

Complete nutrient recovery from source-separated urine by nitrification and distillation

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ABSTRACT

In this study we present a method to recover all nutrients from source-separated urine in a dry solid by combining biological nitrification with distillation. In a first process step, a membrane-aerated biofilm reactor was operated stably for more than 12 months, producing a nutrient solution with a pH between 6.2 and 7.0 (depending on the pH setpoint), and an ammonium to nitrate ratio between 0.87 and 1.15 gN gN⁻¹. The maximum nitrification rate was 1.8 ± 0.3 gN m⁻² d⁻¹. Process stability was achieved by controlling the pH via the influent. In the second process step, real nitrified urine and synthetic solutions were concentrated in lab-scale distillation reactors. All nutrients were recovered in a dry powder except for some ammonia (less than 3% of total nitrogen). We estimate that the primary energy demand for a simple nitrification/distillation process is four to five times higher than removing nitrogen and phosphorus in a conventional wastewater treatment plant and producing the equivalent amount of phosphorus and nitrogen fertilizers. However, the primary energy demand can be reduced to values very close to conventional treatment, if 80% of the water is removed with reverse osmosis and distillation is operated with vapor compression. The ammonium nitrate content of the solid residue is below the limit at which stringent EU safety regulations for fertilizers come into effect; nevertheless, we propose some additional process steps that will increase the thermal stability of the solid product.

KEYWORDS

Membrane-aerated biofilm reactor (MABR); Evaporation; Primary energy demand; Nutrient recovery; Fertilizer; Ammonium nitrate; No-Mix technology

1. INTRODUCTION

Providing adequate sanitation is a major challenge for fast growing cities, especially in emerging and developing countries. However, the current technology of choice – waterborne conveyance of human excreta and centralized wastewater treatment – is inappropriate for many cities, because it requires large initial investments and high amounts of water (Corcoran et al., 2010). Many researchers and practitioners agree that new designs and technologies are needed, which focus on the recovery of resources such as water, nutrients and energy instead of merely preventing pollution (Guest et al., 2009). One very promising approach is the separation of wastewater streams and their specific treatment in decentralized reactors. Urine is of particular interest, because it contains most of the nutrients, which could be used in fertilizers (Larsen et al., 2009). Since fertilizers have a market value, separate collection and treatment of urine has the potential to stimulate private business initiatives, which help to promote sanitation (Koné, 2010).

Direct application of urine as a fertilizer has been common in many rural societies around the world, but this straightforward technique is unsuitable for modern cities: the high water content makes the transport to agricultural land costly, ammonia volatilization from stored urine is unpleasant and causes high nitrogen losses, and pathogens pose a health risk to farmers and consumers of agricultural products (Udert et al., 2006). Maurer et al. (2006) reviewed a multitude of technologies, which could be used to produce a more convenient urine fertilizer. So far, struvite (MgNH₄PO₄·6H₂O) has received the most attention (Etter et al., 2011): by adding a suitable magnesium source, more than 90% of the phosphate and some ammonia are recovered, but most ammonia and basically all potassium and sulfate stay in solution. Based on fertilizer prices in Nepal, Etter et al. (2011) calculated

that struvite production only allows to recover 13% of the monetary fertilizer value of urine.

Physical water removal is the only process that allows to recover all urine nutrients in one final product. Maurer et al. (2006) described four processes to separate water and dissolved compounds: electrodialysis, reverse osmosis, freeze/thaw concentration and distillation. In the present paper, we will show that distillation is the most promising of the four processes. In previous studies, distillation was studied with fresh and stored urine. With both solutions, the urine was pretreated with strong acid to prevent ammonia volatilization. The acid addition to fresh urine inhibited the urea hydrolyzing enzyme urease (Maurer et al., 2003). In stored urine, acid converted free ammonia into non-volatile ammonium (Ek et al., 2006 and Tettenborn et al., 2007). To recover 95% of the nitrogen during distillation, Ek et al. (2006) added 13 g H₂SO₄ to 1 L of stored urine and reached a pH value of 4.5. Since urea hydrolysis increases the alkalinity approximately by a factor of 20 (Udert et al., 2006), significantly more acid has to be added to stored urine than to fresh urine. However, urea hydrolysis is a very fast process in urine-collection systems (Udert et al., 2003a), so that the strong acid would already have to be added in the toilet, which is as dangerous as technically challenging.

An alternative method for stabilizing nitrogen is biological nitrification. The alkalinity of stored urine allows to nitrify about 50% of ammonium to nitrate, while the pH decreases to values around 6.3 (Udert et al., 2003b). Nearly all ammonium can be oxidized to nitrate if additional alkalinity is added (Oosterhuis and Loosdrecht, 2009 and Feng et al., 2008). Biological nitrification requires a well tuned interplay of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), which is very challenging in high strength ammonia solutions such as urine (Udert et al., 2003b). Alternatively, nitrification can be split up into two pro-

cesses: biological ammonium oxidation and chemical nitrite oxidation. Chemical nitrite oxidation with oxygen occurs at low pH values, which can either be reached with acid-tolerant ammonia oxidizers (Udert et al., 2005) or by adding acid (Verhave et al., 2007). The drawback of the process is the substantial volatilization of nitrogen oxides. Another alternative is the electrochemical oxidation of nitrite on graphite electrodes. This method has been successfully tested in the lab, though as yet, no longterm experiments exist (Faraghi et al., 2011).

The aim of this paper is to test the hypothesis that a combination of biological nitrification and distillation is a technically suitable and energetically sensible process for complete nutrient recovery from urine. We will also discuss the chemical stability of the final product, which mainly consists of ammonium nitrate.

2 MATERIALS AND METHODS

2.1 Urine solutions

The urine for the nitrification experiments was taken from the men's tank of the NoMix system in the Eawag main building (Forum Chriesbach). The average concentration of the urine solution is given in Table 1. Although the urine was practically not diluted with flushing water, nitrogen concentrations were significantly lower than in fresh urine due to ammonia volatilization (Goosse et al., 2009). Distillation experiments were conducted with effluent from the nitrification reactor, spiked effluent and synthetic solutions. Typical concentrations are given in Table 3. In the spiked solution, ammonium nitrate was added to correct for ammonia volatilization. Synthetic urine solutions were used to evaluate the effect of the pH value on nitrogen loss during distillation. The basic synthetic urine had a pH of 6.0. The recipe for the synthetic solution is given in the Supplementary Information (Table S1). From this stock four additional solutions with pH values of 6.3, 6.6, 6.9 and 7.2 were prepared. The pH values were adjusted with 2 M NaOH. All chemicals used for the synthetic solutions were of pro analysi grade.

