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Optimalizace dvoustupňové úpravy fugátu

Diplomová práce

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Optimization of Two-Stage Treatment of the Liquid Phase of Digestate

Diploma Thesis

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Field of study: Technology processing and utilization of wastes

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Declaration

I declare that the Diploma Thesis "Optimization of Two-Stage Treatment of the Liquid Phase of Digestate" is my own work and all the sources I cited in it are listed in the Bibliography. Permission to write the diploma thesis in English language was granted.

Prague, April 13, 2018

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Liz Mabel Vargas Cáceres

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Optimization of Two-Stage Treatment of the Liquid Phase of Digestate

Summary

This diploma thesis is focused in the determination of nitrogen losses from the long-term storage of the untreated liquid phase of digestate (LPD) versus the long-term storage of the nitrified LPD at lab-scale conditions, highlighting the differences between the aforementioned experimental setups. It was hypothesised that the rate of nitrogen losses during long-term storage of the nitrified LPD will be significantly lower compared with the storage of untreated LPD.

Moreover, this diploma thesis seeks to verify the feasibility of the combination of previous nitrification and subsequent thermal thickening by vacuum evaporation of the LPD in order to concentrate the nutrients and other chemical compounds in the thickened LPD, while simultaneously obtaining clean water and reducing the volume of the LPD. It was hypothesised that a nitrogen-rich concentrate, which can be used as a complex liquid fertiliser, will be produced, and a distillate characterised by low concentrations of nitrogen and other chemical compounds, which can be used as a process liquid in the biogas plants (BGPs) for the dilution of feedstocks or for irrigation, will be recovered through the thermal thickening of the nitrified LPD by vacuum evaporation.

To achieve these goals, the nitrification of the LPD in a continuously stirred tank reactor (CSTR) was performed as a first step. Subsequently, four glass beakers were filled with 750 mL of untreated LPD and other four were filled with 750 mL of nitrified LPD. In each model, different temperature storage conditions were simulated by storing two of the four beakers at room temperature, one of which was continuously stirred to verify the behaviour of the sample under moderate wind conditions. The remaining beakers were stored in a thermostatic cabinet at 10.0 ± 1.0 °C with one being constantly stirred. The concentrations of total ammonia nitrogen (TAN), $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and chemical oxygen demand (COD), as well as pH and dissolved oxygen (DO), were measured at a minimum of two-week intervals. It was proved that during the long-term storage of the untreated LPD approximately 7% of nitrogen in the form of TAN was lost weekly whereas during the long-term storage of the nitrified LPD the losses of total inorganic nitrogen (TAN + $N\text{-}NO_2^-$ + $N\text{-}NO_3^-$) did not exceed 0.3% per week.

Two different series of evaporation were carried out using the nitrified LPD. Samples of 200 mL of nitrified LPD each were subjected to evaporation under reduced pressure (300 mbar) and high temperature (60°C) using a heating water bath set to 95 °C. Evaporation was ceased when the volume of the thickened LPD and distillate were equal to 50% of the nitrified LPD. Next, the pH, electrical conductivity (EC), and concentrations of COD_{Total} and $COD_{Soluble}$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, and TAN were measured, and mass balance of the aforementioned parameters was calculated. The results of the analyses of the thickened LPD were then compared with those obtained from the untreated LPD and nitrified LPD. The total inorganic nitrogen preserved in the thickened LPD of all the samples increased in concentration more than double after the vacuum evaporation, with $N\text{-}NO_3^-$ being the dominant nitrogen form (99.9%), whereas in the distillate did not exceed 2 mg/L in all the samples. Mass balance calculations indicated that 99.9% of the total inorganic nitrogen was maintained in the thickened LPD and the percentage of total inorganic nitrogen in the distillates of all the samples did not exceed 0.06%.

Keywords: Liquid Phase of Digestate, nitrification, thermal thickening, denitrification, volatilisation

Optimalizace dvoustupňové úpravy fugátu

Souhrn

Anaerobní digesce (AD) efektivně převádí biologicky rozložitelné odpady na bioplyn sestávající převážně z methanu, který se používá k výrobě elektřiny a tepla v kogeneračních jednotkách. Na konci procesu zůstává tvz. fermentační zbytek (digestát) se sušinou obvykle okolo 10 %.

V důsledku podpory obnovitelných zdrojů energie a v důsledku skutečnosti, že produkce metanu prostřednictvím AD spadá mezi účinné způsoby snižování emisí skleníkových plynů, se počet bioplynových stanic v Evropě v průběhu posledního desetiletí neustále zvyšuje. Například Evropská asociace pro biomasu uvedla, že v současné době je v Evropě v provozu přibližně 17 000 bioplynových stanic. Z toho 554 je jich provozováno v České republice, přičemž 383 z nich spadá do kategorie zemědělských bioplynových stanic. Přestože bioplyn představuje velkou příležitost k výrobě energie z obnovitelných zdrojů, ekologická účinnost výroby bioplynu závisí také na udržitelném hospodaření s digestátem.

Digestát může být podroben separaci na základní frakce, které jsou snadněji skladovatelné a přepravované. Pevná frakce je označována jako separát, kapalná frakce pak jako fugát. Většina sloučenin fosforu je po separaci obsažena v separátu, hlavní podíl sloučeni dusíku pak ve fugátu. Fugát obsahuje relativně velké množství živin, zejména N-amon (NH_4^++ NH_3). Je to proto, že během AD jsou organické látky degradovány na různé konečné produkty, zejména pak na CH_4 a CO_2. Organická forma dusíku je při tom z velké části mineralizována do amoniakální formy. Navíc fugát obecně má pH přibližně 7,5 až 8,5 a proto má vysoký volatilizační potenciál. Nejběžnějším využitím fugátu je jeho přímá aplikace na zemědělskou půdu. Použití fugátu v zemědělství je však přísně omezeno a je upraveno Evropskou nitratovou směrnicí (Směrnice Rady 91/676/EHS o ochraně vod před znečištěním způsobeném dusičnany ze zemědělských zdrojů), jejímž cílem je ochrana podzemních a povrchových vod před znečištěním dusičnanem produkovaným zemědělskými zdroji. To často vede k nutnosti dlouhodobého skladování fugátu, což má za následek nedostatečné skladovací kapacity a únik NH_3 do ovzduší. Ten nejenže snižuje kvalitu fugátu jako hnojiva, ale také znečišťuje životní prostředí.

Z výše uvedených důvodů se pozornost stále více soustředí na různé varianty zpracování fugátu, které snižují jeho objem a maximalizují koncentraci v něm obsažených živin, například tepelné zahušťování fugátu. Tepelné zahušťování fugátu je technikou

používanou k výrobě zahuštěného fugátu bohatého na živiny, který může být použit jako hnojivo. Zároveň vede k získávání destilátu s nízkými koncentracemi živin a dalších chemických sloučenin. Tento destilát pak může být použit například jako procesní kapalina v bioplynových stanicích pro zředění vstupních surovin.

Úprava hodnot pH fugátu na mírně kyselé je však nutným krokem, aby se omezily případné úniky těkavého NH_3 během tepelného zahuštění. Hodnoty pH lze snadno upravit přidáním minerálních kyselin, ale k tomu je zapotřebí značné množství chemikálií, což zvyšuje provozní náklady. Jako alternativní postup můžeme zmínit nitrifikaci, kdy dochází k předúpravě fugátu tak, aby se snížily hodnoty pH a aby fugát byl vhodný pro tepelné zahušťování. Nitrifikace je biochemická oxidace amoniakalního dusíku na dusičnany (NO_3^-). Ty jsou charakteristické tím, že jsou stabilnějším a mobilnějším zdrojem dusíku pro rostliny než N-amon.

Tato diplomová práce se zabývá stanovením a porovnáním ztrát dusíku při dlouhodobém skladování surového fugátu oproti dlouhodobému skladování nitrifikovaného fugátu v laboratorních podmínkách, přičemž je kladen důraz na rozdíly mezi výše uvedenými variantami. Hypotéza vycházela z předpokladu, že rychlost ztrát dusíku při dlouhodobém skladování nitrifikovaného fugátu bude výrazně nižší ve srovnání se skladováním surového fugátu.

Dále se tato diplomová práce zaměřuje na ověření proveditelnosti kombinace nitrifikace a následného tepelného zahušťování fugátu za účelem zakoncentrování živin a dalších chemických sloučenin v zahuštěném fugátu, za současného získávání čisté vody. Předpokládalo se, že výstupem bude koncentrát bohatý na dusík, který může být použit jako komplexní kapalné hnojivo, a destilát charakterizovaný nízkými koncentracemi sloučenin dusíku a dalších chemických sloučenin, který může být použit jako procesní kapalina pro ředění vstupních surovin v bioplynových stanicích nebo pro zavlažování.

Prvním krokem k dosažení výše uvedeného cíle bylo provedení nitrifikace fugátu v nitrifikačním reaktoru pracujícím na principu směšovací aktivace. Fugát pocházel z bioplynové stanice Rebios s.r.o. (Vyškov, Česká republika), která zpracovává biologicky rozložitelné odpady z kuchyní a stravoven (gastroodpady) a další bioodpady.

Čtyři skleněné kádinky byly naplněny 750 ml surového fugátu a další čtyři byly naplněny 750 ml nitrifikovaného fugátu. V každém modelu byly simulovány různé podmínky skladování, přičemž teploty dvou ze čtyř kádinek byly udržovány při pokojové teplotě, z nichž jedna byla kontinuálně míchána, aby se ověřilo chování vzorku za mírně větrných

podmínek. Zbývající dvě kádinky byly skladovány v termostatované skříni při teplotě 10,0 ± 1,0 °C, přičemž jedna byla nepřetržitě míchána. Koncentrace amoniakálního dusíku (N-amon), $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ a chemická spotřeba kyslíku (CHSK), stejně jako pH a rozpuštěného kyslíku byly měřeny minimálně v dvou-týdenních intervalech. Bylo prokázano, že při dlouhodobém skladování surového fugátu bylo během jednoho týdne ztraceno přibližně 7% dusíku ve formě TAN, zatímco ztráty celkového anorganického dusíku (N-amon + $N\text{-}NO_2^-$ + $N\text{-}NO_3^-$) nepřesáhly 0.7% týdně.

Analytické metody byly provedeny v souladu se standardními metodami v laboratořích Katedry agroenvirometální chemie a výživy rostlin České zemědělské univerzity v Praze. Jednoduchá lineární regrese byla použita k hodnocení tzv. denitrifikačního testu a volatilisačního testu za použití programu R.

Dále byly provedeny dvě různé série odpařování za použití nitrifikovaného fugátu. Vzorky 200 mL nitrifikovaného fugátu byly tepelně zahuštěny odpařováním za sníženého tlaku (300 mbar) a vysoké teploty (60 °C) za použití topné vodní lázně nastavené na teplotu 95 °C. Odpaření nebylo ukončeno do doby, dokud objem zahuštěného fugátu a destilátu nedosáhl 50 % objemu původního nitrifikovaného fugátu. Dále bylo měřeno pH, měrná elektrická vodivost a koncentrace N-amon, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, a CHSK. Následně byla vypočtena hmotnostní bilance výše uvedených parametrů. Výsledky analýz zahuštěného fugátu byly následně porovnány s výsledky získanými ze surového a nitrifikovaného fugátu. Celková koncentrace anorganického dusíku ve všech vzorcích zahuštěného fugátu po tepleném zahušťování vzrostl ve srovnání s koncentrací v nitrifikovaném fugátu před jeho zahuštěním více než dvojnásobně, přičemž $N\text{-}NO_3^-$ byl dominantní formou dusíku (99,9%). V destilátu koncentrace anorganického dusíku u žádného vzorku nepřekročila 2 mg/L. Výpočty hmotnostní bilance ukázaly, že v zahuštěném fugátu bylo zakoncentrováno více než 99,9 % celkového anorganického dusíku a procento celkového anorganického dusíku v destilátech všech vzorků nepřekročilo 0,06%

Výsledky této diplomové práce naznačují, že kontinuální míchání může zvýšit emise NH_3 během skladování, a proto je třeba se mu vyhnout. Dále výsledky ukazují, že při nitrifikaci jako předúpravě fugátu mohou být ztráty dusíku při dlouhodobém skladování výrazně nižší než při skladování surového fugátu. Budoucí výzkum, který se zaměří na skladování nitrifikovaného LPD v terénních podmínkách, je však nezbytný k potvrzení tohoto předpokladu.

V rámci dvoustupňové úpravy fugátu nitrifikací a následným tepelným zahuštěním popsané v této diplomové práci je finálním produktem fugát s vyššími koncentracemi anorganického dusíku přítomného dominantně ve formě $N\text{-}NO_3^-$, ve které je snadno dostupný pro příjem rostlin. Tato dvoustupňová úprava minimalizuje náklady spojené s použitím chemických látek. Nicméně, $N\text{-}NO_3^-$ se rychle vyplavuje z půdy a při denitrifikaci, která se přirozeně vyskytuje v půdě, může dojít k emisím N_2O. Kromě toho při skladování zahuštěného fugátu může docházet k emisím N_2O a CH_4. S ohledem na tato omezení je zapotřebí dalšího výzkumu, aby mohly být sledovány důsledky aplikace zahuštěného fugátu na půdu při vyplavování $N\text{-}NO_3$ a emise N_2O. Kromě toho je zapotřebí dalšího výzkumu během skladování zahuštěného fugátu pro porovnání emisí dvou hlavních skleníkových plynů, tj. N_2O a CH_4.

Klíčová slova: fugát, nitrifikace, tepelné zahušťování, volatilizace, denitrifikace

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1. Introduction

Anaerobic digestion (AD) efficiently converts biodegradable wastes into biogas consisting mainly of methane, which is used to generate electricity and heat in Combined Heat and Power units (CHP). AD additionally produces a post-digestion matter that can potentially be used as fertiliser and soil improver i.e. the digestate. As a result of the promotion of renewable energy sources and the recognition of methane production via AD as an effective way to mitigate greenhouse gases (GHG) emissions the number of biogas plants (BGPs) in Europe has steadily increased throughout the last decade. For instance, the European Biomass Association (2016) reported that about 17000 BGPs are currently operating in Europe, including 554 BGPs in the Czech Republic, 383 of which are agricultural. Although biogas represents a great opportunity to produce energy from renewable sources, the environmental efficacy of the biogas production also relies on the sustainable management of the digestate remaining after the AD of biodegradable wastes.

The digestate can be subjected to separation in different fractions that are easier to store and transport, i.e. a solid fraction (SPD) and a larger-in-volume liquid fraction (LPD), with phosphorus being more concentrated in the SPD, and nitrogen in the LPD. The LPD contains relatively high amounts of nutrients, in particular, TAN (NH_4^++ NH_3). This is because, during the AD, the organic molecules are mainly biodegraded to CH_4 and CO_2 while the organic form of N (N_{org}) is mineralised into TAN or partially conserved. Moreover, the LPD generally has a pH of around 7.5 to 8.5 and therefore has high NH_3 volatilisation potential. The most common utilisation of the LPD is its direct application on agricultural land. However, the use of LPD in the agricultural sector is strictly limited and is regulated by the EU Nitrate Directive (91/676/EEC) that aims to protect ground and surface water from nitrate pollution caused by agricultural sources. This often results in long LPD storage periods, leading to insufficient storage capacity and NH_3 volatilisation which not only reduce the fertiliser quality of LPD but also pollute the environment.

For the aforementioned reasons, increasing focus is being placed on various LPD treatment options for reducing its volume and concentrating the nutrients, namely the thermal thickening of LPD by vacuum evaporation. Vacuum evaporation of the LPD is a technique used to produce a nutrient-rich thickened LPD, which can be used as a fertiliser, to recover a distillate with low concentrations of nutrients and other chemical compounds, which can mainly be used as a process liquid in the BGPs for the dilution of feedstocks, and to significantly reduce the LPD's volume.

However, the adjustment of the pH values of the LPD to slightly acidic is a necessary step in order to limit eventual stripping of NH_3 during evaporation. The pH values can be easily adjusted by the addition of mineral acids, but considerable amounts of chemicals are needed, which increase the costs. Alternatively, nitrification as an LPD pre-treatment seems to be an interesting approach in order to decrease the pH values and make the LPD suitable for vacuum evaporation. Nitrification is the biochemical oxidation of TAN into nitrates (NO_3^-) that is characterized by being more stable and mobile nitrogen source for plants.

This diploma thesis seeks to verify the applicability of nitrification combined with thermal thickening by vacuum evaporation of the nitrified LPD in order to concentrate the nitrogen and other chemical compounds in the thickened LPD while simultaneously obtaining clean water and reducing the volume of the LPD. Moreover, the aim of this diploma thesis is the comparison of nitrogen losses during the long-term storage of the untreated LPD and the nitrified LPD.

2. Aim, objectives of the study and scientific hypothesis

This diploma thesis aims to scientifically determine nitrogen losses from the long-term storage of the liquid phase of digestate (LPD) at lab-scale conditions, highlighting the differences between two experimental setups (i.e. the storage of nitrified LDP and the storage of the untreated LPD). In addition, this diploma thesis seeks to verify the feasibility of the thermal thickening by vacuum evaporation of the nitrified LPD in order to concentrate the nitrogen in the thickened LPD while simultaneously obtaining clean water and reducing the volume of the LPD.

It is hypothesised that the rate of nitrogen losses during long-term storage of the nitrified LPD will be significantly lower compared with the storage of untreated LPD. A second hypothesis is that a nitrogen-rich concentrate, which can be used as fertiliser, will be produced, and a distillate characterised by low concentrations of nitrogen and other chemical compounds, which can be used as a process liquid in the BGPs for the dilution of feedstocks or for irrigation, will be recovered through the thermal thickening of the nitrified LPD by vacuum evaporation.

3. Literature overview

3.1. Digestate

3.1.1. Origin

Anaerobic digestion (AD) is a process of biogas production that takes place in a biogas plant (BGP). Under controlled anaerobic conditions, bacterial populations convert a wide range of biodegradable materials (e.g. livestock waste, energy crops, animal slurries, the organic fraction of municipal solid waste, municipal sewage sludge) mainly into methane that is afterwards used to produce renewable energy through biogas (Nkoa, 2014; Teglia et al., 2011a; Möller and Müller, 2012). As illustrated in Figure 1, the AD additionally produces a post-digestion matter that can potentially be used as a fertiliser and soil improver i.e. the digestate, which is a nutrient-rich material, principally composed of indigestible substances and microbial biomass remaining after the anaerobic digestion (Al Seadi et al., 2013; Alburquerque et al., 2012; Nkoa, 2014; Risberg et al., 2017). Furthermore, the digestate volume commonly varies between 90-95% of the biomass initially fed into the digester (Kathijotes et al., 2015). According to the processed substrate, biogas plants can be categorised into agricultural, industrial, and communal (Kučera and Bednář, 2014; Rigby and Smith, 2013). Nevertheless, it is particularly beneficial to link this technology to agriculture, where a large number of by-products of biological origin are produced, providing the possibility of using the digestate as fertiliser (Loria et al., 2007; Holm-Nielsen et al., 2009).

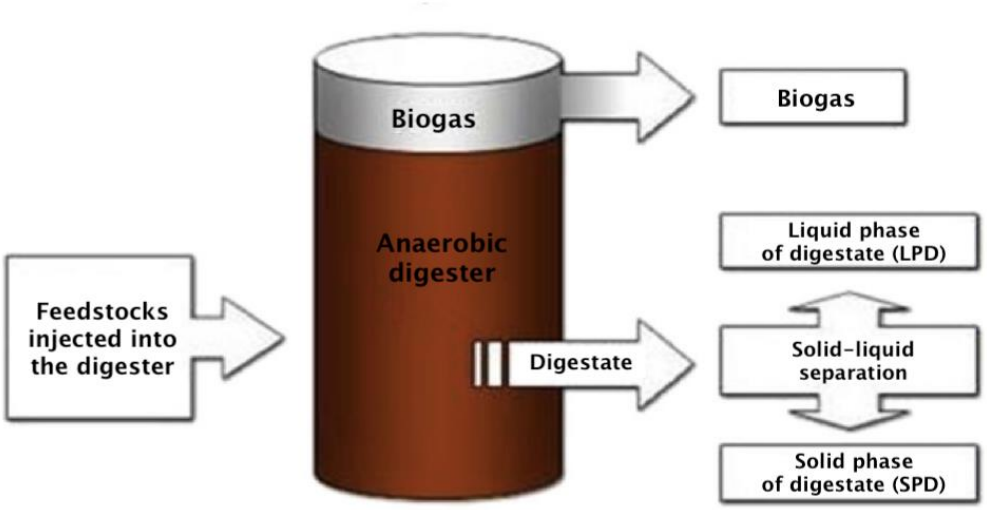

Figure 1. Anaerobic digestion process simplified and modified from Nkoa (2014).

3.1.2. Digestate characteristics and composition

The digestate composition and quality are directly linked to the AD operational conditions, such as organic loading rate (OLR), operating temperature, and hydraulic retention time (HRT) (Al Seadi et al., 2013; Sheets et al., 2015; Zirkler et al., 2014), as well as the feedstock components (Makádi et al., 2012; Provenzano et al., 2011; Möller and Müller, 2012). However, the digestate is generally a dense, heterogeneous, and dark grey to black liquid (Tlustoš et al., 2014), with a dry matter content that ranges from 2% to 9% (Sheets et al., 2015). Furthermore, high biological stability (Alburquerque et al., 2012; Provenzano et al., 2011) and likewise, a significant proportion of undigested organic matter (Tlustoš et al., 2014) and inorganic soluble nutrients (Alburquerque et al., 2012; Tambone et al., 2010) are among the digestate's generic characteristics.

The nutritional value of the digestate is determined by the fact that during anaerobic digestion, essential nutrients present in the raw materials in organic form are mineralised into inorganic forms more available to plants (Schievano et al., 2009). On the contrary, digestates have negative characteristics (e.g. heavy metals, pathogen contamination, and other potential hazards) that can decrease their agricultural value and reduce their commercial acceptability (Holm-Nielsen et al., 2009; Teglia et al., 2011a; Dragicevic et al., 2017). Hence, the aforementioned characteristics determine whether previous or subsequent treatment of the digestate are needed to improve its quality (Alburquerque et al., 2012; Teglia et al., 2011a). Considering these facts, the digestate characteristics and composition must be taken into account to assess their agronomic use. Determining the digestate characteristics will guarantee the safety of the digestate's use as an effective digestion by-product in agriculture (Teglia et al., 2011a). In this manner, possible soil and food chain contamination can be avoided (Holm-Nielsen et al., 2009; Al Seadi et al., 2013; Zirkler et al., 2014), and their eventually-required post-treatment (see chapter 3.2. and 3.5.) will be more efficient (Teglia et al., 2011a).

3.1.2.1. pH

Typically, the digestate pH value ranges from neutral to slightly alkaline as a result of the increment of the concentrations of total inorganic carbon (TIC) (TIC = CO_2 + HCO_3^- + CO_3^{2-}), NH_3 production and the reduction of volatile fatty acids (VFAs) during the AD process (Melamane et al., 2007; Ward et al., 2008). In terms of the substrate source, according to Alburquerque et al. (2012), the pH value of digestates derived from animal manures is generally slightly alkaline, whereas the pH of digestates obtained from food and green wastes

are neutral or slightly alkaline (Teglia et al., 2011b). The neutral pH allows the agronomic use of digestate (Tampio et al., 2016) whereas in contrast, the alkaline digestates could increase NH_3 emissions when applied onto land (Crolla et al., 2013) as a result of ammonia volatilisation (Nkoa, 2014). On the other hand, Otabbong et al. (1997) stated that when spread on the soil, digestates with low pH values may reduce the soil pH and, as a consequence, heavy metal mobilisation may occur. Based on these considerations, the pH value depends on the biomass inputs as well as the operational conditions during the AD, not to mention the soil characteristics (Makádi et al., 2012).

Table 1 summarizes the pH values of digestates resulting from different types of feedstocks at different operating temperatures. It is important to emphasize that the values represented are mere examples and may change conforming to the aforementioned parameters.

Table 1. pH values of digestates resulting from different feedstocks at different operating temperatures

Feedstock	Process temperature	pH Digestate	Reference
Primary sludge and the organic fraction of municipal solid wastes (OFMSW)	Mesophilic	7.4	Gómez et al., 2005
Pharmaceutical industry sludge	Mesophilic	7.8	Gómez et al., 2007
Cattle manure	Mesophilic	7.6	
Beef cattle slurry. maize or sorghum silage. agro-industrial residues	Mesophilic	7.9	Provenzano et al., 2011
Pig slurry plus energy crop residues and 9.6% rape residue	Mesophilic	7.8	Alburquerque et al., 2012
Cattle slurry plus agroindustrial residues (11.6% maize-oat silage)	Mesophilic	7.5	
Swine manure and vegetable processing wastes	Mesophilic	8.3	Molinuevo-Salces et al., 2013
Mixture of vegetable waste and waste-activated sludge	Thermophilic	7.6	Tampio et al., 2016

3.1.2.2. Macroelement contents

The content of macroelements in the digestate is in like manner regulated by the fermentation process, the biomass source, the dry matter and the subsequent digestate storage conditions (Kuusik et al., 2017; Lukehurst et al., 2010; Makádi et al., 2012). Table 2 presents some of the concentrations of main nutrients of digestates (total nitrogen (N_{tot}), TAN, potassium (K), carbon (C) concentrations) from different sources and different fermentation conditions.

Digestate is rich in nitrogen (N), an important plant nutrient and, paradoxically, the most recurrent limiting factor for plant growth (Kuusik et al., 2017; Makádi et al., 2012). During the AD, the organic molecules such as carbohydrates, proteins, lipids and cellulose among others, are mainly biodegraded to CH_4 and CO_2 (Tambone et al., 2009; Schievano et al., 2009; Teglia et al., 2011a) while the organic form of N (N_{org}) is mineralised into TAN or partially conserved. Thereby, the inorganic and organic N concentrations in the digestate are attributable to the initial N_{org} contents in the substrate (Søresen and Møller, 2008). Apart from that, the total N concentrations can be influenced by additional factors such as the process design, namely the amount of fresh water and the used recirculation effluent (Fuchs and Drosg, 2013). On average, the total TAN contents reach around 50-80 % of the digestate total N (N_{tot}) (Makádi et al., 2012; Teglia et al., 2011a) while the remainder represents the percentage of nitrogen in organic forms (Søresen and Møller, 2008). However, studies conducted by Teglia et al. (2011b) reported that the TAN represented only 30% of the total N of their studied digestates obtained from agricultural solid wastes, food-processing wastes, and organic fraction of municipal solid wastes. Hence, the use of digestate as a mineral fertiliser may be limited if organic forms of nitrogen are predominant and therefore the N_{org}/TAN ratio must be taken into account (Teglia et al., 2011b). With the increase of the mineral N to N_{org} ratio after AD, the crop N assimilation efficiency is enhanced since ammonia is a soluble form of N that is easily available to plants (Søresen and Møller, 2008). Conversely, large amounts of the N-NH_4^+ present in the digestate may represent risks associated with NH_3 emissions during storage or land spreading (Botheju et al., 2010) mainly due to the alkaline pH of the digestate (Teglia et al., 2011a), and may also raise the risk of phytotoxicity, depending on the dose and timing of land application, and the plant species or crops concerned (Teglia et al., 2011b). Hence, the digestate may need to be subjected to a convenient post-treatment (see chapter 3.5.) so that characteristics suitable for agricultural use will be insured (Botheju et al., 2010; Teglia et al., 2011a). A further important characteristic

related to the digestate nitrogen content is the carbon to nitrogen ratio (i.e. C/N ratio) which determines the digestate's agricultural use (Nkoa, 2014). If the mineral nitrogen fraction of the digestates is higher than that of the organic fraction, it is very likely that its best use will be as fertiliser (Tambone et al., 2009), whereas, on the contrary, if the mineral nitrogen fraction is lower, it is most likely that organic amendment will be its best use (Teglia et al., 2011b).

Besides nitrogen, the digestate is likewise rich in mineral nutrients such as inorganic phosphorus (P) and potassium (K) that can be easily assimilated by plants (Koszel and Lorencowicz, 2015; Tambone et al., 2009). Since P and K are generally included in the animal diet, animal slurries contain large amounts of these elements (Bachmann et al., 2016; Lukehurst et al., 2010). K is a highly influential part of plant water balance, enzymatic activity, photosynthetic processes, and nutrient transportation. Meanwhile, P contributes to plant growth and increases yield and quality, but repeated fertilisation may lead to high phosphorus accumulation in the soil (Koszel and Lorencowicz, 2015). As a consequence, it can be transported from the soil and subsequently reach surface water (Verheyen et al., 2015). Digestate is also composed of magnesium (Mg), which is the central chlorophyll atom and therefore influences the photosynthesis processes (Koszel and Lorencowicz, 2015). Mg is present in the digestate mainly in dissolved form and can therefore be more easily assimilated by plants (Kuusik et al., 2017). Digestate also supplies useful quantities of sulphur (S) and calcium (Ca). S is a structural component of three major amino acids; cysteine, methionine, and glutathione, which are essential in plant primary and secondary metabolism. Moreover, S functions in a wide variety of physiological processes such as photosynthetic processes, growth and development of cells, metabolism of carbon and nitrogen, and synthesis of plant proteins (Ceccotti, 1996). Ca is an equally essential plant nutrient. The main function of Ca in plant growth is to provide structural stability and plasticity of the membrane cell walls. Moreover, Ca activates many enzyme systems in protein synthesis and carbohydrate transfer (White and Broadley, 2003).

