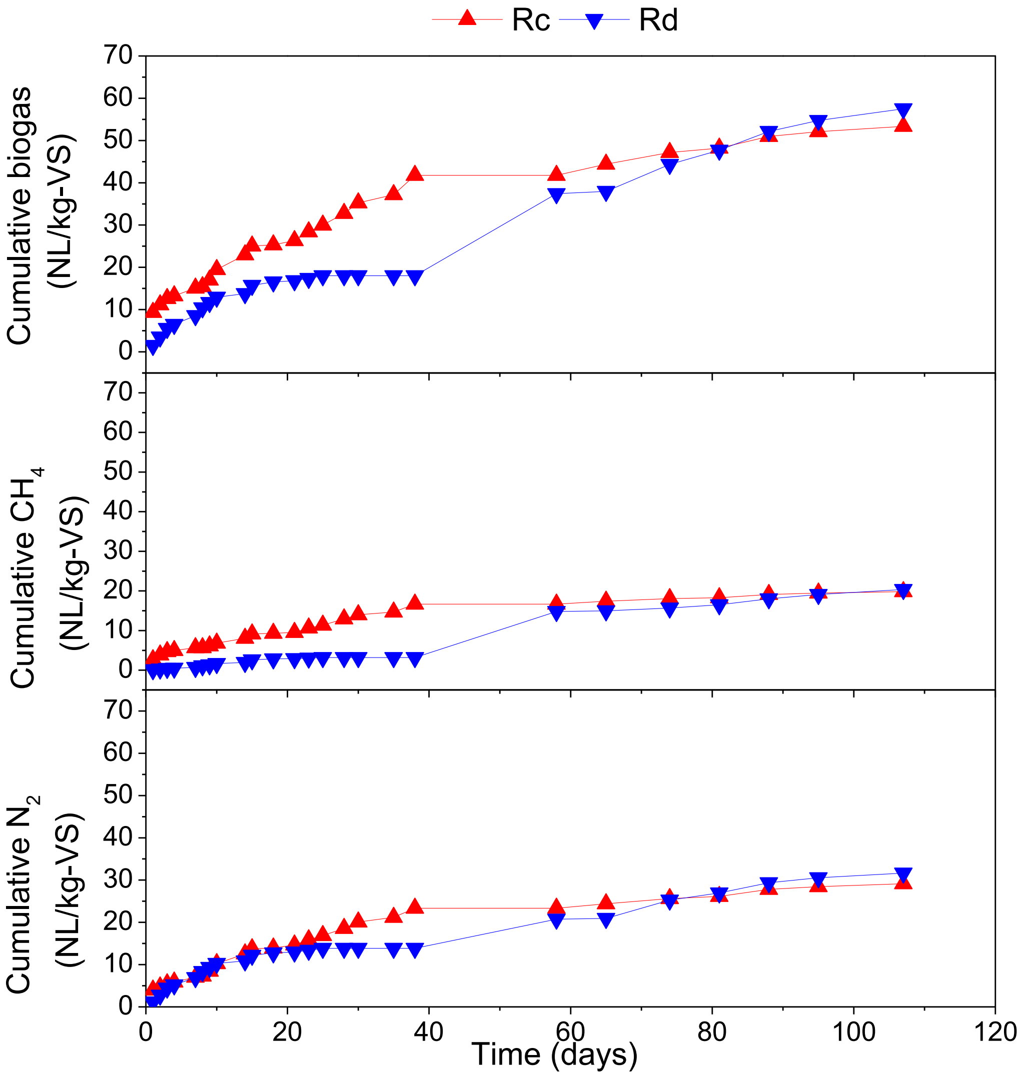

Figure 3.3.5. Dynamics of biogas, CH_4 and N_2 production in simulated landfill bioreactor columns

Denitrification Capacity of the Solid Digestate

The denitrification rates of Rc and Rd were 204 mg N/kg TS/d and 194g mg N/kg TS/d, respectively. The N-NO_2^- removal rates for Rc and Rd were 145 mg N/kg TS/d, 139 mg N/kg TS/d, respectively. The N-NO_3^- removal rates for Rc and Rd were only 59 mg N/kg TS/d and 55 mg N/kg TS/d, respectively. The relatively low N-NO_3^- removal rate could be attributed to the low N-NO_3^-concentration (428 mg-N/L) of the PNL additions. We et al. (2009b) and Cerminara et al. (2017) demonstrated that increasing the initial N-NO_3^- concentrations, from 80-850 mg-N/L to 700-3000 mg-N/L, resulted in a higher N-NO_3^- removal rate. Furthermore, competition for substrate electrons between N-NO_3^- and N-NO_2^- might also explain the low N-NO_3^- removal rates (Glass and Silverstein, 1998). As shown in **Table 3.3.3**, the average denitrification capacity of 199 mg N/kg TS/d achieved in this study shows a significantly higher efficiency compared with a bioreactor filled with either fresh or old municipal solid waste (Chen et al., 2009; He et al., 2006; Price et al., 2003; Zhong et al., 2009). However, the denitrification capacity in this study (199 mg N/kg TS/d) was lower than 256 mg N/kg TS/d achieved in a study by Peng et al., 2018 in which completely nitrified leachate was added. This difference can be attributed to the fact that N-NO_3^- is a preferred electron acceptor relative to N-NO_2^- when biodegradable organic matter is limited (Glass and Silverstein, 1998)

Table 3.3.3. Denitrification capacity of bioreactors filled with waste or digestate

	TON concentration (mg-N/L)	TON composition	Waste type	ANRR (mg N/kg TS/d)
(Price et al., 2003)	400	100%NO_3^-	Composed refuse	140
(He et al., 2006)	1335	58% NO_3^-+42% NO_2^-	Fresh waste +composed refuse	92*
	1504	97% NO_3^-+3% NO_2^-		
	1329	81% NO_3^-+19% NO_2^-		
Zhong et al (2009)	2000-2200	NO_3^-+ NO_2^-**	Landfill refuse	28.6
(Chen et al., 2009)	1000	100% NO_3^-	1-year-old refuse	163.2*
			6-year-old refuse	72.0*
			11-year-old refuse	26.4*
(Cerminara et al., 2017)	763	100% NO_3^-	Old landfill refuse	101
	3188			162
(Peng et al., 2018)	1438	99.9% NO_3^-	Solid digestate	256
In this study	1432	70.4% NO_2^-+29.6% NO_3^-	Solid digestate	199

*the data were calculated by the authors.

** The TON composition is not described in the cited paper.

3.4 Conclusion

$N\text{-}NO_2^{-}$ can be effectively removed in a solid digestate simulated landfill reactors columns with the recirculation of PNL. The average TON removal efficiency was 95.2±0.01% during the first 31 days of operation while it decreased to 79.9±0.09% until 109 days of operation. Meanwhile, the significant fraction of the solid digestate organic carbon was consumed under anoxic conditions with methane production. These results suggest that PNL from an old landfill could be cost-effectively denitrified in external reactors fed with digestate. Results also demonstrate that solid digestate can act as a functional denitrification layer that could be embedded into an old landfill to remove the nitrogen from old leachate. One drawback observed with this approach was the leaching of ammonia from the solid digestate. Although this increase in ammonia occurred, further studies would need to identify the possibility to simultaneously treated $N\text{-}NO_2^{-}$ from the PNL through the Anammox process.