2.2 Nitrification reactor

A hybrid membrane-aerated biofilm reactor (MABR) was used for the nitrification experiment. The reactor had a liquid volume of 2.6 L. Silicon tubing coiled on a PVC rack (Supplementary Information, Figures S1 and S2) served for diffusive aeration and as substratum for biofilm. The tubing had a length of 21.7 m, a diameter of 4 mm and a wall thickness of 0.5 mm. The total surface available for biofilm growth in the reactor was 0.39 m², thereof 0.25 m² or 65% on silicone tubing. The surface to volume ratio was 149 m¹. In addition to the membrane aeration, air was also supplied as bubbles through an air diffuser, which was attached to the lower end of the silicone tubing. The aim of combining silicone and bubble aeration was to minimize denitrification in the biofilm by supplying air from the substratum and the bulk. During the experiment reported in this paper, the air flow was fixed to 450 mL min⁻¹. The temperature in the reactor (23 ± 2 °C) was not controlled.

The oxygen transfer coefficient K_{La} was determined to be 430 ± 20 d⁻¹ (average and standard deviation of three experiments).

2.3 Nitrification experiments

After some preliminary tests, the reactor was emptied, cleaned and reinoculated with activated sludge from the Eawag experimental wastewater treatment plant. Stored urine from the Forum

Table 1: Average concentrations in the nitrification reactor influent (real stored urine).

	Average [mg L ⁻¹]	Std. Dev. [mg L ⁻¹]
Total Ammonia-N	2390	250
Total Phosphate-P	208	49
Calcium	16	3
Magnesium	<5	-
Potassium	1410	320
Sodium	1740	360
Sulfate	778	184
Chloride	3210	530
Total inorganic C	1210	220
Diss. organic C	1830	360
Dissolved COD	4500	910
COD/N ratio [gO ₂ gN ⁻¹]	1.9	0.5
pH [-]	8.69	0.11

Chriesbach was supplied continuously and half of the ammonium was oxidized to nitrate, but the pH had to be controlled frequently with carbon dioxide aeration to prevent process instabilities due to high pH values. Two months after inoculation, an alternative pH control scheme was started: the high buffer capacity and pH value of the influent urine was used to correct for the pH decrease caused by nitrification: as soon as the pH raised 0.1 units below a certain set-point, the influent pump was switched on, until the set-point was reached again. This control mechanism was automated with the process control tools of the data-logger (see below). After an initial phase with set-point 6.1 the actual experiment phase - a series with pH set-points 6.9, 6.7, 6.5, 6.3 and 6.1 - was run to test the influence of the pH value on the nitrification performance. The reactor was operated at each pH set-point for at least three hydraulic retention times. The water loss in the system was kept low (4.3–6.7%) by moisturizing the aeration air in a wash bottle before introducing it into the reactor.

2.4 Distillation experiments

All distillation experiments except for the boiling point elevation experiment (see below) were performed at low pressure in a Büchi Rotavapor R-124 with a Büchi Water bath B-480 (Büchi Labortechnik AG, Flawil, Switzerland). Tapwater was used for the cooling coil. The initial volume in the distillation reactor was approximately 200 mL, for both synthetic and real urine solutions.

To guarantee the reproducibility and comparability of the results, the experiments in the Rotavapor were carried out according to the following procedure: 1.) the pressure in the system was lowered to 200 mbar and then the water bath was started to heat up from approximately 20 °C - 78 °C (duration: 19 min); 2.) water was distilled at 78 °C and 200 mbar for 1 h (real urine) or 2 h (synthetic urine); 3.) the pressure was lowered for 5 min to 150 mbar; 4.) the pressure was lowered to 100 mbar for another 5 min; 5.) the water bath was removed and the system was brought to ambient pressure. In all experiments, the solids crystallized in step 4.) or earlier. The humid end product, which had approximately 2% of the initial volume, was dried completely in a desiccator under reduced air pressure and with silica gel as desiccant. Later, the dried solids were dissolved in nanopure water and samples were taken from this solution and the condensate to analyze their composition wetchemically.

To estimate the boiling point elevation during the distillation process, 1 L (1010.2 g solution) of a synthetic solution of nitrified urine (pH 6.0, Supplementary Information Table S1 and Table 3, but with pH adjusted to 6.0) was distilled in a custom-made glass reactor equipped with a reflux condenser, a condenser to trap the distilled water, a thermometer inside the reactor and a balance to weigh the distilled water (Labo-Tech LTS AG, Muttenz, Switzerland) at ambient pressure (approximately 970 mbar in Zurich). The water temperature during distillation was measured frequently until 99.2% of the water had evaporated.

2.5 Thermal stability measurements

The thermal stability of the solid residues of a spiked nitrified urine sample, a commercial ammonium nitrate fertilizer (27% nitrogen, Landor, Birsfelden, Switzerland) and pure ammonium nitrate (Catalogue number 1.01188.1000, pro analysi, Merck, Darmstadt, Germany) was compared with differential scanning calorimetry (DSC). The measurements were carried out on an HP DSC827e (Mettler Toledo, Greifensee, Switzerland) under argon atmosphere at ambient pressure. The temperature range was 25–500 °C and the heating rate 4 °C min⁻¹. To homogenize the samples, the dry solids were milled and sieved. The diameter of the final particles was smaller than 100 µm. About 1 mg of these particles was placed in gold coated crucibles (M20, Swis-si, Basel, Switzerland) and compacted with a closing force of at least 4 kN. The measured power curves were integrated with the integral tangential method implemented in the STARe Software Version 8.10 (Mettler Toledo, Greifensee, Switzerland).