Table 2. The main properties of digestates from different sources and different fermentation conditions.

Feedstock	Process temperature	N_{tot}	TAN	P_{tot}	K_{tot}	C_{tot}	C/N	HRT (days)	Reference
		g/L							
Swine manure	Mesophilic	2.93	2.23	0.93	1.37	n.a.	n.a.	15	Loria et al., 2007
Pig slurry plus energy crop residues (9.6% rape residue)	Mesophilic	3.6	2.9	1.1	3.1	14.7	4.1	30	Alburquerque et al., 2012
Pig slurry plus animal by-products (0.6% pasteurised slaughterhouse residues)	Mesophilic	2.9	2.2	0.5	2.2	5.8	2.0	20	
Cattle slurry plus 6 % glycerine	Mesophilic	2.3	0.9	0.4	1.6	42.8	18.5	40	
Cattle slurry plus agroindustrial residues (11.6% maize-oat silage)	Mesophilic	4.0	2.4	0.8	3.1	33.7	8.5	25	
Food waste	Mesophilic	6.0	4.4	0.33	3.2	26.9	3.1	58	Tampio et al., 2016 [1]
Mixture of vegetable waste and waste-activated sludge (VMAS)	Thermophilic	2.2	1.6	0.35	0.6	13.5	6.1	16	
Cattle manure	Mesophilic	3.8	1.8	0.7	2.7	n.a.	n.a.	n.a.	Kuusik et al., 2017
Pig slurry	Mesophilic	5.2	3.2	1.5	2.1	n.a.	n.a.	n.a.	

[1] The results were converted from g/kg to g/L
n.a. = not available

3.1.2.3. Organic matter contents

In the course of the AD processes around 20 – 95 % of the amount of organic matter (OM) and carbon content of the feedstock is degraded in digesters depending on the feedstock composition and the operational conditions (Makádi et al., 2012; Monlau et al., 2015; Teglia et al., 2011a; Teglia et al., 2011b; Möller and Müller, 2012). For example, Schievano et al. (2009) noticed OM content reductions up to 65±10 % in terms of volatile solids (VS) balance after the AD of swine manure, various energy crops, and other organic residues. Furthermore, the biological stability of the modified OM increases incrementally with higher levels of recalcitrant molecules such as lignin, humic acids, steroids and complex proteins, since most OM is converted into biogas (Schievano et al., 2009; Teglia et al., 2011b). The AD residues are considered to be stable if it is composed mainly of recalcitrant or humus-like matter and therefore it is not capable of maintaining microbial activity (Kirchmann and Bernal, 1997). Consequently, stability prevents nutrients from being embedded in microbial cells, hence it increases the availability of nutrients for plants (Trzcinski and Stuckey, 2011).

The effectiveness of OM degradation depends on the type of feedstock fed to the digester, as well as on the reactor parameters, such as the OLR and the HRT (Monlau et al., 2015; Nkoa, 2014). For instance, the efficiency criteria for methane production may result in a shorter HRT of the biomass in the digester than the time required for the digestate to be fully stabilised (Nkoa, 2014). If the OLR of biogas plant is high and the HRT is short, the digestate will contain high amounts of undigested OM (Nkoa, 2014; Teglia et al., 2011b). As a result, the digestate can cause problems such as odour emissions, higher toxic organic contents, pathogens and phytotoxicity that will not allow it to be considered as an amendment material (Nkoa 2014; Teglia et al., 2011b). Apart from the OM content, the dry matter (DM) content is a likewise important characteristic for the potential use of digestate as amendment, since excessive moisture can have adverse effects also related to odour emissions, elevated transport costs and storage complications. The DM content depends on the initial DM contents of the substrate and the easily degradable OM (Drosg et al., 2015). In general terms, the digestate can contain 50 % to 80 % less DM in comparison with the initial DM of the substrate (Holm-Nielsen et al., 1997).

Founded on these considerations, the acceptability of digestate as soil amendment is acquired from the remaining OM and dry matter content after AD (Teglia et al., 2011b). Therefore, producing the maximum yield of biogas should not be at the expense of the production of a safe, reliable and stable digestate suitable for agricultural utilisation (Maynaud

et al., 2017; Nkoa, 2014). In light of these facts, the appropriate characterisation of organic matter composition of digestates is crucial to guarantee a sustainable way to manage and recycle these biodegradable residues (Teglia et al., 2011b).

3.1.2.4. Risk element contents

Heavy metals are considered to be trace elements because they are present at low concentrations (mg/kg or less) in agroecosystems (He et al., 2005). In addition, heavy metals are elements that have a high atomic weight and 5 times greater density than water (Tchounwou et al., 2012). Heavy metals are also acknowledged to be toxic elements that can potentially accumulate in different environmental compartments (Dragicevic et al., 2017). More so, it is assumed that heaviness and toxicity are interdependent. For that reason, risk elements include heavy metals and also metalloids such as arsenic (As), since they can induce toxicity at a low level of exposure (Tchounwou et al., 2012). Trace amounts of some heavy metals such as zinc (Zn), nickel (Ni) and copper (Cu) are essential to fulfilling biochemical and physiological functions in plants and animals (Dragicevic et al., 2017; He et al., 2005; Tchounwou et al., 2012). However, at elevated concentrations these elements are toxic to plants (He et al., 2005) and therefore there is a very narrow limit of concentrations between beneficial and adverse effects (Tchounwou et al., 2012). Other trace elements such as mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As) represent a high degree of toxicity for living organisms and are considered to be hazardous elements (He et al., 2005; Kuusik et al., 2017; Makádi et al., 2012). Considering these facts, the concentrations of heavy metals must be taken into consideration before the digestate application, on the basis that metal can accumulate in soil and consequently get into the food chain (He et al., 2005; Alburquerque et al., 2012; Kuusik et al., 2017; Al Seadi et al., 2013).

In the Czech Republic, the regulation of heavy metals in organic fertilisers is governed by the Decree of the Ministry of Agriculture of the Czech Republic No. 131/2014 Coll., as amended, on Requirements on fertilisers (Ministry of Agriculture of the Czech Republic 2014). According to the Czech legislation, cadmium (Cd), lead (Pb), mercury (Hg), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), and zinc (Zn) are the heavy metals that raise the highest concerns. In addition, arsenic (As) is also monitored. Table 3 shows the limit concentrations of heavy metals in digestate for application on agricultural land according to regulations in different countries.

Table 3. Limits concentrations of risk elements in digestate (mg/kg DM) for application on agricultural land according to regulations in different countries

	Czech Republic [a]	Germany [b]	Finland [c]	UK [d]	EU proposal [e]
			mg/kg DM		
Cd	2	1.5	1.5	1.5	1.5
Pb	100	150	100	200	120
Hg	1	1	1	1	1
As	20	n.a.	n.a.	n.a.	n.a.
Cr	100	100	300	100	100
Cu	250	100	600	200	200
Mo	20	n.a.	n.a.	n.a.	n.a.
Ni	50	50	100	50	50
Zn	1200	400	1500	400	600

n.a. = not available

a Ministry of Agriculture of the Czech Republic, 2014

b Siebert, 2008

c Ministry of Agriculture and Forestry of Finland, 2011

d PAS 110:2010

e Saveyn and Eder, 2014

Table 4 displays very heterogeneous element concentrations of digestates which indicate that the character of input materials could play a role in the heavy metal contents of digestates (Kupper et al., 2014). Digestible organic materials such as organic waste, wastewater treatment plant sludge, fat residues, and domestic sewage can contain or can be contaminated with heavy metals as a result of anthropogenic activity. Hence, the heavy metal content of the input biomass remains in their digestates after the AD processes (Al Seadi et al., 2013; Govasmark et al., 2011; Makádi et al., 2012). For instance, Tampio et al. (2016) reported that the digestate from a mixture of waste-activated sludge and vegetable waste showed increased heavy metal content that exceeded the legislative limits. Contrastingly, reports from Tambone et al. (2017) indicated that digestates from animal slurry plus by-products and energy crops were in line with the limits suggested by the European Union and have the qualities to be used as a fertiliser. However, it is important to emphasise that the aforementioned examples cannot be generalised because the substrates represent a variety of organic residues that as such can widely differ in character (Tambone et al., 2010)

Kupper et al. (2014) strongly argued that the treatment process had little influence on the heavy metal content of the studied digestates since heavy metals are per se recalcitrant to the anaerobic degradation process. Notwithstanding the foregoing, Trzcinski and Stuckey (2011) found that accumulations of Ni and Cr in digestates were attributable to the attrition of the stainless steel stirrer and found that Zn and Cu content were lower as the HRT decreased and the OLR increased. Moreover, Zirkler et al. (2014) suggested that digestates can present variabilities in their characteristics among biogas plants, and even within one biogas plant. For these reasons, the development of new technologies to diminish the heavy metal content in the digestate might be needed (Al Seadi and Lukehurst, 2012; Selling et al., 2008).

Table 4. Risk element contents of digestate resulting from different feedstocks

Feedstock	Pb	Ni	Hg	Cd	As	Cu	Cr	Zn	Reference
	mg/kg DM								
Organic fraction of municipal solid waste	4.9	49.8	n.a.	0	n.a.	25.1	118.6	76.9	Trzcinski and Stuckey, 2011
Food waste	2.1	17.8	0.1	0.2	0.7	25.6	9.8	116	Tampio et al., 2016
Organic fraction of municipal solid waste (OFMSW)	11.7	6.7	0.3	1.5	3.3	58.7	13	401	
Mixture of vegetable waste and waste-activated sludge	98.0	22.3	1.8	1.1	2.6	626.5	32.9	1006	
Maize	1.3	5.0	n.a.	0.05	n.a.	28.5	16.0	34.3	Selling et al., 2008
Horse manure	3.2	3.8	n.a.	0.26	n.a.	14.0	10.3	43.2	
Pig slurry + energetic crops	1.54	14.4	n.a.	0.46	n.a.	105	7.26	341	Tambone et al., 2017
Cow slurry + energetic crops	3.19	9.2	n.a.	0.21	n.a.	61.5	10.6	374	

n.a. = not available

3.1.2.5. Pathogens

The application of digestates on the soil requires a previous evaluation of the quality with regard to the presence of toxic organic and inorganic compounds, as well as the concentration of organic matter and nutrients. Moreover, in terms of digestate quality, a further noteworthy aspect of digestate is its microbial stability and hygiene (Alburquerque et

al., 2012; Kuusik et al., 2017). The potential risks of digested residues from biogas plants to human and animal health are partially influenced by the processed substrates, since pathogenic bacteria may be present in it (Alfa et al., 2014; Bonetta et al., 2014; Sahlström, 2003). For instance, biowastes from animal origin may contain different species of pathogenic bacteria, e.g. *Salmonella, Enterobacter, Clostridia, Campylobacter, Escherichia coli, Listeria,* and *Mycobacteria* among others (Sahlström, 2003). Moreover, various pathogenic bacteria are very persistent and may result in their multiplication in the digesters (Sahlström, 2003). Above all, pathogenic bacteria can be found also in the digester, and consequently, there is a risk of digestate contamination with pathogenic bacteria after the AD process, even if no pathogenic bacteria were present in the substrate (Kuusik et al., 2017).

It is known that through AD process it is possible to inactivate pathogens present in the substrates (Dumitru, 2014; Makádi et al., 2012). Nonetheless, elimination of plant pathogenic bacteria depends on the synergistic interaction of various operational parameters and conditions, including pH, temperature, the HRT, volatile fatty acids (VFA), bacterial species, available nutrients and digester type (namely batch or continuous digestion) (Dumitru, 2014; Holm et al., 2010; Kuusik et al., 2017; Sahlström 2003), with temperature alongside a reasonable exposure time regarded as the most important factors for microbial growth inhibition during the AD of biodegradable wastes (Sahlström, 2003; Wagner et al., 2008). The AD can be performed either at mesophilic (30-38 °C) or thermophilic (50-55 °C) temperature regimes (Sahlström, 2003). Nevertheless, pathogenic bacteria can be mostly inactivated through elevated temperatures (Kuusik et al., 2017). Among the many advantages of thermophilic operational temperatures (e.g. higher rate of degradation of OM, and as a consequence shorter HRT, and higher biogas production) enhanced elimination of pathogens is one of value (Parawira et al., 2007). Higher digestion temperatures require less time for pathogenic bacteria inactivation, therefore bacteria elimination occurs more quickly in thermophilic than in mesophilic digestion (Dumitru, 2014; Sahlström, 2003). Kuusik et al. (2017) suggested that post-digestion hygienic procedures are not necessary if the operating temperatures are higher than 55 °C and the HRT is longer than 23 hours. Furthermore, Owamah et al. (2014) recommended longer HRT of at least 90 days at mesophilic temperatures and shorter HRT of 30 days at thermophilic temperatures to ensure better digestates quality in terms of destruction of pathogens that may be potentially present in the waste. Hence, the higher temperature plus retention time combination may result in sanitation or pasteurisation of the biodegradable wastes in the course of the AD (Holm et al., 2010).

With this in mind, the hygiene of digestates is not fully guaranteed when the digesters are operated at mesophilic temperatures (Sahlström, 2003; Smith et al., 2005). As reported by Smith et al. (2005), inactivation of *Escherichia coli* and *Salmonella spp.* occurred by thermophilic temperatures whereas they were not damaged by mesophilic temperatures (Smith et al., 2005). Contrastingly, Sahlström (2003) reported that spores of *Bacillus cereus* and *Clostridum perfringens* were not inactivated in either mesophilic or thermophilic digestion, indicating that the elimination rate of pathogenic bacteria is not only dependent on the operating temperatures, but also on the additional above-mentioned variables. For instance, the hygiene problems may increase if the digesters are operated on a semi-continuous feed basis and thereby are vulnerable to a possible pathogens flow when the digestate is mixed with the fresh substrates (Smith et al., 2005). On the other hand, Dumitru (2014) pointed out that the effective hygienisation (i.e. 99% destruction of all pathogens) can be reached at thermophilic temperatures in an elongated plug flow continuous reactor with the suitable HRT, since there is no mixing of digestate with the fresh substrate in that type of digester.

All things considered, efficient pre- or post-treatment such as pasteurisation or by pressure sterilisation for inactivation of pathogens from the digestates may be required depending on the type of feedstock (Alburquerque et al., 2012; Dumitru, 2014) especially in the case of animal by-products (Sahlström, 2003).

3.2. Digestate processing

After being removed from the digesters, the digestate can be directly applied on agricultural land for crop growth as a beneficial fertiliser owing to the high amounts of nutrient contents (Al Seadi et al., 2013; Fuchs and Drosg, 2013; Lukehurst et al., 2010; Nkoa, 2014). However, unsuitable fertilisation practises derived from direct land application can lead to ammonia volatilisation, nutrient loss, fertiliser over use, heavy metal accumulation or pathogen contamination (Nkoa, 2014). Moreover, due to its low dry matter content and large volume, the costs of transportation, storage, and application can be excessively high (Al Seadi et al., 2013). Additionally, with the intention of protecting groundwater resources against pollution caused by nitrates from agricultural sources and to reduce the emissions greenhouse gases to the environment, the European Nitrate Directive 91/676/CEE (European Community, 1991) limits the annual nitrogen load which can be applied on farmland and requires EU member states to establish a minimum storage time. Being rich in nitrogen available for plants, the amount of digestate that can be applied onto agricultural lands is directly influenced.

For these main reasons, the efficient digestate processing is increasingly gaining importance. Digestate processing techniques are mainly focused on the volume reduction, on the separation into fractions (solid-liquid) and therefore, the reduction of transportation costs, and on the recovery or improvement of the nutrients in concentrated forms (Al Seadi et al., 2013; Fuchs and Drosg, 2013). In summary, the benefits of digestate processing are not only the reduced transportation cost, the lower fuel and time required to apply the digestate on land, and the reduction of the necessary storage capacity (Fechter and Kraume, 2016), but also provides the possibility of reusing the nutrients (e.g. nitrogen and phosphorus) present in the digestate in an environmental sustainable way (Sheets et al., 2015).

3.2.1. Solid-liquid separation

3.2.1.1. Separated components of digestate

The solid-liquid separation is the starting point of the digestate processing (Al Seadi et al., 2013; Drosg et al., 2015; Fechter and Kraume, 2016; Fuchs and Drosg, 2013), uncommonly the digestate is processed without a previous solid-liquid separation (Fuchs and Drosg, 2013). The solid-liquid separation is a process wherein the solid phase of digestate (SPD) is separated from the liquid phase of digestate (LPD). Separation is performed in order to obtain a solid material with a high dry matter content up to 35 ± 5 % and a liquid material

characterised by its less than 5 % DM content depending on the separation technology used (Fechter and Kraume, 2016; Kubáňková et al., 2016). The typical distribution of components after solid-liquid separation of digestate is shown in Figure 2.

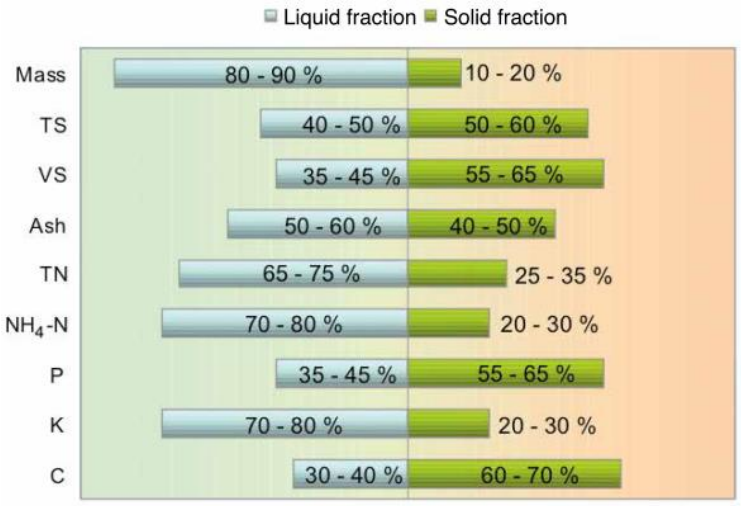

Figure 2. Distribution of the main components after solid-liquid separation (Drosg et al., 2015)

Generally, the phosphorus remains mainly in the SPD, while the nitrogen, generally in the form of dissolved ammonia, is enriched in the LPD (Al Seadi et al., 2013; Dumitru, 2014; Fechter and Kraume, 2016; Lukehurst et al., 2010; Nkoa, 2014; Tambone et al., 2017). The solid-liquid separation enhances the management of plant nutrients, the SPD can be applied directly for agricultural purposes as phosphorus-rich fertiliser or be alternatively stabilised after being dried or composted and used as an organic amendment, additionally, it can be palletised or incinerated for energy use (Fechter and Kraume, 2016; Fuchs and Drosg, 2013; Tambone et al., 2010). On the other hand, the LPD can be applied to land as liquid nitrogen-rich fertiliser as a substitute for mineral fertilisers, it can be recirculated into the digester or can undergo a variety of nutrient recovery and treatment processes (see chapter 3.5.) in order to obtain concentrates or pure water (Al Saedi and Lukehurst, 2012; Al Seadi et al., 2013; Alfa et al., 2014; Fuchs and Drosg, 2013).

3.2.1.2. Solid-liquid separation technologies

There are several available solid-liquid separation technologies (vibrating screens, belt filter presses, bow sieves, decanter centrifuges, screw press separators, etc.) with the decanter centrifuge and the screw press separator the most widely used among farmers in the EU (Al Seadi et al., 2013; Fuchs and Drosg, 2013). Moreover, the separation using the aforementioned techniques can be improved by flocculation (Fechter and Kraume, 2016).

3.2.1.2.1. Solid-liquid separation of digestate by decanter centrifuge

The decanter centrifuge contributes to the highly effective separation of solid and liquid fractions. It is used for the separation of small particles and colloids from the digestate and the separation of the phosphorus contained in the digestate with the solid fraction (Møller, 2001). An overview of the set-up of a decanter centrifuge is provided in Figure 3. The digestate is fed into the centre of the centrifuge where the particles are separated by the influence of centrifugal force. Separation takes place in an encasing drum and a conveyor screw, both rotating in the same direction and at different speeds. Due to the different high rotational speed of the drum, solids (higher density) from liquids (lower density) are separated. The solid particles accumulate in the inner wall of the drum and are transported by the conveyor screw towards the outputs. Simultaneously, the liquid phase is discharged in the direction of the liquid outlet (Drosg et al., 2015; Fechter and Kraume, 2016). Even though the decanter produces a noticeably clear LPD, the solid fraction remains with an elevated water content compared to the screw press (Fechter and Kraume, 2016).

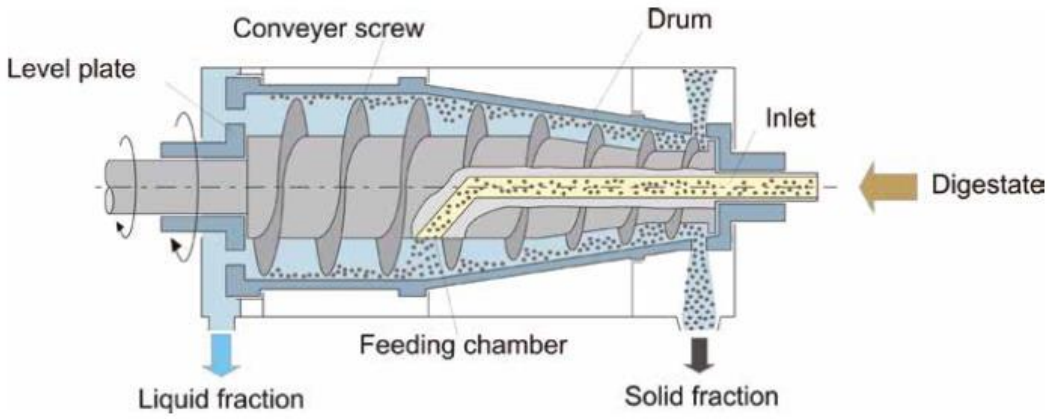

Figure 3. Decanter centrifuge. Source: Fuchs and Drosg, 2010.

3.2.1.2.2. Solid–liquid separation of digestate by screw press separator

The screw press separator is a device designed to mechanically separate solid and liquid fractions of materials with high fibre contents and therefore is generally used for agricultural applications specially for fibre-rich digestates from medium and large biogas plants (Al Seadi et al., 2013; Fechter and Kraume, 2016). As shown in Figure 4, the separation occurs in a drum with a cylindrical wedge wire screen and a screw conveyor. After

the digestate is pumped into the drum, a helical conveyor (screw) transports the digestate through a tube and past a cylindrical wedge wire screen with a slot size that varies between 0.5 and 1.0 mm; thereby the greater particles are retained while the smaller particles and liquid phase pass through. Gradually, the remaining solid is squeezed out by means of the conveyor screw as it enters into the pressure zone of the drum and thereby further liquid is released. A water-free solid material is released towards the outlet, while the released liquid is drained off to the outlet underneath the drum (Drosg et al., 2015; Fechter and Kraume, 2016).

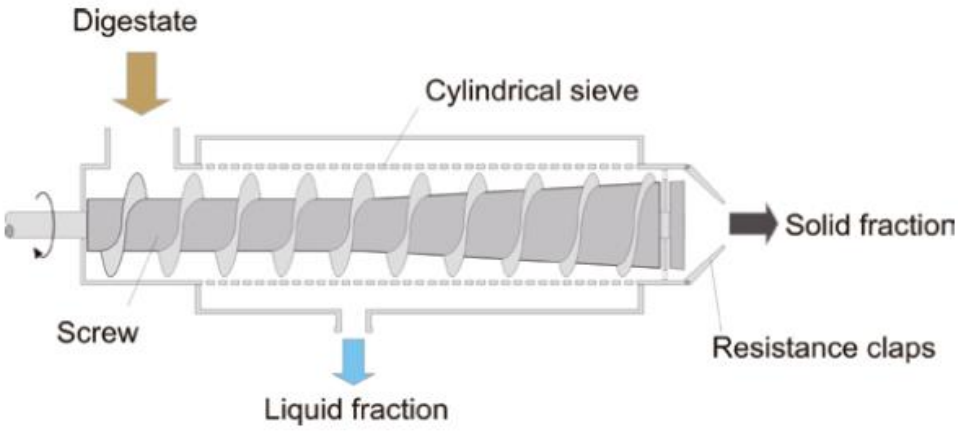

Figure 4. Screw press separator. Source: Fuchs and Drosg, 2010.

3.2.1.2.3. The use of flocculants for enhancement of separation

The agglomeration of digestate particles into bigger particles that can be easily separated is in many cases problematic due to the fact that the particles repel each other by cause of their negatively charged surfaces (Fechter and Kraume, 2016). For that reason, flocculation can be used prior to solid-liquid separation in order to improve the separation efficiency. Flocculation is usually performed in two steps. Initially, the flocculant is added to the digestate. The flocculant generally consists of a water-soluble metal salt such as aluminium sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), ferric sulphate ($Fe_2(SO_4)_3$) or calcium hydroxide ($Ca(OH)_2$). The metal salt form highly-charged cations that agglomerate the negatively charged suspended digestate particles in bigger particles. Nonetheless, most of these particles are still too small for separation, and because of this, polymers are added for further agglomeration of particles. In this manner, there is formed a much bigger particle that can be efficiently separated (Al Seadi et al., 2013; Fechter and Kraume, 2016). However, the disadvantages of the use of flocculants lie in their costs and the limitation of synthetic flocculants in fertilisers (Fechter and Kraume, 2016).

3.3. Agronomic utilisation of digestate and legal frameworks

There is a vast array of digestate uses depending on the quality and the origin of the feedstocks, as well as the characteristics and type of digestate (Dahlin et al., 2015; Plana and Noche, 2016). Nonetheless, the direct land application in agricultural fields is the most common usage of digestate (Fuchs and Drosg, 2013; Nkoa, 2014; Tambone et al., 2009). After the solid-liquid separation, the SPD can be directly used as soil conditioner without further treatment (Alfa et al., 2014; Tambone et al., 2017) or it can be used as plant growing media preparation (Plana and Noche, 2016). Moreover, it can be converted into compost (Arab et al., 2017) and the use of the SPD as solid fuel after its drying and palletising has also been investigated (García-Maroto et al., 2014) as well as the conversion of SPD into biochar under pyrolysis to be used as soil amendment (Hung et al., 2017).

The LPD can be mostly used as a fertiliser due to the high nutrient content (Fuchs and Drosg, 2013; Rehl and Müller, 2011). It has been highlighted that the LPD has been used as a fertiliser instead of mineral fertilisers, proving that it not only enhances soil properties but also crop nutrient uptake (Koszel and Lorencowicz, 2015; Riva et al., 2016; Vázquez-Rowe et al., 2015). Koszel and Lorencowicz (2015) observed an increase in the macroelement contents in the alfalfa leaves fertilised with digestate compared to the alfalfa fertilised with mineral fertilisers. Loria et al. (2007) demonstrated that liquid digestate from swine manure is a valuable source of N that can be used in corn production. Moreover, the low dry matter content of LPD enables the possibility of its application using conventional irrigation methods such as liquid manure spreaders or sprinkling machines (Alfa et al., 2014; Koszel and Lorencowicz, 2015). However, due to its high nutrient contents and potential hazards, the use of the digestate and its separated products are subject to strict legislative restrictions, regularly updated, that govern its use in agriculture. For instance, in order to protect ground and surface water from nitrate pollution caused by agricultural sources, the European Nitrate Directive 91/676/EEC (European Commission, 1991) imposes the annual N spreading amounts that can be applied in agricultural lands (i.e. 170 kg N Ha^{-1} per year in nitrate vulnerable zones (NVZs)). The NVZs are areas identified as affected or threatened by agricultural nitrates used as fertilisers to promote crop yields. In the Czech Republic the NVZs are listed in the Czech Government Regulation No. 262/2012 Coll., on the designation of nitrate vulnerable zones and the action programme (Ministry of Environment of the Czech Republic, 2012). The NVZs are designated and registered by the Ministry of Environment of the Czech Republic, as well as the governance of related action programme. Moreover, according to the Act No.

