Digestate Nitrification for Nutrient Recovery

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Abstract: A large portion of nutrients is dissolved in the liquid fraction of the effluents (digestates) resulting from anaerobic digestion (AD) of wet organic wastes. The aim of this study is to establish an efficient way of converting such digestates into liquid "organic fertilizer". Enhancement of the nutrient concentration is necessary in order to make the final product commercially acceptable. Direct evaporative concentration is not suitable, as it would lead to a significant loss of ammonia. Thus, stabilizing the product by nitrification prior to evaporation was proposed, and a series of experiments was conducted to evaluate the appropriateness of this approach. The study was conducted using the digestate (containing 1.7 g/L NH_4-N) from a full-scale biogas plant in Norway. The process was further analyzed by modelling and simulations using ASM 3, which was found to be an appropriate biochemical model for designing such digestate nitrification plants. The digestate was successfully nitrified to achieve above 75 % NH_4-N conversions without any addition of extra alkalinity. The nitrification brings the pH down to below 5.0 where the remaining ammonia is present as > 99 % NH_4^+. In this condition the nitrified digestate can be evaporated without significant nitrogen (NH_3 gas) loss. The toxic metal content of the nitrified liquid fertilizer is much lower than that of the original digestate. The nitrified digestate gained superior aesthetic quality as an almost translucent and odourless liquid. It is concluded that effluents from anaerobic digesters operating on municipal organic wastes can successfully be converted into a high quality commercial grade liquid fertilizer through post anaerobic nitrification.

Keywords: Anaerobic digestion, ASM 3 model, nitrification, nutrient recovery, organic fertilizer.

1. INTRODUCTION

Nutrient mismanagement can lead to disastrous environmental alterations due to the excessive accumulation of nitrogen in soil and water. Eutrophication of surface water bodies, ammonia toxicity in aquatic life forms, acidification of soil and ground water and surface waters, assisting ground level ozone, greenhouse gas and smog formation are among the major environmental impacts of different nitrogenous compounds resulting from untreated nutrient releases to open environments [1-3]. After the EU directive of 91/271/EEC [4], European member states were guided to adopt more stringent water nutrient standards and incorporate nutrient removal stages into their wastewater treatment facilities. However, instead of following the traditional nitrogen removal treatment strategy, which converts chemically bound nitrogen into N_2 gas, the modern day treatment practice encourages the reuse and recycling of nutrients from wastes. For example, it is estimated that recycling nutrients from domestic wastes can replace 35 - 45 % of the industrially produced and energy intensive fertilizers which are in use today [1]. This level of nutrient recycling will be essential in the future to achieve a sustainable relationship between the natural environment and the ever increasing human interference with it. The non-renewability and resultant exhaustion of mineral nutrients used for food production is another important perspective motivating the development of more complete nutrient recycling schemes. The focus in the present study is on nitrogen, but the scheme proposed will also lead to a more complete recycling of phosphorus and potassium, which at present come almost exclusively from limited mineral reserves [3, 5].

The effluents from anaerobic digesters operating on municipal organic wastes contain relatively high amounts of ammonia nitrogen. This is because ammonium is a product of protein metabolism [6] and municipal organic wastes are rich in proteins from food residues. Methane-producing fermentation processes do not fix nutrients in an effective manner [7, 8] but increase the content of soluble nutrients *via* the dissolution and mineralization of particulate organic matter [8]. Other organic nitrogenous compounds such as amino acids and urea are also mainly reduced to ammonia in AD. Ammonia itself cannot be further degraded without an aerobic treatment stage [2] in order to oxidize ammonium nitrogen to nitrate and/or nitrite. Nitrified ammonium can be denitrified to nitrogen gas by heterotrophic denitrification or by anaerobic ammonium oxidation (*anammox* process [9]) from nitrite under anaerobic conditions. Municipal digestates usually contain 1500 – 4000 mg/L of NH_4-N together with some organic N and negligible amounts of nitrate and nitrite [7; chemical analysis made during this study].

The direct application of anaerobic digestates as nitrogen fertilizers in farmlands [7, 8] is the most straightforward method of nutrient recycling in small scale and closed systems (such as small scale farms, diaries, sugar mills *etc.*). Note that Swedish farmers accept anaerobically digested manure as a valued fertilizer, primarily because of a faster

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nitrogen effect than the raw farmyard manure [10]. However, direct spreading of municipal digestates on farmlands is legally restricted in many countries owing to stringent guidelines on toxic contaminants (e.g. heavy metals) which may enter and accumulate in the human body through bio-magnification along food chains. These kind of direct applications are usually not economically attractive either, due to comparatively low nutrient concentrations which lead to high transport and handling costs [3]. The public acceptance based on the aesthetic quality of this type of raw digestates (odour, color, particulate matter) may further restrict its commercial use. The most critical barrier for using these digestates as direct commercial fertilizers is the instability of the ammonia nitrogen (NH_4-N) at above-neutral pH levels which are typical for digestates. The high ammonia nitrogen content hinders the capability of concentrating these digestates by evaporation as it tends to release ammonia (NH_3 gas), thus reducing the fertilizer quality and also materializing an air pollution problem.

Note that two forms of ammonia nitrogen species NH_3 (free ammonia) and NH_4^+ (ammonium ion) have strong equilibrium relations both with temperature and pH [11]. Untreated digestates usually have a pH of around 7.5 to 8.5. At these above-neutral pH values, the unionized NH_3 form is abundant. Using ammonia as the sole source of nitrogen for plants is not ideal either as it can lead to acidification in the plant root zone. In this perspective, nitrification of the digestate therefore seems to be a logical step towards stabilizing the nitrogen and making the digestate suitable for evaporative concentration.

Nitrification converts ammonia nitrogen into nitrates (NO^-_3) which is more stable in the soil and is a highly mobile nitrogen source for plants. Nitrification is a two step biochemical reaction. In the first step, ammonium is oxidized into nitrite (by a group of bacteria called "nitritifiers" or "ammonia oxidizing bacteria - AOB"). In the second stage, nitrite is further oxidized into nitrate (by a group of bacteria called "nitratifiers" or "nitrite oxidizing bacteria, NOB"). Both of these bacterial groups are categorized as aerobic autotrophic organisms. The overall conversion reaction can be represented by Reaction *(a)* [12].

$$NH_4^+ + 1.863O_2 + 0.098CO_2 \rightarrow 0.0196C_5H_7NO_2 + 0.98NO_3^- + 0.0941H_2O + 1.98H^+ \quad \text{(a)}$$

The aim of the present study was to investigate the applicability of nitrification to overcome the three basic challenges in using anaerobic digestates as a commercial grade fertilizer, namely: 1) the stability issue, especially related to making a high quality concentrated liquid fertilizer; 2) toxic metal content; 3) the aesthetic quality of the product. Regarding the concern about toxic metals, attention was primarily given to the seven heavy metals, Cd, Hg, Pb, Ni, Cr, Zn and Cu which are regulated by Norwegian governmental and European Union norms for controlling the applications of bio-solids in agriculture [13, 14]. An experimental laboratory study was carried out on digestate from a commercial AD plant treating wet organic wastes in order to investigate the effects of nitrification. The experiments were followed up by a theoretical analysis to generalize the results.