Chapter 4: Digestate application in aged refuse bioreactors[4]

Stabilization of solid digestate and nitrogen removal from mature landfill leachate: a combined approach in aged refuse landfill simulation bioreactors

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Abstract

Digestate from biogas plants of municipal solid waste need to be well treated. Aim of this study was to use a digestate layer in aged refuse bioreactors to enhance the denitrification capacity of aged refuse, stabilize digestate and mitigate the ammonia emission from digestate leaching with leachate recirculation. Six identical landfill columns filled with 0% (R0), 5% (R5), and 15% (R15) of solid digestate above aged refuse, were set and nitrified leachate was periodically fed and recirculated. Nitrate removal rate in R5 and R15 were 3.4 and 10.0 times higher than that of control (no digestate added). Solid digestate biostability was confirmed by tests performed under both aerobic and anaerobic conditions. The results showed that instead of land use, solid fraction of digestate could be exploited as an inexpensive functional layer embedded in old landfill site to enhance denitrification capacity and achieve digestate stabilization with little ammonia leaching from digestate.

Keywords: Solid Digestate; Aged Refuse; OFMSW; Landfill Leachate; Nitrogen Removal; Circular economy

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[4] This work has been submitted to the *Journal of Environmental Management*.

4.1 Introduction

The valorization of Organic Fraction of Municipal Solid Waste (OFMSW) can be addressed to the production of renewable energy (biogas) and biofertilizer (digestate), thereby closing the waste-energy-food loop (Sisto et al., 2017; Fuldauer et al., 2018). Digestate obtained from the biogas plants of OFMSW is an unstable material affluent in undigested organic carbon and pollutants (Tampio et al., 2016; Peng and Pivato, 2017). In Italy, digestate from agricultural biomasses (energy crops or animal manures) can be directly applied as biofertilizer while the digestate from OFMSW is classified as organic wastes which need to be aerobically treated (Saveyn and Eder, 2014). However, aerobic post-treatment of digestate should be carefully operated because of the high nitrogen emissions, especially nitrous oxide (Tremier et al., 2013). Furthermore, anaerobically digested OFMSW mechanically separated from unsorted waste needs to be disposed to landfills or incinerators (Bolzonella et al., 2006; Li et al., 2011). Based on the concept of circular economy, those digestates which fail to meet the agricultural requirements, might consider alternative options to completely utilize the digestate (Peng and Pivato, 2017). Digestates from OFMSW might be innovatively applied for nitrogen removal from mature landfill leachate (Peng et al., 2018). Both nitrogen removal from mature landfill leachate and stabilization of municipal solid waste (MSW) can be achieved in facultative landfill bioreactors with recirculating nitrified landfill leachate (Chen et al., 2009; He et al., 2006; Price et al., 2003; Sun et al., 2017; Xie et al., 2013; Zhong et al., 2009). As a result of the absence of easily biodegradable organic carbon in aged refuse, 11-year-old refuse showed significantly lower denitrification capacity compared to 1-year-old refuse (Chen et al., 2009). Even though autotrophic metabolic pathways (e.g. Anammox) might occur in waste landfill bioreactors, its contribution on nitrogen removal was low (Valencia et al., 2011). Thus, biodegradable organic matters, working as electron donors, still play essential roles in nitrate denitrification. Carbon source derived from food waste was successfully applied in mature landfill leachate treatment (Yan et al., 2018). Digestate with undigested food fraction from OFMSW could be used in old landfill sites to enhance the in-situ denitrification capacity for treating oxidized mature landfill leachate. Despite of the high denitrification potential, ammonia leaching from digestate or MSW might be considered as a drawback when digestate is applied in bioreactor landfills (Peng et al., 2018; Lubberding et al., 2012). To solve the problem, aged refuse with adsorption capacity can be used as a biofilter to relieve the ammonia emission (Zhao et al., 2002). Furthermore, soluble ammonia nitrogen in aged refuse bioreactors could be removed through biological nitrification. After leachate recirculation and drainage, the "dry condition" will be created, which restores the high porosity of aged refuse and allow air or oxygen to invade the reactor for nitrification (He et al., 2017).

As limited studies are available on applied digestates in bioreactor landfills, it is necessary to investigate application techniques for landfilling digestate. In this study, digestate stabilization and denitrification of mature landfill leachate were investigated in landfill simulation columns with dual layers consisted of digestate and aged refuse.

4.2 Materials and methods

Mature landfill leachate, aged refuse and solid digestate

Mature landfill leachate was obtained in the landfill site in Northern Italy. The raw leachate underwent a nitrification process in an aerobic reactor. The qualities of raw and aerobically nitrified landfill leachate are summarized in **Table 4.2.1**. The aged refuse was excavated from the same landfill. The aged refuse was regarded as 40-years-old refuse. The aged refuse samples were characterized as Total Solids (TS) = 94.7±0.7 %, Volatile Solids (VS) = 3.5±0.2% TS, Total Kjeldahl Nitrogen (TKN) = 3.3±0.2 g-N/kg-TS and Total Organic Carbon (TOC)= 27.1±11.7 g-C/kg-TS.

The solid fraction of digestate was collected from a biogas plant in Camposampiero (Italy) treating source-segregated OFMSW and sewage sludge. The digestate was centrifuged for solid-liquid separation. The solid digestate were characterized as: TS = 19.4±0.1 %, VS = 62.0±0.3% TS, TKN = 51.0±0.2 g-N/kg-TS and TOC = 285.0±1.2 g-C/kg-TS.

Table 4.2.1. Characteristics of raw mature leachate and nitrified landfill leachate

Parameters	**Raw leachate**		**Nitrified leachate**	
	Mean	Range	Mean	Range
pH	8.87	8.68-9.05	7.86	7.28-8.56
TOC (mg-C/L)	907	478-1336	834	351-1030
TC (mg-C/L)	2570	2110-3030	1221	705-1500
BOD_5 (mg-O_2/L)	60	58-62	20.6	6.5-32.9
COD_{Cr} (mg-O_2/L)	1360	722-1998	1325	444-1590
N-NH_4^+ (mg-N/L)	1250	758-1741	34.5	16.4-38.8
N-NO_2^- (mg-N/L)	1.9	1.6-2.2	16.2	0.9-56.5
N-NO_3^- (mg-N/L)	0	0	1131	517-1332

Experimental setup

The experiment was consisted of a nitrification reactor and six landfill simulation columns. **Figure 4.2.1** described the graphic experiment. The landfill simulation bioreactors were operated through six identical columns with volume 7.85 liters and height 100 cm. The columns were called R0A, R0B, R5A, R5B, R15A and R15B, where *R* indicates reactor, the number indicates the solid digestate percentages (%) based on the TS, *A* or *B* represents the duplicates. Accordingly, solid digestates and aged refuses were filled to each column. The initial nitrate loading rate was set as 0.76 g-N/ (kg-VS day) for each column to ensure the occurrence of a stable denitrification (Peng, et al. 2018). Effluents (denitrified leachate) obtained from the bottom of each column were weekly characterized and then discharged. Nitrified leachates were weekly replenished to each column. Effluents from the landfill columns were drained from the bottom and recirculated to the top of the landfill simulation columns twice a day. The experiment lasted 100 days after 14 feeding cycles (14 weeks).