254/2001 Coll., on waters (Waters Act), as amended (Parliament of the Czech Republic, 2001a), the digestate as a fertiliser is considered a potentially harmful substance, and therefore the digestate application in NVZs is also regulated in order to avoid increases of nitrate concentrations in surface and ground water bodies.

The Act No. 156/1998 Coll., on fertilisers, auxiliary soil agents, auxiliary plant preparations and substrates, and on agrochemical testing of agricultural lands (Fertilisers Act), as amended (Ministry of Agriculture of the Czech Republic, 1998), categorise the digestate as an organic fertiliser that cannot be applied in flooded, over-humid, frozen or snow-covered soil. Moreover, the digestate can be used as fertiliser, but as such its authorised certification and registration by the Central Institute for Supervising and Testing in Agriculture is needed. The Fertilisers Act (Ministry of Agriculture of the Czech Republic, 1998), stipulates the basic principles and conditions for the registration of the digestates as organic fertiliser. As stated by the Fertilisers Act (Ministry of Agriculture of the Czech Republic, 1998), the digestates obtained exclusively from cattle manure or roughage are considered a fertiliser and can be used for own use without any registration. Furthermore, after being registered, the digestate is no longer considered as waste according to the Act on Waste No. 185/2001 Coll., as amended (Parliament of the Czech Republic, 2001b). The registration aims to ensure the quality of the digestate to be used as a safe product in agriculture, to contribute not only to the development of the market for digestate, but also to support the further improvement of biogas technologies.

3.4. Storage of digestate and the risk of nitrogen losses

As mentioned before, different regulations integrated into the agricultural and environmental protection legislation in many European countries govern not only the nutrient management and restrict the periods of digestate application, but also the storage capacity. As a consequence, the continuously produced digestate through the AD processes cannot be applied onto farmlands immediately, but instead, it must be stored until the growing season, which is the proper application time (Al Saedi and Lukehurst, 2012; Lukehurst et al., 2010; Plana and Noche, 2016). According to the Czech Government Decree No. 262/2012 Coll., on the designation of nitrate vulnerable zones and the action programme (Ministry of Environment of the Czech Republic, 2012) the LPD, which contains mainly nitrogen in plant-available forms such as NH_4^+ and NO_3^-, is considered a quick-release fertiliser, and as such its application is restricted from 15.11. until 15.02. for the climatic region 0-5 (i.e. very warm, moderately warm, moderately humid region), and respectively from 05.11. to 28.02 for climatic region 6-9 (moderately warm, humid, cold region). Due to the LPD's large volume and high-water content, biogas plants installations should count on adequate storage facilities with sufficient capacity, or alternatively the digestate should be transported and stored nearby the utilisation area (Al Saedi and Lukehurst, 2012; Plana and Noche, 2016).

Apart from legal frameworks, there are various factors that influence the length of the storage time and the design of the storage facilities e.g. digestate volume and type based on dry matter content (namely solid fraction or liquid faction), soil type and characteristics, geographical and climate conditions (Al Saedi and Lukehurst, 2012; Lukehurst et al., 2010; Plana and Noche, 2016). The digestate volume depends on the feedstock material and how often the storage tanks are emptied (Plana and Noche, 2016). Moreover, the storage facilities are also influenced by the digestate type. Unseparated digestate and the LPD are generally stored in above or below ground storage tanks, lagoons or storage bags in such a way that water and soil contamination does not occur, while the SPD is stored in open heaps, in covered flat concrete areas or inside buildings (Al Seadi et al., 2013; Möller, 2015; Plana and Noche, 2016). Lastly, the crop type defines the best suitable periods for digestate application i.e. during the growing season in order to avoid nutrient leakage and specifically to prevent nitrogen losses to waters (Lukehurst et al., 2010; Sommer, 1997). For instance, the Nitrate Directive (European Commission, 1991) recommends member states to settle limited storage time with the aim of reducing nutrient loss and emissions of GHG to the environment. For

these reasons, for European countries a storage capacity of 6 to 9 months is mandatory (Al Seadi et al., 2013).

In the Czech Republic, the storage and use of fertilizers must be in accordance with the Decree No. 377/2013 Coll., on storage and method of use of fertilisers, as amended (Ministry of Agriculture of the Czech Republic, 2013). According this Decree, the untreated digestate and the LPD must be stored in impermeable over-ground or partly recessed tanks or in earth lagoons. Moreover, the inflow of surface water or rainwater into the tanks or lagoons must be avoided, unless it is otherwise specified in the building approval decision. The solid phase of digestate (SPD) must be stored in buildings secured in the same way as buildings for the storage of solid manure without the inflow of surface or precipitation water and must include a collecting reservoir. The farms usually use their own agricultural wastes as a feedstock in the AD processes and also use the digestate as a fertiliser on their own fields. In this case, SPD obtained from anaerobically digested manure must be stored on agricultural fields for a maximum of 24 months prior to its use. Finally, the storage capacity of the digestate must correspond to the actual digestate production.

The storage of digestate is often related to large emissions e.g. odours, greenhouse gasses (GHG) especially if storage cover is not mandatory and the digestate is intensively produced (Alburquerque et al., 2012; Lukehurst et al., 2010; Möller et al., 2008; Sommer, 1997). AD processes lead to an increase of TAN concentrations, the total inorganic carbon, and pH and the reduction of the VFA in digestates (Melamane et al., 2007). Therefore, one of the most representative features of the digestate is its large proportion of the N occurring as inorganic forms (Monlau et al., 2015). This form of N has high ammonia volatilisation potential during storage owing to the digestate's high pH value and high TAN ($NH_3 + NH_4^+$) concentrations (Möller, 2015; Nkoa, 2014; Sommer and Husted, 1995). Furthermore, ammonia volatilisation can be higher if the storage facilities are uncovered, as stored the digestates do not naturally form a surface crust that helps reduce these emissions (Sommer, 1997; Al Saedi and Lukehurst, 2012; Möller, 2015; Perazzolo et al., 2016). What is more, emerging technologies of digestate management include the solid-liquid separation of digestate, which generally, increases N losses (Möller, 2015). After the separation, the majority of N in the form of dissolved ammonia is concentrated in the LPD (Fechter and Kraume, 2016) and therefore high ammonia volatilisation rates during storage of LPD are expected (Perazzolo et. al., 2015).

N losses in the form of ammonia to the atmosphere reduce the nutrient value of the digestate. Moreover, ammonia deposition to land and water can also cause eutrophication of

water courses and other adverse effects thereof, such as losses in biodiversity (Möller, 2015). Additionally, ammonia is a highly reactive gas able to neutralise acids and form ammonium aerosols, developing small diameter particulate matter of 2.5 μm ($PM_{2.5}$) which has notable adverse effects not only on overall air quality but also human and animal health (Erisman and Schaap, 2004). For these reasons, the Act No. 201/2012 Coll., on air protection, as amended (Parliament of the Czech Republic, 2012) defines the stationary sources of air pollution as sources of pollutant release and establish emission limits for such sources. These sources include the BGPs and storage areas for fermentation residues (i.e. digestate). Furthermore, ammonia volatilisation and denitrification following land application of digestate have been reported as a mechanisms for N loss (Möller and Stinner, 2009; Nkoa, 2014). Not only increasing NH_3 emissions but also N_2O emissions to the atmosphere resulted as an intermediate product of denitrification. N_2O is so-called GHG, associated with the stratospheric ozone depletion and therefore has high global warming potential (Petersen et al., 1998).

In summary, digestates with a high initial N fertiliser value decrease through ammonia volatilisation during storage and denitrification upon application to soil. The N losses especially from the LPD represent one of the main challenges related to digestate storage after anaerobic digestion. In this regard, sustainable treatment techniques dedicated to preventing N losses when storing digestate are required to be developed, so that possible GHG emissions will be avoided and the management of the nutrients will be more efficient.

3.5. The processes for the LPD treatment

After the solid-liquid separation, the generated LPD may still contain significant concentrations of TAN, potassium, VFAs, carbonates, phosphorus and suspended solids (Drosg et al., 2015; Masse et al., 2007; Vázquez-Rowe et al., 2015) depending on the AD feedstock, the digester type and the AD process parameters, as well as the separation technology and flocculants added for improved separation (Drosg et al., 2015). The LPD can be reused as a fertiliser or for irrigation without any further treatment (Lukehurst et al., 2010). However, these approaches may be significant sources of ammonia emissions, odours, pathogens and heavy metals, which may restrict its application to the soil (Holm-Nielsen et al., 2009). Depending on the water content of the substrates, the LPD also can be recirculated in order to moisturise very solid substrates going into the AD process (Drosg et al., 2015; Hu et al., 2014). However, accumulation of ammonia nitrogen and other substances may occur after repeated recirculation of the LPD, leading to microbial activity inhibition (Drosg et al., 2015; Hu et al., 2014). Worse still, it can lead to a complete failure of the AD process (Hu et al., 2014). For these reasons and due to the challenges that represent the sustainable and affordable management of the LPD, many treatment techniques of LPD that focused on water re-utilisation, volume reduction, nutrient recovery, and re-utilisation have been developed, some of which are reviewed in the following chapter and their advantages and disadvantages are highlighted at the end of this review in Table 5.

3.5.1. Membrane processes

Solid-liquid separation resulting in the production of a nutrient-rich LPD via separation and concentration of dissolved nutrients (K, P, N) in the LPD, as well as the possibility of obtaining purified water for reuse or safe discharge to the environment, can be achieved by means of membrane technology (Dumitru, 2014; Hjorth et al., 2010). The membrane is a synthetic semipermeable barrier able to transport particles from the feed more easily than other component or components (Mulder, 1996; Davis, 2010). Particles naturally move from areas of high concentration to low concentration. The process is based on the fact that molecules can flow from areas of low concentration to high concentration when external pressure is applied. The pressure difference between the two sides of the membrane will cause the particles to go through the membrane at a steady state (Davis, 2010; Dumitru, 2014). The separation of a two-phase system is schematically represented in Figure 5.

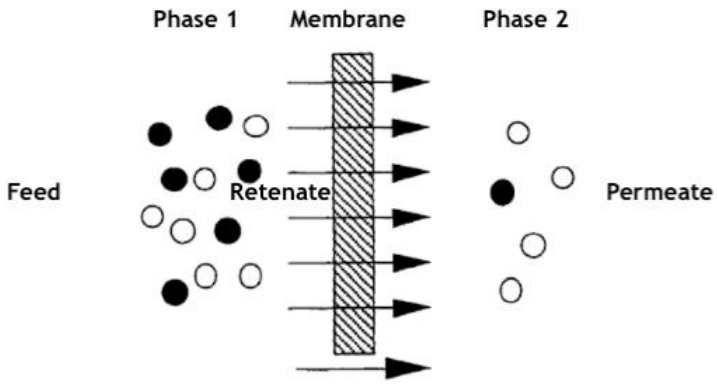

Figure 5. Membrane separation of two phases. Source: Mulder 1996.

As illustrated in Figure 5, the feed stream is separated into two fractions: the fraction that crosses through the membrane (the permeate), and the fraction containing the particles that cannot pass through the membrane, known as the retenate (Mulder, 1996). The structure of the membrane will determine the operating pressures and the type of applications e.g. the separation of very small or microscopic particles, the separation of particles with equal size or shape (Fuchs and Drosg, 2013; Mulder, 1996). There are four types of membrane processes depending on the size of the particles to be separated: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), whose efficiencies are determined by its selectivity and the flow through the membrane (Davis, 2010; Dumitru, 2014). From microfiltration through ultrafiltration, nanofiltration to reverse osmosis, the hydrodynamic resistance increases and also increases the operating pressure. Contrastingly, the size of the particles that are retained decreases (Masse et al., 2007). MF retains solid particles in the range of about 0.1–10 µm. Since the hydrodynamic resistance of these membranes is low, separation efficiency is reached at low hydrostatic pressures (Hjorth et al., 2010, Mulder, 1996). On the other hand, UF separates particles ranging from approximately 0.01 to 0.1 µm (Hjorth et al., 2010) with molecular weights of about 10^4 to more than 10^6, therefore, the structure of the membrane must be denser and in consequence its hydrodynamic resistance must increase. NF separates particles in a range of 0.001–0.01 µm and operates at lower pressures than RO (Masse et al., 2007). RO membranes have a pore size of around 0.0001 µm and can separate low molecular weight particles of identical size. For this purpose, a very dense membrane is needed and, hence, a very high hydrostatic pressure is also required (Mulder, 1996).

In order to fulfil the parameters for an efficient separation, successive connected steps are carried out as depicted in Figure 6 (Al Seadi et al., 2013; Dumitru, 2014). First, enhanced solids removal has to be performed in order to apply membrane technology (Al

Seadi et al., 2013). For that reason, larger particles are removed by mechanical solid-liquid separation or MF and flocculants are added for increased solids removal. Next, UF is used for the removal of all remaining particles and the colloidal dispersed fractions (Masse et al., 2007). After UF, the retenate, which is rich in OM, is generally recycled to the BGP digester in order to reduce its amounts (Al Seadi et al., 2013; Fuchs and Drosg, 2013). On the other hand, the permeate resulting from an ultrafiltration membrane can be composed of considerable amounts of dissolved ions. For that reason RO, and, to a certain degree NF, are used for the removal or recovery of dissolved nutrients and the production of higher quality water (Fuchs and Drosg, 2013; Gerardo et al., 2015; Hjorth et al., 2010). RO is usually used when it is necessary to obtain pure water permeate and is performed in two steps: in the first step, salts and dissolved substances are removed. The permeate of the first step still contains a major fraction of ammonia that is not retained by membranes. Because of this, sulphuric acid is added to the permeate, forming ammonium sulphate ($(NH_4)_2SO_4$) that can be subsequently retained by the membrane in the second step (Al Seadi et al., 2013; Fechter and Kraume, 2016). The permeate of the second step is pure water that can be reused or discharged to surrounding water streams and the retenate can be reintroduced to the first step of RO (Fechter and Kraume, 2016; Rehl and Müller, 2011).

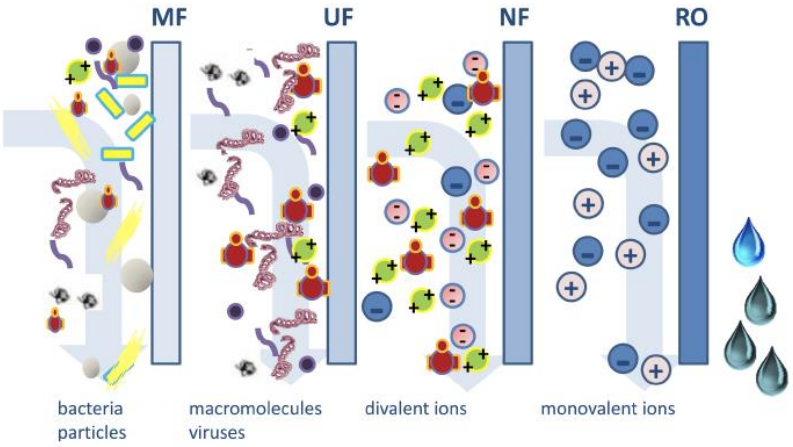

Figure 6. Membrane technology operations. Source: Ortiz et al., 2015.

The benefits of membrane technology for the recovery or removal of nutrients from LPD rests on the fact that pure water can be obtained after a highly selective separation and that little or no chemicals are used (Gerardo et al., 2015). One of the downsides to the membrane technology is that the costs of the membranes can be significantly high (Sheets et al., 2015). Moreover, the main shortcomings of MF and UF are that the pores of the membrane may clog by the adhesion of particles (Hjorth et al., 2010). Furthermore, the flow through the membrane can also be reduced by bacterial growth on the surface of the

membrane (Al Seadi et al., 2013; Hjorth et al., 2010). Therefore, a developed separation technique should be pre-installed (Hjorth et al., 2010). In addition, the energy demand of ultrafiltration is increased by higher concentrations of solids because this thickens the liquid and leads to a higher-pressure loss (Hjorth et al., 2010). Likewise, the main disadvantages of NF and RO are the high costs of energy consumption (16–25 kWh per m^3 treated) related to the higher operating pressure (Fechter and Kraume, 2016) and there is also a risk of fouling during the process and therefore regular cleaning needs to be performed (Hjorth et al., 2010). What is more, NF and RO membranes are generally fabricated from cellulose acetate or polyamide materials (Nguyen et al., 2012). While polyamide membranes are not subject to biodegradation and have less pH operating requirements, cellulose-based membranes have been found to be more susceptible to biodegradation and need a residual of chlorine as protection from the adverse effects of biofouling on the membrane (Nguyen et al., 2012). Cellulose membranes are also extremely sensitive to changes in pH values and are stable only within a narrow pH range of 4 to 8 (Nguyen et al., 2012).

3.5.2. Ammonia stripping

In the LPD and digestate processing, the ammonia stripping is used to remove or recover nitrogen in the form ammonia from the LPD (Drosg et al., 2015; Fechter and Kraume, 2016; Sheets et al., 2015). The stripping of ammonia is a process whereby volatile substances are converted from liquid to gas. During this process, the phase change of NH_3 from liquid to gaseous phase is accomplished when the LPD comes into contact with air or steam containing limited or no NH_3. The process is influenced by the pH, temperature, air/liquid ratio, and pressure (Sheets et al., 2015). The volatility of ammonia increases with increasing pH and temperature (O'Farrell et al., 1972; Killham, 1994); therefore, high pH values (10–11) are needed for an efficient stripping process as well as high temperatures (around 70 °C) (Guštin and Marišek-Logar, 2011; O'Farrell et al., 1972).

Air stripping and vapour stripping are two main processes applied for ammonia stripping. In air stripping, the LPD is heated and the pH value is increased by degasification of CO_2 as a pre-treatment or during the process by the addition of alkali (generally sodium hydroxide) (Drosg et al., 2015; Fechter and Kraume, 2016). Once the sodium hydroxide is added, the NH_3/NH_4^+ equilibrium is moved toward the NH_3 increasing its volatility. Subsequently, the heated digestate is entered into a stripping column where the extraction of the ammonia from the liquid is performed using stripping gas steam. Finally, the nitrogen-reduced LPD flows back into the digester or to a storage tank while the NH_3 is recovered from

the gas phase using a sulphuric acid scrubber that forms ammonium sulphate ($(NH_4)_2SO_4$) which can be used as fertiliser (Jiang et al., 2014). The cleaned gas can afterwards be reused in the stripping column (Al Seadi et al., 2013; Drosg et al., 2015; Fechter and Kraume, 2016). A schematic representation of air stripping is given in Figure 7. Unlike air stripping, a higher operating temperature is required in vapour stripping to produce the vapour and the final scrubber is not needed. The ammonia is directly condensed with the vapour and ammonia-water with a concentration up to 25 - 35 % is produced (Drosg et al., 2015).

One of the main advantages of ammonia stripping is the acquisition of a valuable commercial-standardised fertiliser product that can be used to enrich other digestate fractions in digestate processing to a standardised nitrogen concentration increasing their marketability (Al Seadi et al., 2013; Drosg et al., 2015; Jiang et al., 2014). On the other hand, the main disadvantages of ammonia stripping are the high costs related to energy for heating and compression (the process efficiency is decreased at low temperatures) and the requirement of chemicals for pH adjustment (Jiang et al., 2014). In addition, there is a risk of foaming (Jiang et al., 2014) and residual solids can clog the ammonia stripping columns (Drosg et al., 2015).

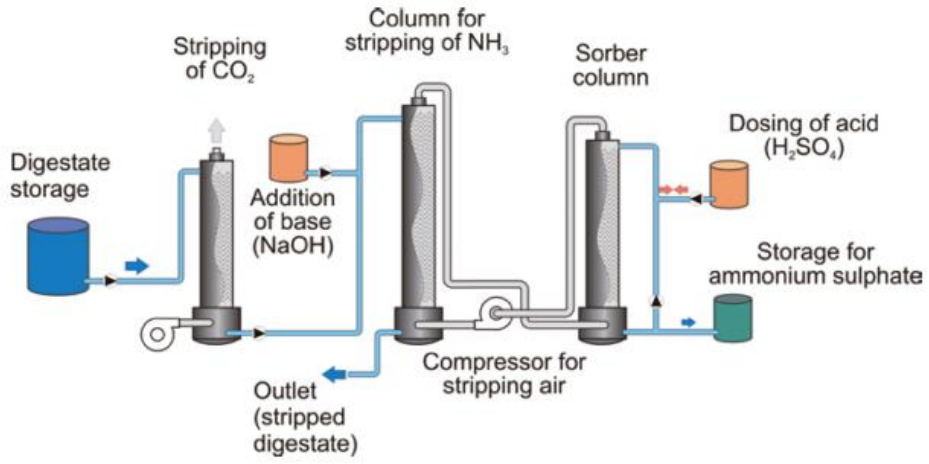

Figure 7. Schematic representation of ammonia air stripping with CO2 removal and ammonia recovery. Source: Fuchs and Drosg, 2010.

3.5.3. Struvite crystallisation

The struvite crystallisation technique has been applied to remove N and P from wastewaters (Harrison et al., 2011) mainly because their discharge to natural water bodies often causes severe environmental problems such as eutrophication (Hidalgo et al., 2015). However, P and N are important nutrients beneficial to agricultural development (Hidalgo et al., 2015). Moreover, P is a limited natural resource while the mineable phosphate rocks used

for P fertiliser production are known to be exhausted within the next 100 years (Shu et al., 2006). In recent years, not only the protection of water resources but also the recovery of N a P from recoverable sources such as the LPD has been pursued (Sheets et al., 2015; Uludag-Demirer et al., 2005). For these reasons, removal has been shifted to the recovery of nutrients from the LPD in order to improve the sustainability of agricultural activities (Uludag-Demirer et al., 2005). The crystallisation of N and P in the form of struvite ($MgNH_4PO_4.6H_2O$), which is an effective slow-release fertiliser (Harrison et al., 2011; Uludag-Demirer et al., 2005), represents the possibility of the recycling of P and N from the LPD (von Münch and Barr, 2001). The crystallization of struvite occurs under supersaturated conditions according to the following simplified equation (Eq. 3.1) (Uludag-Demirer et al., 2005):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \qquad \text{(Eq. 3.1)}$$

Struvite is a naturally occurring white crystalline solid that is highly soluble in water at acidic pH and less soluble in water at alkaline pH (Harrison et al., 2011; von Münch and Barr, 2001). With increasing pH, the concentration of P also increases while the concentrations of Mg^{2+} and NH_4^+ decrease, producing an optimum pH for struvite formation (von Münch and Barr, 2001). Therefore, the most important parameters influencing the struvite formation are the increasing operational pH values along with the adopted molar ratios of magnesium, ammonium and phosphate (Song et al., 2011; von Münch and Barr, 2001). Moreover, the growth rate, crystal size, and the supersaturation are also other important parameters (Harrison et al., 2011; Sheets et al., 2015). For these reasons, studies have focused on the optimisation of the aforementioned parameters, as well as the nucleation (crystal birth) and crystal growth using computer models such as MINTEQA2 for understanding the behaviour of phosphate crystallization (Harrison et al., 2011).

However, the recovery of nutrients by struvite crystallization from LPD has been reported to be difficult (Sheets et al., 2015). The LPD does not have considerable amounts of dissolved Mg and in some cases the content of dissolved phosphate can be low also for proper struvite crystallization. Consequently, not only external Mg^{2+} ion sources such as magnesium chloride ($MgCl_2$), magnesium oxide (MgO), and magnesium hydroxide ($Mg(OH)_2$), but also external sources of phosphate. May be required to induce struvite crystallization and therefore operational costs increase (Sheets et al., 2015; Song et al., 2011). Furthermore, LDP obtained from digested cow manure may have also a high concentration of calcium (Ca) (Martí et al., 2010). Ca^{2+} competes with Mg^{2+} and leads to the formation of calcium phosphate precipitate instead of the formation of struvite (Hidalgo et al., 2015; Martí et al., 2010).

3.5.4. Algae cultivation

The LPD from agricultural biogas plants is rich in micro and macronutrients valuable as crop fertiliser (Nkoa, 2014). Likewise, it can be used as a nutrient source for the growth of lipid-rich algae biomass (Bjornsson et al., 2013; Monlau et al., 2015; Sheets et al., 2015; Veronesiv et al., 2015). In recent years, the interest for the use of LPD in algal cultivation has been driven by the fact that the costs of nitrogen and phosphorus fertilisers have considerably increased, turning algal biomass yield costly (Bjornsson et al., 2013; Veronesiv et al., 2017). Therefore, the re-utilisation of other liquid streams such as the LPD as sources of nutrients for algal cultivation became a very attractive alternative (Bjornsson et al., 2013). The energy potential of algae has been at the centre of attention. For that reason, studies focused interest on the improvement of the intracellular lipid content of algae, the extraction of the oils, and the subsequent conversion to biodiesel (Bjornsson et al., 2013; Prajapati et al., 2014). Therefore, the use of the LPD as a source of nutrients for algal growth can be considered as a viable alternative energy production pathway (Monlau et al., 2015). Moreover, the high removal and recovery efficiency of major nutrients such as P and N using algae have been demonstrated making it potentially suitable for digestate and LPD treatment also (Franchino et al., 2013).

However, there are several factors that lead to important limitations in the development of this technology (Marazzi et al., 2017; Monlau et al., 2015; Sheets et al., 2015). Algae are autotrophic microorganisms that have the ability to synthesise biomass compounds (i.e. lipids, proteins, carbohydrate, and pigments), and that are strongly dependent on light energy exposure, temperature, and inorganic nutrients, namely CO_2, N and P (Sheets et al., 2015). The LPD is characterized by a high concentration of total suspended solids that cause high turbidity (the colour of the LPD) limiting light penetration for adequate algae growth and survival (Marazzi et al., 2017; Monlau et al., 2015; Sheets et al., 2015). Moreover, the LPD is also characterized by a high concentration of NH_3 that could be inhibitory, or even toxic to algae (Marazzi et al., 2017; Monlau et al., 2015; Veronesiv et al., 2015). Furthermore, bacterial contamination may occur when using LPD as culturing media that can lead to either positive (i.e. symbiotic) or negative interactions, such as competition for nutrients that can negatively affect the algae production rate (Monlau et al., 2015; Sheets et al., 2015). In addition, the algal biomass composition can also be negatively affected by the nutrient availability favouring the synthesis of proteins instead of lipids and sugars (Monlau et al., 2015). Therefore, some pre-treatment approaches as potential solutions have been suggested

to improve the LPD characteristics. The pre-treatments commonly used to reduce the turbidity level and simultaneously to decrease of NH_3 concentration include dilution with freshwater or deionized water (Bjornsson et al., 2013), filtration (Veronesiv et al., 2017), solid/liquid separation, and the use of activated carbon (AC) (Marazzi et al., 2017). Nonetheless, these pre-treatments may increase costs, making full-scale algal cultivation challenging (Monlau et al., 2015; Sheets et al., 2015).

3.5.5. Nitrification for nitrogen recovery

Nitrification followed by denitrification is one of the most common methods used for the removal of nitrogen from wastewaters. Within this process, chemically bound nitrogen present in wastewaters is converted into N_2 which is then released (Reeves, 1972). However, a novel approach is the nutrient recycling and recovery, especially from residual streams with great potential for the recovery of nutrients such as LPD (Botheju et al., 2010). Nitrification is a sequential biochemical process wherein TAN is oxidised into nitrite (NO_2^-) and NO_2^- into nitrate (NO_3^-), with molecular oxygen as electron acceptor. Two separate and distinctive steps take place in nitrification and are illustrated in Figure 8. First, the oxidation of TAN to NO_2^- is accomplished by ammonia oxidising bacteria (AOB) such as *Nitrosomonas, Nitrosospira* or *Nitrosocystis*. Next, NO_2^- is oxidised into NO_3^- by nitrite oxidising bacteria (NOB), often *Nitrobacter*, *Nitrospira* or *Nitrocystis* (Anthonisen et al., 1976; Gerardi, 2002). These bacterial groups are both chemoautotrophic gram-negative bacteria that use CO_2 as a source of carbon for the synthesis of cellular material and energy production (Gerardi, 2002; Reeves, 1972). They are also strict aerobes and therefore require molecular oxygen in order to oxidise the substrate (Gerardi, 2002).

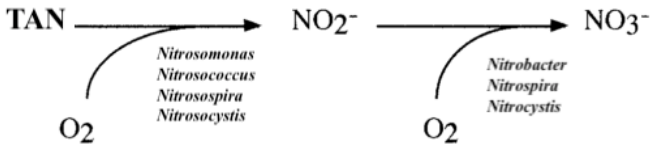

Figure 8. Oxidation of TAN and oxidation of NO_2^-. Source: Gerardi, 2002.