2. MATERIALS AND METHODS

2.1. Feed Source

The source digestate was obtained from a full scale active anaerobic digestion plant (*Hadeland and Ringerike Avfallselskap, Jevnaker,* Norway). This plant has a total reactor volume of 2300 m^3 in three reactor stages; one hydrolysis tank (350 m^3) followed by two consecutive methanogenic reactors (1500 and 450 m^3 respectively). The plant operates at a (total) hydraulic retention time of 20 days. This plant had been operating on municipal source separated organic residues for more than one year when this study commenced. The first methanogenic reactor is maintained at thermophilic conditions (52 - 55 ^oC) and the second digester is operated under ambient conditions without temperature control. At the time of the experiments reported here, the effluent from this second reactor contained approximately 1700 mg /L of NH_4-N (Table **1**), and was used as the feed source for the experiments described here.

Table 1. Characteristics of Anaerobic Digestate Used

Parameter	Value	Units
NH_4-N	1700	mg/L
pH	8.05	-
COD (soluble)	3260	mg/L
Total solids	23.5	g/L
Volatile solids	15.5	g/L
Kjeldahl -N	15.9	g /100 g TS
Total P	233	mg/L
Total S	95.2	mg/L

2.2. Nitrification Setup

The reactor assembly consisted of five identical glass columns (1 m height and 5 cm internal diameter) each equipped with aeration diffusers and tube connections (*Tygon*® tubes of 6 mm outer diameter) for feeding and removing samples. The diffusers placed at the bottom of the columns provided the air supply and were also used for mixing. Continuous aeration was provided by aquarium aerators (*Eheim 400*, 4 Watts) with two channels in each unit.

The used inoculum was a mixture of sludge from a nitrifying wastewater treatment facility (ESSO petroleum refinery at *Slagentangen*, *Vestfold*, Norway), sludge from a municipal wastewater treatment plant with biological N and P removal stages (*Risor*, Norway), and sludge from a bench top scale nitrification reactor operated on a synthetic nutrient feed (4.438 g/L of $(NH_4)_2SO_4$, 3.581 g/L of K_2HPO_4, 0.344 g/L of KH_2PO_4, and 7.445 g/L of $NaHCO_3$). This inoculum mixture was pre-acclimated with the anaerobic digestate in an aerated vessel for 20 days before being introduced into the reactor columns.

2.3. Operation of Reactors

Five reactors (named columns 1 - 5) were operated as sequential batch reactors under laboratory-controlled

conditions at 25 °C. Feeding was done once per day after removal of the same volume of effluent before each feeding. The effluent removal was done after stopping the aeration and allowing the columns to settle for 15 minutes. This procedure ensures low sludge removal from the reactors in order to avoid the washing out of the slow-growing nitrifying organisms [2].

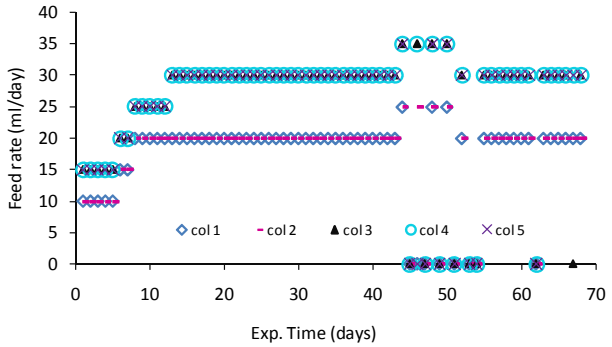


Fig. (1). Volumetric feed patterns for the five columns.

As depicted in Fig. (**1**), two different NH_4-N loading levels were applied. In order to avoid shock loading of the culture, a stepwise increase in daily feeding was done so that the activated sludge could adapt to the higher concentrations of digestate with time. Starting from the lowest feeding levels of 10 and 15 ml/d, feeding volumes were increased until they reached 20 and 30 ml/d through the first 12 days time period. The feeding was kept constant at these levels for the next 31 days, which comprises the main phase of this experimentation (note that days are counted from the start up of the column reactors – not considering the prior acclimation period). Two of the five columns (columns 1 and 2) were fed 20 ml/d of digestate while the other three (columns 3, 4 and 5) were fed 30 ml/d of digestate during this 31 day period. The difference in feeding volumes leads to two different initial pH levels (after each feeding) in the reactor assay. The feeding volumes were so chosen to keep pH at approximately 6.0 and 7.0 in the respective reactor columns.

All columns were fed with the same digestate, but heavier particles were first removed from the feed of two of the columns (columns 1 and 5). This was done by first allowing the digestate to sediment for one day (settled in a 100 ml volumetric cylinder filled to a liquid height of 20 cm). In the case of other three columns (columns 2, 3 and 4), the digestate was taken from its original container after rigorous mixing to avoid any settling. This unsedimented and sedimented feed difference was set to reveal any possible effects of the heavy particulate fraction of the digestate on the process and the quality of the final product.

At the end of the main (steady feeding) phase of the experiment (day 43), another step increase in feeding was applied to the columns; i.e. to 25 and 35 ml/d for 7 days. From day 52 to the end of the experiment (on day 68), feed volumes were reduced back to 20 and 30 ml/d but, with less regular feeding.

2.4. Analytical Methods

Daily pH measurements were made before and after feeding using a Beckman Φ 390 pH meter. More detailed pH measurements (usually on a two-hour basis) were made at selected feeding cycles (between two consecutive feedings). The concentrations of NH_4-N, NO_3-N and NO_2-N in the five columns were measured at selected feeding cycles. NH_4^+, NO_3^-, and NO_2^- analyses were performed using absorption colorimetry with a mobile spectro-photometer (*Lasa 100*). Soluble COD measurements were made using the closed reflux colorimetric method. For the analyses of NH_4^+, NO_3^-, NO_2^- and COD (s), 10 ml samples were taken from each column and centrifuged at 9000 rpm for 10 minutes and then the supernatants were filtered through 0.45 μm syringe filters and finally diluted to the required ranges (10, 20 or 50 times) using deionized water. The levels of dissolved oxygen in the reactors were measured using a WTW Oxi 340-A oxygen meter in order to confirm that a sufficient and constant aeration was maintained in the reactor assay. Sludge settling rates of the different reactor columns were estimated at the start and at the end of the 32 day long steady feeding phase. Standard methods [15] were used to determine the total suspended solids (TSS) and volatile solids (VS) contents of the feed digestate.

Analyses were also carried out to characterize the presence of various metals and heavy metals in the digestate. Similar analyses were done on the nitrified effluent collected at the end of the experimental duration. Metal and heavy metal analyses were carried out according to accredited procedures (7 M HNO_3 extraction based on [16, 17]) and determined using ICP.

2.5. Modelling and Simulation

A simulation model was developed by approximating the reactor columns by a simple CSTR system with a complete sludge retention (sludge recycle ratio, R = 1). The daily feeding and effluent removal were simulated as continuous flow through the reactor. The necessary reaction equations and kinetic rate expressions were adopted from the ASM 3 (Activated Sludge Model no. 3 [18]).