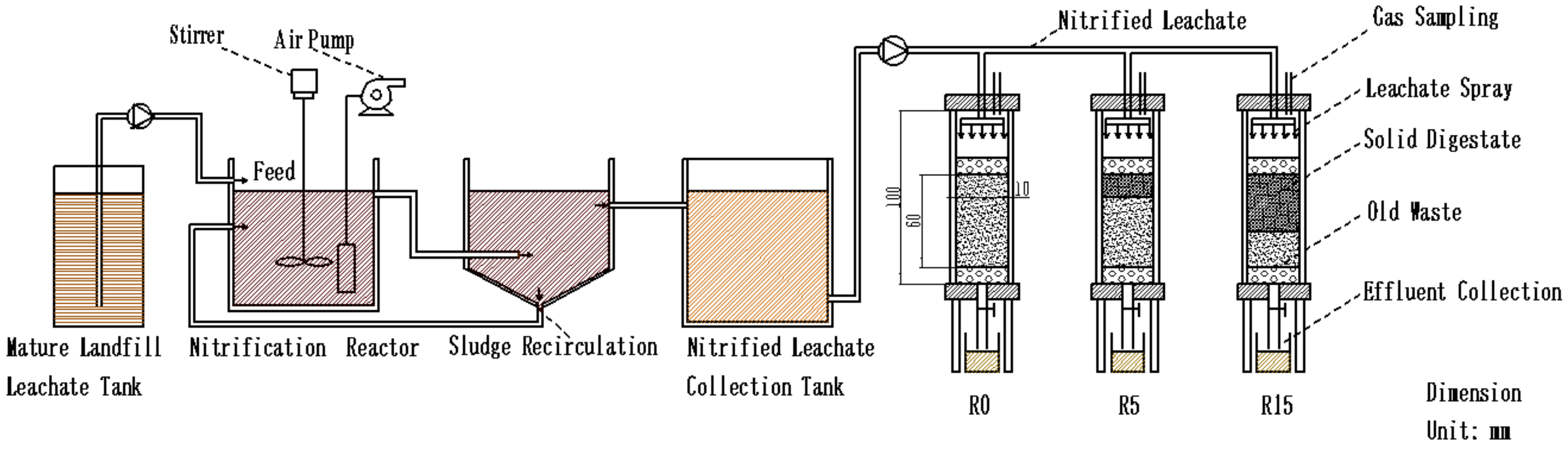


Figure 4.2.1 Schematic diagram of experimental design

The N-NO_3^- removal efficiencies (%), N-NO_3^- removal capacity (g-N/g-TS-solid digestate) and average nitrogen removal rate (ANRR, mg N/kg-TS/d) were calculated using the following equation.

$$\mathrm{N-NO_3^-}\ \text{removal efficiency} = \frac{\sum_1^n (C_{inf,i} \cdot V_{inf,i} - C_{eff,i} \cdot V_{eff,i})}{\sum_1^n C_{inf,i} \cdot V_{inf,i}} \times 100\% \quad (1)$$

$$\mathrm{N-NO_3^-}\ \text{removal capacity} = \frac{\sum_1^n (C_{inf,i} \cdot V_{inf,i} - C_{eff,i} \cdot V_{eff,i})}{M} \quad (2)$$

$$\mathrm{ANRR} = \frac{\sum_1^n (C_{inf,i} \cdot V_{inf,i} - C_{eff,i} \cdot V_{eff,i})}{M \cdot t} \quad (3)$$

where:

$C_{inf,I}$, $C_{eff,i}$=influent and effluent concentrations of nitrate in the landfill columns at feed cycle i;

$V_{inf,i}$, $V_{eff,i}$=influent and effluent volumes of nitrate in the landfill columns at feed cycle i;

n=total feeding cycles; n equal to 14 in this study;

M=the dry mass of solid digestate in the simulated landfill columns, kg;

t= the operation time, days.

Adsorption test

Adsorption of ammonium ions onto the aged refuse were studied using batch tests (OECD, 2000). The aged refuses samples are air-dried at ambient temperature (20-25 °C) before being used. Batch experiments were carried out using 10 g aged refuse sample and 250 cm^3 ammonium solution (100 mg-NH_4^+/L in 0.01 M $CaCl_2$) added to a capped plastic bottle (270ml) and rotated at 20 rpm. The corresponding L/S were 25 ml/g. Triplicate experiments are done at laboratory ambient temperature (20±2 °C). After 3h, 6h, 24h, 72h, 96 h, the ammonium concentration in the supernatant was determined. Two control samples (only the ammonium in 0.01 M $CaCl_2$ solution without aged refuse sample) and two blank samples (with the aged refuse and 0.01 M $CaCl_2$ solution without ammonium) were subjected to the same test procedure.

Adsorption capacity of aged refuse (Q_e, mg-NH_4^+/g-TS) was calculated as following equation:

$$Q_e = [C_i - (C_e - C_{e,blank})] \times \frac{V/1000}{M}$$

C_i=Initial concentrations of ammonium in contact with aged refuse (mg-NH_4^+/L),

C_e=equilibrium concentrations of ammonium in contact with aged refuse (mg-NH_4^+/L),

$C_{e,blank}$=equilibrium concentrations of ammonium in blank (mg-NH_4^+/L),

V= solution volume (ml),

M= dry mass of aged refuse (g-TS).

Analytical method

Liquid samples were determined by the IRSA-CNR methods (IRSA-CNR, 2003). Effluent samples from the landfill simulation columns were periodically analyzed for TOC, Total Carbon (TC), Chemical Oxygen Demand (COD_{Cr}), Biochemical Oxygen Demand (BOD_5), N-NH_4^+, TKN, N-NO_2^- and N-NO_3^-. TOC and TC were determined through a TOC analysis meter (Shimadzu TOC-V CSN). COD_{Cr} was measured by digestion with $K_2Cr_2O_7$ in acid solution (Spectroquant® COD Cell Test and Spectroquant® 320) and determined by a COD analyzer (Spectroquant® NOVA 60). BOD_5 was determined by measuring five days' oxygen consumption by a dissolved oxygen probe. TKN was determined by a distillation (VELP® Scientifica UDK 127 Distillation Unit) and titration (HACH® Crison TitroMatic 2S) procedure after acid digestion. N-NH_4^+, N-NO_2^- and N-NO_3^- were analyzed by a spectrophotometer (Shimadzu UV-1601).

Solid digestate and aged refuse were characterized at the beginning and at the end of experiments. TS, VS, TOC, Respiration Index (RI_4 and RI_7) and TKN were measured. TS and VS were analyzed through Standard Analytical Methods (IRSA-CNR, 2003). TOC of dried solid samples were determined by a TOC analyzer (Shimadzu TOC-V CSN). Respiration Index were determined through the four days’ cumulative oxygen consumption in a Sapromat apparatus (Labortechnik, Germany). The Kjeldahl method was used to determine the TKN. To evaluate the anaerobic biostability of original solid digestate and treated digestate, the biochemical methane potential (BMP) of all solid samples were carried out in 500 ml serum bottles. Granular sludge was used as inoculum and the initial ratio of inoculum and substrate was set as 2.0 on basis of VS. All analyses on the solid-state samples were operated in triplicate.