Nitrification occur according to the following simplified equations (Eq. 3.2 and 3.3):

$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+$ or $NH_3 + 1.5O_2 + NO_2^- + H_2O + H^+$ (Eq. 3.2)

$NO_2- + 0.5O_2 \rightarrow NO_3^-$ (Eq. 3.3)

The LPD contains significant amounts of TAN that were produced by the degradation of N_{org} during AD (Melamane et al., 2007). TAN consists of two forms: NH_4+ and NH_3, whose quantities in the LPD are dependent on pH values and temperature (Botheju et al.,

2010). The LPD has a pH level that ranges from 7.5 to 8.5 and generally, at above-neutral pH range, a relatively high proportion of ammonia is present in unionised form as depicted in Figure 9 (Botheju et al., 2010; Gay and Knowlton, 2009). Therefore, either when the LPD is stored or after land application, there is a risk of ammonia volatilisation (Botheju et al., 2010; Švehla et al., 2017). Moreover, the use of LPD as liquid fertiliser rich in NH_3 can lead to toxicity in many plant species (Takemura et al., 2016; Teglia et al., 2011b) and soil acidification due to proton release, which naturally occur in soils through the microbial process of nitrification (Whelan et al. 2010). During nitrification the pH tends to decrease due to H^+ production, and with this decrease of pH value the NH_4^+/NH_3 move towards the NH_4^+ side (Anthonisen et al., 1976) thereby limiting the loss of nitrogen due to volatilisation of NH_3 during storage or land application of LPD (Botheju et al., 2010). For these reasons, nitrification of the LPD seems to be feasible in order to obtain a product rich in NO_3^- which is characterised by being more stable in the soil and by being a highly mobile nitrogen source for plants (Botheju et al., 2010; Švehla et al., 2017; Takemura et al., 2016). Furthermore, Botheju et al. (2010) observed decreased amounts of heavy metals in the nitrified LPD, which enhances the LPD quality, due to the presence of considerable amounts of sulphur in the LPD that contributed to the metal precipitation forming $PbSO_4$, or $Cr_2(SO_4)_3$) under aerobic conditions.

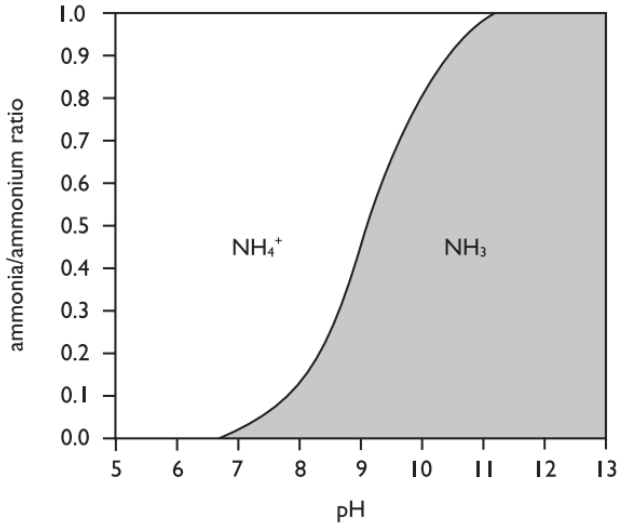

Figure 9. The dependence of the NH_4^+/ NH_3 ratio as a function of pH. Source: Gay and Knowlton, 2009.

Nevertheless, nitrification of the TAN in the LPD may cause significantly increased nitrate leaching from agricultural soils since NO_3^- is soluble and mobile and susceptible to transport to groundwater (Haraldsen et al., 2011). On the other hand, several factors have

been identified that selectively inhibit or limit bacterial growth and that therefore complicates the nitrification process in the environment of the LPD. These factors include high TAN concentration and high HNO_2 concentration which may accumulate during the nitrification process (Anthonisen et al., 1976; Gerardi, 2002). Generally, AOB is less sensitive to the aforementioned factors than NOB, hence leading to the production of an end product of nitrification of LPD where nitrates are not dominant (Anthonisen et al., 1976). Moreover, heterotrophic denitrification may occur during long-term storage of a nitrified LPD which may lead not only to the loss of nitrogen in the form of N_2 but also may lead to an increase of N_2O emissions that result as an intermediate product of denitrification. Additionally, the high costs related to energy consumption for the supply of air into the reactor must be taken into consideration (Švehla et al., 2017).

3.5.6. Thermal thickening by vacuum evaporation

After the solid/liquid separation, the obtained LPD can be further thickened by vacuum evaporation (Fechter and Kraume, 2016). Vacuum evaporation is performed at a pressure lower than atmospheric pressure, hence the boiling point of water is also much lower than at atmospheric pressure (Chiumenti et al., 2013), thereby resulting in energy savings (Fechter and Kraume, 2016). Figure 10 shows the relationship between boiling point and pressure for water.

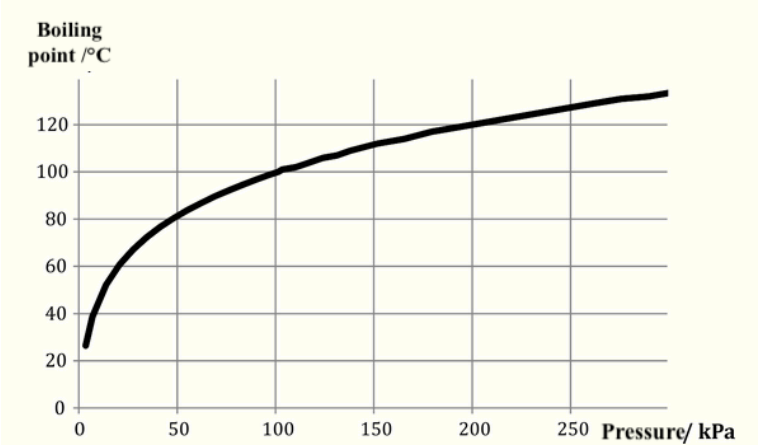

Figure 10. Dependence of the boiling point of water on pressure. Source: http://fyzikalnipokusy.cz/

Once the LPD enters the evaporator, the boiling point is reduced to around 60 °C due to the influence of the applied vacuum (approximately 30 kPa) (Fechter and Kraume, 2016). Evaporation of water and consequent concentration of the LPD occurs. By cooling, the evaporated water is afterwards condensed and collected in the condensate tank (Chiumenti et

al., 2013). The condensed vapour is called distillate or condensate, while the remaining LPD represents the thickened or concentrated LPD (Chiumenti et al., 2013). Vacuum evaporation of the LPD is a technique used to produce a nutrient-rich thickened LPD, to recover a distillate with low concentrations of nutrients, and to significantly reduce the LPD's volume (Bonmatí et al., 2003; Bonmatí and Flotats 2003; Lebuf et al., 2012; Al Seadi et al., 2013; Vondra et al., 2016). The considerable reduction in the volume of the LPD (Chiumenti et al., 2013; Heviánková et al., 2014; Vondra et al., 2016), which allows the reduction of costs and fossil fuel consumption needed for its transportation, is one of the main advantages (Chiumenti et al., 2013; Li et al., 2016; Vondra et al., 2016). Moreover, within this process, is possible to obtain a thickened LPD with higher nutrient concentration and therefore higher fertiliser potential than the untreated LPD (Chiumenti et al., 2013; Heviánková et al., 2014; Li et al., 2016) as well as a distillate with low $N\text{-}NH_4^+$ concentrations that can be used for irrigation (Heviánková et al., 2014) or as a process liquid that can be used in the BGPs for the dilution of feedstocks (Míchal et al., 2016). Another benefit of using vacuum evaporation is that emissions from the process are reduced since it occurs in enclosed systems (Bonmatí and Flotats, 2003), and that total inactivation of pathogenic bacteria may occur under such high operational temperatures (Kuusik et al., 2017).

On the other hand, the adjustment of the pH values of the LDP to slightly acidic (6 or below) is a necessary step in order to limit eventual stripping of NH_3 during evaporation (Chiumenti et al., 2013). Acidification ensures that the NH_3 remains in the thickened LPD and limits its transfer to the distillate (Chiumenti et al., 2013; Lebuf et al., 2012). The pH values can be easily adjusted by the addition of mineral acids (Míchal et al., 2016). However, considerable amounts of chemicals are needed which involves high costs (Al Seadi et al., 2013). Alternatively, the biological pre-treatment of LPD by nitrification can be used that not only decreases the pH values and minimises the nitrite production, but can also be applied in order to successfully limit the leakage of ammonia into the air during evaporation of the LPD (Švehla et al., 2017). Another possible downside of this technology can be its high heat energy requirement (Míchal et al., 2016; Vondra et al., 2016) that may vary depending on the evaporator type (Vondra et al. 2017). Nevertheless, BGPs generally uses only 20-40 % of the heat that is produced in the cogeneration units and the remaining heat becomes waste heat which is not used in any way (Vondra et al., 2016). Therefore, the evaporation of the LPD can be performed with little or no costs while simultaneously becoming an interesting approach to re-using waste heat to give the BGPs a productivity boost (Al Seadi et al., 2013; Fechter and Kraume, 2016; Vondra et al., 2016).

Table 5. Comparison of technologies for the treatment of LPD. Modified and extended from Sheets et al., 2015.

Treatment process	Advantages	Disadvantages
Membrane technology	Obtainment of pure water	High membrane costs
	Highly selective separation	High energy demands
	Little or no use of chemicals	Need for pH control
	NH_4^+ in retentate can be used as fertiliser, dissolved nutrients (K, P, N) recovered in retentate	Risk of biofouling
Ammonia stripping	High NH_3 removal efficiencies	High energy demands for heating and compression
	The resulted product $(NH_4)_2SO_4$) can be used as fertiliser	Need for pH control
		Need for chemicals for pH adjustment
		Risk of foaming and clogging
Struvite crystallisation	High NH_4^+ and dissolved P removal efficiencies	Agricultural digestates have low dissolved Mg and P
	Produces a solid fertiliser	Need for external Mg and P sources
Algae cultivation	Reuse of N	Microbial contamination
	Biofuel production	High turbidity of the LPD
		High concentration of NH_3 could be toxic to algae
		High costs of biomass processing
		Additional costs related to LPD pre-treatment and post-treatment
Nitrification for nitrogen recovery	Minimisation of NH_3 volatilisation during storage and land application	Risk of increased nitrate leaching from agricultural soils
	Production of NO_3^- that is more stable in the soil and highly mobile nitrogen source for plants	Complications related to bacterial growth inhibition
		Risk of N losses and N_2O emissions during storage
		High costs of energy
	Decreased amounts of heavy metals in the nitrified LPD	Need for chemicals for pH adjustment
Vacuum evaporation	Volume reduction and the reduction of costs and fossil fuel consumption	High heat energy requirement
	Obtainment of pure water	
	Re-use of the BGP's waste heat	
	Produces a high-nutrient fertiliser	Need for chemicals for pH adjustment

The combination of nitrification and subsequent thermal thickening by vacuum evaporation was already proposed by Botheju et al. (2010) and Švehla et al. (2017) but has not been widely tested yet. This diploma thesis aims to go one step further by carrying out the practical part of the mentioned theoretical proposal. Nitrification can provide a product with reduced pH resulting in chemical conditions unfavourable for NH_3 volatilisation during evaporation of LPD so that no chemical will be needed for pH adjustment. Additionally, the heat energy requirements of vacuum evaporation can be fulfilled by re-using waste heat from BGPs thereby turning this disadvantage into something beneficial.

Nonetheless, the nitrified LPD is rich in a nitrogen form (NO_3^-) which is considered to be more stable than TAN, in terms of volatilisation. For that reason, this diploma thesis also wants to demonstrate that N losses are less intensive when nitrified LPD is stored for a long period than when untreated LPD is stored for a long period of time.

4. Materials and methods

4.1. Source of the LPD

The experiments described in this diploma thesis were run using LPD obtained from a biogas plant (Rebios s. r. o., Vyškov, Czech Republic) that uses wet fermentation technology and is operated at mesophilic temperature process. The biogas plant is configured as a two-stage system with three horizontal digesters with a capacity of 80 m^3 each that operates as a first fermentation stage and a 2470 m^3 conventional digester with a 1200 m^3 double-skinned gas holder installed as a second stage. It specializes in the treatment of separated biodegradable waste including separate collected organic leftovers, fruit and vegetable wastes, and grass clippings. Moreover, its substrates also include gastro waste such as animal by-products generated in restaurants, canteens, and other raw materials like expired food from supermarkets, used frying oils, etc. to produce electricity and heat.

Table 6 summarises the composition of the LPD used as the feed source for the nitrification and volatilisation tests (see chapter 4.2. and 4.3.) described in this thesis.

Table 6. Characteristics of the untreated LPD.

Parameter (Units)	**Value**
pH	8.1 ± 0.1
COD (mg/L)	9080 ± 1240
TAN (mg/L)	2470 ± 190
N_{tot} (mg/L)	2780 ± 230
TS (mg/L)	3130 ± 370
VS (mg/L)	2780 ± 320
Ca (mg/L)	264 ± 15
K (mg/L)	3730 ± 150
Mg (mg/L)	18.4 ± 4.9
P (mg/L)	269 ± 9
S (mg/L)	399 ± 21

4.2. Nitrification

As depicted in Figure 11, the nitrification of raw LPD was performed in a 5 L continuously stirred tank reactor (CSTR) aerated with coarse bubble diffusers (1). The LPD was continuously fed into the reactor using a peristaltic pump (2). The activated sludge from a wastewater treatment plant (Prague central wastewater treatment plant, Czech Republic) was used as inoculum. Via peristaltic pump, the activated sludge was recirculated from a 1 L sedimentation tank into the reactor (3). The reactor was operated under laboratory

temperatures (25.0 ± 2.0 °C) and the level of dissolved oxygen in the reactor ranged from 3.0 and 7.4 mg/L. The pH level was controlled by feeding NaOH (2.5 mol/L) solution using a peristaltic pump (4) to maintain the pH values at 6 during the first 157 days and at 5.5 from day 158 until day 184. To bring the pH to the desired values a GRYF sensor PCL 321 XB2 and GRYF MAGIC XBC measuring and controlling system (GRYF HB, Czech Republic) were employed.

The samples from the influent and effluent were taken twice a week to be centrifuged at 9500 rpm for 12 minutes by a Rotina 420 centrifuge (Andreas Hettich GmbH & Co.KG, Germany). Following that, to measure the TAN, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ and chemical oxygen demand (COD), the samples were diluted to the proper dilution ratio using demineralised water. Furthermore, the average values and standard deviations were calculated by measuring three times the Cd, Pb, Hg, As, Cr, Cu, Mo, Ni and Zn concentrations of the influent and effluent samples during the operation of the reactor.

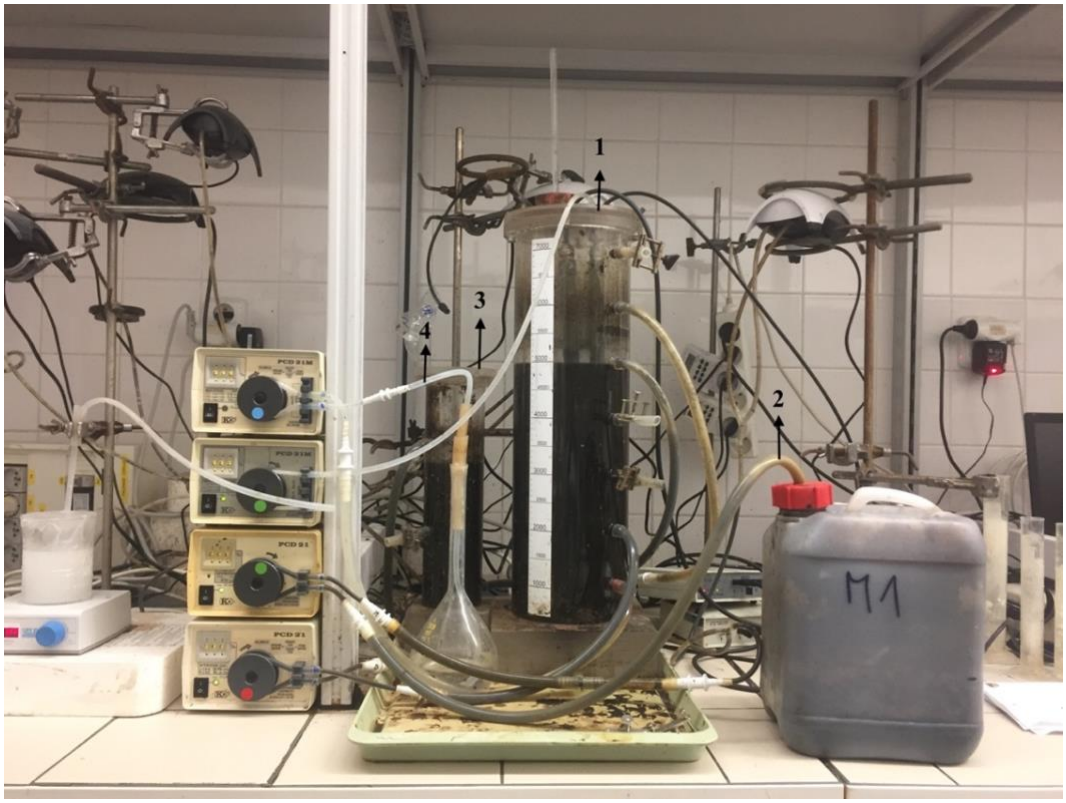

Figure 11. Continuous Stirred Tank Reactor (CSTR). Source: Author.

The results of the main measurements are summarized in Table 17 (situated in the chapter Enclosures). Table 7 shows the mean values of the measured parameters and Table 8 the risk element contents of the nitrified LPD used as the source for the denitrification tests and thermal thickening by vacuum evaporation (see chapter 4.4. and 4.5.) described in this thesis.

Table 7. Characteristics of the nitrified LPD.

Parameter (Units)	Value
COD_{Total} (mg/L)	4868.3 ± 822.1
$COD_{Soluble}$ (mg/L)	3193.3 ± 550.5
TAN (mg/L)	14.4 ± 8.6
NO_2^- (mg/L)	1.4 ± 1.1
NO_3^- (mg/L)	5444 ± 262.4
TS (mg/L)	49.1 ± 5.3
DS (mg/L)	49.7 ± 5.7
SS (mg/L)	0.6 ± 1.1
VS (mg/L)	5.1 ± 0.9
pH	6.0 ± 0.4

Table 8. Risk element contents of the LPD before and after the nitrification and limit values for risk element contents established by the Czech legislation (Ministry of Agriculture of the Czech Republic, 2014)

Element	Untreated LPD	Nitrified LPD	Czech Republic
	Concentration mg/kg DM		
Cd	0.13 ± 0.06	0.11 ± 0.04	2
Pb	2.54 ± 1.24	2.47 ± 1.54	100
Hg	0.56 ± 0.33	0.57 ± 0.04	1.0
As	1.95 ± 0.39	2.02 ± 0.73	20
Cr	3.70 ± 1.63	4.18 ± 3.17	100
Cu	39.93 ± 18.93	34.93 ± 11.87	250
Mo	1.62 ± 0.65	1.46 ± 0.48	20
Ni	7.72 ± 3.26	7.17 ± 2.98	50
Zn	100.52 ± 58.27	88.38 ± 41.61	1200

4.3. Volatilisation tests

Volatilisation simulation tests were set up to ascertain the average potential for ammonia losses of untreated LPD during storage by the comparison with the nitrified LPD. For this purpose, four glass beakers were filled with 750 mL of untreated LPD, following which the beakers were sealed using aluminium foils with holes. Different temperature

storage conditions (i.e. winter and summer) were simulated by incubating two of the four beakers (V1 and V2) at room temperature (25.0 ± 2.0 °C), one of which (V2) was moderately and continuously stirred with a stirring speed of 100 rpm (revolutions per minute) using a magnetic micro-stirrer (Velp Scientifica, Italy) to verify the behaviour of the sample under moderate wind conditions. The beakers V3 and V4 were stored in a thermostatic cabinet (Lovibond, Germany) at 10.0 ± 1.0 °C with V4 being constantly stirred at 100 rpm by a magnetic micro-stirrer (Velp Scientifica, Italy) as shown in Figure 12.

Samples from each beaker were analysed at a minimum of two-week intervals in the course of the experiment. The aluminium foil was removed from the beakers to measure the pH, dissolved oxygen (DO) and temperature. The difference in volume caused by natural evaporation was compensated by the addition of demineralised water in each model. Subsequently, the samples from the beakers V1 and V3 were mixed for 1 min and then all the samples were taken for analysis. Following that step, the level of remaining LPD was marked to compensate the potential volume reduction caused by natural evaporation in the following measurement and then the beaker was resealed with aluminium foil. In the next step, the samples were centrifuged at 9500 rpm for 12 minutes by means of a Rotina 420 centrifuge (Andreas Hettich GmbH & Co.KG, Germany). After being centrifuged, the samples were diluted to the suitable dilution ratio in accordance with the calibration range of the given assay and the current concentration using demineralised water. Finally, the TAN, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ concentrations and the COD were measured.

Figure 12. Volatilisation tests. V1, V2 (left), V3 and V4 (right). Source: Author.

4.4. Denitrification tests

The denitrification process during the storage of nitrified LPD were carried out using four glass beakers each filled with 750-mL nitrified LPD and sealed with aluminium foil. In order to simulate different storage conditions (i.e. summer and winter respectively), two of the four beakers (D1 and D2) were incubated at room temperature (25.0 ± 2.0 °C), one of which (D2) was moderately and continuously stirred at 100 rpm with a magnetic micro-stirrer (RH basic 2, IKA, Selangor, Malaysia) in order to simulate air–sample interaction under moderate wind conditions. The remaining beakers (D3 and D4) were stored at 10.0 ± 1.0 °C in a thermostatic cabinet (Lovibond, Germany) with D4 being constantly stirred at 100 rpm by a Velp Scientifica magnetic micro-stirrer (Velp Scientifica, Italy) as depicted in Figure 13.

Analyses were performed at a minimum of two-week intervals during the experimental period. From day 184 D1 and D2 were analysed at monthly intervals and D3 and D4 were analysed until the 83rd day storage. Analyses of D3 and D4 were carried out by Behnad Ahmari, Mr.sc. MSc.

For the purpose of taking samples, the aluminium foil was removed from the beakers and subsequently pH, dissolved oxygen (DO) and temperature were measured. Before the samples were taken, the difference in volume caused by natural evaporation was compensated for by the addition of demineralised water in each model. Subsequently, the samples from the beakers D1 and D3 were mixed for 1 min and then all the samples were taken for analysis. Once the samples were taken, the level of remaining nitrified LPD was marked to compensate the potential volume reduction caused by natural evaporation in the following measurement and then the beaker was resealed with aluminium foil. Afterwards, the samples were centrifuged at 9500 rpm for 12 minutes by means of a Rotina 420 centrifuge (Andreas Hettich GmbH & Co.KG, Germany). Finally, the samples were diluted to the appropriate dilution ratio using demineralised water and the TAN, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$ concentrations, and the COD were measured. These analyses allow assessment of nitrogen losses in different storage conditions.

Figure 13. Denitrification tests. D1, D2 (left), D3 and D4 (right). Source: Author.

4.5. Vacuum evaporation

The vacuum evaporation of the nitrified LPD was conducted using a BÜCHI rotavapor R-215 (BÜCHI, France) as illustrated in Figure 14. First, the heating water bath was set to 95 °C (BÜCHI heating bath B-491, France) to encourage the evaporation (1). Second, 200 mL of nitrified LPD and 10-12 drops of defoamer, which was used to avoid foaming and possible contamination of the distillate, were poured into a round bottom flask (boiling flask) for connection to the rotor-vac apparatus (2). Third, the boiling flask was lowered into the rotavapor heating bath using an elevation rail that allows sliding the entire system up and down to put it into or raise it out of the bath (3). The boiling flask was rotated continuously at 40 rpm, at a temperature that was set in accordance with the boiling point of water at certain vacuum level (65 ± 5 °C at 350±40 mbar pressure) (4) by means of a BÜCHI vacuum controller V-850 and vacuum pump V-700 (BÜCHI, France). Rotation serves two purposes: first, a thin film of solvent (distillate) forms on the inner surface of the boiling flask, resulting in a higher rate of evaporation; second, it ensures homogenous mixing of the sample, which reduces the risk of bumping or flash boiling which can cause solvent contamination or otherwise adversely affect the rotary evaporation. At that point the sample was under reduced pressure which means that the boiling points of all the volatile materials from the sample were reduced and went into the vapour phase. Afterwards, the LPD vapour flowed at high speed into the condenser (5). At that moment, the energy inside the solvent vapour was transferred to the cooling medium (i.e. tap water) and the distillate condensed. Subsequently, the

condensed distillate then flowed by force of gravity into the receiving flask (6). Finally, after the vacuum was unsealed the flasks were removed. The process lasted approximately 30 minutes per sample, in which around 50 % (approximately 100 mL) of the nitrified LPD volume was evaporated. After the evaporation thickened LPD and distillate were obtained (Figure 15) and the resulting volumes were measured using a graduated cylinder to assess potential volume losses.

Next, the pH and electrical conductivity (mS/cm) were measured for the nitrified LPD, the thickened LPD, and distillate. Penultimately, the nitrified LPD and the thickened LPD were centrifuged at 9500 rpm for 12 minutes using a Rotina 420 centrifuge (Andreas Hettich GmbH & Co.KG, Germany). Then, the nitrified LPD, the thickened LPD and the distillate were diluted using demineralised water and the concentrations of TAN, N-NO_2^-, N-NO_3^- and the COD were determined for all the samples. The concentrations of VFA were measured only for sample No. 1.

Finally, the mass (i.e., weight) of each parameter (COD, TAN, NO_3^-, NO_2^-) in the nitrified LPD, the thickened LPD and distillate was calculated using Eq. 4.1:

$$M_N, M_T, M_D\ (mg) = \frac{V_S\ x\ \rho_{ps}}{1000} \qquad \text{(Eq. 4.1)}$$

where M_N, M_T, and M_D (mg) are the weight of a given parameter in the nitrified LPD, thickened LPD and distillate, respectively. V_S is the total volume of a particular stream (the nitrified LPD, the resulted volume after the vacuum evaporation for the thickened LPD and distillate, respectively for each sample), ρ_{ps} (mg/L) is the measured concentration, and coefficient 1000 was used to convert mL to L.

The percentage distribution of each parameter (COD, TAN, NO_3^-, NO_2^-, VFAs) concentrated in the thickened LPD (% concentrated) and transferred into the distillate (% transferred) after the vacuum evaporation was calculated for each sample using the following Eq. 4.2 and Eq. 4.3:

$$\%_{concentrated}: \frac{M_T}{M_N}\ x\ 100 \qquad \text{(Eq. 4.2)}$$

$$\%_{transferred}: \frac{M_D}{M_N}\ x\ 100 \qquad \text{(Eq. 4.3)}$$

Figure 14.BÜCHI rotavapor R-215. Source: Author

Figure 15. Thickened LPD (right) and distillate (left) obtained from the vacuum evaporation of 200 mL nitrified LPD. Source: Author.

4.6. Analytical methods

The methods were performed conforming to standard guidelines established by Horáková et al. (2003) in the laboratories of the Department of Agro-Environmental Chemistry and Plant Nutrition of the Czech University of Life Sciences Prague.

4.6.1. Determination of inorganic forms of nitrogen

To evaluate the nitrification and denitrification progresses, as well as the nitrified LPD, the thickened LPD and distillate compositions, the measurement of various nitrogen forms ($N\text{-}NH_4^+$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$) was determined by spectrophotometry on a HACH DR/4000V spectrophotometer (Hach-Lange, Germany).

4.6.1.1. Determination of TAN concentrations

The TAN concentrations were estimated colorimetrically using the indophenol method in conformity with Horáková et al. (2003) standards procedures. This method detects both $N\text{-}NH_4^+$ and NH_3 forms of N and is based on the reaction of ammonia and salicylate that in the presence of sodium dichloroisocyanurate forms a green-coloured complex under alkaline pH conditions. The samples were spectrophotometrically measured using a 10-mm square cuvette at 655 nm wavelength.

4.6.1.2. Determination of $N\text{-}NO_2^-$ concentrations

Nitrite nitrogen ($N\text{-}NO_2^-$) concentrations were determined through formation of a pink azo dye produced at pH 1.9 by coupling diazotised sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The product was spectrophotometrically measured using a 1" square glass of 25-mL at 540nm wavelength (Horáková et al., 2003).

4.6.1.3. Determination of $N\text{-}NO_3^-$ concentrations

Nitrate nitrogen ($N\text{-}NO_3^-$) concentrations were determined using the 2,6-Dimethylphenol spectrometric method. This method is based on the reaction of nitrate with 2,6-dimethylphenol in the presence of sulfuric and phosphoric acids to produce 4-nitro-2,6-dimethylphenol. Afterwards, the spectrophotometric measurement of the absorbance of the reaction product was conducted at 324 nm.