2.6 Chemical and physical analyses

The concentrations of nitrate, nitrite, phosphate, sulfate and chloride were measured with an ion chromatograph (IC 881 Compact IC pro, Methrom, Zofingen, Switzerland).

Sodium, potassium, calcium and magnesium were analyzed with optical emission spectroscopy (OES) with inductively coupled plasma (ICP) (ICP-OES, Ciro, Spectro Analytical Instruments, Kleve, Germany). Cuvet tests (LCK 614, Hach-Lange, Berlin, Germany) were used to measure chemical oxygen demand (COD), while total organic carbon (TOC), dissolved organic carbon (DOC) and total inorganic carbon (TIC) were determined on a TOC-TN analyzer (IL 550 TOC-TN, Hach-Lange, Berlin, Germany). Ammonium was measured photometrically on a flow injection analyzer (Application Note 5520, FOSS, Hillerød, Denmark). The free ammonia (NH₃) concentrations were simulated with the computer program PHREEQC Version 2.15.0.2697 using the “phreeqc.dat” database.

Electrodes and handheld meters were used to measure pH (pH 191 and pH 340 meters, Sentix 20 electrode, WTW, Weilheim, Germany) as well as oxygen and temperature (Oxi 340 meter, Cellox 325 electrode, WTW, Weilheim, Germany). Online measurements of pH and oxygen were recorded on a data-logger (Memograph S, Endress+Hauser, Reinach, Switzerland).

The standard deviations of all physical and chemical analyses were 2% or less.

3 Nitrification

3.1 Stable nitrate production

The nitrification reactor was operated stably for more than twelve months. The only exception was one short period with nitrifi-

te accumulation, which will be discussed in Section 3.5. Since nitrification generally consumes twice as much alkalinity (2 mol alkalinity per 1 mol ammonium) as is produced by urea hydrolysis (Udert et al., 2003a), about 50% of the ammonia was oxidized to nitrate. The ratio of nitrate to ammonium was slightly lower above pH set-point 6.5 and slightly higher below (Table 2, Fig. 1). Independent of the pH set-point, 90% of the organic substances were degraded (90 ± 26% TOC, and 89 ± 27% COD).

Influent control alone was a good means to keep the pH stable at a certain value in the reactor. In a previous study (Udert et al., 2003b), we reported that stable nitrification is possible without any pH control at all, but process instabilities are more likely. Influent control can also increase the nitrification rate by raising the pH value in the reactor.

Other studies described the use of base for pH control (Oosterhuis and Loosdrecht, 2009; Feng et al., 2008). In these studies, stable nitrification was only one of the two motivations for the use of chemicals: adding base also increased the alkalinity, so that all ammonia could be oxidized. However, the use of chemicals is costly and requires additional instrumentation. Both requirements make the process more complex and prone to malfunction. Therefore, a reactor setup without continuous base dosage is preferable.

3.2 pH influence on nitrification rate

The nitrification rate correlated strongly with the pH value in the reactor (Fig. 1). This pH dependency can be explained with substrate limitation for AOB. Since free ammonia NH₃ is generally assumed to be the true substrate of AOB (Suzuki et al., 1974) we fitted the nitrification rates as function of free ammonia with Monodkinetics. The fit was very good (R²=0.98, Figure S3 Supplementary Information), with a half saturation constant of 0.66 mgN L⁻¹ (maximum nitrification rate of 2.3 gN m⁻² d⁻¹), which is close to the half saturation constant (0.46 mgN L⁻¹) that Hellinga et al. (1999) proposed in their model for biological nitrogen transformation in high-strength ammonium wastewaters. The higher nitrification rates at higher pH values did not substantially change the product quality. While the nitrification rate doubled between pH 6.2 and pH 7.0, the average nitrate to ammonium ratio decre-

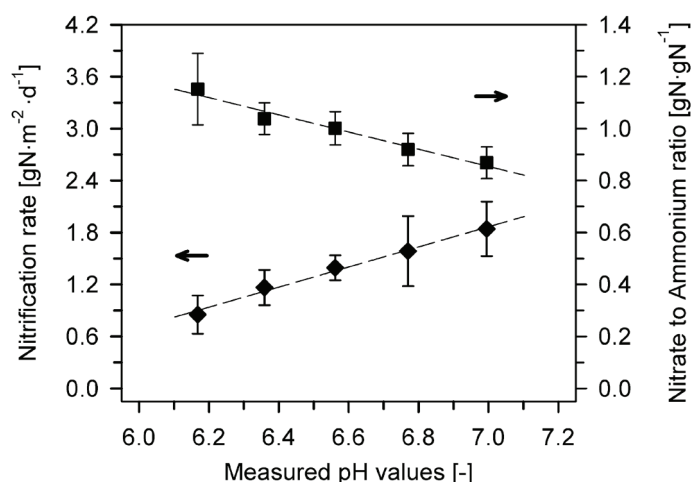


Fig. 1: Comparison of the nitrification rate (R² = 0.99) and the nitrate to ammonium ratio (R² = 0.97) in the nitrification reactor at different pH set-points. Error bars depict standard deviations.

Table 2: Performance data of the nitrification reactor for different pH set-points. The nitrification rate is given per total surface available for biofilm growth (on tubing, stand and reactor wall). The nitrification rate was calculated using the difference between ammonia load in the inflow and in the outflow. Multiplication with 149 mgN L⁻¹ m² gN⁻¹ gives the nitrification rate per fluid volume (in mgN d⁻¹). The nitrogen loss was calculated by comparing the ammonia load in the influent and the sum of nitrite, nitrate and ammonia load in the effluent.

pH setpoint	Measured pH [-]		Nitrification rate [gN m ⁻¹ d ⁻¹]		Nitrate/Ammonia [gN gN ⁻¹]	
	Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
6.9	6.99	0.08	1.8	0.3	0.87	0.06
6.7	6.77	0.10	1.6	0.4	0.92	0.06
6.5	6.56	0.12	1.4	0.1	1.00	0.06
6.3	6.36	0.07	1.2	0.2	1.04	0.06
6.1	6.17	0.10	0.9	0.2	1.15	0.14

pH setpoint	Nitrogen loss [%]		Nitrite in bulk [mgN L ⁻¹]		Oxygen in bulk [mg L ⁻¹]	
	Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
6.9	20	14	37	21	3.0	0.7
6.7	24	9	51	26	3.1	0.9
6.5	23	8	17	1	4.0	0.5
6.3	17	4	13	3	5.0	0.7
6.1	0	9	5	1	5.5	0.5

ased only by 24% and was always in a range of 1.00 ± 0.15 gN gN⁻¹. Higher pH set-points, however, had other adverse effects, which will be discussed in the following section.