The standard method, EN-12457-2 (BSI, 2002), was used to guide the leaching test. All eluates were measured for TOC, TC, COD_{Cr}, BOD_5, N-NH_4^+, TKN, N-NO_2^- and N-NO_3^-. All the results of the duplicate columns are reported as the arithmetic means.

4.3 Results and discussion

Nitrogen characteristics of the effluents

N-NO_3^- and N-NO_2^- concentrations

Variations of N-NO_3^- and N-NO_2^- for the reactors are presented in **Figure 4.3.1**. As illustrated, all the columns achieved low nitrate effluent at the first sampling which can be attributed to the adsorption of digestate and aged refuse (Fu et al., 2009; Peng et al., 2018). Nitrate concentrations in samples from columns without digestate addition (R0) fluctuated around the influent throughout the entire duration of the experiment, which suggested that aged refuse has limited denitrification capacity. Zhao et al. (2007) also found that the aged refuse had a weak denitrification ability. Contrarily, nitrate removal efficiency of both R5 and R15 were averagely 43.8% and 59.6% (calculated by eq. (1)) higher than 23.2% of R0, respectively, which suggested the digestate addition enhanced the denitrification capacity of aged refuse in landfill simulation columns. The optimal nitrate removal efficiency was achieved in R15, which suggests that increase of digestate addition can enhance the nitrate removal under the same nitrate loading rate.

The nitrite concentration in the influent drastically dropped after 16 days because of the full nitrification of landfill leachate. Effluents nitrite concentrations in all columns were much lower than those of nitrate because of the low nitrite input. The significant removal of nitrite in all columns were observed at the first 16 days, which could be due to the adsorption and denitrification. However, the nitrite concentrations in effluents were comparable with those of the influent after day 16. Nitrite accumulation in R15 in the day 37 indicated that the over-loading of nitrate could occur as nitrite might increase because the carbon sources was limited (Oh and Silverstein, 1999).

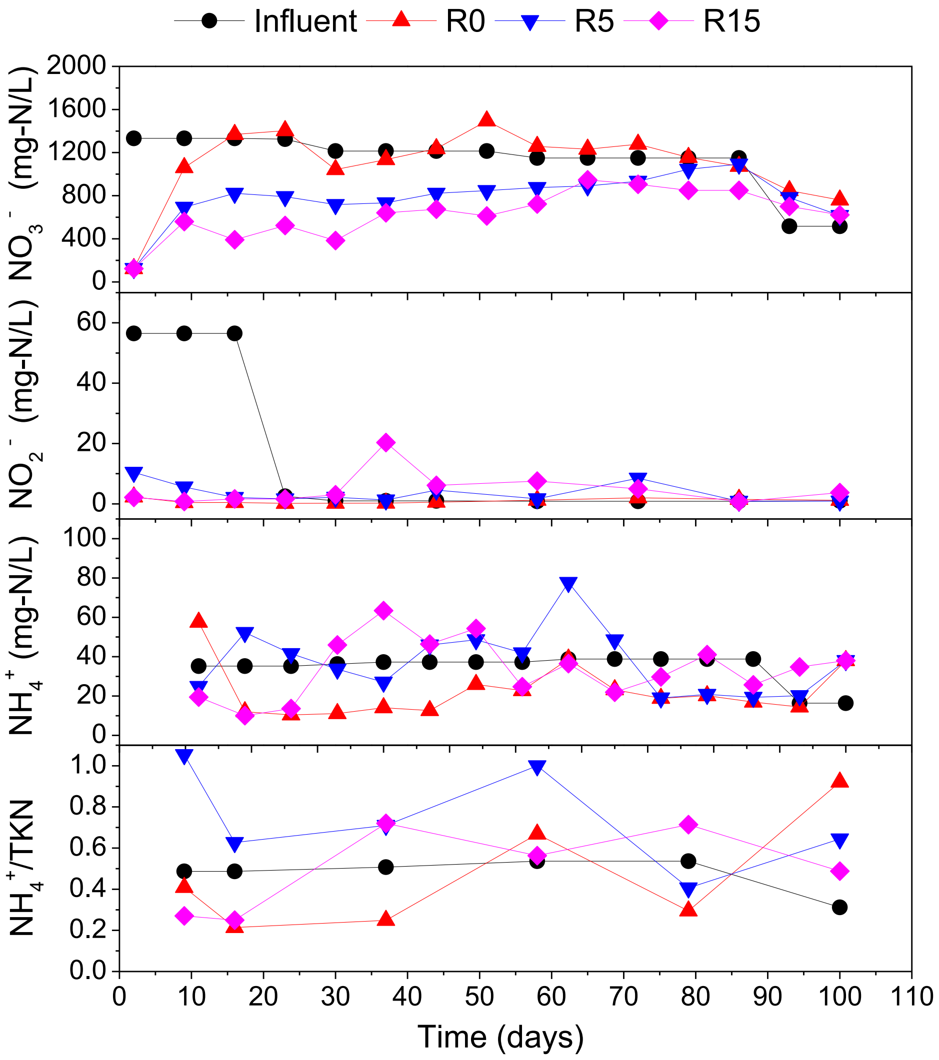


Figure 4.3.1. Dynamics of N-NO_3^- and N-NO_2^- of influent and effluent concentrations in landfill simulation columns

$N\text{-}NH_4^+$ *and TKN*

Ammonia concentrations in the effluents of R0, R5 and R15 fluctuated around 40 mg/L that was similar to the ammonia concentrations of the influent, as shown in **Figure 4.3.1**. In the previous study, the ammonia concentrations in the effluent approximated 2000 mg/L in a simulated landfill bioreactor with sole solid digestate packed (Peng et al., 2018). These results suggested that aged refuse used in this study can abate the ammonia release originated from digestate. Aged refuse has a high ammonia adsorption capacity (Chen et al., 2009; He et al., 2017). As shown in **Figure 4.3.2**, the ammonia adsorption capacity was 0.49±0.02 mg/g lower than the 0.83 mg/g reported by He et al. (2017), which could be explained by the different characteristics of aged refuse. The ammonia adsorption by aged refuse was reversible as the desorption capacity was 0.12±0.06 mg/g. The ammonia adsorption by aged refuse occurs when aged refuse layer in the columns undergoes a “water distribution period” after the feeding with nitrified leachate or recirculating the effluent leachate. After leachate drainage, aged refuse layer will be porous and permeable, which could allow air to enter for ammonia nitrification. The average $N\text{-}NH_4^+$/ TKN ratio for R0 was 0.459, which is comparable with 0.475 of the influents. The average $N\text{-}NH_4^+$/ TKN ratios for R5 and R15 were 0.773 and 0.501, respectively. The high $N\text{-}NH_4^+$/ TKN ratios for R5 and R15 could be contributed to the ammonia release from digestate solubilization.