4.6.2. Determination of chemical oxygen demand

The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO_2 and H_2O. COD measures the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant (Chudoba et al., 1991). The method uses potassium dichromate as the oxidising agent to determinate the COD_{Cr}. The oxidation is catalysed by silver ions and takes place in a strongly acidic environment of sulfuric acid. Often, the test involves the addition of mercury sulphate in order to reduce the interference from oxidation of chloride ions. Subsequently, the sample is digested for two-hours at 150 °C. During the reaction, potassium dichromate is reduced to Cr^{3+}, whose concentration is proportional to the organic matter content of the sample.

After performing the aforementioned procedures, the COD (mg/L) was measured by spectrophotometry at 600 nm wavelength. In addition, it was necessary to correct positive errors caused by nitrite oxidation, since potassium dichromate also oxidises nitrites when high nitrite concentrations are present in the sample (Horáková et al., 2003). The equation used was the following (Eq. 4.4):

$$COD_{Cr\ (real)} = COD_{Cr\ (measured)} - (1{,}1422 * N\text{-}NO_2^-) \quad mg/L \qquad \text{(Eq. 4.4)}$$

4.6.3. Determination of volatile fatty acids

VFAs were measured using a Thermo Scientific TRACE 1300 Gas Chromatograph (GC) (Thermo Fisher Scientific, UK) equipped with an FID detector. Samples were separated by a DB – FFAP capillary column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness, Agilent Technologies Inc., USA) with hydrogen as a carrier gas. First, 800 μL. of the sample was pipetted and mixed with 0.033 mL of H_3PO_4. Finally, 10 μL. of the mixed sample was injected into the GC.

4.6.4. Determination of risk elements

Cd, Pb, As, Cr, Cu, Mo, Ni, and Zn were determined according to guidelines established by Zaková et al. (2016) using inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720, Agilent Technologies Inc., USA) equipped with a two-channel peristaltic pump, a Sturman-Masters spray chamber and a V-groove pneumatic nebulizer. In this manner, the so-called pseudo-total content of the elements expressing the amount of the elements extractable with aqua regia was analysed.

The pseudo-total content of Hg was measured according to Šípková et al. (2016) using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x, Agilent Technologies Inc., USA), equipped with an autosampler ASX-500, a three-channel peristaltic pump and a MicroMist nebulizer.

4.6.5. Determination of total solids, dissolved solids, suspended solids, and volatile solids.

By gravimetric analysis, the total solids (TS) which include organic and inorganic dissolved solids (DS) and suspended solids (SS) were determined. Samples from the influent, reactor, and effluent were collected from the nitrification reactor during its operation. The analysis was performed on non-centrifuged samples. 10 mL (V) from each sample was pipetted into pre-weighed aluminium foil bowls (m_1), then the samples were evaporated in a water bath heated with a hotplate (STUART CB 500, UK). These were then placed in a drying oven (Ecocell 55, BMT Medical Technology, Czech Republic) for 2 hours and afterwards were once again weighed (m_2). TS concentrations (g/L) were thus calculated using the equation bellow (Eq. 4.5):

$$\rho_{(TS)} = \frac{m_2 - m_1}{V} * 1000 \qquad \text{(Eq. 4.5)}$$

The coefficient 1000 was used to convert mL to L.

The determination of DS was performed on centrifuged samples from the influent, reactor and effluent from the nitrification reactor during its operation. The procedure and calculation for DS was analogous to the TS determination (Eq. 4.6):

$$\rho_{(DS)} = \frac{m_2 - m_1}{V} * 1000 \qquad \text{(Eq. 4.6)}$$

The SS were calculated according to the equation (Eq. 4.7):

$$\rho_{(SS)} = \rho_{TS} - \rho_{DS} \qquad \text{(Eq. 4.7)}$$

The concentration of volatile solids (VS) was determined by the loss-on-ignition (LOI) method (Horáková et al., 2003). This method is based on the determination of organic matter and involves the heated destruction of all organic matter in the sample. The dried samples (m_2) were placed in a muffle furnace MF5 (ELSKLO s.r.o., Czech Republic) which was then heated to 550 °C for one hour. The sample was then cooled in a desiccator and weighed (m_3). The VS was calculated using the Eq. 4.8

$$\rho_{(LOI)} = \frac{m_2 - m_3}{V} * 1000 \qquad \text{(Eq. 4.8)}$$

4.6.6. Measurement of pH, dissolved oxygen, and conductivity

Dissolved oxygen (DO) concentrations were measured employing a WTW Oxi 340i oxygen meter (WTW, Germany) to verify proper operation of the aerators in the CSTR nitrification reactor and to monitor the expected anoxic conditions of the denitrification models. In like manner, pH measurements were performed using a WTW pH 340i pH meter (WTW, Germany). Electrical conductivity (EC) was determined by means of a conductometer inoLab Cond 730 (WTW, Germany).

4.6.7. Statistical analysis

Simple linear regression was used to ascertain the existence of linear trends between the concentrations of $N\text{-}NO_3^-$ and total N_{inorg} of the denitrification models D1, D2, D3, and D4 (dependent variables) and the storage time (independent variable), and the concentrations $COD_{Soluble}$ of the volatilisation models V1, V2, V3 and V4 (dependent variables) and the storage time (independent variable), with a confidence limit of 95% ($p < 0.05$). For this purpose, the statistical analysis was performed using the computing environment R (R Development Core Team 2012).

5. Results

5.1. Storage of untreated LPD and nitrified LPD

5.1.1. Volatilisation tests

The volatilisation tests were carried out for a total of 99 days (V3 and V4) and 104 days (V1 and V2). The results of all the measurements made during the experimental period can be seen in Tables 22 – 25 (situated in the chapter Enclosures).

5.1.1.1. Temperature and DO

The average temperature of the samples stored at room temperature V1 and V2 was 24.8±3.1°C and 26.3±3.0°C, respectively, while the average temperature of the samples stored at a thermostatically controlled cabinet (V3 and V4) was 10.8±0.6°C and 10.6±0.5°C, respectively (Tables 22 – 25 situated in the chapter Enclosures). The differences between temperatures of the continuously stirred samples and the samples that were not continuously stirred were insignificant.

The concentration of DO of the samples that were not continuously stirred (V1 and V3) was 0.1 mg/L and remained constant during the experimental period (Tables 22 and 24 situated in the chapter Enclosures). On the other hand, V2 and V4, which were continuously stirred during the experimental period, began to rapidly increase after the 6^{th} (V4) and 77^{th} (V2) days, reaching 9.5 mg/L and 2.5 mg/L, respectively at the end of the experiments (Tables 23 and 25 situated in the chapter Enclosures).

5.1.1.2. pH values

As can be seen in Figures 16 and 17, the pH values of all the samples increased steadily throughout the experiments from slightly alkaline (8.25) to alkaline (up to 9) and then began to decrease two weeks before the end of the experiment. It can be observed that the samples that were not continuously stirred (V1 and V3) and those that were continuously stirred (V2 and V4) followed very similar trends.

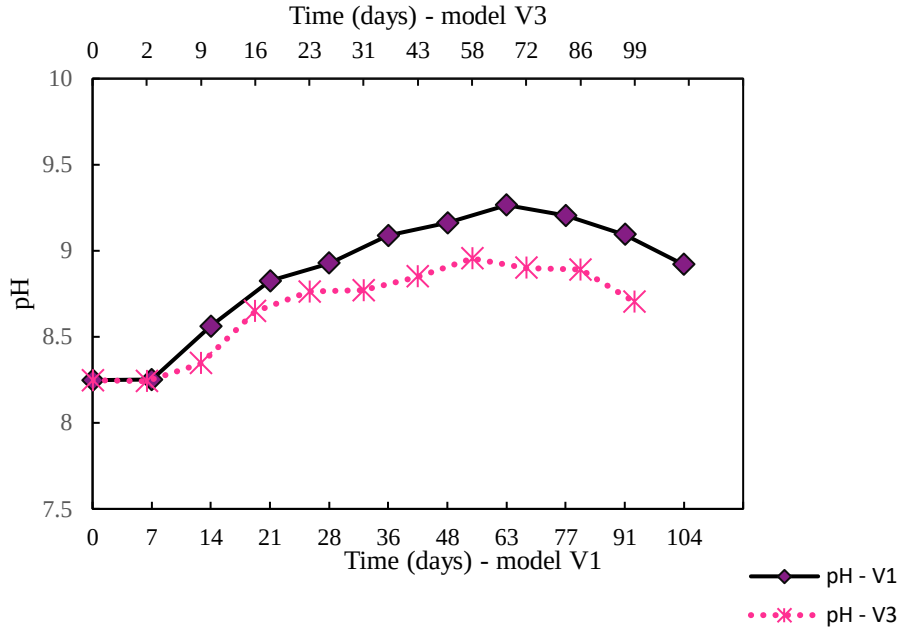

Figure 16. Comparison of the changes in pH values of V1 and V3 during storage

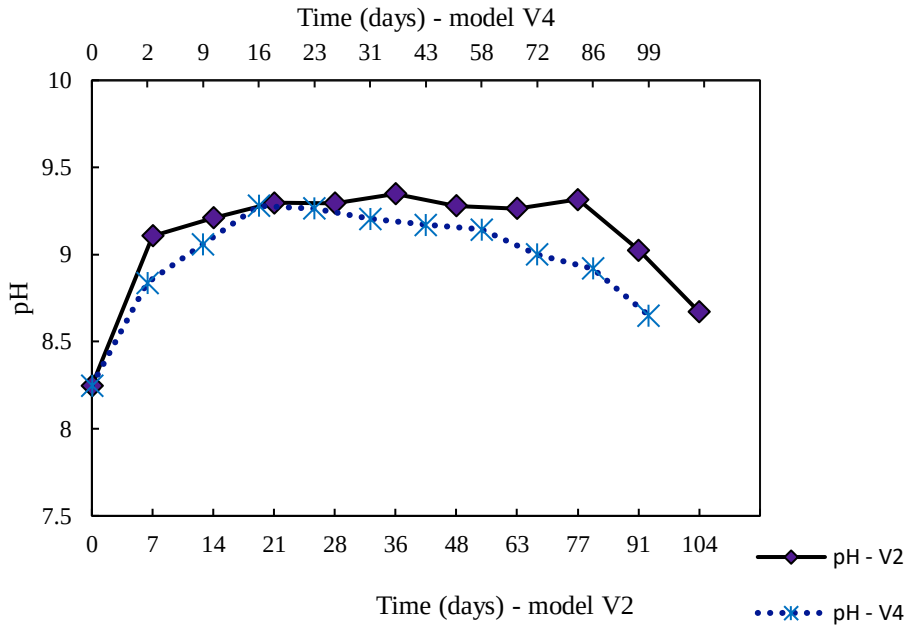

Figure 17. Comparison of the changes in pH values of V2 and V4 during storage

5.1.1.3. Total ammonia nitrogen

All the samples were characterised by containing high initial concentrations of TAN up to 5200 mg/L. Although the samples were stored in different storage conditions (i.e. temperature), the samples that were not continuously stirred (V1 and V3) and the samples that were stirred continuously (V2 and V4), followed similar trends over time. For instance, when comparing V1 with V3, Figure 18 reveals that there was a steady increase in the percentage of

TAN losses during both experimental periods of about 87% of the initial TAN concentrations. This represents a decrease from 5200 mg/L (day 0) to around 700 mg/L (days 99 and 104, respectively). On the other hand, TAN losses from V2 and V4 markedly increased during the experiment (Figure 19). Both samples decreased by 91% and 96%, respectively compared to their initial TAN concentration from 5200 mg/L to around 400 mg/L and 200 mg/L, respectively.

However, significant differences in the volatilisation rate can be observed between different samples stored at room temperature (V1 and V2), and those stored in the thermostatically controlled cabinet, being the decreases in concentration in those continuously stirred higher. The average percentage of change in the concentrations TAN was calculated from the slope of the linear relationship between the concentrations of TAN and storage time. There was found a concentration loss of approximately 6% (V1 and V3) and 7% (V2 and V4) per week during the experimental period (Table 28 situated in the chapter Enclosures).

5.1.1.4. Nitrite and nitrate

Very low concentrations of $N\text{-}NO_2^-$ that does not exceed 2 mg/L were detected in all the samples. All the samples were characterised by practically immeasurable $N\text{-}NO_3^-$ concentrations. The results can be seen in Tables 22 – 25 (situated in the chapter Enclosures).

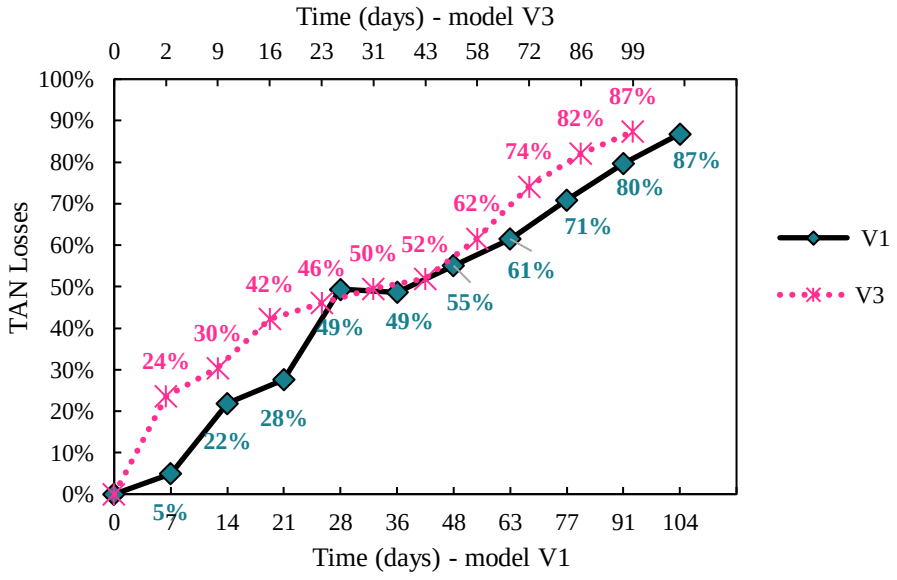

Figure 18. Comparison of percent loss of TAN in V1 and V3

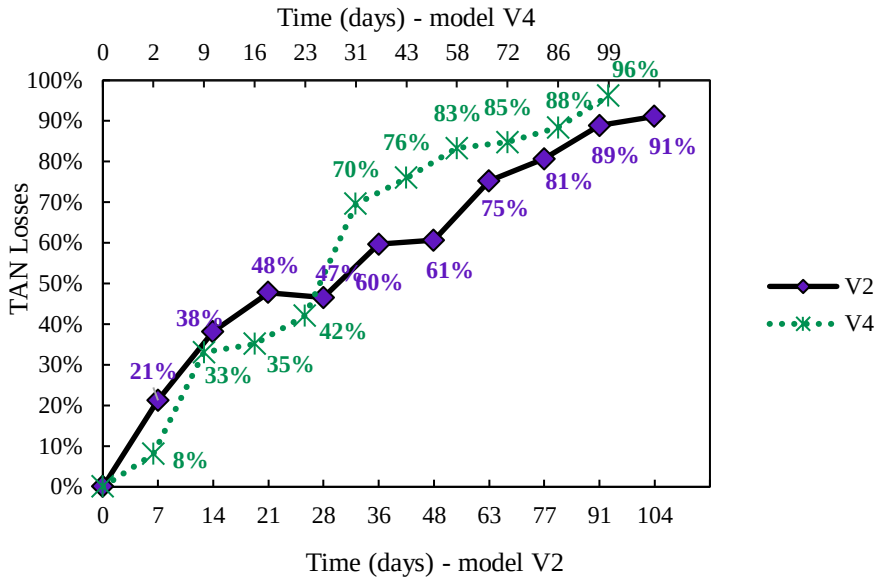

Figure 19. Comparison of percent loss of TAN in V2 and V4

5.1.1.5. Chemical oxygen demand

Non-significant linear relationships were found between the $COD_{Soluble}$ concentrations of V1 ($F(1, 9) = 1.85$, $p = 0.20$, $R^2 = 0.19$) and V3 ($F(1, 9) = 1.34$, $p = 0.27$, $R^2 = 0.19$) and the storage time (Figure 20 and 22). Nevertheless, a linear relationship was found between the concentration of $COD_{Soluble}$ and the storage time of V2 ($F(1, 9) = 12.27$, $p = 0.006$, $R^2 = 0.68$) and V4 ($F(1, 9) = 13.37$, $p = 0.005$, $R^2 = 0.71$) as can be seen in Figures 21 and 23. Both samples negatively correlated and therefore indicate a decreasing trend with time.

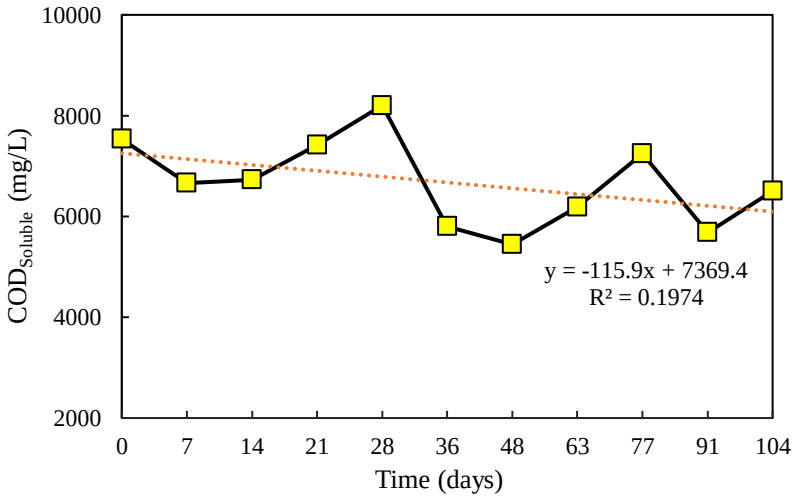

Figure 20. Relationship between the COD concentrations of V1 and the storage time

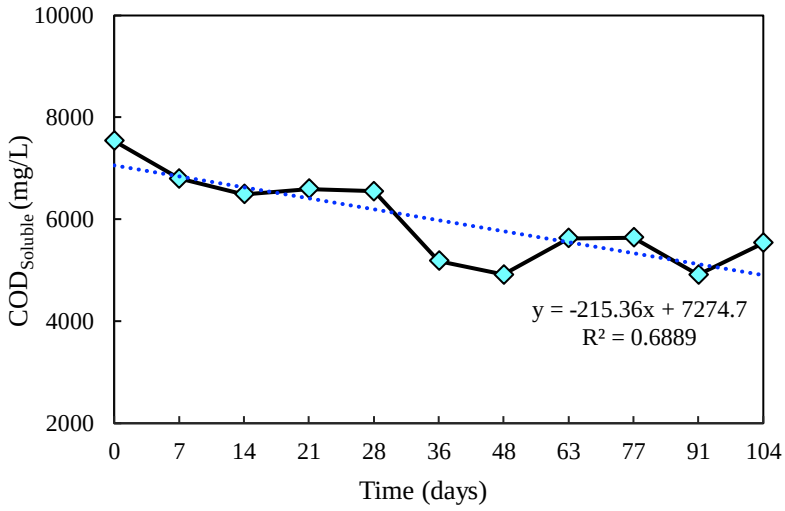

Figure 21. Relationship between the COD concentrations of V2 and the storage time

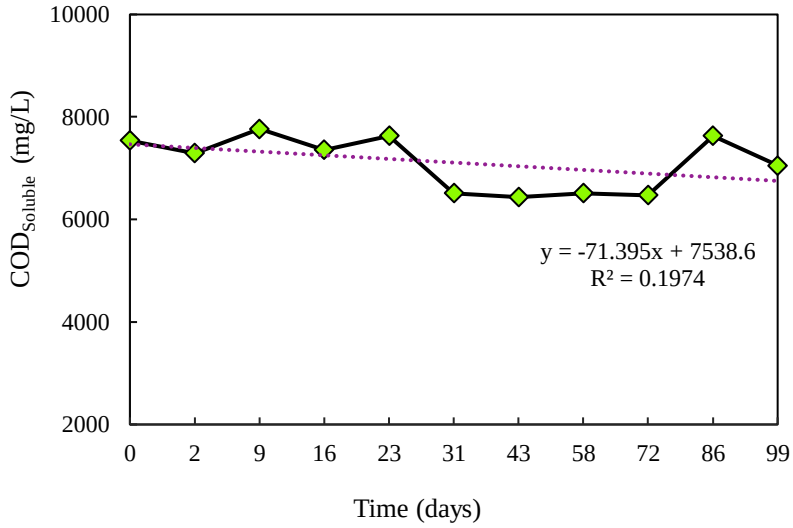

Figure 22. Relationship between the COD concentrations of V3 and the storage time

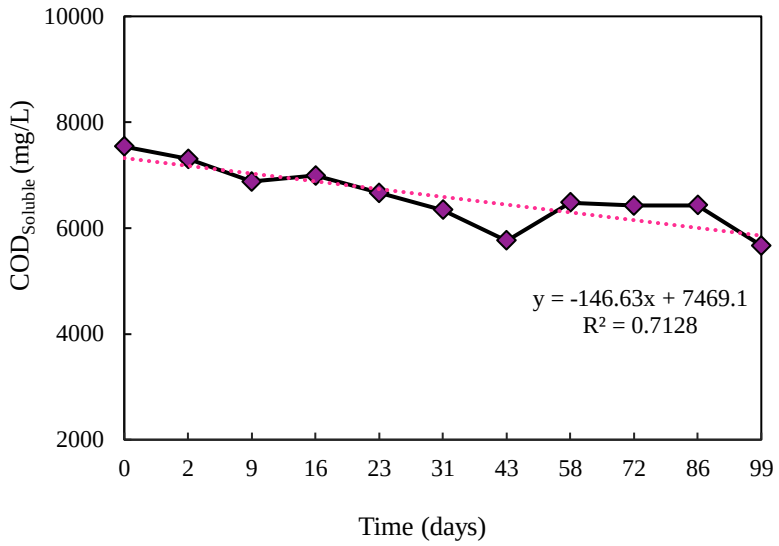

Figure 23. Relationship between the COD concentrations of V4 and the storage time

5.1.2. Denitrification tests

The denitrification tests were carried out for a total of 236 days (D1 and D2) and 83 days (D3 and D4). The results of all the measurements made during the experimental period can be seen in Tables 18 – 21 (situated in the chapter Enclosures).

5.1.2.1. Temperature and pH

The samples stored at room temperature (D1 and D2) had an average temperature of 26.2±0.4°C, while the samples stored at a thermostatically controlled cabinet (D3 and D4) had an average temperature of 11.2±1.1°C (Tables 18 – 21 situated in the chapter Enclosures).

The pH values varied among samples. Initially, pH values of D1 tend to increase from 6.9 to 7.7 until the 4th week storage. From the 4th week pH values lay within the range of 7.9 to 8.2 pH and remained constant until the end of the experiment. Unlike D1, the pH values of D2 gradually decreased during the experimental period from 6.9 (day 0) to 5.6 (day 236). On the other hand, pH values of D3 remained neutral (7.3±0.2) during the course of the experiments. Over the same time period, pH values of D4 decreased very slightly from neutral (6.9) at the beginning of the storage to slightly acidic (6.2) at the end of the experiment (day 83) (Tables 18 – 21 situated in the chapter Enclosures).

5.1.2.2. Dissolved oxygen

The concentrations of DO of the samples that were not continuously stirred (D1 and D3) can be seen in Figure 24. D1 is characterised by DO concentrations of 0.1 mg/L, which after the 15th week storage suddenly rose from 0.1 mg/L to 1.5 mg/L and then remained rather unstable. DO levels of D3 also fluctuated and ranged from within 0.9 to 1.5 mg/L. Another important finding is that DO concentrations in D2 fluctuated greatly and ranged from less than 1 mg/L to more than 8 mg/L, while DO concentrations in D4 increase gradually, as one can observe in Figure 25.

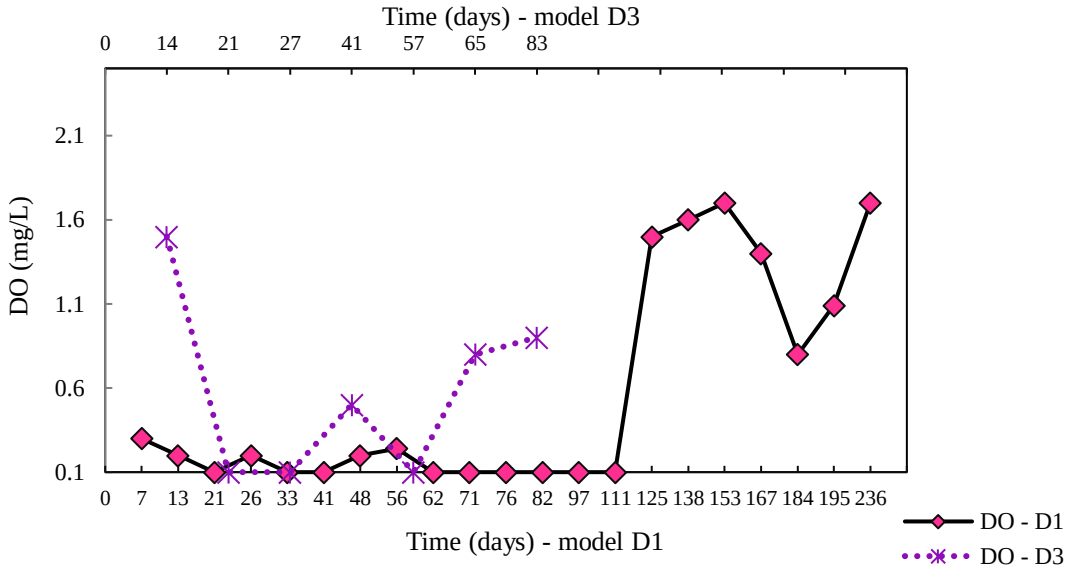

Figure 24. Comparison of DO concentrations in D1 and D3

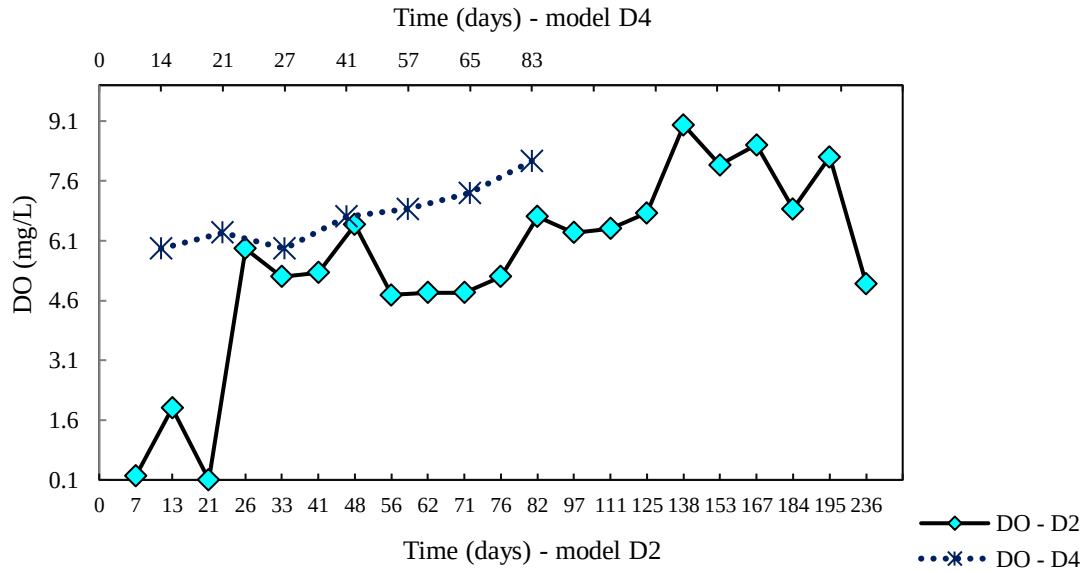

Figure 25. Comparison of DO concentrations in D2 and D4

5.1.2.3. Nitrate

A non-significant regression equation was found ($F(1, 20) = 0.72$, $p = 0.40$), with an R^2 of 0.03. Therefore, there is insufficient evidence to suggest that there is a linear relationship between the $N\text{-}NO_3^-$ concentrations of D1 and the storage time (Figure 26). Likewise, no statistically significant relationships were found between the storage time and the $N\text{-}NO_3^-$ concentrations of D2 ($F(1, 20) = 1.91$, $p = 0.18$, $R^2 = 0.09$); D3 ($F(1, 6) = 0.0072$, $p = 0.93$, $R^2 = 0.001$); and D4 ($F(1, 6) = 0.1342$, $p = 0.72$, $R^2 = 0.02$) as can be observed in Figures 27, 28 and 29. The percentage of change in $N\text{-}NO_3^-$ in the nitrified LPD was calculated from the slope of the linear relationship between the concentrations of $N\text{-}NO_3^-$ and storage time. There was found a concentration loss of approximately 0.08% and 0.1% per week in D1 and D2, respectively. On the other hand, there was found a concentration increase of about 0.08% and 0.2% per week in D3 and D4, respectively (Table 26 situated in chapter Enclosures).