3.3 Nitrogen loss

Substantial nitrogen losses occurred at high pH set-points. The maximum nitrogen loss was 24% at a pH set-point of 6.7 (Table 2). Ammonia volatilization cannot explain this high nitrogen loss, because other aerated bioreactors treating urine did not experience nitrogen losses in the same pH range (Udert et al., 2003b). The most likely cause is heterotrophic denitrification. At high pH values, the ammonia and COD load in the inflow was so high that the oxygen supply became limiting in some parts of the biofilm. Oxygen limitation can also explain the nitrite accumulation, which we observed at high pH set-points. Nitrogen loss is one of the disadvantages of this reactor setup: to prevent anoxic zones, oxygen was supplied concomitantly from the substratum and the bulk, but the shear stress was too small to prevent the growth of thick biofilms with anoxic zones between substratum and bulk.

3.4 Comparison with a moving bed biofilm reactor

A moving bed biofilm reactor (MBBR) in an earlier study (Udert et al., 2003b), performed significantly better than the MABR presented in this paper. At an average pH value of 6.3, the MBBR achieved a surface specific nitrification rate of 1.7 ± 0.1 gN m⁻² d⁻¹, while the MABR only reached 1.2 ± 0.2 gN m⁻² d⁻¹. The volumetric nitrification rate was higher as well: 380 mgN L⁻¹ d⁻¹ compared to 180 ± 30 mgN L⁻¹ d⁻¹. Additionally, no nitrogen loss was detected in the MBBR. The lower performance of the MABR is partly due to the reactor setup, which allowed biomass to accumulate. In the MBBR, strong mixing prevented thick biofilms on the biofilm carriers. Another reason for the lower performance of the MABR, especially for the high nitrogen loss, was the higher COD to ammonia ratio in the influent. The MABR was fed with urine that had a ratio of 1.9 ± 0.5 gCOD gN⁻¹, while the urine used in the MBBR experiment had a COD/N ratio of only 0.47 ± 0.27 gCOD gN⁻¹. The high COD/N ratio in the influent to the MABR supported strong heterotrophic growth. The strong differences

in the COD/N ratio can be explained with processes during urine storage and urine preparation. The high COD/N ratio for the MABR is due to ammonia volatilization, while the low value for the MBBR was caused by addition of ammonia to diluted urine. In stored urine without ammonia loss, one would expect a COD to ammonia ratio of about 1.2 gCOD gN⁻¹, which lies between the values for the MABR and the MBBR (Udert et al., 2006).

3.5 Process instabilities

The activities of NOB and AOB strongly depend on the pH value, because the concentrations of their substrates of AOB (NH₃) and NOB (HNO₂) are in a pH dependent equilibrium with their acid (NH₄⁺) or base (NO₂⁻). NH₃ and HNO₂ cannot only be limiting but also inhibiting (Anthonisen et al., 1976; Wiesmann, 1994). Additionally, AOB can be inhibited by their product HNO₂ (Hunik et al., 1992), while inhibition of NOB by their product NO₃ is usually negligible (Hunik et al., 1993). The complex pH dependency of nitrifiers is particularly pronounced in urine treatment, because of the high substrate concentrations and the large pH difference between influent and effluent.

Fig. 2 exemplifies that a sudden increase of the pH can be detrimental for urine nitrification. After the reactor had been operated for several weeks at pH 6.1, the pH set-point was raised to 6.9. Due to the higher availability of NH₃ at higher pH values, AOB activity increased immediately. NOB reacted too slowly to the rise of nitrite, probably because of oxygen limitation. Nitrite kept on increasing and the HNO₂ concentrations approached values that would have caused complete NOB inhibition. To prevent process breakdown, inflow and aeration were switched off and acetate added to remove nitrite (and nitrate) by denitrification. The concomitant pH increase was counteracted by dosing hydrochloric acid. As soon as all nitrite was removed, inflow and aeration were switched on again. In the following days, the process recovered and nitrate approached former levels, while nitrite concentrations stayed low.

As this example shows, a sudden increase of the reactor pH value endangers process stability. Therefore, the pH control via