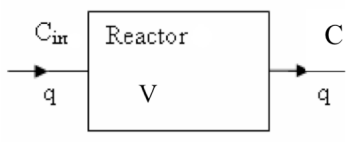
The ASM 3 kinetic model consists of a stoichiometric matrix with 12 biochemical processes and 13 different compounds. The compounds are divided into 7 soluble compounds and 6 particulate compounds (refer to ASM 3 [18] for details on the stoichiometric matrix, kinetic rate expressions and other relevant descriptions). The schematic reactor model developed here addresses the relevant transformation processes of these soluble and particulate components by two different generic ordinary differential equations. In addition a third equation was applied for dissolved oxygen in order to accommodate the aeration process.

Considering an arbitrary soluble component *A* and formulating the species mass balance,

Accumulation of component "A" in reactor column = *Inflow of component "A" into reactor column* - *Outflow of component "A" out of reactor* + *Generation/consumption of component "A"*

Using the usual notations (see Nomenclature), we can represent this word statement by the equation:

$$\Rightarrow \frac{dn_A}{dt} = \dot{n}_{A,in} - \dot{n}_{A,out} + \dot{n}_{A,gen} \quad (1)$$



Using the concentrations and flow rates, *Eq. 1* can be expressed as:

$$\frac{d}{dt}(C_A V) = qC_{in,A} - qC_A + r_A V \quad (2)$$

Assuming a constant flow rate through the reactor system,

$$V\frac{d}{dt}(C_A) = qC_A - qC_A + r_A V \quad (3)$$

$$\Rightarrow \frac{d}{dt}(C_A) = \frac{q}{V}(C_{in,A} - C_A) + r_A \quad (4)$$

Using the vector notation, the generic equation for every soluble component in the reactor column can be written as:

$$\Rightarrow \frac{dC^s}{dt} = \frac{q}{V}(C^s_{in} - C^s) + r \quad (5)$$

Here r is the vector of the rate of generation and can be expressed as:

$$r = S^T \cdot r_b \quad (6)$$

Here, r_b = vector of the rate of reaction

S = stoichiometric matrix of the reaction system

S^T denotes the transpose of the stoichiometric matrix S

Now the generic equation representing all soluble components can be expressed as:

$$\frac{dC^s}{dt} = \frac{q}{V}(C^s_{in} - C^s) + S^T \cdot r_b \quad (7)$$

Now repeating the species mass balance analysis for an arbitrary particulate component A leads to the equation:

$$\Rightarrow \frac{dn_A}{dt} = \dot{n}_{A,in} + \dot{n}_{A,gen} \quad (8)$$

Note that here, there is no term representing the outflow of the component A, since all the sludge is retained in the reactor column (no sludge removal).

Using concentrations and flow rates, *Eq. 8* may be expressed as:

$$\frac{d}{dt}(C_A V) = qC_{in,A} + r_A V \quad (9)$$

$$\Rightarrow \frac{d}{dt}(C_A) = \frac{q}{V}C_{in,A} + r_A \quad (10)$$

Now using the vector notation and by substituting r_A by *Eq. 6*, a generic equation for all particulate components is obtained:

$$\frac{dC^p}{dt} = \frac{q}{V}C^p_{in} + S^T \cdot r_b \quad (11)$$

A separate equation for the soluble component oxygen is also required in order to represent the physiochemical process of aeration; in addition to the biochemical consumption/generation processes.

Once again, starting from the species mass balance for dissolved O_2,

Accumulation of O_2 in reactor column = *O_2 inflow with influent* + *O_2 addition by Aeration* - *O_2 outflow with effluent* + *O_2 generation/ consumption*

$$\Rightarrow \frac{dn_{O_2}}{dt} = \dot{n}_{O_2,in} + \dot{n}_{O_2,Aeration} - \dot{n}_{O_2,out} + \dot{n}_{O_2,gen} \quad (12)$$

$$\Rightarrow \frac{d}{dt}(C_{O_2} V) = qC_{in,O_2} + r_{Aeration} V - qC_{O_2} + r_{O_2} V \quad (13)$$

Here r_{O2} includes the oxygen generation/consumption rates related with any other component. Thus in reality, $r_{O2} = r$. Then, using *Eq. 6*,

$$\Rightarrow \frac{d}{dt}(C_{O_2} V) = q(C_{in,O_2} - C_{O_2}) + r_{Aeration} \cdot V + S^T \cdot r_b V \quad (14)$$

$$\Rightarrow \frac{dC_{O_2}}{dt} = \frac{q}{V}(C_{in,O_2} - C_{O_2}) + r_{Aeration} + S^T \cdot r_b \quad . \quad (15)$$

According to the mass transfer theory [12], aeration rate can be expressed as:

$$\Rightarrow r_{Aeration} = k_L a(C_S - C_{O2}) \quad (16)$$

Here $k_L a$ = oxygen transfer coefficient; C_S = saturation concentration of oxygen in water (at the given temperature).

$$\Rightarrow \frac{dC_{O_2}}{dt} = \frac{q}{V}(C_{in,O_2} - C_{O_2}) + k_L a(C_S - C_{O_2}) + S^T \cdot r_b \quad (17)$$

$$\Rightarrow \frac{dC_{O_2}}{dt} = \frac{1}{V}[q \cdot C_{in,O_2} + V \cdot k_L a(C_S - C_{O_2}) - q \cdot C_{O_2}] + S^T \cdot r_b \quad (18)$$

The complete reactor model consisting of *Eq. 7*, *Eq. 11* and *Eq. 18* can be solved using an appropriate numerical tool such as the *ode45* ordinary differential equation solver available in Matlab (7.0). The stoichimetric coefficients required for the matrix S and the kinetic rate expressions required for r_b are taken from ASM 3 [18]. Also the typical kinetic parameter values suggested in ASM 3 are used (these values are, however, not a part of the ASM 3 itself).

3. RESULTS AND DISCUSSION

3.1. System Monitoring *via* pH Measurements

The variation of pH during each consecutive feeding interval (1 day) was monitored as an appropriate way of following the nitrification dynamics of the reactors. The pH drop follows nitrification as nitrification consumes 7.07 g alkalinity (as $CaCO_3$ equivalent) per gram of NH_4-N converted [12]. According to Fig. (**2a**), it is clear that the pH responds consistently to feeding cycles. A closer look at the pH measurements for all 5 reactors during two consecutive

feeding cycles confirms the consistent pH response and shows that differences between the reactors can be detected (Fig. **2b**). Since any addition of extra alkalinity was not made, the reactors had limited buffer capacity and a drop of almost 3 pH units was observed due to nitrification during each cycle. From the view point of process economy, and also for safeguarding the status of the intended fertilizer as "fully organic", it is thought to be an advantage to conduct the nitrification process with a minimum or no addition of extra chemicals (as alkalinity or pH buffers).

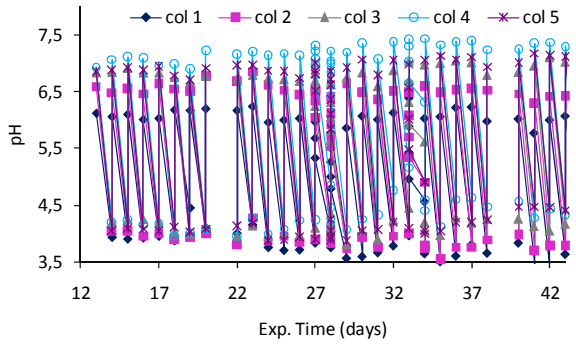


Fig. (2a). pH variation for the duration from day 13 to day 44 (steady feeding phase).