5.1.2.4. TAN and nitrite

The initial concentrations of TAN were rather low (approximately 30 mg/L) and steadily decreased during the course of the experiment in D1, D2, D3 and D4 to around 2 mg/L, 10 mg/L, 12 mg/L, and 5 mg/L, respectively. Very low concentrations of $N\text{-}NO_2^-$ that varied greatly during the experimental period were detected in all the samples. The results of both parameters can be observed in Tables 18 – 21 (situated in the chapter Enclosures).

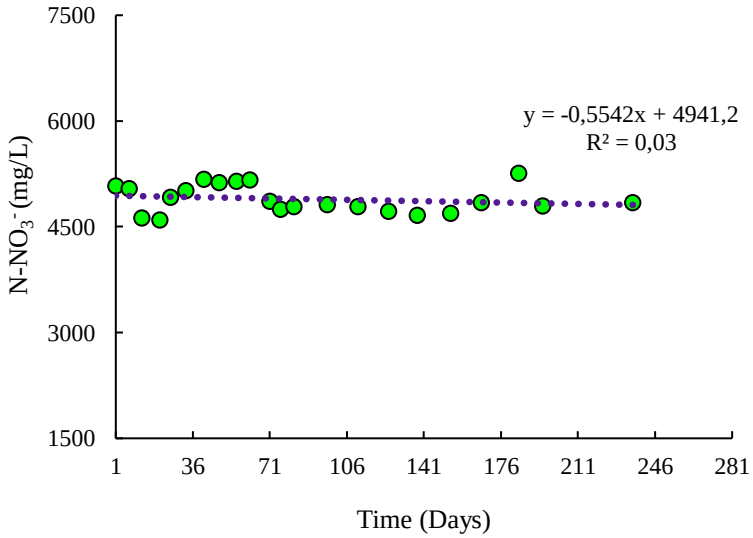

Figure 26. Relationship between $N\text{-}NO_3^-$ concentrations of D1 and the storage time

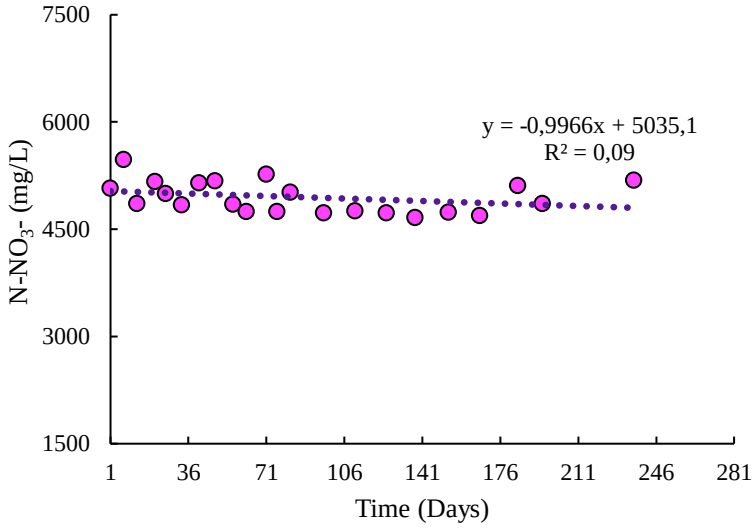

Figure 27. Relationship between $N\text{-}NO_3^-$ concentrations of D2 and the storage time

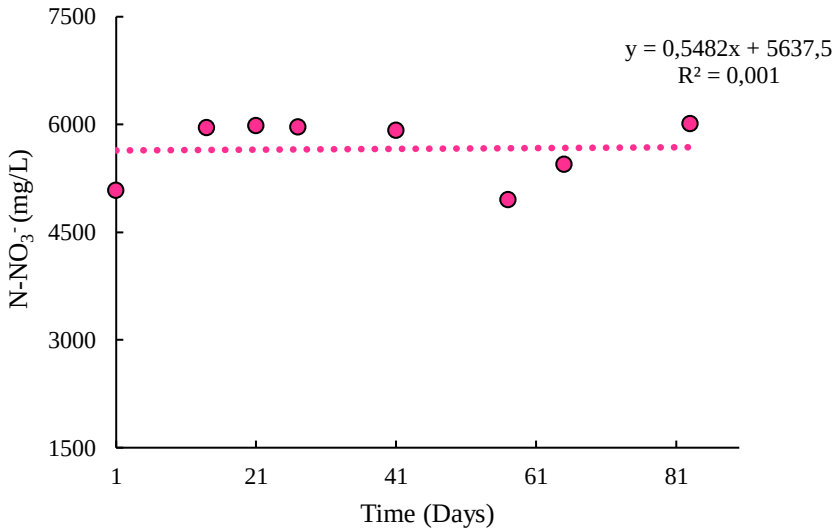

Figure 28. Relationship between $N\text{-}NO_3^-$ concentrations of D3 and the storage time

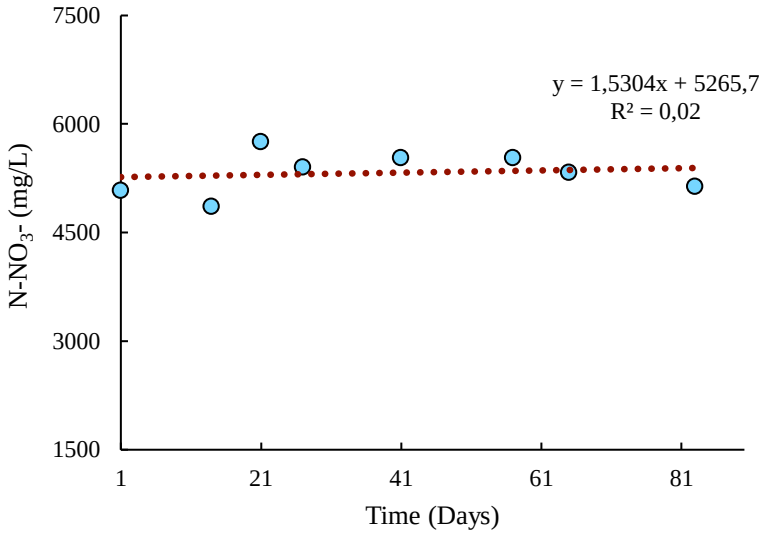

Figure 29. Relationship between $N\text{-}NO_3^-$ concentrations of D4 and the storage time

5.1.2.5. Total inorganic nitrogen

Total N_{inorg} was mainly composed of $N\text{-}NO_3^-$. The percentage of change in total N_{inorg} in the nitrified LPD was calculated from the slope of the linear relationship between the concentrations of total N_{inorg} (TAN + NO_2^- + $N\text{-}NO_3^-$) and storage time. There was found a concentration loss of approximately 0.1% and 0.3% per week in D1 and D2, respectively. On the other hand, there was found a concentration increase of about 0.06% and 0.2% per week in D3 and D4, respectively (Table 27 situated in the chapter Enclosures).

5.1.2.6. Chemical oxygen demand

A linear relationship between the $COD_{Soluble}$ concentrations of D1 and the storage time ($F(1, 20) = 5.2$, $p = 0.03$), with an R^2 of 0.20). The linear regression equation that derived from the data can be seen in Figure 30. A significant relationship was found ($F(1, 20) = 37.21$, $p = 1.10^6$, with an R^2 of 0.65) between the $COD_{Soluble}$ concentrations of D2 and the storage time (Figure 31). On the other hand, no statistically significant relationships were found between the concentrations of $COD_{Soluble}$ and the storage time of D3 ($F(1, 6) = 2.6$, $p = 0.2$, $R^2 = 0.30$) and D4 ($F(1, 6) = 0.1342$, $p = 0.4$, $R^2 = 0.14$) as can be observed in Figures 32 and 33.

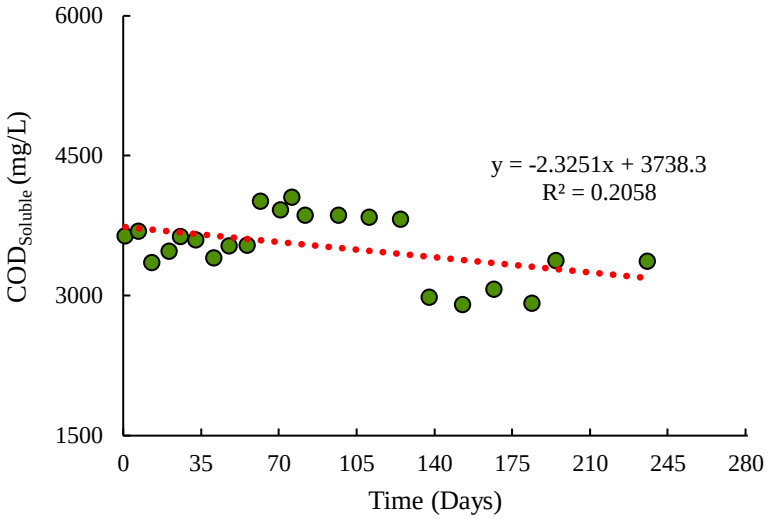

Figure 30. Relationship between COD concentrations of D1 and the storage time

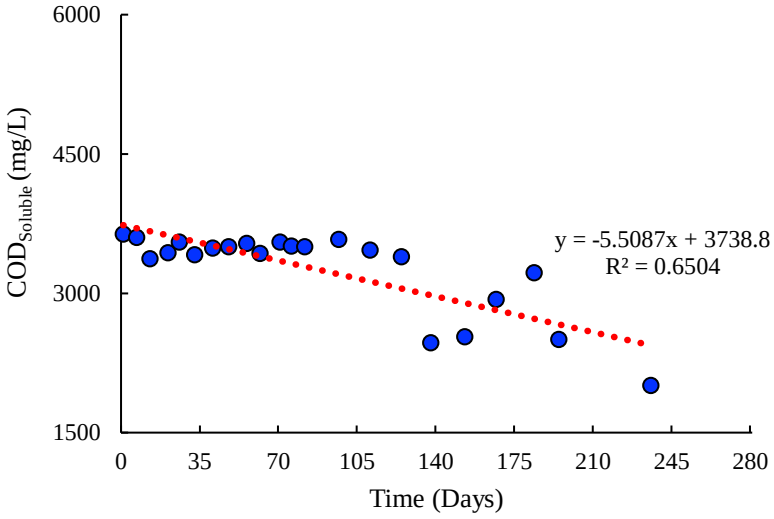

Figure 31. Relationship between COD concentrations of D2 and the storage time

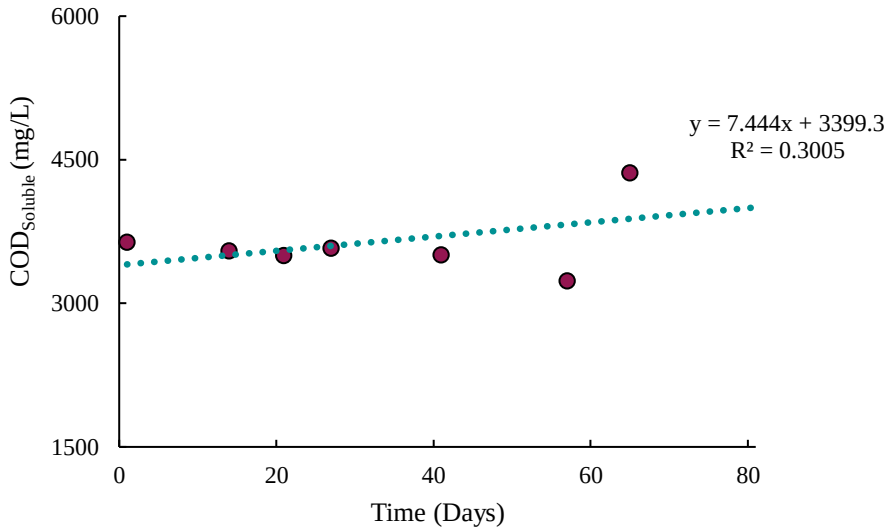

Figure 32. Relationship between COD concentrations of D3 and the storage time

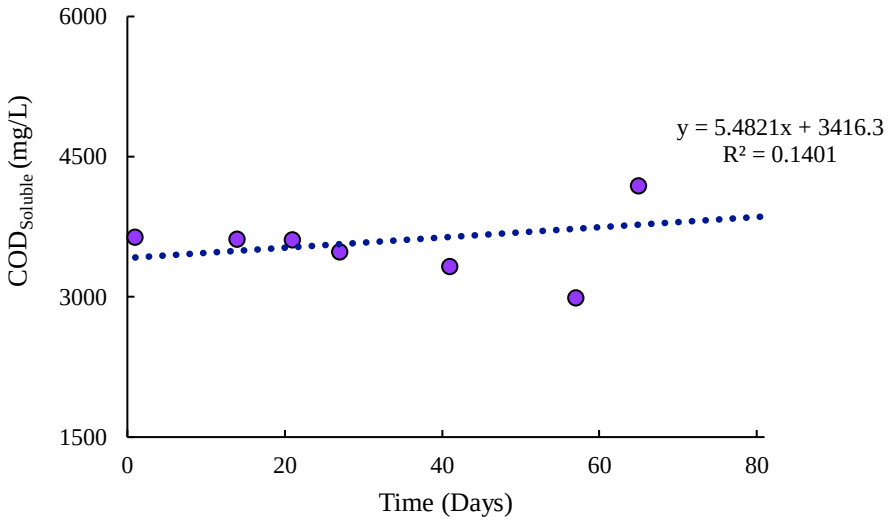

Figure 33. Relationship between COD concentrations of D4 and the storage time

5.2. Vacuum evaporation

Two different series of evaporation were carried out using the nitrified effluent (nitrified LPD) from the CSTR nitrification reactor. The evaporation series No. 1 was performed on July 31, 2017, where three samples (Sample Nos. 1, 2 and 3) of the nitrified LPD were subject to vacuum evaporation. In the evaporation series No. 2, the evaporation of two samples (Sample Nos. 4 and 5) of the nitrified LPD was performed on August 29, 2017. The initial approach was to cease the evaporation until a volume of distillate equal to 100 mL was obtained. However, as can be observed from Table 9, in not all the samples was it possible to achieve this goal. The measured parameters of each sample (pH, EC, COD_{Total} and $COD_{Soluble}$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, TAN) and the calculated mass balance of the aforementioned parameters are shown in Table 29 (situated in the chapter Enclosures).

Table 9. Volume of the nitrified LPD before and after the vacuum evaporation, and the volume of the resulting products.

Parameter	Units	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
Volume nitrified LPD	mL	200	200	200	200	200
Volume thickened LPD		65	86	80	100	103
Volume distillate		134	113	119	100	95
Volume losses		1	1	1	0	2

5.2.1. pH and EC

From the data presented in Table 10, there can be seen a decrease in pH values of the LPD as a result of the nitrification in the CSTR reactor. On average, the pH values of the untreated LPD, the nitrified LPD, the thickened LPD, and the distillate were 8.1±0.0, 6.5±0.2, 6.0±0.3, 7.9±0.5, respectively. Due to pH adjustment during the nitrification in the CSTR reactor, the pH values of the untreated LPD decreased on average 1.7. Likewise, it can also be observed that the pH values of the nitrified LPD in all five samples slightly decreased by 0.3 (on average) after the vacuum evaporation. Contrastingly, the pH level of the resulting distillate from samples No. 1 and 3 was close to neutral (7.2), and the pH values of samples No. 2, 4 and 5 were slightly alkaline with values of 8.2, 8.3, and 8.7, respectively.

As is also shown in Table 10, the conductivity of sample No. 1 increased from 33.7 mS/cm to 49.8 mS/cm after the nitrification. In the same way, the EC of the nitrified LPD

rose from 49.8 mS/cm to 109.1 mS/cm after the vacuum evaporation. Similar results can be observed for all the samples. It can also be observed that the EC values of the distillate reach the arithmetic average of 0.03 mS/cm.

Table 10. pH and EC values resulting from the untreated LPD, nitrified LPD, thickened LPD, and distillate

	pH				EC (mS/cm)			
Sample No.	**Untreated LPD**	**Nitrified LPD**	**Thickened LPD**	**Distillate**	**Untreated LPD**	**Nitrified LPD**	**Thickened LPD**	**Distillate**
1	8.1	6.1	5.8	7.2	33.7	49.8	109.1	0.03
2	8.1	6.1	5.9	8.2	33.7	49.8	88.8	0.02
3	8.1	6.1	5.7	7.2	33.7	49.8	99.1	0.02
4	8.1	6.8	6.4	8.3	33.7	55.0	95.4	0.03
5	8.1	6.8	6.4	8.7	33.7	55.0	88.9	0.03

5.2.2. Nitrate

The $N\text{-}NO_3^-$ concentrations in the nitrified LPD and the products resulting from the vacuum evaporation (i.e. thickened LPD and distillate) are depicted in Figure 34. It can be seen that significant concentrations of $N\text{-}NO_3^-$ were preserved in the thickened LPD of all the samples after the evaporation of the nitrified LPD. Sample No. 1 reached the highest concentration and rose from around 5600 mg/L to 17000 mg/L. Similarly, samples No. 2, 3, 4 and 5 also increased in concentration. It can be also seen that the $N\text{-}NO_3^-$ concentration in the distillate did not exceed 2 mg/L.

Based on mass balance (Table 11), 103% of the $N\text{-}NO_3^-$ from the nitrified LPD is maintained in the thickened LPD of sample No. 1, while the increases the $N\text{-}NO_3^-$ of sample Nos. 2, 3, 4, and 5 represent 85%, 101%, 112% and 96% of the $N\text{-}NO_3^-$ from the nitrified sample concentrated in the thickened LPD, respectively. In contrast, the amount of $N\text{-}NO_3^-$ transferred to the distillate did not exceed 0.02%.

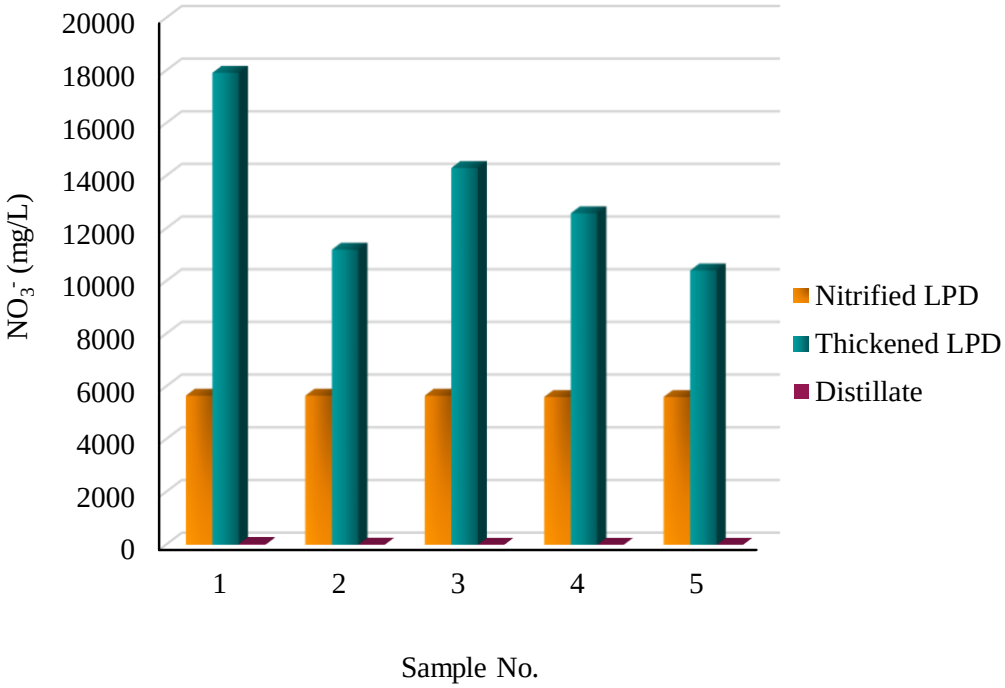

Figure 34. The N-NO_3^- concentrations in the nitrified LPD, thickened LPD and distillate.

Table 11. N-NO_3^- mass balance of the five measured samples

Sample No.	Nitrified LPD	Thickened LPD	Distillate	Thickened LPD	Distillate
	mg			%	
1	1130.8	1164.7	0.3	103	0.02
2	1130.8	963.0	0.3	85.2	0.02
3	1130.8	1144.0	0.2	101.2	0.02
4	1120.8	1258.2	0.1	112.3	0.01
5	1120.8	1072.2	0.1	95.7	0.01

5.2.3. Total ammonia nitrogen

The TAN concentrations of the input (nitrified LPD) and the products (i.e. thickened LPD and distillate) resulting from vacuum evaporation are illustrated in Figure 35. It can be observed that the TAN concentrations of the untreated LPD decreased after the nitrification from around 2400 mg/L to 6 mg/L (evaporation series No. 1) and 11 mg/L (evaporation series No. 2), respectively. On the other hand, it can be seen that the concentrations of TAN increased by almost double after the evaporation of the five samples of the nitrified LPD and that the concentration of TAN of the distillates did not exceed 4 mg/L.

As shown in the table below (Table 12), the results of mass balance calculations of TAN reveal that 57% of TAN remained in the thickened LPD of sample No. 1, while 31% was recovered in the distillate. The results of samples No. 2, 3, 4 and 5 followed the same pattern with 66%, 85%, 104%, and 92% of TAN preserved in the thickened LPD, respectively, and around 36%, 25%, 12%, 15% transferred to the distillate, respectively. It is important to emphasize that the representation of TAN in the total inorganic nitrogen is very low (see chapter 5.2.5).

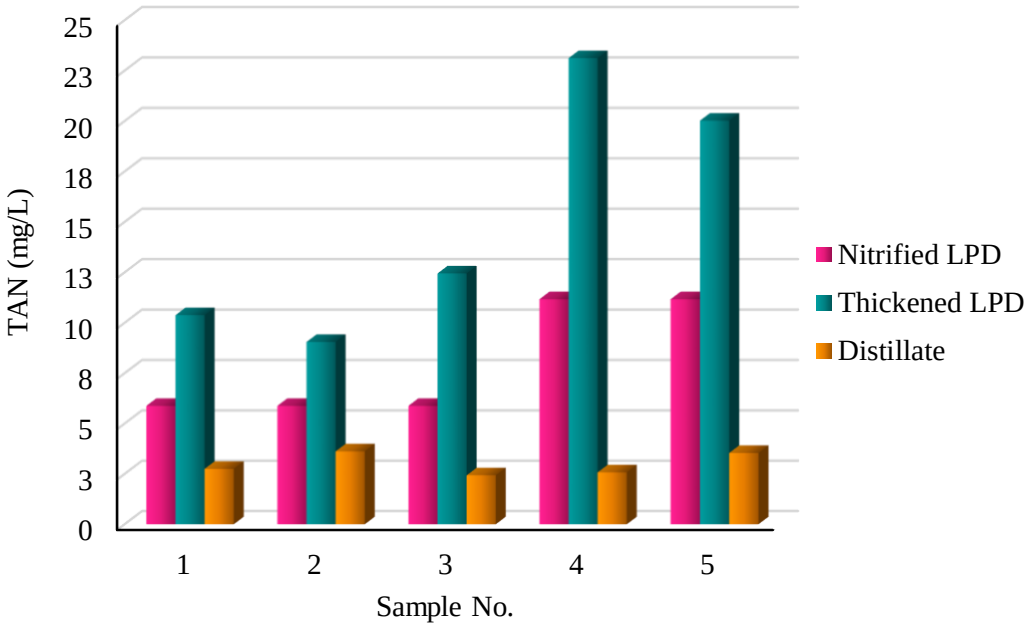

Figure 35. The TAN concentrations of the nitrified LPD, thickened LPD and distillate

Table 12. TAN mass balance of the five measured samples

Sample No.	Nitrified LPD	Thickened LPD	Distillate	Thickened LPD	Distillate
	mg			%	
1	1.2	0.7	0.4	57.4	31.3
2	1.2	0.8	0.4	66.2	34.7
3	1.2	1.0	0.3	84.7	24.6
4	2.2	2.3	0.3	103.5	11.5
5	2.2	2.1	0.3	92.3	15.1

5.2.4. Nitrite

The results of mass balance calculations of $N\text{-}NO_2^-$ concentrations conserved in the thickened LPD and transferred into the distillate after the vacuum evaporation of the nitrified LPD can be seen in Table 29 (situated in the chapter Enclosures). The results of sample No. 1 indicate that around 93% of the $N\text{-}NO_2^-$ remained in the thickened LPD, while only 3% was transferred to the distillate. On the other hand, the results of samples No. 2, 3, 4 and 5 indicate that more than 100% of the NO_2^- remained in the thickened LPD, and a very low percentage was transferred into the distillates. Like TAN, the representation of $N\text{-}NO_2^-$ in the total inorganic nitrogen is very low (see chapter 5.2.5).

5.2.5. Total inorganic nitrogen

Figure 36 and Table 13 clearly show that the inorganic nitrogen (N_{inorg}) concentrations of the nitrified LPD increased more than double after the vacuum evaporation. In contrast, the distillate was characterised by low concentrations. It can also be observed that the concentration of N_{inorg} in the nitrified LPD in sample No. 1 increased 3 times more from around 5600 mg/L to 17000 mg/L in the thickened LPD, and only around 5 mg/L was detected in the distillate. Samples No. 2, 3, 4 and 5 followed the same pattern.

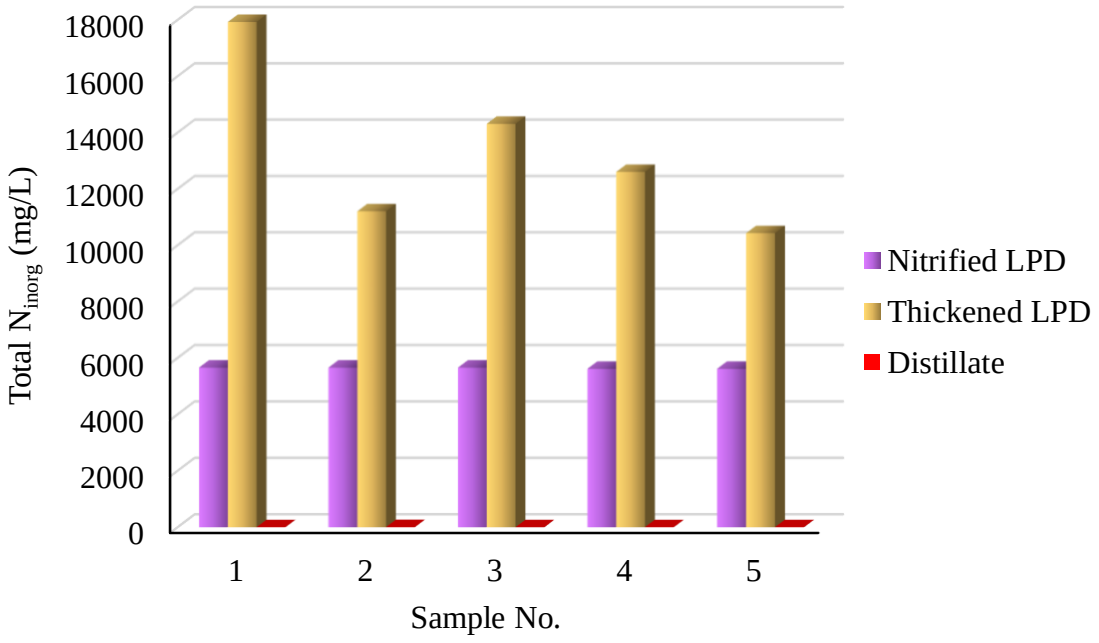

Figure 36. The total N_{inorg} concentrations in the nitrified LPD, thickened LPD and distillate.

Table 13. Total N_{inorg} concentrations in the untreated LPD, thickened LPD and distillate

Sample No.	Nitrified LPD	Thickened LPD	Distillate
	mg/L		
1	5660	17929	4.6
2	5660	11208	5.9
3	5660	14314	2.0
4	5616	12607	3.9
5	5616	10432	4.4

The results of total N_{inorg} mass balance of the thickened LPD are presented in Table 14. $N\text{-}NO_3^-$ represents around 99.9% of the total N_{inorg} of the nitrified LPD concentrated in the thickened LPD, while $N\text{-}NO_2^-$ and TAN represent approximately only the 0.02% and 0.2%, respectively. On the other hand, very little amounts of total N_{inorg} were detected in the distillates of all the samples, with TAN being the dominant nitrogen form (see Table 29 situated in chapter Enclosures).