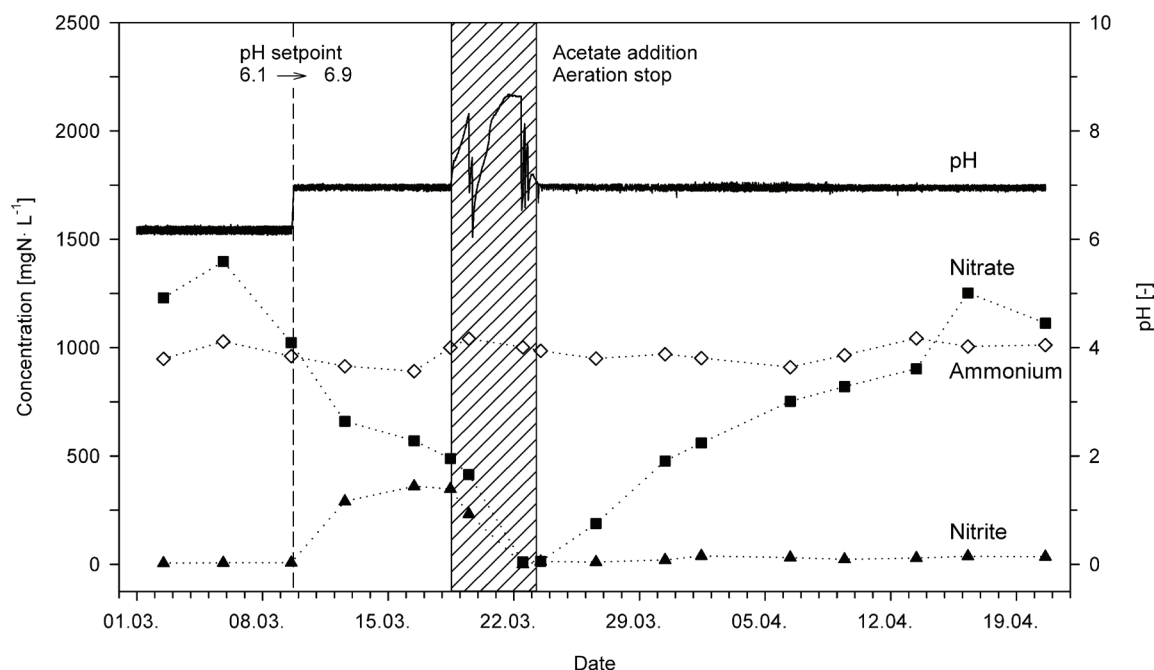


Fig. 2: Nitrite build-up after a sudden increase of the pH set-point from 6.1 to 6.9. The nitrite was removed and the process stabilized by switching off the air and adding acetate and acid.

the influent has to be very reliable. Furthermore, an automated monitoring system would be useful, which detects and announces sudden increases of the influent rate and of the pH value. pH decreases, for example caused by an inflow stop, are less critical, because ammonium oxidation usually comes to a halt at pH values of 6 or slightly below (Udert et al., 2003b). Rare exceptions are reactors, where acidtolerant AOB are present (Udert et al., 2005). However, according to our current knowledge, the acid-tolerant AOB only occur, when the reactor is operated for several weeks at pH values below 6.

4 Distillation

4.1 Mass balance

The recovery of most dissolved compounds in the solid residue was very high, regardless of whether synthetic solutions or real nitrified urine was used (Table 3). Only total inorganic carbon was lost completely due to the strong pH decrease to values around 4 (data not shown). In the real nitrified urine, organic compounds were reduced by 23%. Visual inspection of the glass bulb used in the experiment revealed a dark brown, presumably organic layer on the glass wall during the distillation. The transformation of the organic substances could cause scaling problems in large scale operation, but it also shows the possibility of targeted removal of organic substances during the distillation step. For all other dissolved compounds, losses due to distillation or scaling were negligible, considering that the minimum standard deviation for all analytical methods was 1%. However, in experiments with solutions that had a higher initial pH value, ammonia volatilization was relevant, as we will discuss in Section 4.2.

Foaming was not a problem, neither with synthetic nor with real urine. Other researchers (Tettenborn et al., 2007; Ek et al., 2006) experienced foaming when distilling urine that had not been treated biologically. We assume that foaming is mainly caused by organic substances, which are removed during the nitrification step (see Section 3.1).

4.2 Ammonia loss

The composition of the condensate was analyzed for trace compounds. As was expected, only ammonia and carbonate were detected (Fig. 3 and Figure S5 in the Supplementary Information). Although the mass balances in Table 3 did not reveal that significant amounts of ammonia volatilized, ammonia concentrations in the condensate were above 40 mgN L⁻¹. The ammonia concentrations in the condensate correlated strongly with the pH value in the initial synthetic nitrified urine (Fig. 3). When the initial pH value was 7.2, about 3% of the total nitrogen was captured in the condensate, while at an initial pH of 6.0, only 1.5% was

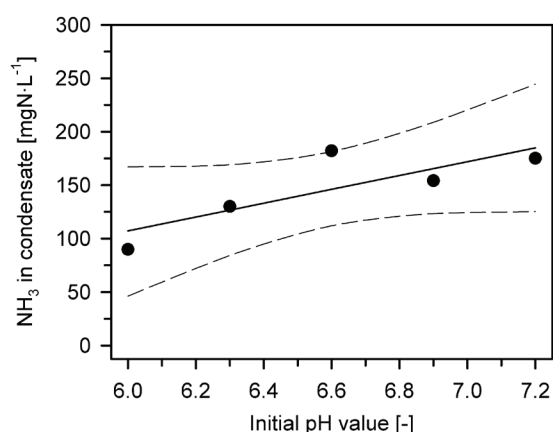


Fig. 3: Ammonia in the condensate as function of the pH value in the initial synthetic nitrified urine. Initial composition of the synthetic nitrified urine according to Table 3 and Table S1 (Supplementary Information) except for pH and sodium (NaOH used for pH adjustment). The slope of the linear regression curve is 65 ± 25 mgN L⁻¹. A correlation between the ammonia in the condensate and the initial pH of the nitrified urine is highly probable (p-value 0.085 for zero slope hypothesis). The dashed lines indicate the 95% confidence intervals.

captured. The low losses can be explained with a steady pH decrease to values below 4 (data not shown). Experiments with real nitrified urine solutions confirm the values obtained with synthetic nitrified urine. For example, the condensate of the experiment with real urine given in Table 3, contained approximately 40 mgN L⁻¹, which corresponds to less than 0.6% nitrogen loss.

The nitrogen loss we recorded for nitrified urine was lower than in experiments with acidified stored urine. Using reverse osmosis to reduce the volume by a factor of five, Ek et al. (2006) reported 9% nitrogen loss with stored urine acidified to pH 7, and 2% nitrogen loss, when the pH value was lowered to 6. The same authors found higher nitrogen loss when more water was removed with the help of distillation (volume reduction by a factor 20). Here, the nitrogen losses were 11% (acidification to pH 5.5) and 5% (acidification to pH 4.5). More significant than the losses during urine treatment is the ammonia volatilization during urine storage. A study in Forum Chriesbach showed that more than 50% of the ammonia was lost by volatilization (Goosse et al., 2009). Ammonia volatilization and not dilution is probably the reason why nitrogen concentrations in stored urine are generally much lower than in fresh urine (see e.g. Etter et al., 2011).

The condensate can be a second valuable product besides the nutrient-rich solid residue, because it contains hardly any dissolved compounds. Possibly, purified water for technical applications could be produced with only little additional treatment. According to our current knowledge, the main impurity is ammonia, which could be removed by for example electrolysis (Kapalka et al., 2010a, b) or stripping.