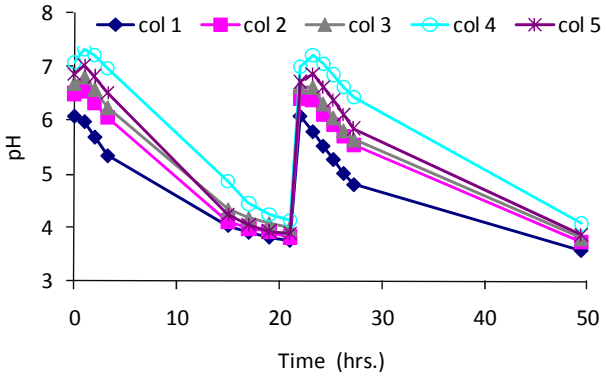


Fig. (2b). Detailed pH measurements during two consecutive feeding cycles (day 27– day 29).

Columns fed 30 ml of digestate (columns 3, 4 and 5) show a larger pH drop, compared to the columns fed 20 ml of digestate (columns 1 and 2), and they maintain a higher average pH (Fig. **2b**). The columns fed pre-sedimented digestate (1 and 5) had less alkalinity compared to the columns fed unsedimented digestate (2, 3 and 4), resulting in a steeper pH drop. This is illustrated by comparing the pH curves of columns with the same feed volume; *i.e.,* 5 with 4 and 1 with 2 (Fig. **2b**). The particulate fraction present in the digestate evidently contributes additional buffer capacity, probably *via* the dissolution of solids to soluble ions.

At the end of the 32 day long steady feeding duration, the two feeding levels were increased from 20 and 30 ml/d to 25 and 35 ml/d. The corresponding pH measurements suggest that the nitrification rate had dropped significantly after the load increase. For example, before the load increase (on day 43 and day 44) pH drops observed in a single day (between two consecutive feedings) for five columns (col. 1 to col. 5) were 6.1 to 3.9, 6.4 to 3.8, 7.0 to 4.1, 7.3 to 4.4 and 7.1 to 4.4 respectively. After the load increase (on day 44), it took four days for the pH in columns 1 and 5 to drop from 7.3 to 4.1 and from 7.3 to 4.5 respectively (without any feeding in between). This condition can be defined as an overload, since the higher feed load lead to less nitrification. Meanwhile, for columns 2, 3 and 4, pH value drops were 6.9 to 3.3, 7.2 to 3.9, and 7.5 to 4.5 respectively, and these drops took place during a two day period (without feeding in between). However, during the next two feeding cycles (on day 48 and day 50), all the columns behaved in a more similar manner and pH dropped below 4.5 within a two day period (without feeding in between). The initial (just after feeding) pH values started to increase beyond the previously intended 6.0 and 7.0 limits and ascended towards 7.5 for most of the reactors. This pH is close to the optimum pH suggested for nitrification (7.9±0.4 – 8.2±0.3 [19]), but nitrification still decreased, probably due to free ammonia (NH_3) inhibition of the nitrifying organisms. A theoretical calculation based on the NH_4^+ - NH_3 equilibrium data ([12]) shows that the free ammonia concentration could have exceeded 10 mg/L under the above mentioned operating conditions. The free ammonia at pH < 7 should be near zero [12]. Therefore, it is concluded that the observed overload behaviour is caused by NH_3 inhibition. Thus, on day 52, it was decided to reduce the feed rates back to 20 and 30 ml/day and to observe the recovery of the reactors to earlier conditions. This phase continued for another 14 days and the detailed pH measurements made during a single feeding cycle (days 68 - 69) are illustrated in Fig. (**3**). It is evident that these pH curves correspond well with the curves shown in Fig. (**2b**) except for the behaviour of column 3. It is concluded that the culture in reactor column 3 had been permanently damaged by the overload while the others were able to recover. Column 3 never recovered and consecutive feedings led to higher and higher initial (after feed) pH values until a complete failure occurred (Fig. **4**). The exact reason for the sudden loss of nitrification in column 3 on day 63 was not clear but the complete failure could have been avoided if the feeding in the next cycle had been stopped. Feed accumulation can lead to higher pH and increased amounts of free ammonia (NH_3) and even low concentrations (such as 0.1 mg/L, free ammonia) can inhibit nitrifying organisms [7; 20]. However this is a clear example of the nature of bioreactor failures commonly found in practice and it emphasizes the importance of detecting the early signs of failures by simple measurement techniques (like pH) and the necessity of taking direct corrective measures promptly in order to avoid complete system failures.

These results show that continuous feed can be advantageous compared to the sequential batch operation tested, in order to maintain low pH and low ammonia concentrations. Ammonia stripping and ammonia inhibition of the nitrifying organisms could thereby be avoided even at high loading rates.

3.2. Nitrification During a Single Cycle

Figs. (**5a**, **5b**) show the variation of NH_4-N and NO_3-N concentrations (in mg/L) respectively in reactor columns during a single feeding cycle (days 33 - 34). The degree of

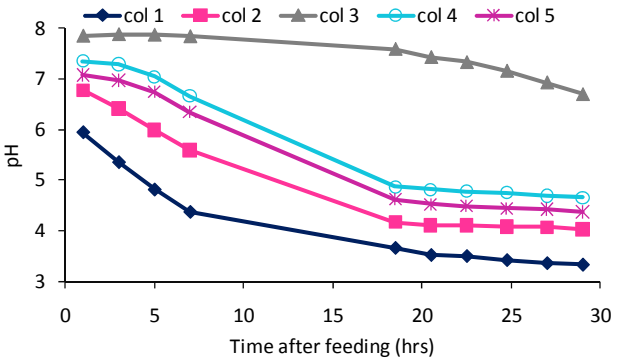


Fig. (3). Detailed pH measurements for a single feeding cycle (days 68 – 69).

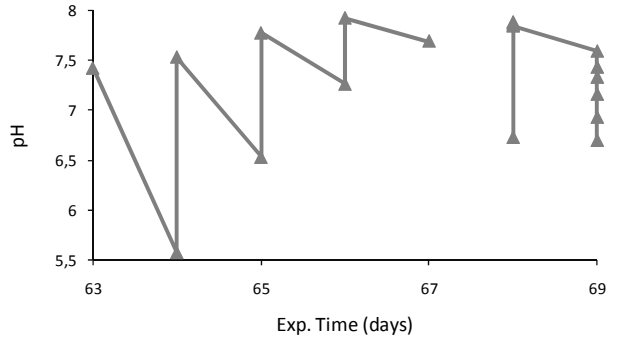
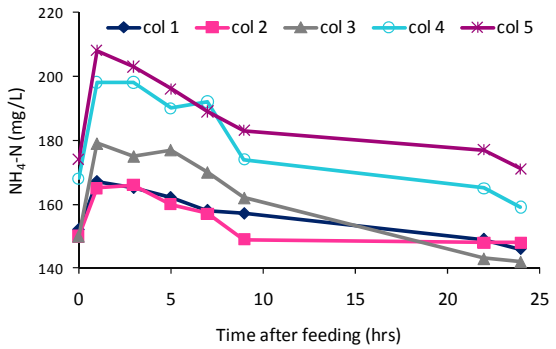


Fig. (4). Progressive failure of reactor column 3 (days 63 – 69).