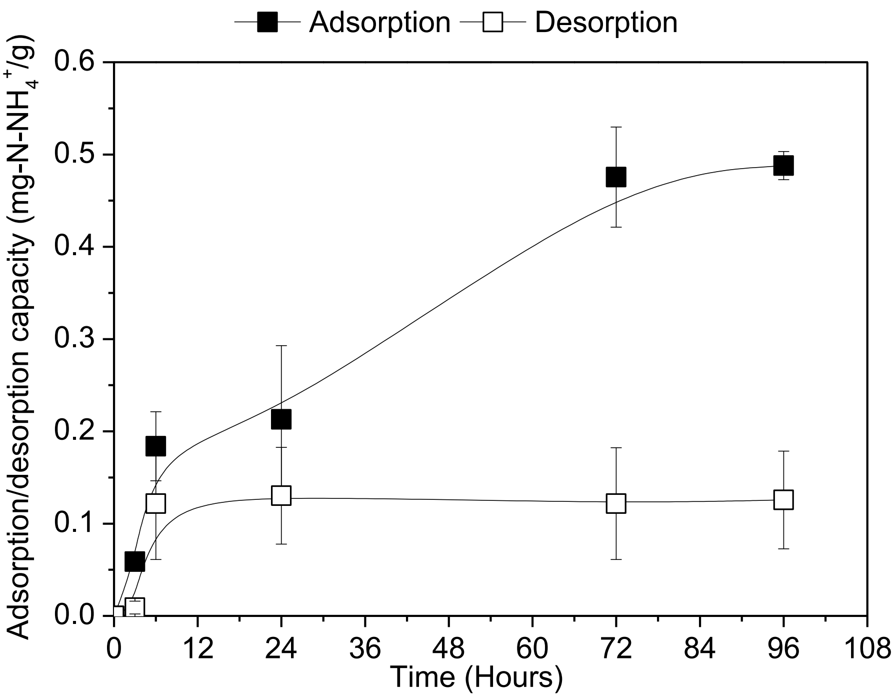


Figure 4.3.2 Ammonium adsorption/desorption kinetics from the aged refuse within 96 hours

Biological Parameters of the effluents

The variations of TOC were similar to those of TC among R0, R5 and R15 (**Figure 4.3.3**). The low level of TOC in the effluents of R0 could be due to the TOC removal capacity of aged refuse (Lei et al., 2007). As aged refuse worked as a filter in the bottom layer, TOC in the effluents of both R5 and R15 were comparatively lower than those of previous study (Peng et al., 2018), which can suggest that the addition of aged refuse layer impeded the TOC emission from the digestate to the effluent. Additionally, it was observed that the original dark brown nitrified leachate became a pale-yellow effluent because of filtration of aged refuse in the bottom layer. The TOC removal by aged refuse reactors with or without digestate resulted from the combined effect of biological removal and physico-chemically adsorption. Because of TOC leaching from digestate and depletion of TOC removal capacity of aged refuse, TOC reduction in all the six columns gradually weakened over time, as shown in **Figure 4.3.3**.

As shown in **Figure 4.3.3**, all the COD_{Cr} in the effluents were lower than those in the influent at the beginning, which could be due to the adsorption of aged refuse. The following COD_{Cr} increase could not be resulted from the emission from solid digestate but originate from aged refuse since the COD_{Cr} of the control (R0) also increased. The effluent BOD_5 in all treatments were lower than 20 mg-O_2/L. The low BOD_5 values, on one side, were due to the low BOD_5 content of the influent. Besides, BOD_5 from leaching of solid digestate were presumably consumed in the aged refuse layers. The average influent BOD_5/COD_{Cr} was 0.016 assumed as low biodegradability (Sekman et al., 2011). Nonetheless, the average BOD_5/COD_{Cr} of the effluent in R0, R5 and R15 were 0.008, 0.005, 0.003, respectively. The lower BOD_5/COD_{Cr} of the effluents suggested that nitrified leachate was slightly degraded in the columns.

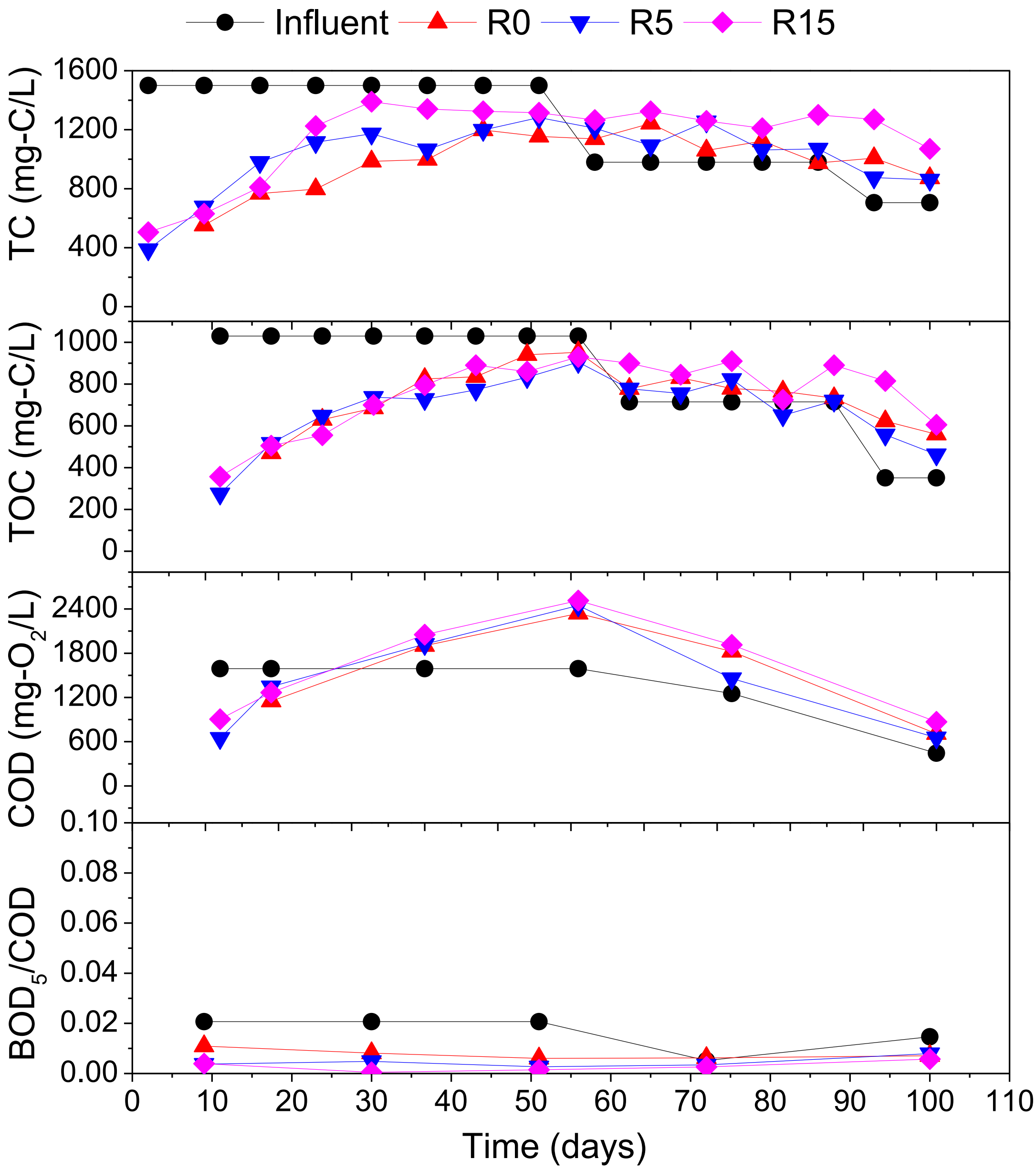


Figure 4.3.3. Changes of TC, TOC, COD_{Cr} and $BOD5/COD_{Cr}$ of influent and effluent concentrations in landfill simulation bioreactors