4.3 Energy demand

The minimum energy demand for evaporative water removal consists of the energy required to heat the water to the boiling point and the energy to evaporate the water at the boiling point:

$$\Delta H_{\text{boil}} = m_{\text{water}} \cdot c_p \cdot \Delta T \quad (1)$$

$$\Delta H_{\text{evap}} = m_{\text{vapor}} \cdot \Delta h_v \quad (2)$$

ΔH_{boil} : energy required to heat the water to the boiling point from room temperature (20 °C) [kJ]
 ΔH_{evap} : energy required to evaporate the water [kJ]
 m_{water} : mass of heated water [kg]
 m_{vapor} : mass of vapor produced [kg]
 c_p : heat capacity of water, 4.19 ± 0.01 kJ kg⁻¹ K⁻¹ (average between 20 °C and 100 °C, Marsh, 1987)
 ΔT : temperature increase [K]
 Δh_v : heat of vaporization [kJ kg⁻¹], 2259 kJ kg⁻¹ (for ambient pressure of 1 atm, Lide, 2009)

Due to the high amount of dissolved compounds the boiling point increases during evaporation. The increase of the boiling point is important, because it changes the amount of energy required to heat up a certain volume of water. At ambient pressure, the boiling point of synthetic urine increased only by 1.4 °C up to a water removal of 82%, and an additional 9.0 °C for a water removal of 97% (Figure S4, Supplementary Information). For the remaining 2.2% water removal the boiling point temperature increased exponentially, reaching 130.1 °C. Mayer (2002) found a similar boiling point elevation for acidified fresh urine (ca. 9 °C for a final 57% total solids which corresponds to 97.5% evaporated water) as we did for synthetic nitrified urine (12.5 °C for 57% total solids content), if total solids are taken as reference. We therefore conclude that the boiling point elevation is mainly determined by the total solids in the liquid and does not differ substantially for differently treated urine.

The energy demand for removing 99.2% water from synthetic nitrified urine at ambient pressure was calculated to be 710 W h L⁻¹ (90 W h L⁻¹ (13%) for heating the solution from ambient temperature (20 °C) to boiling point, 620 W h L⁻¹ (87%) for steam production), which corresponds to 44 W cap⁻¹ (assuming a urine production of 1.5 L cap⁻¹ d⁻¹). With vapor compression, about 85% of the energy can be recovered at small scale (Wood, 1982), which means that the energy requirement could be reduced to 110 W h L⁻¹ (6.9 W cap⁻¹), but electric energy is required. If one assumes a conversion efficiency of 31% for electricity production (average

Table 3: Recovery of major compounds in two distillation experiments. On the left synthetic nitrified urine, on the right real nitrified urine (spiked with ammonium nitrate). The total inorganic solids are calculated from analyses. To measure the pH of the solids after distillation, the solid residue was diluted in 1 L of nanopure water.

	Synthetic nitrified urine			Real nitrified urine		
	Input [g]	Product [g]	Diff. [%]	Input [g]	Product [g]	Diff. [%]
Water	986	0.00	-100	989	0.0	-100
Phosphate-P	0.52	0.53	1.3	0.22	0.21	-0.5
Carbonate-C	0.20	0.00	-100	<0.002	0.00	-100
Sulfate	1.46	1.45	-0.8	0.83	0.83	-0.3
Chloride	3.79	3.76	-0.7	3.39	3.36	-1.1
Potassium	2.20	2.21	0.4	1.54	1.56	1.6
Sodium	2.79	2.86	2.3	1.82	1.84	1.2
Ammonia-N	3.28	3.28	-0.1	3.23	3.22	-0.3
Nitrate-N	3.22	3.21	-0.5	3.65	3.60	-1.2
Tot. inorg. solids	30.6	30.4	-0.6	28.5	28.3	-0.7
DOC	-	-	-	0.13	0.10	-23
pH	6.60	4.03	-	6.00	3.84	-

European electricity mix, UCPTE, 1994), the primary energy demand amounts to 340 W h L^{-1} or 21 W cap^{-1} . Additionally, nitrification in a small-scale MBBR (100 person equivalent) has a primary energy demand of about 8.9 W cap^{-1} (Supplementary Information, Section S6). The total energy demand of nitrification and distillation (with energy recovery) amounts to 30 W cap^{-1} , which is about 0.6% of the average energy consumption rate in Switzerland (4690 W cap^{-1} in the year 2009, calculated from BFE, 2010). The energy demand is two and a half times the energy demand estimated for removing nitrogen and phosphorus in a centralized wastewater treatment plant and producing the equivalent amount of nitrogen and phosphorus fertilizer: 190 W h L^{-1} or 12 W cap^{-1} (calculated based on Maurer et al. (2003) assuming phosphorus precipitation with iron (II) sulfate, phosphorus fertilizer production in Europe, nitrification/pre-denitrification, urea production, a urine composition according to spiked nitrified urine (Table 3) and a urine production of $1.5 \text{ L}_{\text{urine}} \text{ cap}^{-1} \text{ d}^{-1}$). This energy comparison shows that a nitrification/distillation process would probably require more energy than conventional wastewater treatment, but it also shows that the energy demand is still low compared to the overall energy demand in a country like Switzerland. This comparison alone is not a sufficient basis to decide, whether a sanitation system based on nitrification/distillation requires more energy than conventional wastewater management. For a proper comparison, one has to include the energy demand for additional system components, such as the transport of urine, water and wastewater, the production of synthetic potassium and sulfate fertilizers and the handling of the feces and gray water.

4.4 Alternative processes for water removal

To the best of our knowledge, lyophilization is the only other industrial technology for complete water removal from salt solutions. During lyophilization, moist material is frozen at atmospheric pressure; later the water is sublimated at low temperatures (-40°C and below in the condenser) and low pressure (millibars to microbars) (Rowe, 1960). This technology is often used to dry heat sensitive products in the food and pharmaceutical industry, but consumes high amounts of energy. According to Gehrmann et al. (2004) (cited in Claussen et al. (2007)) an electrical energy input of 1000 W h is needed to remove 0.4 kg water. This corresponds to 8100 W h L^{-1} primary energy, which is 22 times higher than the energy demand for distillation with energy recovery.