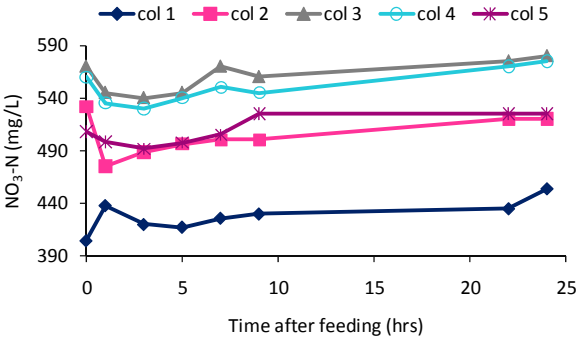
nitrification cannot be read directly from Fig. (**5**) since the process was far from the steady state due to the long hydraulic retention time (> 33 days). It was calculated that about 75 % ammonia nitrogen removal was obtained, mainly by conversion to nitrate nitrogen, by accounting for the "dilution effect" of adding the given volumes of feed every day for 33 days. Significant ammonia losses are also observed in some columns (24 % in column 1 and 27 % in column 5) and can be linked to the assimilation into microbial cells and stripping out as NH_3 at the higher pH conditions prevailing in the early phase of the feeding cycle. Pambrun *et al.* [21] observed that ammonia loss due to the combined effects of assimilation and stripping could be as high as 10 – 20 %. Instant ammonia stripping was also observed by Yamamoto *et al.* [7]. They further reported that nitrification conditions were restored to a greater degree by lowering the pH from 9.0 to below 7.5. Any significant ammonia loss due to *anammox* process is unlikely here, mainly due to the high oxygen level maintained and the strict anaerobic nature of *anammox* organisms ([9]).

As should be expected, the columns fed 30 ml/d (3, 4 and 5) showed higher nitrate concentrations compared to the columns fed 20 ml/d (1 and 2), (Fig. **5b**). The columns fed pre-sedimented digestate had lower nitrate accumulation than the columns fed unsedimented digestate. For example, column 5, which was fed sedimented digestate, had significantly lower nitrate content than columns 3 and 4 (parallel to each other), which were fed the same amount of unsedimented digestate. The comparison of columns 1 and 2 further confirms this observation. It is plausible that suspended solids (SS) may release extra NH_4-N during the

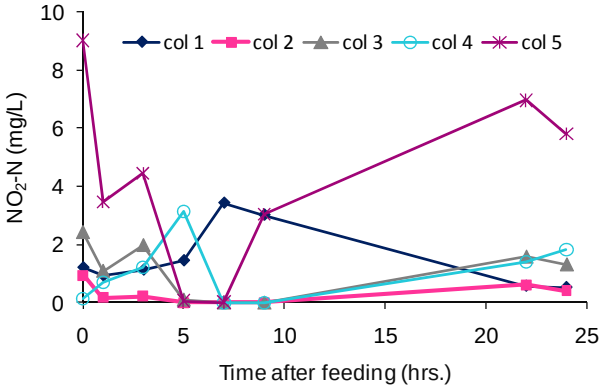
(**a**) NH_4-N Reduction



(**b**) NO_3-N Increase



(**c**) NO_2-N Levels



(**d**) COD (s) Variation

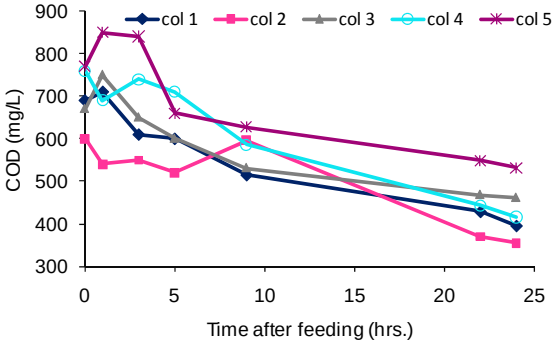


Fig. (5). Parameter variations during a single feeding cycle (days 33 – 34). (Note: The first data points at time zero indicate the reactor condition just before feeding).

process leading to higher NO_3-N levels. This may also explain the NH_4-N and NO_3-N imbalance observed in columns 2 and 4 where more NO_3-N was produced than the NH_4-N consumed (Figs. **5a**, **5b**). This suggests the release of additional NH_4-N from suspended solids. Meknassi *et al.* [22] observed that large amounts of NH_4-N can be present in the solid phase of sludge. The mineralization of bound nitrogen in the solids was also confirmed in analyses made during this study. The portion of plant-available nitrogen in the digestate increased after nitrification (data not shown). Thus it can be deduced that conducting the nitrification without pre-filtration /settling of the raw digestate is beneficial.

The amount of nitrogen present as nitrite (NO_2 -N) was measured and found to be low (below 10 mg/L – Fig. **5c**). Since nitrite is an intermediate product, it will be consumed and converted rapidly to nitrate (NO_3-N) under most nitrification conditions. However, under certain operating conditions, such as low sludge retention time (SRT), low dissolved oxygen (DO) and high level of free NH_3, nitrite oxidizing organisms can be inhibited and outcompeted by NH_4-N oxidizers, leading to considerable nitrite accumulation. Nitrite oxidation was promoted in the present study with high SRT and high DO (up to 8.0 mg/L, at the temperature of 25 ^{o}C).

COD (soluble) measurements were also made as an additional indicator of the biological activity (Fig. **5d**). The overall reduction of soluble COD during the cycle (~ 40 %) shows significant heterotrophic bacterial activity. Such activity can break down recalcitrant compounds surviving the anaerobic digestion. Based on the digestate COD (soluble) concentration of 3260 mg/L, the reactor concentrations at 33 days, and the daily COD loads applied, it was calculated that about 80 % of the soluble COD was removed in all reactor columns. Parravicini *et al.* [23] observed COD reductions ranging from 13 % to 23 % in post aerating anaerobically digested sewage sludge at much less intensive aeration conditions (below 1 mg/L dissolved oxygen). The COD degradation in the five columns depended on the loading rate. Columns 3, 4 and 5, which were fed 30 ml digestate per day have slightly higher final COD values compared to the columns (1 and 2) which were fed 20 ml per day.

The above results confirm that anaerobic digestates can be nitrified to obtain a more stable product which may be further concentrated without a deterioration in the quality of the fertilizer.

3.3. Sedimentation Quality

The sedimentation effectiveness of the sludge in the reactor columns was quite good on day 11 (Fig. **6a**) and was better at the end of the 32 day-long steady feeding phase (Fig. **6b**).