Carbon and Nitrogen Mass balance

Table 4.3.1 and **Figure 4.3.4** demonstrated the mass balance of carbon and nitrogen. At the first week, biogas production was observed in the R15 (data not shown) while afterwards no significant biogas was generated as the inhibition effect from high nitrate concentrations. Because of the possible diffusion of atmospheric nitrogen gas into gas collecting bags and little amounts of biogas production, nitrogen gas collection for denitrification quantification was difficult in this study (Berge et al., 2006). The low methane emission of solid digestate due to the inhibition of high nitrate concentrations might be a benefit for avoiding greenhouse gas (e.g. CH_4) emission, which is a growing concern of digestate management (Baldé et al., 2016). The mass balances (**Table 4.3.1**) revealed that on average, 50.7% of carbon in R0, 17.6% of carbon in R5 and 4.8% of carbon in R15 were unaccounted. However, the unaccounted or losing TC in the R5 and R15 were mainly due to the TC reduction of solid digestate and influent leachate, as shown in **Table 4.3.1** and **Figure 4.3.4**. The TC reduction were coincident with the degradation of organic matters in solid digestate. On average, 58.5% of nitrogen in R0, 51.6 % of nitrogen in R5 and 50.6 % of nitrogen in R15 were lost, as reported in **Table 4.3.1**. Like the TC in R0, the TN reduction in R0 might be due to the TN loss from aged refuse (**Figure 4.3.4**). Differently, TN reduction of liquid leachate and solid digestate in R5 and R15 contributed to the TN losses by denitrification.

Table 4.3.1 Mass balance distribution in landfill simulation bioreactors

	R0		R5		R15	
Carbon (C)	g C	%	g C	%	g C	%
$C_{input.l}$ (C input from leachate)	8.5	11.7	12.8	10.6	19.5	11.4
$C_{initial.s\text{-}AR}$ (Initial C in aged refuse)	63.9	88.3	51.1	42.3	32	18.7
$C_{initial.s\text{-}SD}$ (Initial C in solid digestate)	0	0	56.8	47.1	119.1	69.8
$C_{output.l}$ (C output from leachate)	5.7	7.8	9.4	7.7	14.7	8.6

$C_{final.s\text{-}AR}$ (Final C in aged refuse)	30.0	41.5	51.3	42.5	38.3	22.4
$C_{final.s\text{-}SD}$ (Final C in solid digestate)	0	0	38.8	32.2	109.4	64.1
$C_{unaccounted}$ (Unaccounted)	36.7	50.7	21.25	17.6	8.2	4.8
Nitrogen (N)						
$N_{input.l}$ (N input from leachate)	8.5	35.3	12.7	35.9	19.5	40.1
$N_{initial.s\text{-}AR}$ (Initial N in aged refuse)	15.6	64.7	12.5	35.3	7.8	16
$N_{initial.s\text{-}SD}$ (Initial N in solid digestate)	0	0	10.2	28.8	21.3	43.8
$N_{output.l}$ (N output from leachate)	6.95	28.85	7.8	22.1	8.7	17.9
$N_{final.s\text{-}AR}$ (Final N in aged refuse)	3.05	12.7	3.6	10.1	2	4.1
$N_{final.s\text{-}SD}$ (Final N in solid digestate)	0	0	5.75	16.2	13.3	27.4
$N_{unaccounted}$ (Unaccounted)	14.1	58.5	18.25	51.6	24.6	50.6