Maurer et al. (2006) described three additional processes that can be used to remove a particular amount of water from urine: electrodialysis, freeze and thaw, and reverse osmosis.

In the electrodialysis process, ions are concentrated in an electric field by interrupting the ion flow with alternating anion and cation exchange membranes. For the treatment of stored urine, Dodd et al. (2008) estimated a gross primary energy demand of $145 \text{ W h cap}^{-1} \text{ d}^{-1}$, which corresponds to 97 W h L^{-1} (assuming a urine production of $1.5 \text{ L cap}^{-1} \text{ d}^{-1}$ and exclusive energy for pumping). This is substantially lower than the estimated primary energy demand for distillation with energy recovery. However, the achievable concentration is low because water is also transported into the concentrate by osmosis and electro-osmosis. Furthermore, some dissolved compounds remain in the diluate. For stored urine, Pronk et al. (2006) reported a maximum concentration factor of 3.3 in continuous mode with 15% of the ions remaining in the diluate.

The freeze and thaw method is based on the physical effect that during freezing most dissolved substances are excluded from the crystal lattice of ice and instead are concentrated in the remaining liquid phase. Lind et al. (2001) applied this method to

fresh urine and synthetic fresh urine. They achieved 75% water removal, but only 80% of the nutrients were recovered. Gulyas et al. (2004) reported that the nutrient recovery from fresh urine decreased when more water was removed. In this study, the authors cited that a small scale falling film freezing reactor (250 L h^{-1} , Type “W33”, Niro Process Technology bv, ‘s-Hertogenbosch, The Netherlands) requires 244 W h L^{-1} . Assuming that this is electrical energy, the primary energy demand is 790 W h L^{-1} , which is in the same range as the energy demand for distillation without energy recovery.

Today, reverse osmosis is the leading technology for water production from seawater. Due to the increasing osmotic pressure the typical water removal in seawater treatment is between 35 and 45% (Greenlee et al., 2009). Ek et al. (2006) used commercially available reverse osmosis units to concentrate untreated and acidified stored urine by a factor of 5 (80% water removal, 5 MPa, 29°C). With urine of an initial pH value of 9.2 (probably untreated urine) the nitrogen recovery was only 79%, while with acidified urine the recovery was increased to 91% and 98% at pH values of 7.0 and 6.0, respectively. The overall phosphorus loss was 10%, because some of the phosphorus, probably in the form of particulate compounds, was restrained in the pre-filtration step. For 80% water removal from acidified urine (pH 7), Ek et al. (2006) reported an energy demand of 8 W h L^{-1} electricity and 4 W h L^{-1} heat, which amounts to 30 W h L^{-1} primary energy. This is considerably lower than the energy demand we estimated for distillation. Fig. 4 summarizes the energy demand estimations for the various water removal technologies. Reverse osmosis has by far the lowest energy demand, but it is unsuitable for complete water removal. However, it can be combined with

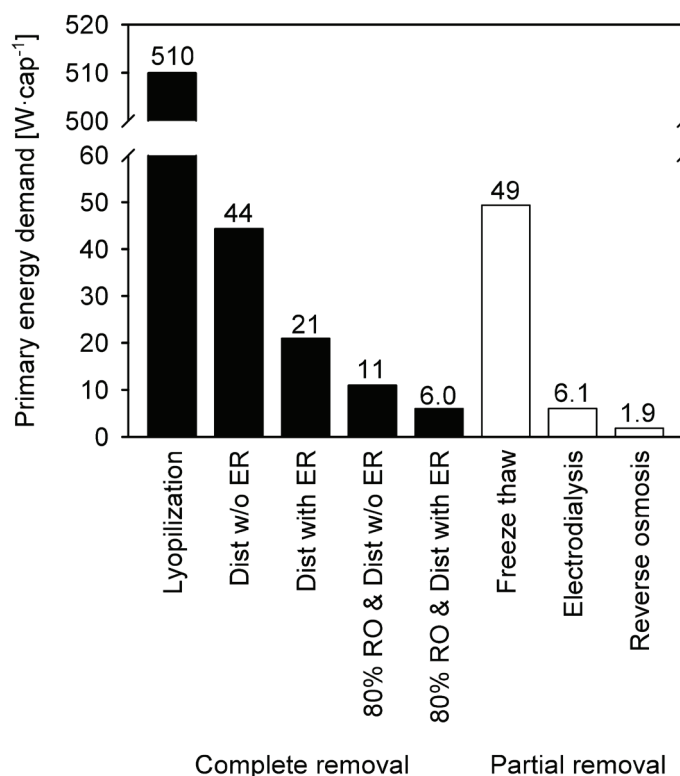


Fig. 4: Estimated primary energy demand for different processes for water removal from nitrified urine ($1.5 \text{ L cap}^{-1} \text{ d}^{-1}$). Dist.: distillation, ER: energy recovery (with vapor compression), RO: reverse osmosis. See text for a description of the processes. 1 W cap^{-1} equals $16.0 \text{ W h L}^{-1}_{\text{urine}}$.

distillation to save energy. In a reactor setup that uses reverse osmosis to remove the first 80% of the water, the primary energy demand could be reduced to 170 W h L⁻¹ (11 W cap⁻¹ or 76% energy reduction) without energy recovery and 96 W h L⁻¹ (6.0 W cap⁻¹, 86% energy reduction) with energy recovery. Together with the energy for nitrification (8.9 W cap⁻¹, Section 4.3), this is only 25% higher than the energy demand for today's wastewater treatment and fertilizer production (12 W cap⁻¹, see Section 4.3).

5 Product stability

5.1 Critical compounds

According to Table 3, ammonium nitrate accounts for 61% of the solid residue of the synthetic nitrified urine and 71% of the solid residues of the spiked nitrified urine. As ammonium nitrate is the most important nitrogen fertilizer in Europe (IFA, 2011), the use of the solid residue in agriculture seems to be an obvious choice for nutrient recycling. However, it has to be considered that ammonium nitrate is unstable at increased temperatures and pressures (Saunders, 1922).