Generally, it is clear that a significant improvement of sedimentation of the reactor mixed liquor has occurred with the establishment of an efficient nitrification process. The anaerobic digestate had very poor sedimentation qualities. Even after centrifugation at 9000 rpm for 15 minutes, a clear liquid phase was not obtained (the same dark colour as the original digestate remained). Filtration of the supernatant (resulting from centrifugation) through a 0.45 μm filter, however, produced a filtrate with a yellowish colour. This indicates that the digestate contains a significant amount of colloidal solids which cannot easily be settled. The mixed liquor from the nitrified reactor columns produced a clear phase with the same yellowish colour as obtained by filtering the original digestate through 0.45 μm filters, just by allowing it to settle for 15 minutes. This improvement of effluent quality by accelerated sedimentation (hence enhanced clarity) after nitrification can play a major role in producing a commercially acceptable liquid fertilizer. The sedimentation rates of all the five columns are similar (Figs. **6a**, **6b**), implying that the effect of pre-sedimentation of the digestate is marginal on the final sedimentation characteristics of the effluent

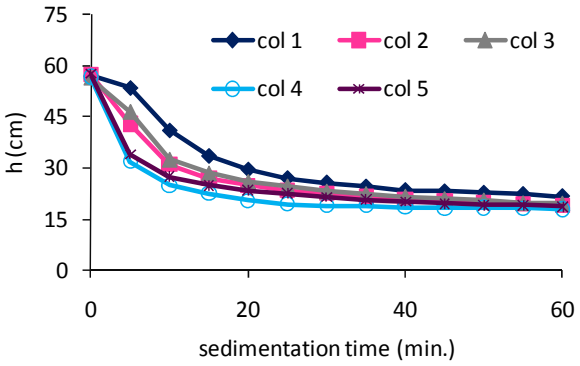


Fig. (6a). Sedimentation tests on day 11. *(h = sludge liquid interface height)*

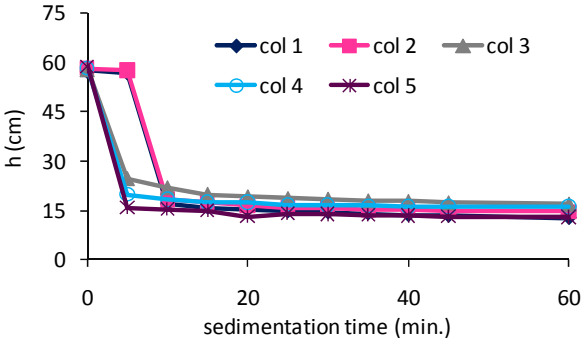


Fig. (6b). Sedimentation tests on day 44.

The nitrified effluent has a mild smell similar to the smell of humus soil and is free from the strong repulsive smell of the raw digestate. The light yellowish colour also seems appropriate for a commercial product, and it can be concluded that post-anaerobic nitrification has led to an aesthetically improved fertilizer product.

3.4. Effect of Nitrification on the Metal and Heavy Metal Content in the Digestate

Another major impediment for the application of anaerobic digestates as fertilizer is the potential presence of toxic metals and heavy metals [3; present study]. Table **2** shows the metal concentrations detected in the feed (raw) digestate used in this study.

According to the Norwegian guidelines imposed on organic fertilizers [13], four quality classes of bio-wastes are

defined, based on the content of seven heavy metals (i.e. Cd, Hg, Pb, Ni, Cr, Zn and Cu) which are identified as priority eco-toxicants. The four classes; 0, *I, II*, and *III* are distinguished by the heavy metal content measured as *mg* per *kg* of dry matter (DM) of the bio-waste (Table **3**). The specific use, and also the degree of usage, of an organic fertilizer is legally restricted based on its classification category; however the regulations mainly focus on the use of organic waste products as soil improvers [13]. In contrast to this Norwegian class categorisation, the European Union (EU) directives [14] suggest single point standards for each of these heavy metals for the land application of bio-wastes (Table **3**).

Table 2. Concentrations (in *mg/L*) of Various Metals Detected in the Digestate

Metal	Average Conc.	SD	Metal	Average Conc.	SD
Al	80.6	13.3	Mg	145.4	2.7
As	0.20	0.0	Mn	14.8	0.2
B	1.6	0.2	Mo	0.07	0.01
Ba	5.00	0.1	Na	630.4	9.1
Be	0.001	0.0	Ni	0.3	0.1
Ca	768.1	7.3	Pb	0.3	0.03
Cd	0.02	0.004	Sb	n.d*	n.d
Co	0.08	0.01	Sn	0.15	0.04
Cr	0.5	0.1	Sr	3.24	0.04
Cu	2.00	0.04	Ti	2.6	0.4
Fe	99.5	2.8	Tl	0.12	0.05
K	1019.0	16.1	V	0.23	0.10
Li	0.1	0.01	Zn	11.4	0.3

*Not detected.

Table 3. Norwegian [13] and EU Standards [14] on Limiting Heavy Metal Concentrations in Organic Fertilizers

Quality Class/Standard	Metal Concentration (mg Metal/kg Dry Matter of Bio-Waste)						
	Cd	Hg	Pb	Ni	Cr	Zn	Cu
Nor. class 0	0.4	0.2	40	20	50	150	50
Nor. class I	0.8	0.6	60	30	60	400	150
Nor. class II	2	3	80	50	100	800	650
Nor. class III	5	5	200	80	150	1500	1000
EU standard	0.7	0.4	45	25	70	200	70

A comparison of the concentrations of heavy metals before and after the nitrification is presented in Table **4**. It was found that a significant class improvement occurred when the digestate was nitrified. For the case of Cd and Hg, the quality class improved from class *II* to class 0, and in the case of Cu, it was upgraded from class *I* to class 0. Now the only heavy metal constituent which keeps the nitrified effluent from becoming an overall quality class 0 organic fertilizer is the high concentration of Zn (272 mg/kg DM) which is categorized as class *I*.

Table 4. Concentrations of Regulated Heavy Metals (mg/kg Dry Matter) and Categorized Quality Class Before and After Nitrification

Heavy Metal	Feed Digestate		Nitrified Effluent	
	Conc.	Quality Class	Conc.	Quality Class
Cd	1.2	II	0.4	0
Hg	0.9	II	0.02	0
Pb	18.4	0	6.2	0
Ni	19.1	0	9.4	0
Cr	27.4	0	1.4	0
Zn	672.6	II	272.3	I
Cu	118.4	I	24.6	0

It should be further emphasized that the Norwegian standards for the classification of "sludge" used for agricultural purposes are made with sewage sludge in mind. When used as a soil improver, sewage sludge has far less N than the digestates originating from the wet municipal organic wastes; the type treated in this project. Thus, the use of this digestate-based nitrified fertilizer would not lead to significant heavy metal contamination if nitrogen application rates are used as the basis for standardizing the metal contamination effect. Therefore, in practice, this nitrified digestate fertilizer would have a negligible effect on heavy metal content in soil even after decades of annual fertilization.

Contrary to the common awareness that low pH values must favour metal ion solubilisation, we observed decreased amounts of metals/heavy metals in the nitrified effluent. The removal of metals from the liquid in the nitrification process can be explained by adsorption, reaction and sedimentation. The presence of considerable amounts of sulphur in the digestate (95.2 mg/L, Table **1**) will contribute to the metal precipitation under the aerobic conditions. S compounds are oxidized to sulphates and insoluble metal sulphates (*e.g.* $PbSO_4$, $Cr_2(SO_4)_3$) are formed and precipitated [22]. These reactions are favoured at low pH conditions. These heavy precipitating components add structure and weight to the sludge, which improves sedimentation (Figs. **6a**, **6b**), and increased sedimentation can sweep away suspended colloidal particles carrying metals. Undesirable metals are thereby fixed in sludge and a liquid fertilizer with low metal content is produced. Excess sludge from the nitrification process can be used as a source of metals or as a low quality fertilizer (category *III* – Table **3**) intended for specific purposes (e.g. forest fertilization).