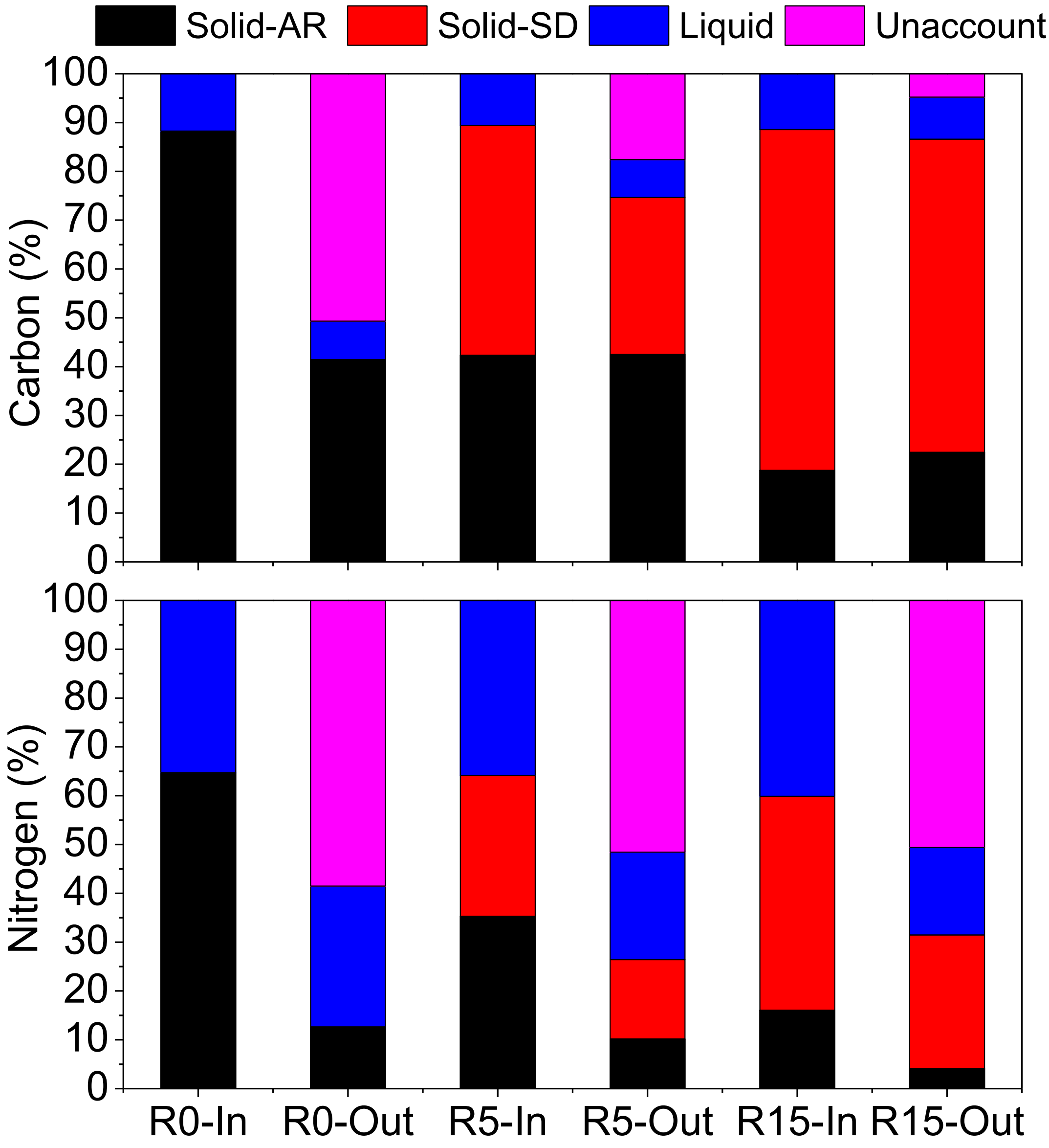


Figure 4.3.4 Carbon and nitrogen partitions in landfill simulation bioreactors

Degradation of solid digestate and aged refuse

The initial and final characteristics of the digestate and aged refuse from the landfill columns are presented in **Table 4.3.2**. Compared to initial solid digestate, VS of solid digestate in the end of R5 and R15 were on average reduced by 13.7% and 9.8%, respectively. Those VS reductions partly can be due to the organic matters transferring from solid digestate to the aged refuse as the VS of the aged refuse in R5 and R15 slightly increased compared to the initial ones. Additionally, the eluate of BOD_5 from the leaching test of treated digestate in R5 and R15 separately decreased 81.8% and 87.1% compared to that of initial digestate. The anaerobically degradation by methanation and anoxic activities of denitrifiers could contribute to the reduction of VS and BOD_5. RI is generally used as a descriptor of the biostability of organic wastes. RI_4 and RI_7 clearly shows the degradation of solid digestate as RI of both solid digestate and aged refuse in R5 and R15 was reduced. Compared to the initial, the final RI_7 of solid digestate in R5 and R15 decreased by 33.9 % and 32.6 %, respectively. Meanwhile, the final RI_7 of aged refuse in R5 and R15 reduced 58.3% and 52.1%, respectively, compared to the initial conditions. As the ratio of BOD_5/COD_{Cr} in all effluent was kept quite low as mentioned before, the reduction of RI was not a result of moving the biodegradable matter of aged refuse to the effluents with leachate recirculation, thus deteriorating the bio-stability of effluent leachate.

Except for the aerobic stability, the anaerobic stability of solid digestate were also achieved as the decrease of BMP. Compared with the BMP of initial solid digestate, 31.5% of BMP reduction in R5 and 35.9 % of BMP reduction in R15 were achieved. These decreased proportions of BMP were comparable with those of RI_7, which suggested both aerobic stability and anaerobic stability of solid digestate were obtained in the aged refuse reactors packed with solid digestate. The partial BMP reduction could result from the biodegradable organic carbon transferring from the digestate to the aged refuse as the slight increase of BMP occurred in aged refuse samples (**Table 4.3.2**).

Table 4.3.2 Characteristics of solid digestate, aged refuse and their eluates from leaching test at the start and the end of the experiment

Solid Digestate				**Aged Refuse**			
		R5	R15		R0	R5	R15
	Start	End	End	Start	End	End	End
Solid samples							
TS (%)	19.4±0.1	22.2	19.9	94.7±0.7	89.9	86.3	82.3
VS (%TS)	62.0±0.3	53.5	55.9	3.5±0.2	2.4	3.4	4.1
RI_4 (mg O_2/g-TS)	13.8±0.4	9.7	10.1	2.4±0.2	2.0	1.6	1.6
RI_7 (mg O_2/g-TS)	22.4±1.0	14.8	15.1	4.8±1.9	3.0	2.0	2.3
TKN (g N/kg-TS)	51.0±0.2	26.4	31.2	3.3±0.2	0.6	1.0	0.9
TOC (g C/kg-TS)	285±1.2	180	258	14±0	6	14	18
BMP(L-CH_4/kg-VS)	27±0.3	18.5	17.3	0.015	2.9	3.9	5.1
Eluates from leaching test							
pH	8.73	8.77	8.41	8.06	8.34	8.29	7.58
TC (mg C/L)	2670	1144	1595	31	114	139	154
TOC (mg C/L)	725	211	359	18	55	50	41
COD_{Cr} (mg O_2/L)	964	432	732	37	112	101	85
BOD_5 (mg O_2/L)	452	82	58.4	<5	<5	<5	< 5
N-NH_4^+ (mg N/L)	801	<30	<30	<30	<30	<30	<30

N-NO_3^- (mg N/L)	<5	11	16	12	10	11	12
N-NO_2^- (mg N/L)	<0.2	0.8	0.5	0.5	0.2	0.2	0.2

Enhancement of denitrification capacity of aged refuse without ammonia emission

Table 4.3.3 represented the average nitrogen removal rate (ANRR) (Calculated by eq. (2)) of different studies. Even though partly degraded aged refuse have a strong denitrification capacity (Chen et al., 2009), the aged refuse in this study, approximately 40 years old, has only 4.2mg N/ (kg-TS day) of capability for denitrification as lack of biodegradable organic matter (**Table 4.3.2**). Nonetheless, the aged refuse excavated from a 40-year old landfill can be used as the biofilter in the column to reduce ammonia concentration (**Figure 4.3.1**) in the effluent and improve the hydraulic condition of leachate recirculation as no clogging problem happened in R0 columns. Based on the TS in the landfill simulation columns, the ANRR of R5 and R15 were 3.4 and 10.0 times higher than that of R0, respectively. After deducting the contribution of aged refuse on the nitrate removal, the ANRR of solid digestate in R5 and R15 were 203 mg-N / (kg-TS day) and 257 mg-N / (kg-TS day), which were comparable with the 256 mg-N / (kg-TS day) achieved in reactors packed with single solid digestate (Peng, et al. 2018).

Despite of the high denitrification capacity, the ammonia leaching from solid digestate as a drawback might impede the application of landfilling digestate. Compared to the ammonium concentrations in the influents, no significant increase of ammonium concentrations in the effluents was observed during the operation (**Figure 4.3.1**). However, ammonium concentrations in the eluate of treated digestates in R5 and R15 were lower than 30 mg-N/L while ammonium concentrations in the eluate of original solid digestate was as high as 801 mg-N/L. Unlike the high ammonia leaching in sole digestate columns (Peng, et al. 2018), the ammonia emission was dramatically mitigated by applying the excavated aged refuse in this study.

The significant enhancement of denitrification capacity by digestate addition in aged refuse will benefit the in-situ nitrogen removal from mature landfill leachate. It can be concluded that the solid digestate integrated with the aged refuse could be superior to the sole aged refused landfill columns.