Table 14. Total Ninorg mass balance of the thickened LPD of the five measured samples

Sample No.	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN	ΣN_{inorg}	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN
	mg				%		
1	1164.7	0.06	0.7	1165.4	99.9%	0.005%	0.06%
2	963.0	0.08	0.8	963.9	99.9%	0.008%	0.08%
3	1144.0	0.09	1.0	1145.1	99.9%	0.008%	0.09%
4	1258.2	0.20	2.3	1260.7	99.8%	0.016%	0.18%
5	1072.2	0.19	2.1	1074.5	99.8%	0.018%	0.19%

5.2.6. Chemical oxygen demand

It can be seen from Figure 37 that the vacuum evaporation produced a thickened LPD characterised by a concentration of COD_{Total} between 4 to 5 times higher than the nitrified LPD. For example, in sample No. 1, the concentration COD_{Total} of the nitrified LPD increased from around 3800 mg/L to 27000 mg/L. The results of samples No. 2, 3, 4 and 5 exhibit the

same pattern. On the other hand, the concentration of COD_{Total} in the distillates did not exceed 200 mg/L.

In terms of mass balance, the results presented in Table 15 indicate that a large proportion of the COD_{Total} was preserved in the thickened LPD characterised by representing more than 200% of the nitrified LPD in each sample, while the COD_{Total} amounts transferred to the distillate did not exceed 2%.

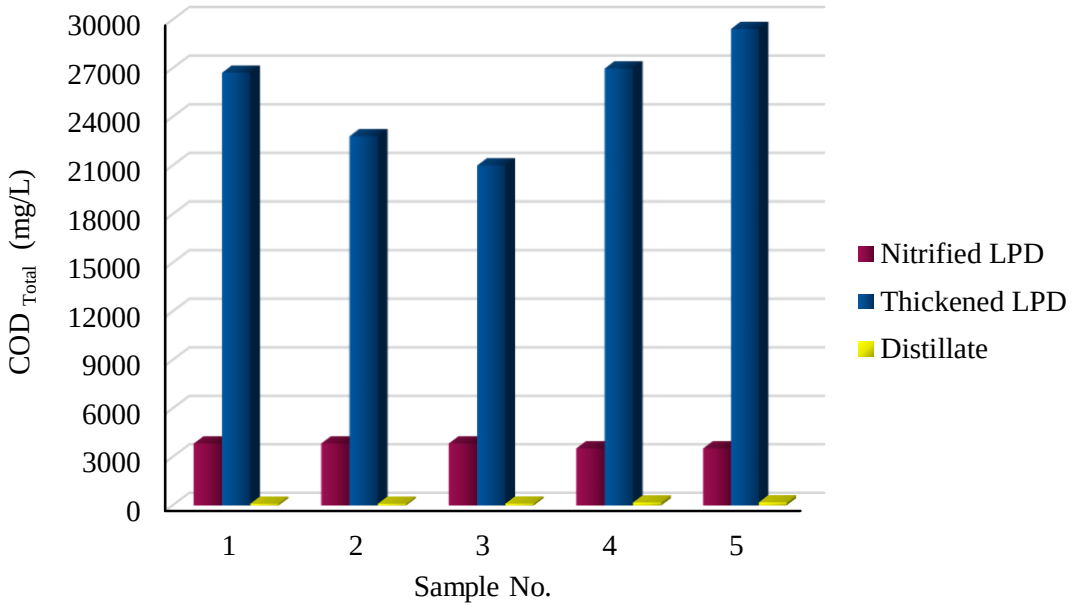

Figure 37.Total COD concentrations in the untreated, the nitrified LPD, thickened LPD and distillate.

Table 15. COD_{Total} mass balance of the five measured samples

Sample	Nitrified LPD	Thickened LPD	Distillate	Thickened LPD	Distillate
	mg			%	
1	766.6	1737.5	14.3	226.6	1.9
2	766.6	1961.7	11.9	255.9	1.6
3	766.6	1680.8	13.3	219.3	1.7
4	985.6	2699.0	18.0	273.8	1.8
5	985.6	3031.3	17.9	307.6	1.8

As shown in Table 29 (see chapter Enclosures), the $COD_{Soluble}$ concentrations of the LPD significantly decreased in value after the nitrification from around 9000 mg/L to 2400 mg/L (evaporation series No. 1) and from 9000 mg/L to 3500 mg/L (evaporation series No.

2). On the other hand, significant increases after the vacuum evaporation can be observed in sample No. 1, where the COD increased from 2400 mg/L to 10500 mg/L, which represents 142% of the nitrified LPD based on mass balance. Samples No. 2, 3, 4 and 5 followed similar patterns. The increases represent 185%, 194%, 175%, and 197% of the nitrified LPD, respectively. From the Table 29, it can also be observed that a relatively small amount of $COD_{Soluble}$ was transferred from the nitrified LPD to the distillate. The five samples represent 3%, 2.5%, 2.7%; 2.6%, and 2.5% of COD from the nitrified LPD, respectively.

5.2.7. Volatile fatty acids

The most remarkable result to emerge from the data in Table 16 are the changes in the concentrations of VFAs in the thickened LPD after the evaporation of the nitrified LPD. For instance, the propionic acid increase from 0 mg/L to around 40 mg/L and butyric acid increase from 0 mg/L to 7 mg/L, while the concentrations of isovaleric acid, valeric and caproic acid decrease almost entirely. On the other hand, it can be seen that the VFAs concentrations transferred into the distillate are considerably lower.

Table 16. VFA concentrations in sample No. 1

Parameter	Untreated LPD	Nitrified LPD	Thickened LPD	Distillate
	mg/L			
Acetic acid	3555	16.4	16	7.6
Propionic acid	731	0	43	0
Isobutyric acid	144	15.5	4.5	9.9
Butyric acid	448	0	6.5	0
Isovaleric acid	296	19.5	0	0
Valeric acid	36	19	0	0
Caproic acid	18	0	0	0

6. Discussion

6.1. Nitrogen losses

6.1.1. Changes during the storage of the untreated LPD

Based on the low concentrations of $N\text{-}NO_2^-$ of the untreated LPD (the $N\text{-}NO_2^-$ not exceeding 2 mg/L) and the practically immeasurably low concentrations of $N\text{-}NO_3^-$, the concentrations of TAN were considered as total N_{inorg} in the untreated LPD. Moreover, based on the untreated LPD's initial pH it was assumed that a significant portion of TAN concentration was present in the form of unionised NH_3, and therefore N losses were considered to be losses in the form of NH_3, since the nitrification process in the storage environment was not expected to occur (Patni and Jui, 1991).

The decrease in the concentrations of TAN was quick and fairly steady in all the samples during the experimental period. Indeed, the first sign that volatilisation of NH_3 was occurring was the emissions of the characteristic pungent odour of the NH_3 a week after the start of the storage period. As time progressed, the concentrations of TAN decreased and so did the odour intensity. The average percentage of change in concentrations of TAN, calculated from the slope of the linear relationship between the concentrations of TAN and storage time, indicated that the average rate of volatilisation was of approximately 6% (V1 and V3) and 7% (V2 and V4) per week, as can be seen in Figure 38 and Table 28 (situated in the chapter Enclosures). Similar results were also obtained by Whelan et al. (2010), who reported significant reductions in TAN concentrations during storage of about 7.6% per week.

There were no significant differences found between the samples that simulated summer (i.e. V1 and V2) and winter (i.e. V3 and V4) storage, but there were differences found between the samples that were not continuously stirred (i.e. V1 and V3) and the samples that were continuously stirred (i.e. V2 and V4). The concentration of TAN in V1 showed a decrease of 87%, while the concentration of TAN in V2 had decreased by 91 % at the end of storage compared to the concentration of TAN at the start of storage. Likewise, the samples that simulated winter storage followed similar patterns with V3 decreasing by 87% and V4 by 96% at the end of storage. These results differ from those of Perazzolo et al. (2017) who reported limited N losses of approximately 9% in the stirred sample and around 2% in the unstirred sample during the winter storage of LPD in field conditions (90 days), versus N losses from LPD that were stirred and unstirred during the summer storage in field conditions (90 days) of 35% and 32%, respectively. Generally, high temperatures increase the risk of N

losses because the representation of volatile NH_3 within TAN increases with increasing temperature (Patni and Jui, 1991). The discrepancy between the results of this diploma thesis and those of Perazzolo et al. (2017) may be attributable to the fact that the samples described in this diploma thesis were stored under lab-scale conditions, and therefore were not affected by the varying field conditions of climate such as air temperature, precipitation, solar radiation, air relative humidity, wind speed and direction, etc., like those of the aforementioned author.

The concentrations of DO in V2 tend to increase from the 11^{th}-week storage, whereas in V4 they began to increase after two days of storage and kept increasing, reaching nearly 10 mg/L by the end of the experimental period. A possible explanation for this is that the solubility of oxygen increases as temperature decreases, and vice versa. Moreover, at higher temperatures, the biodegradation of organic matter is more intensive (Pitter, 2009). Therefore, the oxygen that passed to the sample through the surface could have been consumed more quickly in V2 than in V4. On the other hand, the concentrations of DO in both V1 and V3 reached a maximum concentration of 0.1 mg/L and remained unchanged until the end of the experiments. In addition, the concentrations of $COD_{Soluble}$ in the samples that were continuously stirred (V2 and V4) show a tendency to decrease during the storage period. As Perazzolo et al. (2017) pointed out, under continuous stirring, the initial anaerobic conditions were probably altered in both samples and changed into aerobic. On the other hand, even though there is insufficient statistical evidence to conclude that the concentrations of $COD_{Soluble}$ in the samples that were not continuously stirred (V1 and V3) tended to decrease with time, the similar variations in concentrations of $COD_{Soluble}$ in both samples may indicate that some biological activity was taking place (Figures 20 and 21). Moreover, the detection of such low concentrations of DO in V1 and V3 alone may not be sufficient evidence to suggest that only anaerobic biodegradation of organic matter could occur. As reported by Wong et al. (1997) even if severely limited by available oxygen, aerobic biodegradation was also observed at such low dissolved oxygen concentrations. Comparing the results, this suggests that aerobic biodegradation of OM may have been taking place during the storage period in all the samples, and was probably more intensive in V2 and V4, where the concentrations of DO was significantly higher than in V1 and V3.

It was also observed that the pH values of all the samples gradually increased from the first-week storage and began to decrease two weeks before the end of the experimental period (Figures 18 and 19). High pH levels can lead to higher NH_3 emissions. Higher pH results in a shift of the equilibrium from ionized NH_4^+ to unionised NH_3, which enhances volatilisation

(Koirala et al., 2013). As demonstrated by Hafner et al. (2013) biodegradation of OM causes production or emissions of CO_2 which may create a variation of pH over time. Moreover, pH values may be also influenced by emissions of NH_3 and loss or production of VFA during storage. Emissions of CO_2 will be expected to lead to an increase in pH values and therefore lead to an increase in the rate of NH_3 volatilisation (Hafner et al., 2013). On the other hand, NH_3 emissions tend to reduce pH as alkaline gas is lost. Furthermore, with the production of VFA, which remain in the LPD, pH levels also tend to decrease (Perazzolo et al., 2015). Hence, the aerobic biodegradation possibly occurring in all the samples may explain the gradual increment of pH values in all the samples and high rate of volatilisation. The decrease in pH two weeks before the end of the experiments could be caused by the prevalence of the aforementioned factors that causes a decrease in pH, over those factors that cause an increase in pH levels. However, it is difficult to quantify completely the proportions of each individual factor influencing the pH levels.

To sum up, factors contributing to driving the volatilisation of NH_3 are complex and may be caused by a synergistic interaction of many volatilisation drivers. For the experiments which were conducted in this diploma thesis, these factors are mainly pH, aerobic biodegradation and the CO_2 emissions and VFA loss associated with it, and continuous stirring of the samples V2 and V4. Reducing nutrient losses from LPD storage by covering the storage tanks is very advisable. Moreover, reducing the pH value of the LPD has been proposed by Perazzolo et al. (2016). However, the application of LPD with low pH as a fertiliser on agricultural soils might be questionable.

6.1.2. Comparison between the losses of N from the untreated LPD and nitrified LPD

As reported by Martens (2005), sufficient $N\text{-}NO_3^-$ to act as electron acceptor must be available for denitrification to occur. Moreover, denitrification occurs in the absence of oxygen and readily biodegradable carbon sources are required for bacterial metabolism. Characterised by hardly decomposable organic matter content, the nitrified LPD did not contain a sufficient amount of high soluble carbon sources required to achieve nitrate reduction (Möller and Müller, 2012). After the nitrification, the concentrations of OM were even lower, hence denitrification was not expected to occur. Furthermore, there is sufficient statistical evidence to suggest that very little or no denitrification took place during the storage of the nitrified LPD.

Unlike V1, V2, V3 and V4, where the losses of N in the form of TAN were 87%, 91%, 87% and 96%, respectively of the initial concentration after 104 and 99 days storage,

the losses of N in the form of total N_{inorg} during the storage of the nitrified LPD were low in all the samples. For instance, after 83 days storage, the percentage of N losses was approximately 1% and 4% in D1 and D2, respectively and after 236 days storage 4% and 11% of the initial concentration of total N_{inorg} in D1 and D2, respectively based on calculations made from the slope of the linear relationship between the concentrations of total N_{inorg} and storage time. On the other hand, after 83 days storage, the concentration of total N_{inorg} increased by approximately 1% and 2% in D3 and D4, respectively, according to calculations made from the slope of the linear relationship between the concentrations of total N_{inorg} and storage time (Table 27 situated in the chapter Enclosures).

Based on calculations made from the slope of the linear relationship and between the concentrations of total N_{inorg} in the nitrified LPD, and storage time of D1, D2, D3 and D4, the average rate of N loss was significantly lower than the losses resulting from the storage of untreated LPD. The average rate of loss of total $N_{inorg}$was 0.1% and 0.3% per week in D1 and D2, respectively. On the other hand, the average rate of N increases was 0.06% and 0.2% per week in D3 and D4, respectively (Figure 39 and Table 27 situated in the chapter Enclosures), whereas the average rate of N losses was approximately 6% (V1 and V3) and 7% (V2 and V4). The increases of total N_{inorg} concentrations in D3 and D4 could have been caused by mineralisation of N_{org}. Patni and Jui (1991) also reported that low temperatures did not inhibit mineralisation of N_{org} from two stores filled with dairy slurry. However, it is plausible that small measurement errors could have influenced the results obtained. Moreover, contrasting with V1, V2, V3 and V4, neither the temperature nor the stirring had any greater influence on the losses of N.

The evidence from this diploma thesis suggests that continuous stirring may increase losses of nitrogen compounds and therefore should be avoided. Additionally, the results demonstrate that with the nitrification as a pre-treatment of LPD, nitrogen losses during long-term storage could be significantly lower than when untreated LPD is stored. However, future research that focused on the storage of nitrified LPD under field conditions is needed to obtain more accurate results.

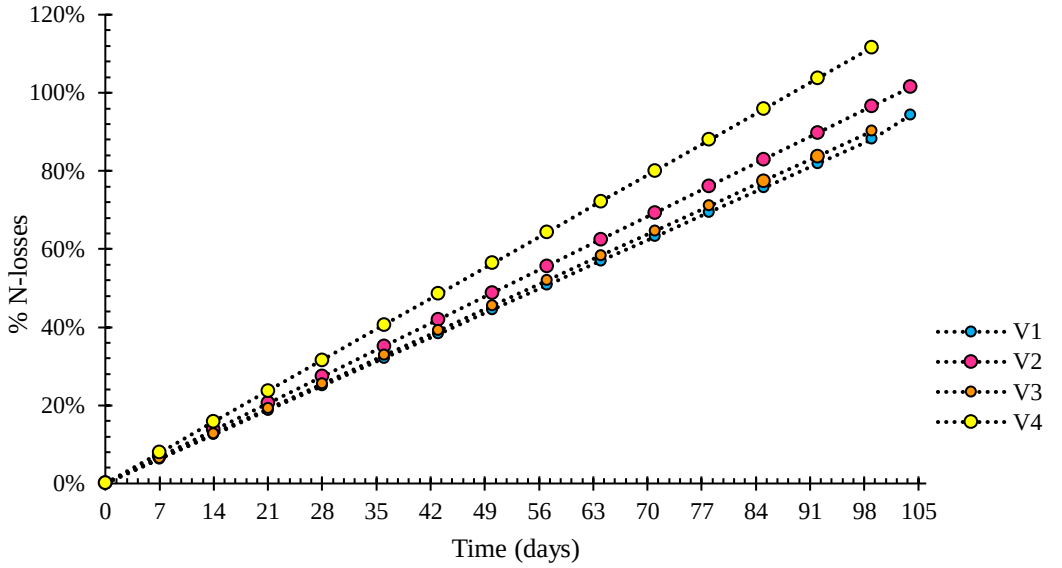

Figure 38. The average percentage of change in concentrations of TAN during the storage of the untreated LPD.

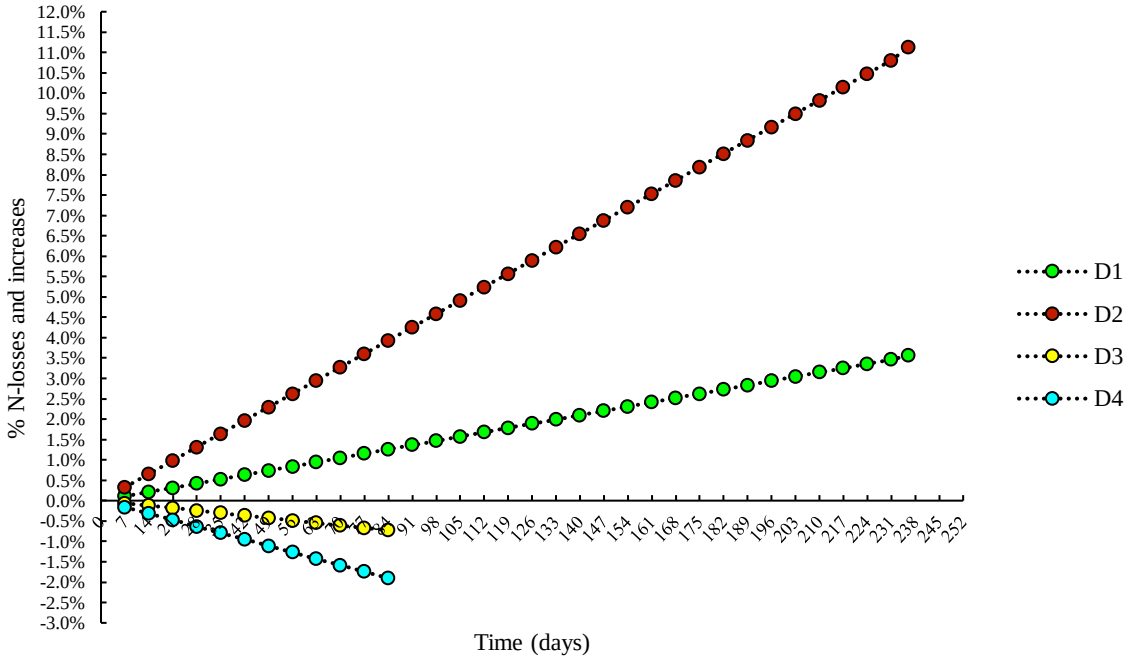

Figure 39. The average percentage of change in concentrations of total N_{inorg} during the storage of the nitrified LPD.

6.2. Vacuum evaporation tests

6.2.1. The concentration of total inorganic nitrogen and other chemical compounds in the thickened LPD and distillate after vacuum evaporation

As mentioned in the literature review, the thermal thickening of LPD by vacuum evaporation aims not only to reduce the volume of the LPD but also to produce a thickened LPD with a higher concentration of nutrients than the original LPD and a distillate characterised by a low concentration of nutrients and other chemical compounds. The combination of nitrification and subsequent thermal thickening by vacuum evaporation was already proposed by Botheju et al. (2010) and Švehla et al. (2017) based on the assumption that with nitrification as a pre-treatment is possible to obtain a product with reduced pH resulting in chemical conditions unfavourable for NH_3 volatilisation during evaporation of LPD. In addition, a product rich in NO_3^- which is characterised by being more stable in the soil and by being a highly mobile nitrogen source for plants will be obtained without the use of chemicals for pH adjustment. In this diploma thesis, this theory was put into practice.

Overall, the most important finding is that the total N_{inorg} preserved in the thickened LPD of all the samples increased in concentration more than double after the vacuum evaporation, with $N\text{-}NO_3^-$ being the dominant nitrogen form (99.9%), whereas in the distillate the concentrations of the total N_{inorg} were rather low (Figure 36). Moreover, based on mass balance calculations, approximately 99.9% of the total inorganic nitrogen was maintained in the thickened LPD of all the samples even when the volume of the thickened LPD was only one-third of the nitrified LPD before the vacuum evaporation as is the case of sample No. 1. On the other hand, the percentage of total inorganic nitrogen in the distillates of all the samples did not exceed 0.06%, even when the volumes of the resulted distillates were more than 50% of the nitrified LPD as is shown in the results of sample No. 1 (Table 14). This is evidence that under the operational conditions and pH of the nitrified LPD described in this diploma thesis (i.e. T= 65°C; P= 300 mbar; pH ≈ 6), the total N_{inorg} was totally preserved in the thickened LPD. There have been many attempts to concentrate the nutrients in the thickened LPD and to obtain a distillate with low concentration of nutrients by means of vacuum evaporation (Bonmatí and Flotats, 2003; Bonmatí et al., 2003; Palatsi et al., 2005; Chiumenti et al., 2013; Li et al., 2016). But, LPD without previous nitrification was subject to evaporation and therefore to achieve that goal, acidification of the LPD was needed in order to avoid the stripping of NH_3. Only with acidification of pH to 3.5 by means of sulfuric acid (35%) Chiumenti et al. (2013) was able to obtain similar results like those described in this

diploma thesis (i.e. a product with 99.2% of N maintained in thickened LPD and 0.8% N in the distillate after the vacuum evaporation).

On the other hand, both the amounts of $N\text{-}NO_2^-$ and TAN maintained in the thickened LPD were very low compared to $N\text{-}NO_3^-$. Although 60% to 80% of the initial TAN (6 mg/L and 11 mg/L, respectively) were transferred to the distillate, indicating that some stripping of NH_3 has occurred, the concentrations did not exceed 4 mg/L.

Like $N\text{-}NO_3^-$, the concentrations of COD_{Total} and $COD_{Soluble}$ significantly increased after the vacuum evaporation and were by 3-5 times higher than the nitrified samples (Table 29 situated in the chapter Enclosures). The data presented in Table 29 indicate that even if low, certain amounts of organic matter were transferred in the distillates (i.e. approximately 2% of the initial COD_{Total}) and that the concentrations detected in the distillates ranged from approximately 100 mg/L to 200 mg/L. That could have been in part caused by the presence of VFAs in the distillate. As can be seen in Table 16, the total concentration of VFA in the distillate obtained from sample No. 1 was approximately 18 mg/L. Even though the untreated LPD contained significant concentrations of each VFA and that significantly decreased due to the aerobic degradation of organic matter during the nitrification in the CSTR nitrification reactor, surprisingly, after the vacuum evaporation, the concentrations of some of the VFA increased (Table 16). This may indicate that the OM was subject to physicochemical changes during vacuum evaporation under such elevated temperatures and low pressure. However, it is plausible that experimental errors could have influenced the results obtained and therefore further analysis is required to confirm this assumption. Nevertheless, the low concentrations of COD (200 mg/L) detected in the distillates should not pose a problem for their use as a process liquid in the BGPs for the dilution of feedstocks or for irrigation.

In summary, the aforementioned works aimed at improving the optimal conditions for vacuum evaporation by acidification of the LPD. However, the use of a fertiliser with such low pH level may lead to inhibition of microorganisms responsible for the nitrification of NH_4^+ to $N\text{-}NO_3^-$ in soils and consequently accumulation of NH_4^+ may occur (Rorison, 1973). In the approach described in this diploma thesis, a product with higher concentrations of $N\text{-}NO_3^-$ readily available for plant uptake was obtained while avoiding the costs associated with the use of chemicals. However, $N\text{-}NO_3^-$ is also rapidly leached from soils and possible emissions of N_2O can result due to the a naturally occurring process of denitrification in soils after land application. Furthermore, emissions of N_2O and CH_4 may occur during the storage of the thickened nitrified LPD. Even though during the nitrification in the CSTR nitrification reactor the CH_4 remaining in the LPD after the AD process can be stripped with the aeration

in the reactor, and the organic substances that can be a source of CH_4 during storage are removed, the possibility of CH_4 emissions during the storage of the thickened LPD from the organic matter, which can emerge after vacuum evaporation, cannot be excluded.

Notwithstanding these limitations, the effects of soil application of the thickened nitrified LPD on $N\text{-}NO_3^-$ leaching and N_2O emissions needs further investigation. Moreover, further research is needed to compare emissions of two major GHGs i.e. N_2O and CH_4 during the storage of the thickened LPD.

7. Conclusions

- It was proved that during the long-term storage of the untreated LPD approximately 7% of the nitrogen in the form of TAN was loss weekly, whereas during the long-term storage of the nitrified LPD the losses of total N_{inorg} (TAN + $N\text{-}NO_2^-$ + $N\text{-}NO_3^-$) did not exceed 0.3% per week.

- It was confirmed that the total N_{inorg} preserved in the thickened LPD of all the samples increased in concentration more than double after the vacuum evaporation, with $N\text{-}NO_3^-$ being the dominant nitrogen form (99.9%), whereas in the distillate it did not exceed 2 mg/L in all the samples.

- Mass balance calculations indicated that more than 99.9% of the total inorganic nitrogen was maintained in the thickened LPD and the percentage of total inorganic nitrogen in the distillates of all the samples did not exceed 0.06%.

- With the nitrification as a pre-treatment of LPD, nitrogen losses during long-term storage could be significantly lower than when untreated LPD is stored. Moreover, the combination of nitrification and subsequent thermal thickening by vacuum evaporation is suitable in order to controllably reduce the pH value and avoid volatilisation of NH_3 and to obtain product rich in NO_3^- which is characterised by being more stable in the soil and by being a highly mobile nitrogen source for plants.

- The products resulting from the thermal thickening by vacuum evaporation have suitable properties for further use; the thickened LPD can be used as a nutrient-rich liquid fertiliser and the distillate can be used mainly as a process liquid in the BGPs e.g. for the dilution of feedstocks.