3.5. Simulations Based on ASM 3

The experimental data for NH_4-N and NO_3-N for a single cycle were compared with the simulations (Fig. **7**) obtained using the schematic reactor model which was developed based on mass balance analysis (section 2.5) and by using the stoichiometric matrix and kinetic rate expressions presented in ASM 3 kinetic model [18]. The generic equation system (*Eq. 7, 11 and 18*) is then solved by a program script formulated in Matlab (7.0), utilizing the

ode45 ordinary differential equation solver. Some of the main parameter values used in the simulation are summarized in Table **5**. Most of the kinetic constants are adopted from the typical values listed with ASM 3 [18]. The simulation program used in this study is freely available from the authors.

Table 5. Main Parameter Values Used in the Simulation

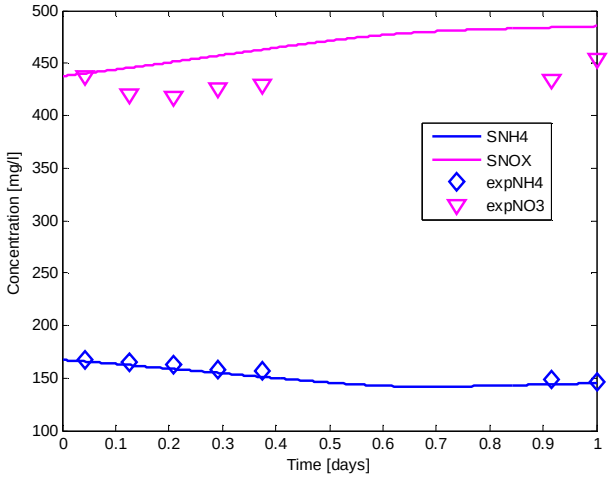
Parameter	Value
Reactor volume, V	0.001 m^3
Flow rates, q	20/30 ml/d
Oxygen saturation coefficient at 25 °C, C_s	8.5 mg/L
Autotrophic max. growth rate, μ_A	1 day^{-1}
Ammonium saturation for autotrophes, $K_{a,NH4}$	1 g N/m^3
Oxygen saturation for nitrifiers, $K_{a,O2}$	0.5 g O_2/m^3
Bicarbonate saturation for nitrifiers, $K_{a,alk}$	0.5 mole HCO_3^-/m^3
Aerobic endogenous respiration rate of autotrophes, $b_{a,O2}$	0.15 day^{-1}
Oxygen mass transfer coefficient, k_La	250 $days^{-1}$

As seen in Fig. (**7**), experimental data for the different reactor columns fit well with the simulation curves giving a good indication of the applicability of the ASM 3 model and the associated typical kinetic parameters for highly nutrient concentrated digestates. This model is ordinarily recommended only for domestic wastewaters in activated sludge systems [18]. Note that ASM 3 considers nitrification dynamics as a single step process ignoring the intermediate formation of nitrites, which is reasonable in the present study where nitrite accumulation is low.

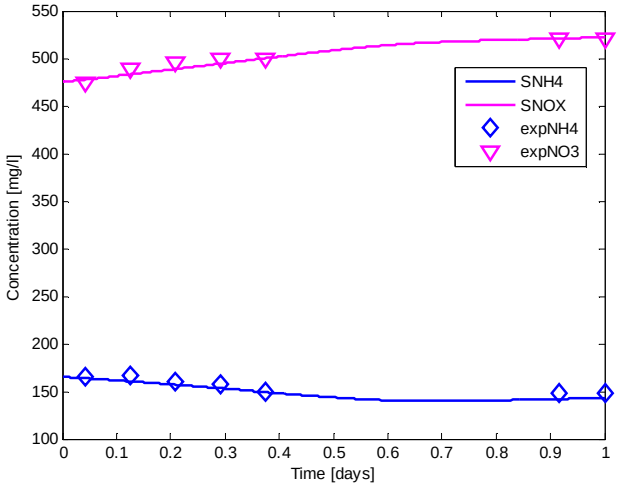
Further, Fig. (**8**) displays the simulation graphs for a longer time duration until the reactors reach steady operation under the feeding conditions maintained during the steady feeding phase of this experimentation. Typically, nitrification processes need extended durations to reach steady operation due to the slower growth rate of autotrophic biomass. Two experimental points, at which the full cycle analysis of nitrification dynamics was carried out, were also included in these graphs. The lower values of NO_3 –N measured than simulated at day 33 indicates N loss possibly due to NH_3 stripping. The simulated dissolved oxygen curves show almost constant oxygen level of about 7.4 mg/L (graphs not shown), in agreement with the experimentally maintained oxygen saturated condition.

The main conclusions from the modelling and simulations presented here are: *(i)*. The standard processes accounted for in nitrogen removal wastewater treatment can also be used to account for the behaviour in digestate nitrification processes. *(ii)*. Standard kinetic and stoichiometric parameters from wastewater treatment can be used in digestate nitrification processes. ASM 3 can therefore be used to generalize the results from the present lab reactor study and to design full scale digestate nitrification plants.

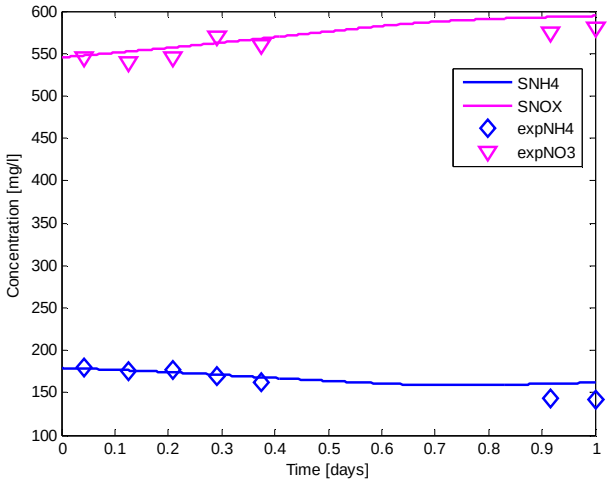
(**a**) Column 1



(**b**) Column 2

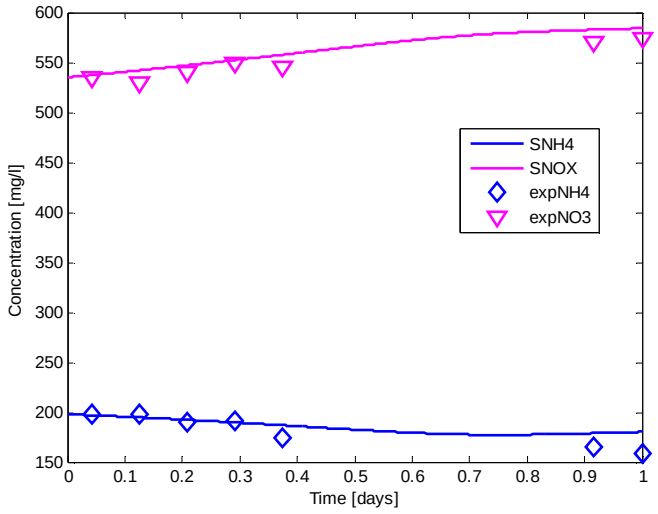


(**c**) Column 3



(Fig. 7) contd…..