Table 4.3.3 Nitrate removal rates of landfill simulation columns with different types of wastes

Waste Types	Nitrate Content	ANRR	ANRR[a]	Reference
	(mg-N/L)	mg N/ (kg-TS day)		
Composed MSW	400	140	-	(Price et al., 2003)
MSW	200-2200	28.6	-	(Zhong et al., 2009)
1-year-aged MSW	1000	163.2[b]	-	(Chen et al., 2009)
6-year-aged MSW	1000	72.0[b]	-	(Chen et al., 2009)
11-year-aged MSW	1000	26.4[b]	-	(Chen et al., 2009)
Solid Digestate (SD)	1438	256	256	(Peng et al., 2018)
100% Aged Refuse (AR)	517-1332	4.2	-	This study
95% AR+5% SD	517-1332	14.1	203	
85% AR+15% SD	517-1332	42.1	257	

[a] the ANRR was calculated based on the TS of solid digestate. The results had deducted the contribution by aged refuse

[b] the data were calculated by the authors

4.4 Conclusions

After 100 days' recirculation of nitrified leachate in the aged refuse bioreactors packed with solid digestate, approximately 4.2 mg N/ (kg-TS day), 14.1 mg N/ (kg- TS day) and 42.1 mg N/ (kg-TS day) of the nitrate removal rate were separately achieved in R0, R5 and R15. Additionally, both the aerobic biostability and anaerobic biostability of treated solid digestate in R5 and R15 increased 31.5-35.9%. These results suggest that the solid digestate with high denitrification capacity could be applied as a denitrification layer in old landfill site for in-situ nitrogen removal from mature landfill leachate and obtain stabilized digestate.

Conclusions and Perspectives

The development of integrating landfill leachate treatment into digestate management could achieve both economic and environmental benefits. The facultative bioreactor landfill consists of two core components: Solid digestate layer for denitrification; Aged refuse layer for avoiding ammonia leaching. Additionally, recirculating the partial or complete nitrified landfill leachate in the facultative bioreactor landfill is also indispensable.

Based on the main results obtained in this study, some general conclusions can be drawn:

Organic matter stabilization:

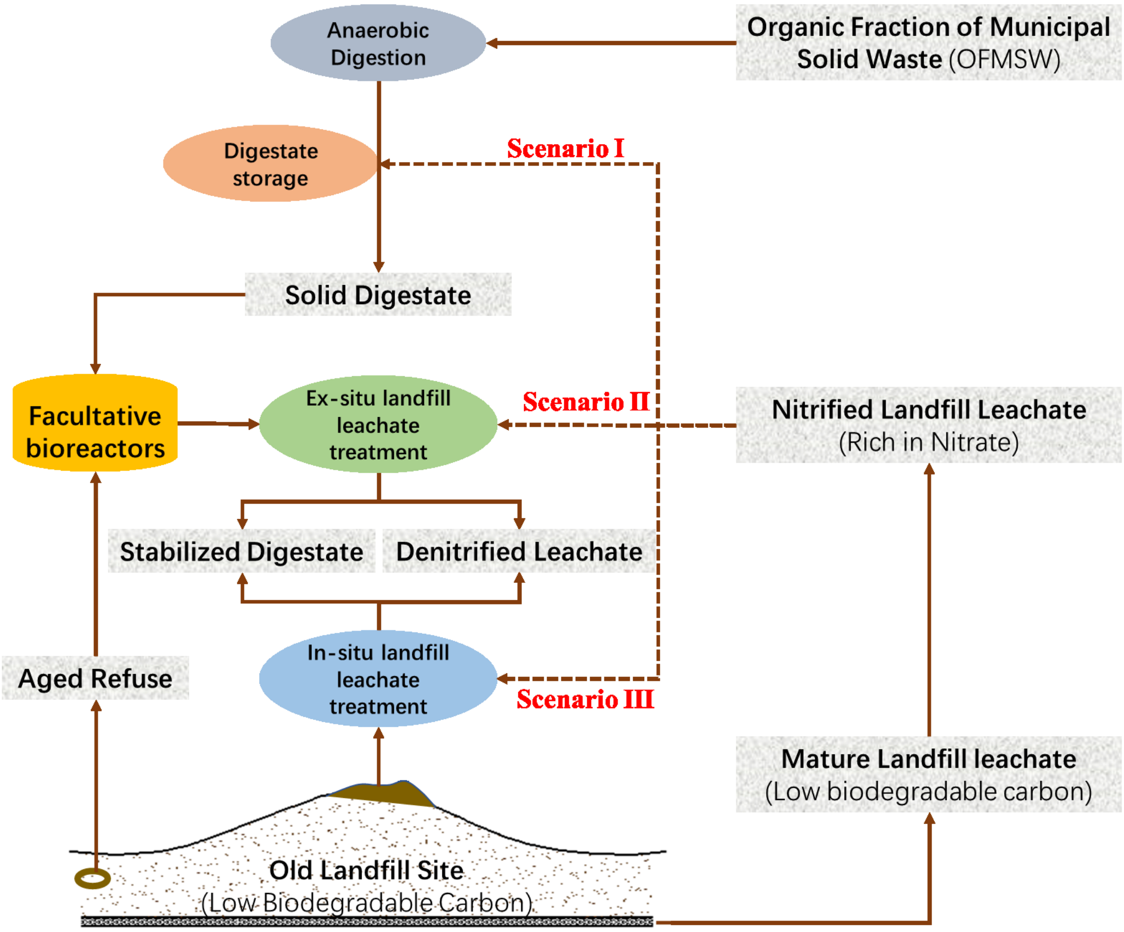
- The application of FBLs with recirculating partially or completely nitrified leachate stabilizes the organic matter in the solid digestate. The degree of oxidation (partial or complete nitrification) and whether integrating aged refuse will affect the both aerobic and anaerobic bio-stability.
- With the leachate recirculation, the high leaching TOC from the digestate at the initial stage can be transferred to the effluent leachate, thereby deteriorating the quality of effluent leachate. However, the TOC of effluent does not increase when an aged-refuse layer is filled under the digestate layer.

Nitrogen Management:

- Digestate from OFMSW shows high denitrification capacity, varied from 199 to 257 mg-N/ (kg-TS day), which is much higher than those of MSW with different ages.
- Although less energy consumed to produce partially nitrified leachate, FBL with recirculating nitrified leachate did not show any advantage by evaluating the denitrification capacity and digestate stability. However, nitrite pathway can help to develop the autotrophic denitrification via the Anammox process.
- Comparing to the aged refuse FBL, tenfold denitrification capacity is enhanced in aged refuse FBL 15% digestate addition.

- With the leachate recirculation, the high leaching ammonium from the digestate at the initial stage can be transferred to the effluent leachate, thereby deteriorating the quality of effluent leachate. However, the ammonium of effluent does not increase when an aged-refuse layer is filled under the digestate layer.

Applicability of the study to full-scale landfills or AD plants



Scenarios for digestate application to remove nitrogen from mature landfill leachate

- Scenario I: Nitrified landfill leachate added into the digestate storage tank to in-situ mitigate the greenhouse gas emission.
- Scenario II: Ex-situ nitrogen removal of landfill leachate in biogas plants and application of stabilized digestate as soil amendment
- Scenario III: In-situ nitrogen removal of landfill leachate in old landfill sites and

application of stabilized digestate as final cover for landfill remediation

Suggestions for further studies

- The pilot-scale application of solid digestate to treat landfill leachate is necessary to conduct according to the three scenarios.
- Short-cut nitrogen removal of landfill leachate through autotrophic denitrification like Annammox should be developed in the digestate-based facultative bioreactors because heterotrophic denitrification cannot last for long time when the biodegradable organic matters exhausted.
- The nitrous oxide emission and fate of possible heavy metals from landfill leachate should be considered in the future research.
- The final quality of treated digestate should be well evaluated for its further use as soil improver or landfill cover.

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