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9. List of abbreviations

AD	Anaerobic Digestion
AOB	Ammonium-oxidising bacteria
BGP	Biogas plant
CHP	Combined Heat and Power units
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
DM	Dry matter
DO	Dissolved oxygen
EC	Electrical conductivity
Eq.	Equation
GHG	Greenhouse gas
HRT	Hydraulic retention time
LPD	Liquid Phase of Digestate
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
N_{org}	Organic nitrogen
NOB	Nitrite-oxidising bacteria
NVZ	Nitrate vulnerable zone
OLR	Organic loading rate
OM	Organic matter
Q	Volumetric flow rate
RO	Reverse osmosis
SPD	Solid Phase of Digestate
TAN	Total ammonia nitrogen
TIC	Total inorganic carbon
TS	Total solids
TKN	Total Kjeldahl nitrogen
UF	Ultrafiltration
VFA	Volatile fatty acid
VS	Volatile solids

10. Enclosures

10.1. List of enclosures

Table 17. Measured values of various parameters in the influent and effluent for monitoring the progress of nitrification (1/3)

Date	Days	Q	T	DO	pH	Influent			Effluent				
						COD Total	COD Soluble	TAN	COD Total	COD Soluble	TAN	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$
		(mL/day)	° C	mg/L		mg/L			mg/L				
25/04/2017	1	240	23	2.5	6.1	22505	7898	6798	6736	44610	24.7	5171	6.9
28/04/2017	3	240	23	7.1	5.8	16820	10690	4792	3432	4491	15.7	4690	10.1
03/05/2017	8	240	24	2.2	6.0	20090	12640	4877	6574	4044	14.6	5189	9.5
08/05/2017	13	240	24	0.5	6.0	22580	30770	5218	11996	3838	24.7	4754	16.5
12/05/2017	17	240	24	2.5	5.9	24640	12775	4668	6008	4133	22.9	4692	37.8
15/05/2017	20	0	24	2.4	6.6	19100	14310	4223	13136	389	74.4	5461	168.2
22/05/2017	27	0	24	6.3	6.6	10010	6354	4495	5809	2852	10.8	5266	6.2
29/05/2017	34	0			5.6	10010	6354	3639	5809	2852	7.4	2982	0.9
01/06/2017	37	240	26	0.9	7.7	19130	10110	4570	3724	2313	8.6	4440	3.6
05/06/2017	41	240	24	4.5	5.9	5960	4840	6380	2152	1662	10.4	5396	1.1
09/06/2017	45	240	24		5.7	15900	9830	5175	4484	2138	10.3	4039	0.9
15/06/2017	51	0	26	6.5	6.1	25190	11108	5363	3130	1975	11.3	5089	2.2
16/06/2017	52	216	26	6.5	6.0	8065	4288	4195	5486	1053	12.9	4628	0.8
21/06/2017	57	216	28	1.5	6.7	27937	8906	4067	2861	1785	15.5	3769	1.0
23/06/2017	59	240	26	5.1	5.4	11735	7190	3420	3666	2127	14.0	4191	2.3
27/06/2017	63	216	26	6.2	6.0	15960	8984	3885	4668	2639	75.0	5097	104.5

Table 17. Measured values of various parameters in the influent and effluent for monitoring the progress of the nitrification (2/3)

Date	Days	Q	T	DO	pH	Influent			Effluent				
						COD Total	COD Soluble	TAN	COD Total	COD Soluble	TAN	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$
		(mL/day)	° C	mg/L		mg/L			mg/L				
29/06/2017	65	216	27	7.7	6.1	12757	8488	6200	5320	2866	39.2	4885	287.8
03/07/2017	69	0	24	4.7	6.0	9910	6342	4620	4976	2813	9.8	4179	27.0
07/07/2017	73	0	27	4.7	5.9	6575	4916	3299	2964	2088	6.9	3845	1.2
10/07/2017	76	216	26	5.5	6.1	17110	10776	5713	4506	2434	6.7	4800	1.0
14/07/2017	80	216	23	5.7	6.1	17495	10338	4122	3888	2248	8.7	4977	1.1
17/07/2017	83	216	25	5.1	6.1	16625	12554	4251	4128	2141	5.4	6094	0.7
20/07/2017	86	0	27	5.5	6.1	16370	10596	3931	3002	2313	8.8	5338	2.6
25/07/2017	91	212	24	5.3	6.0	15065	10968	4430	3628	2465	177.0	5900	39.0
27/07/2017	93	216	25	5.3	5.9	15470	9084	4584	3500	2428	51.1	5434	28.3
01/08/2017	98	252	25	4.6	5.9	18395	11908	3846	3210	2270	32.5	5236	2.7
03/08/2017	100	240	27	5.2	6.1	18030	11982	3601	3720	2357	11.1	5601	3.9
07/08/2017	104	252	24	5.2	6.1	13385	9604	4244	4970	2309	10.9	5590	2.7
10/08/2017	107	252	28	5.0	5.9	16190	11116	4009	3698	2458	9.3	5518	2.9
14/08/2017	111	222	25	6.0	6.0	12160	7934	3835	4188	2295	6.3	6215	0.8
18/08/2017	115	228	27	5.2	5.9	15215	11172	3720	4022	2417	6.9	5557	3.4
24/08/2017	121	228	24	5.4	6.0	15015	8580	4235	6940	3267	12.7	5366	0.6

Table 17. Measured values of various parameters in the influent and effluent for monitoring the progress of the nitrification (3/3)

Date	Days	Q	T	DO	pH	Influent			Effluent				
						COD Total	COD Soluble	TAN	COD Total	COD Soluble	TAN	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$
		(mL/day)	° C	mg/L		mg/L			mg/L				
28/08/2017	125	226	24	4.9	6.0	17640	11662	3898	6872	3173	8.9	5146	0.9
31/08/2017	128	228	25	5.0	6.1	16345	9202	3352	5894	3618	6.5	5619	2.4
04/09/2017	132	233	25	2.5	5.9	20115	12728	5648	9002	3663	14.7	5054	19.3
07/09/2017	135	228	24	5.9	4.8	20375	11666	4057	7570	3657	11.2	5114	7.7
15/09/2017	143	228	24	5.9	6.0	20375	11666	4057	7068	3802	13.3	5487	0.3
18/09/2017	146	209	23	4.4	5.9	20335	10006	3975	6570	3753	16.2	5098	1.7
21/09/2017	149	228	24	5.9	6.0	28250	10176	4714	6826	3962	14.6	5342	0.3
25/09/2017	153	212	24	5.0	5.4	17515	8538	3573	6088	3593	14.6	5059	4.9
29/09/2017	157	216	24	5.4	6.2	19780	11436	4806	6648	3732	17.8	5379	5.1
02/10/2017	160	199	25	6.0	5.3	17570	9674	4842	7750	3583	14.7	4644	5.1
05/10/2017	163	204	25	5.3	5.3	15870	9216	3796	7516	3696	13.8	4612	4.3
11/10/2017	169	216	26	3.7	5.7	18020	10444	3702	7180	3727	19.3	5272	4.9
16/10/2017	174	204	23	4.4	5.5	20265	8172	3623	7266	4129	15.4	4460	0.7
19/10/2017	177	204	26	3.6	5.6	15955	8118	3676	7216	4095	11.1	5074	1.8
23/10/2017	181	210	24	6.4	5.5	26070	8600	3893	8804	3902	12.3	4850	5.1
26/10/2017	184	216	24	6.4	5.4	22955	8388	3691	7584	4277	12.3	5024	13.9

Table 18. Measured values of various parameters for monitoring the progress of denitrification during lab-scale storage (D1)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	TAN	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
			°C	mg/L					
21/06/17	1	6.9			7844	3632	26.2	2.9	5074
28/06/17	7	7.4	26	0.3	5180	3684	47.9	2.0	5041
04/07/17	13	7.7	27	0.2	4100	3349	37.5	2.2	4624
12/07/17	21	7.9	28	0.1	4992	3467	36.7	2.1	4590
17/07/17	26	8.0	26	0.2	5014	3626	33.9	2.3	4915
24/07/17	33	8.0	28	0.1	4686	3589	36.4	2.3	5007
01/08/17	41	8.1	27	0.1	4808	3402	25.9	4.3	5175
08/08/17	48	8.0	28	0.2	5246	3527	28.5	6.9	5126
16/08/17	56	8.0	26	0.2	5184	3537	19.9	8.8	5146
22/08/17	62	8.0	25	0.1	6120	4005	19.8	9.6	5165
31/08/17	71	7.9	27	0.1	5954	3911	13.0	11.8	4857
05/09/17	76	7.9	27	0.1	7168	4047	10.3	12.7	4750
11/09/17	82	7.8	25	0.1	6212	3853	9.9	12.0	4781
26/09/17	97	7.8	26	0.1	6162	3860	1.9	4.9	4812
10/10/17	111	8.2	25	0.1	5904	3838	1.9	2.9	4780
24/10/17	125	8.1	23	1.5	7810	3814	1.0	1.8	4714
06/11/17	138	8.1	19	1.6	7190	2977	1.3	1.9	4656
21/11/17	153	8.1	26	1.7	4494	2900	11.4	2.2	4687
05/12/17	167	8.3	27	1.4	4644	3061	4.5	2.0	4837
22/12/17	184	8.2	27	0.8	6820	2912	4.9	2.2	5256
02/01/18	195	8.2	24	1.1	6930	3367	6.9	1.9	4795
12/02/18	236	8.2	25	1.7	7660	3366	1.5	1.5	4842

Table 19. Measured values of various parameters for monitoring the progress of denitrification during lab-scale storage (D2)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	TAN	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
			°C	mg/L					
21/06/17	1	6.9			7844	3632	26.2	2.9	5074
28/06/17	7	7.0	30	0.2	6212	3599	32.4	9.0	5474
04/07/17	13	6.7	32	1.9	6590	3368	2.2	0.6	4861
12/07/17	21	6.7	29	0.1	5402	3431	13.0	1.2	5168
17/07/17	26	6.8	27	5.9	7450	3547	7.3	0.5	5003
24/07/17	33	6.6	29	5.2	6902	3413	2.2	0.4	4838
01/08/17	41	6.5	28	5.3	6556	3483	5.5	0.4	5149
08/08/17	48	6.5	29	6.5	6128	3496	8.6	0.4	5180
16/08/17	56	6.4	27	4.7	5184	3537	2.3	0.6	4849
22/08/17	62	6.5	26	4.8	7806	3423	2.0	0.6	4745
31/08/17	71	6.5	27	4.8	7870	3549	2.5	0.4	5268
05/09/17	76	6.4	26	5.2	7608	3508	1.9	0.3	4748
11/09/17	82	6.3	25	6.7	7550	3500	2.0	0.4	5018
26/09/17	97	6.1	27	6.3	7504	3577	2.1	0.4	4732
10/10/17	111	6.1	26	6.4	7506	3463	2.0	0.3	4755
24/10/17	125	5.9	23	6.8	8394	3390	2.0	0.3	4728
06/11/17	138	5.9	20	9.0	5544	2461	3.0	0.3	4662
21/11/17	153	5.8	26	8.0	5854	2528	3.4	0.3	4740
05/12/17	167	5.8	27	8.5	6160	2927	6.3	0.4	4688
22/12/17	184	5.9	28	6.9	5192	3214	6.6	0.5	5113
02/01/18	195	5.8	24	8.2	5336	2503	6.4	0.5	4858
12/02/18	236	5.6	25	5.0	5358	2001	9.6	0.6	5186

Table 20. Measured values of various parameters for monitoring the progress of denitrification during lab-scale storage (D3)

Date	Days	pH	Temperature	DO	COD Soluble	TAN	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
			°C	mg/L				
21/06/17	0	6.9	10		3632	26.2	2.9	5074
05/07/17	14	7.2	10	1.5	3545	29.7	1.3	5953
12/07/17	21	7.4	10	0.1	3495	23.8	1.3	5979
18/07/17	27	7.5	10	0.1	3569	23.5	1.3	5955
01/08/17	41	7.5	10	0.5	3497	23.3	2.1	5912
17/08/17	57	7.4	10	0.1	3225	19.7	4.2	4950
25/08/17	65	7.3	11	0.8	4355	14.4	4.8	5437
12/09/17	83	7.2	10	0.9	4177	12.3	4.3	6010

Table 21. Measured values of various parameters for monitoring the progress of denitrification during lab-scale storage (D4)

Date	Days	pH	Temperature	DO	COD Soluble	TAN	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$
			°C	mg/L				
21/06/17	0	6.9			3632	26.2	2.9	5074
05/07/17	14	6.4	14	5.9	3614	45.9	0.5	4859
12/07/17	21	6.4	13	6.3	3606	1.8	0.6	5749
18/07/17	27	6.4	14	5.9	3478	1.8	0.4	5397
01/08/17	41	6.4	12	6.7	3323	1.2	0.3	5532
17/08/17	57	6.4	10	6.9	2983	2.7	0.4	5526
25/08/17	65	6.3	13	7.3	4185	2.1	0.4	5330
12/09/17	83	6.2	12	8.1	4204	4.5	0.5	5132

Table 22. Measured values of various parameters for monitoring the progress of volatilisation during lab-scale storage (V1)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	$N\text{-}NO_2^-$	TAN	$N\text{-}NO_3^-$	N-losses
			°C	mg/L						
16/11/17	1	8.3		0.1	16375	7538	1.1	5236	0	0%
23/11/17	7	8.2	19	0.1	14120	6661	1.1	4978	0	4.9%
30/11/17	14	8.6	27	0.1	11915	6728	0.9	4088	0	21.9%
07/12/17	21	8.8	20	0.1	13960	7418	1.0	3792	0	27.6%
14/12/17	28	8.9	28	0.1	16675	8202	1.5	2650	0	49.4%
22/12/17	36	9.1	28	0.1	14270	5804	0.9	2690	0	48.6%
03/01/18	48	9.2	25	0.1	14255	5444	0.9	2353	0	55.1%
18/01/18	63	9.3	26	0.1	21035	6186	0.8	2017	0	61.5%
01/02/18	77	9.2	22	0.1	16555	7246	1.1	1525	0	70.9%
15/02/18	91	9.1	27	0.1	16295	5682	0.9	1065	0	79.7%
28/02/18	104	8.9	26	0.1	10770	6505	0.6	690	0	86.8%

Table 23. Measured values of various parameters for monitoring the progress of volatilisation during lab-scale storage (V2)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	$N\text{-}NO_2^-$	TAN	$N\text{-}NO_3^-$	N-losses
			°C	mg/L						
16/11/17	1	8.3		0.1	16375	7538	1.1	5236	0	0%
23/11/17	7	9.1	20	0.1	18565	6802	0.9	4122	0	21.3%
30/11/17	14	9.2	28	0.1	19575	6492	0.8	3236	0	38.2%
07/12/17	21	9.3	21	0.1	19650	6598	0.8	2734	0	47.8%
14/12/17	28	9.3	29	0.1	17560	6554	0.7	2798	0	46.6%
22/12/17	36	9.4	29	0.1	17110	5186	0.8	2110	0	59.7%
03/01/18	48	9.3	26	0.1	16030	4918	0.7	2059	0	60.7%
18/01/18	63	9.3	27	0.1	15170	5630	0.8	1297	0	75.2%
01/02/18	77	9.3	27	0.5	13310	5640	0.8	1012	0	80.7%
15/02/18	91	9.0	28	0.6	13440	4914	0.7	581	0	88.9%
28/02/18	104	8.7	28	2.5	13880	5536	0.7	465	0	91.1%

Table 24. Measured values of various parameters for monitoring the progress of volatilisation during lab-scale storage (V3)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	$N\text{-}NO_2^-$	TAN	$N\text{-}NO_3^-$	N-losses
			°C	mg/L						
21/11/17	1	8.3		0.1	16375	7538	1.1	5236	0	0%
23/11/17	2	8.0	11	0.1	14965	7296	1.1	4002	0	23.6%
30/11/17	9	8.4	11	0.1	15820	7768	0.9	3642	0	30.4%
07/12/17	16	8.7	11	0.1	16150	7362	1.0	3024	0	42.2%
14/12/17	23	8.8	12	0.1	17230	7630	0.9	2823	0	46.1%
22/12/17	31	8.8	11	0.1	16055	6512	1.1	2642	0	49.5%
03/01/18	43	8.9	11	0.1	16280	6436	0.9	2518	0	51.9%
18/01/18	58	9.0	12	0.1	15170	6510	0.9	2012	0	61.6%
01/02/18	72	9.0	12	0.1	17640	6473	1.3	1354	0	74.1%
15/02/18	86	8.9	10	0.1	17330	7634	1.1	940	0	82.0%
28/02/18	99	8.7	14	0.1	18785	7054	1.1	661	0	87.4%

Table 25. Measured values of various parameters for monitoring the progress of volatilisation during lab-scale storage (V4)

Date	Days	pH	Temperature	DO	COD Total	COD Soluble	$N\text{-}NO_2^-$	TAN	$N\text{-}NO_3^-$	N-losses
			°C	mg/L						
21/11/17	1	8.3		0.1	16375	7538	1.1	5236	0	0%
23/11/17	2	8.8	10	0.1	14775	7308	1.0	4812	0	8.1%
30/11/17	9	9.1	11	2.3	15165	6878	0.9	3504	0	33.1%
07/12/17	16	9.3	10	2.3	15805	6988	1.0	3394	0	35.2%
14/12/17	23	9.3	11	4.8	15570	6662	0.9	3030	0	42.1%
22/12/17	31	9.2	11	3.8	15630	6342	1.1	1594	0	69.6%
03/01/18	43	9.2	11	5.6	15090	5763	0.9	1257	0	76.0%
18/01/18	58	9.1	11	5.9	14140	6480	0.9	876	0	83.3%
01/02/18	72	9.0	10	8.0	14185	6424	1.3	796	0	84.8%
15/02/18	86	8.9	10	7.9	15285	6430	1.0	609	0	88.4%
28/02/18	99	8.7	11	9.5	15760	5670	0.9	199	0	96.5%

Table 26. Concentration changes of total NO_3^- per week and the average rate of N loss from the nitrified LPD during storage.

Days	D1			D2			D3			D4		
	mg/L	%Losses	%Losses per week	mg/L	%Losses	%Losses per week	m/L	%Losses	%Losses per week	mg/L	% Losses	% Losses per week
0	4941	0%	0%	5035	0%	0%	5634	0%	0%	5265	0%	0%
7	4937	0.1%	0.1%	5028	0.1%	0.1%	5638	-0.1%	-0.1%	5276	-0.2%	-0.2%
14	4933	0.2%	0.1%	5021	0.3%	0.1%	5643	-0.2%	-0.1%	5287	-0.4%	-0.2%
21	4930	0.2%	0.1%	5014	0.4%	0.1%	5647	-0.2%	-0.1%	5298	-0.6%	-0.2%
28	4926	0.3%	0.1%	5007	0.6%	0.1%	5652	-0.3%	-0.1%	5309	-0.8%	-0.2%
35	4922	0.4%	0.1%	5000	0.7%	0.1%	5656	-0.4%	-0.1%	5319	-1.0%	-0.2%
42	4918	0.5%	0.1%	4993	0.8%	0.1%	5661	-0.5%	-0.1%	5330	-1.2%	-0.2%
49	4914	0.5%	0.1%	4986	1.0%	0.1%	5665	-0.6%	-0.1%	5341	-1.4%	-0.2%
56	4910	0.6%	0.1%	4979	1.1%	0.1%	5670	-0.6%	-0.1%	5352	-1.7%	-0.2%
63	4906	0.7%	0.1%	4972	1.2%	0.1%	5675	-0.7%	-0.1%	5363	-1.9%	-0.2%
70	4902	0.8%	0.1%	4965	1.4%	0.1%	5679	-0.8%	-0.1%	5374	-2.1%	-0.2%
77	4899	0.9%	0.1%	4958	1.5%	0.1%	5684	-0.9%	-0.1%	5385	-2.3%	-0.2%
83	4895	0.9%	0.1%	4952	1.6%	0.1%	5687	-1.0%	-0.1%	5394	-2.5%	-0.2%
90	4891	1.0%	0.1%	4945	1.8%	0.1%						
97	4887	1.1%	0.1%	4938	1.9%	0.1%						
104	4884	1.2%	0.1%	4931	2.1%	0.1%						
111	4880	1.2%	0.1%	4924	2.2%	0.1%						
118	4876	1.3%	0.1%	4918	2.3%	0.1%						
125	4872	1.4%	0.1%	4911	2.5%	0.1%						
132	4868	1.5%	0.1%	4904	2.6%	0.1%						
139	4864	1.6%	0.1%	4897	2.8%	0.1%						
146	4860	1.6%	0.1%	4890	2.9%	0.1%						
153	4856	1.7%	0.1%	4883	3.0%	0.1%						
160	4853	1.8%	0.1%	4876	3.2%	0.1%						
167	4849	1.9%	0.1%	4869	3.3%	0.1%						
174	4845	2.0%	0.1%	4862	3.4%	0.1%						
181	4841	2.0%	0.1%	4855	3.6%	0.1%						
188	4837	2.1%	0.1%	4848	3.7%	0.1%						
195	4833	2.2%	0.1%	4841	3.9%	0.1%						
202	4829	2.3%	0.1%	4834	4.0%	0.1%						
209	4825	2.3%	0.1%	4827	4.1%	0.1%						
216	4821	2.4%	0.1%	4820	4.3%	0.1%						
223	4818	2.5%	0.1%	4813	4.4%	0.1%						
230	4814	2.6%	0.1%	4806	4.6%	0.1%						
236	4810	2.6%	0.1%	4800	4.7%	0.1%						
MEAN (83 days)			**0.08%**			**0.1%**			**-0.08%**			**-0.2%**
MEAN (236 days)			**0.08%**			**0.1%**						

Table 27. Concentration changes of total N_{inorg} per week and the average rate of N loss from the nitrified LPD during storage.

Days	D1			D2			D3			D4		
	mg/L	%Losses	%Losses per week	mg/L	%Losses	%Losses per week	mg/L	%Losses	%Losses per week	mg/L	% Losses	%Losses per week
0	4980	0%	0%	5267	0%	0%	5664	0%	0%	5290	0%	0%
7	4975	0.1%	0.1%	5249	0.3%	0.3%	5668	-0.1%	-0.1%	5299	-0.2%	-0.2%
14	4970	0.2%	0.1%	5232	0.7%	0.3%	5671	-0.1%	-0.1%	5307	-0.3%	-0.2%
21	4964	0.3%	0.1%	5215	1.0%	0.3%	5674	-0.2%	-0.1%	5315	-0.5%	-0.2%
28	4959	0.4%	0.1%	5198	1.3%	0.3%	5678	-0.2%	-0.1%	5324	-0.6%	-0.2%
35	4954	0.5%	0.1%	5180	1.6%	0.3%	5681	-0.3%	-0.1%	5332	-0.8%	-0.2%
42	4949	0.6%	0.1%	5163	2.0%	0.3%	5685	-0.4%	-0.1%	5341	-1.0%	-0.2%
49	4944	0.7%	0.1%	5146	2.3%	0.3%	5688	-0.4%	-0.1%	5349	-1.1%	-0.2%
56	4938	0.8%	0.1%	5129	2.6%	0.3%	5692	-0.5%	-0.1%	5357	-1.3%	-0.2%
63	4933	0.9%	0.1%	5111	2.9%	0.3%	5695	-0.5%	-0.1%	5366	-1.4%	-0.2%
70	4928	1.0%	0.1%	5094	3.3%	0.3%	5699	-0.6%	-0.1%	5374	-1.6%	-0.2%
77	4923	1.2%	0.1%	5077	3.6%	0.3%	5702	-0.7%	-0.1%	5383	-1.7%	-0.2%
83	4917	1.3%	0.1%	5060	3.9%	0.3%	5705	-0.7%	-0.1%	5391	-1.9%	-0.2%
90	4912	1.4%	0.1%	5042	4.3%	0.3%						
97	4907	1.5%	0.1%	5025	4.6%	0.3%						
104	4902	1.6%	0.1%	5008	4.9%	0.3%						
111	4896	1.7%	0.1%	4991	5.2%	0.3%						
118	4891	1.8%	0.1%	4974	5.6%	0.3%						
125	4886	1.9%	0.1%	4956	5.9%	0.3%						
132	4881	2.0%	0.1%	4939	6.2%	0.3%						
139	4876	2.1%	0.1%	4922	6.5%	0.3%						
146	4870	2.2%	0.1%	4905	6.9%	0.3%						
153	4865	2.3%	0.1%	4887	7.2%	0.3%						
160	4860	2.4%	0.1%	4870	7.5%	0.3%						
167	4855	2.5%	0.1%	4853	7.9%	0.3%						
174	4849	2.6%	0.1%	4836	8.2%	0.3%						
181	4844	2.7%	0.1%	4818	8.5%	0.3%						
188	4839	2.8%	0.1%	4801	8.8%	0.3%						
195	4834	2.9%	0.1%	4784	9.2%	0.3%						
202	4829	3.0%	0.1%	4767	9.5%	0.3%						
209	4823	3.1%	0.1%	4749	9.8%	0.3%						
216	4818	3.3%	0.1%	4732	10.1%	0.3%						
223	4813	3.4%	0.1%	4715	10.5%	0.3%						
230	4808	3.5%	0.1%	4698	10.8%	0.3%						
236	4802	3.6%	0.1%	4680	11.1%	0.3%						
MEAN (83 days)			**0.1%**			**0.3%**			**-0.06%**			**-0.2%**
MEAN (236 days)			**0.1%**			**0.3%**						

Table 28. Concentration changes of TAN per week and the average rate of N loss from the untreated LPD during storage

Days	V1		V2		V3		V4	
	mg/L	%Change	mg/L	%Change	mg/L	%Change	mg/L	%Change
0	4676	0%	4116	0%	4121	0%	4182	0%
7	4384	6.2%	3835	6.8%	3858	6.4%	3852	7.9%
14	4093	6.2%	3554	6.8%	3595	6.4%	3522	7.9%
21	3802	6.2%	3273	6.8%	3333	6.4%	3192	7.9%
28	3511	6.2%	2992	6.8%	3070	6.4%	2862	7.9%
36	3178	7.1%	2671	7.8%	2770	7.3%	2485	9.0%
43	2886	6.2%	2390	6.8%	2507	6.4%	2155	7.9%
50	2595	6.2%	2109	6.8%	2244	6.4%	1825	7.9%
57	2304	6.2%	1828	6.8%	1982	6.4%	1495	7.9%
64	2012	6.2%	1547	6.8%	1719	6.4%	1165	7.9%
71	1721	6.2%	1267	6.8%	1456	6.4%	835	7.9%
78	1430	6.2%	986	6.8%	1194	6.4%	505	7.9%
85	1139	6.2%	705	6.8%	931	6.4%	175	7.9%
92	847	6.2%	424	6.8%	668	6.4%	-155	7.9%
99	556	6.2%	143	6.8%	405	6.4%	-485	7.9%
104	265	6.2%	-138	6.8%				
Mean		**5.9%**		**6.5%**		**6.0%**		**7.4%**
SD		**0.02**		**0.02**		**0.02**		**0.02**

Table 29. Measured concentrations before and after the vacuum evaporation and mass balance calculations of different parameters (1/3)

Variable	Date	Sample	pH	EC	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN
				mS/cm			mg/L			mg				
Nitrified LPD	31/07/17	1	6.1	49.8	3833	2417	5654	0.338	5.878	766.6	483.4	1130.8	0.068	1.2
Thickened LPD	31/07/17	1	5.8	109.1	26730	10570	17918	0.97	10.38	1737.5	687.1	1164.7	0.063	0.7
Distillate	31/07/17	1	7.2	0.03	106.8	106.8	1.86	0.013	2.75	14.3	14.3	0.25	0.002	0.37
								% Thickened LPD		227%	142%	103%	92.9%	57%
								%Distillate		1.9%	2.9%	0.02%	2.6%	31%
								% Total		229%	145%	103%	95%	89%
								% Losses or % Increases		**-129%**	**-45%**	**-3%**	**5%**	**11%**
Nitrified LPD	31/07/17	2	6.1	49.8	3833	2417	5654	0.338	5.88	766.6	483.4	1130.8	0.068	1.2
Thickened LPD	31/07/17	2	5.9	88.8	22810	10392	11198	0.87	9.05	1961.7	893.7	963	0.075	0.8
Distillate	31/07/17	2	8.2	0.02	105.5	105.5	2.302	0.0116	3.62	11.9	11.9	0.26	0.0013	0.4
								% Thickened LPD		256%	185%	85%	110.5%	66.2%
								%Distillate		1.6%	2.5%	0.02%	1.9%	34.7%
								% Total		257%	187%	85%	112%	101%
								% Losses or % Increases		**-157%**	**-87%**	**15%**	**-12%**	**-1%**

Table 29. Measured concentrations before and after the vacuum evaporation and mass balance calculations of different parameters (2/3)

Variable	Date	Sample	pH	EC	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN
				mS/cm			mg/L			mg				
Nitrified LPD	31/07/17	3	6.1	49.8	3833	2417	5654	0.338	5.88	766.6	483.4	1130.8	0.068	1.2
Thickened LPD	31/07/17	3	5.7	99.1	21010	11744	14300	1.13	12.45	1680.8	939.5	1144	0.0904	0.996
Distillate	31/07/17	3	7.2	0.02	111.6	111.6	1.433	0.0561	2.43	13.28	13.28	0.17	0.007	0.289
								% Thickened LPD		219%	194%	101%	134%	84.7%
								%Distillate		1.7%	2.7%	0.015%	9.8%	24.6%
								% Total		220%	197%	101%	144%	10.39%
								% Losses or % Increases		**-120%**	**-97%**	**-1%**	**-44%**	**-9.3%**
Nitrified LPD	29/08/17	**4**	6.848	55.0	4928	3531	5604	0.81	11.17	985.6	706.2	1120.8	0.162	2.2
Thickened LPD	29/08/17	**4**	6.390	95.4	26990	12366	12582	2.00	23.12	2699	1236.6	1258.2	0.20	2.3
Distillate	29/08/17	**4**	8.312	0.03	180.2	180.2	1.316	0.0314	2.578	18.02	18.02	0.132	0.003	0.26
								% Thickened LPD		274%	175%	112%	123.5%	103%
								%Distillate		1.8%	2.6%	0.01%	1.94%	12%
								% Total		276%	178%	112%	125%	115%
								% LOSSES OR % INCREASES		**-176%**	**-78%**	**-12%**	**-25%**	**-15%**

Table 29. Measured concentrations before and after the vacuum evaporation and mass balance calculations of different parameters (3/3)

Variable	Date	Sample	pH	EC	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN	COD Total	COD Soluble	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TAN
				µS/cm			mg/L			mg				
Nitrified LPD	29/08/17	**5**	6.848	55000	4928	3531	5604	0.81	11.17	985.6	706.2	1120.8	0.162	2.2
Thickened LPD	29/08/17	**5**	6.412	88900	29430	13486	10410	1.89	20.02	3031.3	1389.1	1072.2	0.195	2.1
Distillate	29/08/17	**5**	8.715	27.8	189		0.798	0.0366	3.54	17.9	17.9	0.076	0.0035	0.3
								% Thickened LPD		308%	197%	96%	120.42%	92.3%
								%Distillate		1.8%	2.5%	0.007%	2.146%	15.1%
								% Total		309%	199%	96%	123%	107%
								% Losses or % Increases		**-209%**	**-99%**	**4%**	**-23%**	**-7%**