(**d**) Column 4



(**e**) Column 5

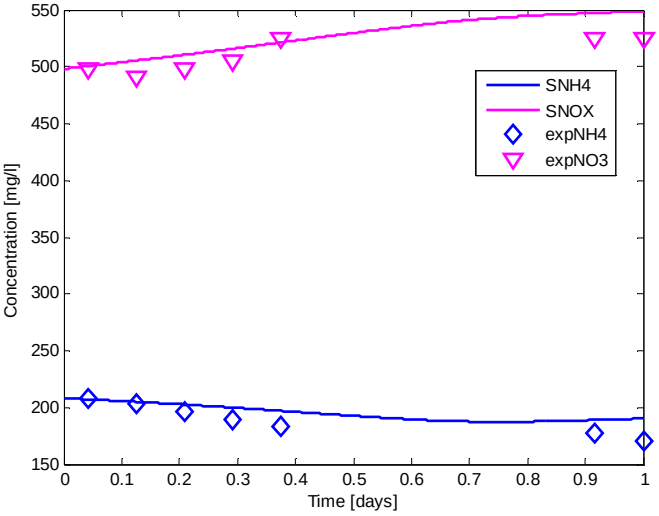
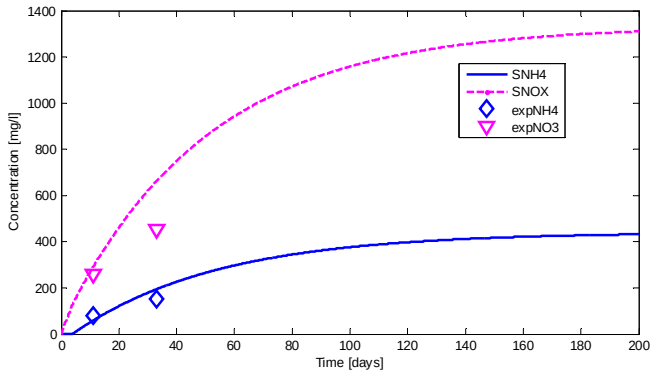


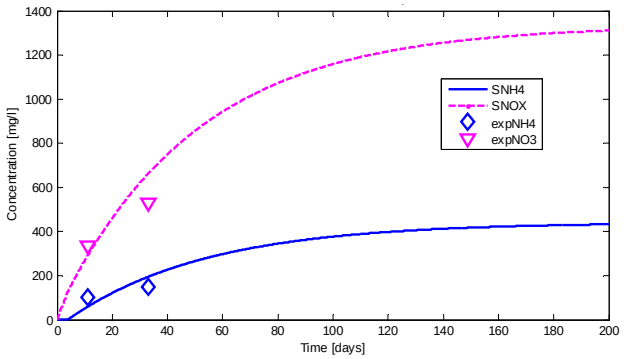
Fig. (7a-e). Experimental data against simulation curves for NH_4, NO_3 and NO_2 (NO_x) for a single cycle of feeding (days 33 - 34) for different reactor columns (1-5).

(**a**) Column 1

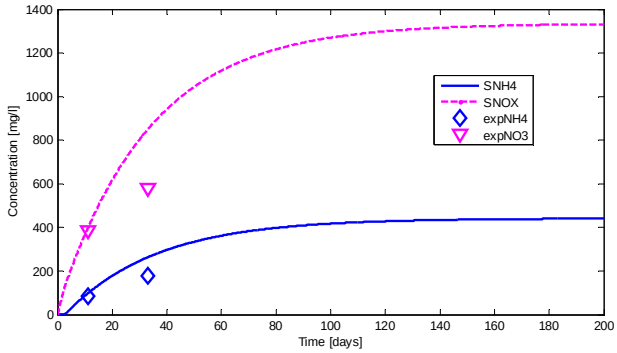


(Fig. 8) contd…..

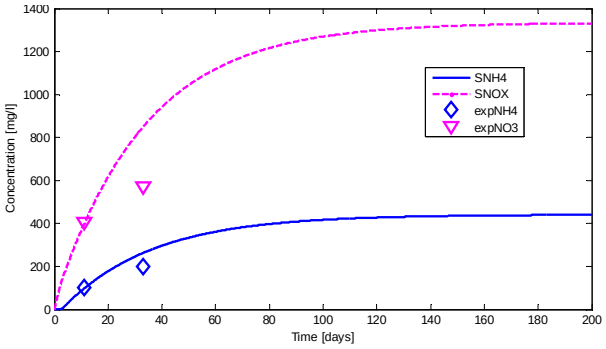
(**b**) Column 2



(**c**) Column 3



(**d**) Column 4



(**e**) Column 5

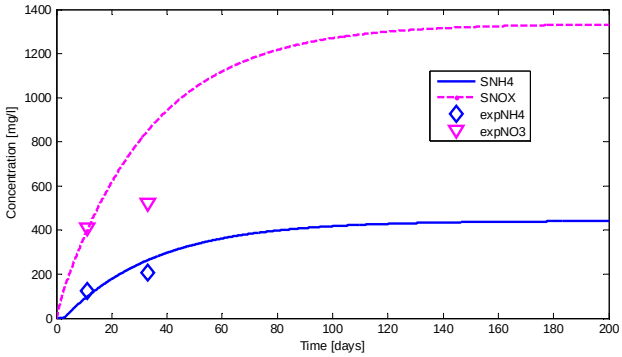


Fig. (8a-e). Simulation curves for NH_4-N and NO_x-N for long time operation of reactor columns (1-5) under steady feeding conditions.

4. CONCLUSIONS

Stable nitrification of digestates from anaerobic digesters operating on source-separated municipal organic wastes containing high amounts of ammonia nitrogen (~1700 mg/L) can be accomplished without the addition of extra buffer capacity in sequential batch reactors.

It is advantageous to conduct the nitrification without (expensive) pre-treatment for the removal of the particulate fraction of the digestate, as the particulates can contribute additional NH_4-N and buffer capacity. Significantly improved sedimentation characteristics are observed after the nitrification of the anaerobic digestate.

A large portion of the toxic heavy metals in the raw digestate was fixed in the sludge of the nitrification process, so that the final liquid product becomes a high quality organic fertilizer. Nitrification also enhances the stability and the aesthetic quality of the digestate.

The nitrification process studied can be modelled by the same reactions as in the ASM 3 model for wastewater treatment. The kinetic and stoichiometric parameters recommended in ASM 3 can also be used in simulating the post-anaerobic nitrification of digestate. ASM 3 can therefore be used in designing digestate nitrification plants.

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NOMENCLATURE

Abbreviations

AD	=	Anaerobic Digestion
ASM	=	Activated Sludge Model
COD	=	Chemical Oxygen Demand
CSTR	=	Continues Stirred Tank Reactor
DM	=	Dry Matter
DO	=	Dissolved Oxygen
EU	=	European Union
gen	=	Generation
ICP	=	Inductively Coupled Plasma analysis
in	=	input
out	=	output
SD	=	Standard Deviation
SRT	=	Sludge Retention Time
SS	=	Suspended Solids
TSS	=	Total Suspended Solids
VS	=	Volatile Solids

General Symbols

$\dot{n}$	=	Time derivative of n
C	=	Concentration
C_s	=	O_2 saturation concentration
k_La	=	Aeration coefficient
n	=	No. of moles
p	=	Particulate component
q	=	Flow rate
r	=	Generation rate vector
r_b	=	Reaction rate vector
S	=	Stoichiometric matrix
s	=	Soluble component
S^T	=	Matrix transpose of S
t	=	Time
V	=	Reactor volume

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