Two types of compounds in the solid residue can decrease the thermal stability even further: The first compound is chloride, which catalyzes the decomposition of ammonium nitrate by reducing the necessary activation energy (or onset temperature) of the exothermic ammonium nitrate decomposition (Keenan et al., 1968). The second set of compounds are organic substances, which can act as additional electron donors besides ammonium (Lurie and Lianshen, 2000) and thereby reduce the activation energy for the decomposition.

To determine whether the solid residue is sufficiently stable to be used as a fertilizer, we conducted calorimetric measurements and consulted the legal regulations for ammonium nitrate fertilizers.

5.2 Differential scanning calorimetry

We used differential scanning calorimetry (DSC) to assess the thermal stability of the solid residue. In a DSC analysis, a sample is heated at a constant rate and the energy amount taken up (endothermic peak) or released (exothermic peak) is measured. The onset temperature of the exothermic peak is an indicator for the sensitivity of a given compound, or in other words, for the amount of energy that is required to initiate a self-accelerating decomposition. Thermally stable materials generally have high onset temperatures. The area under the exothermic peak corresponds to the energy, which is released during the decomposition event. The amount of energy and the rate of heat release are indicators for the severity of the thermal decomposition (Ando et al., 1991). Endothermic peaks indicate phase transitions, which can reduce the stability of the mineral, for example by increasing the shock sensitivity of ammonium nitrate (Hahnefeld et al., 1983).

Three materials were compared with DSC (Fig. 5): the solid residue of spiked nitrified urine (24% N content), a commercial ammonium nitrate fertilizer (27% N, Landor, Birsfelden, Switzerland) and pure ammonium nitrate (35% N, Catalogue number 1.01188.1000, pro analysi, Merck, Darmstadt, Germany). Judging from the onset temperature and the released energy per gram N, the thermal stabilities of the solid residue and pure ammonium nitrate was similar. We assume that the advantage of less ammonium nitrate in the solid residue was counteracted by the presence of chloride and organic substances. The commercial fertilizer had a significantly higher onset temperature than the other two solids. This may be due to powdered dolomite (CaMg(CO₃)₂), limestone (mainly calcite and fewer dolomite, silicates, quartz and gypsum) or pure CaCO₃, which are usually added to ammonium nitrate fertilizers (EU, 2003). Wood and Wise (1955) showed that nitric acid accelerates the decomposition of ammonium nitrate. We assume that the carbonates help to neutralize the nitric acid, thereby increasing the activation energy for the thermal decomposition.

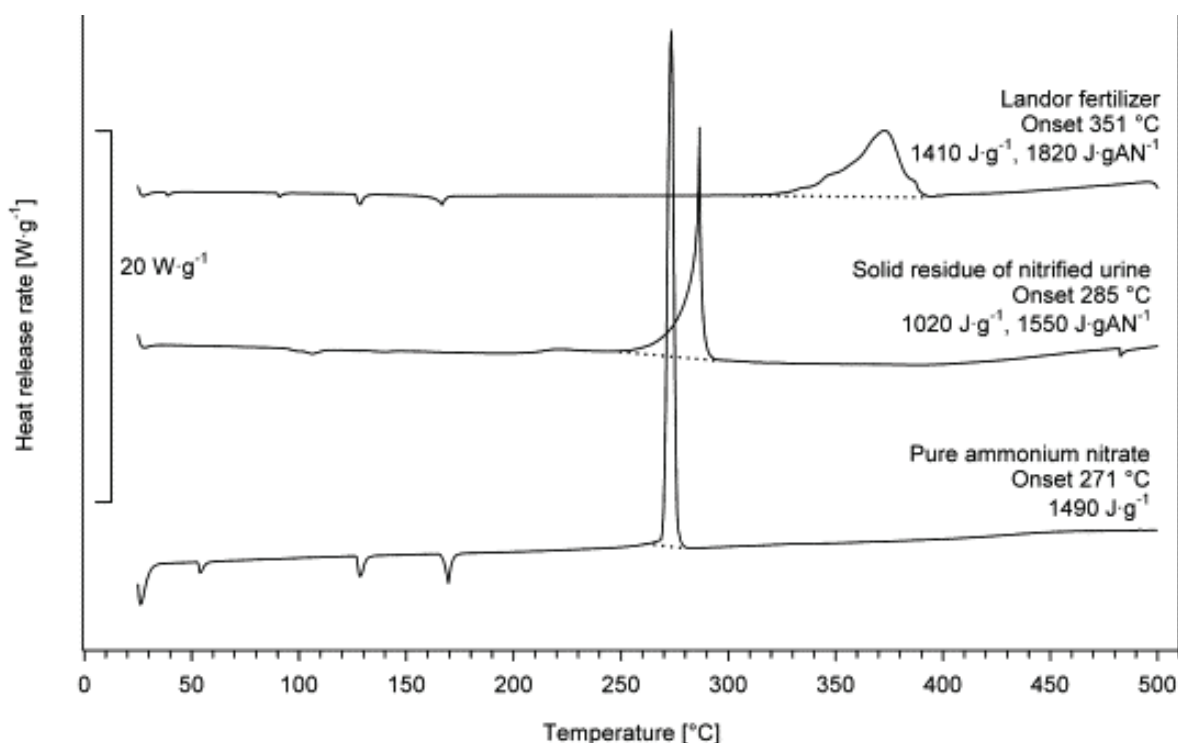


Fig. 5: DSC of three different ammonium nitrate (AN) powders with heating rate of 4 °C per minute. All powders were ground by hand with a pestle before the analysis.

5.3 Legal regulations

Since ammonium nitrate is the main nitrogen fertilizer in Europe, much experience exists for its safe handling and storage. Since disastrous accidents have happened and ammonium nitrate has been misused as explosive, there are strict regulations for the use of ammonium nitrate. The EU Decision 1348/2008/EC (EU, 2008) states that ammonium nitrate fertilizers with a nitrogen content higher than 16% are limited to farmers and other professional users, such as gardeners. Special regulations are given for ammonium nitrate fertilizers with more than 28% nitrogen content (EU, 2003). The solid residue of spiked urine (Table 3) and the theoretical solid residue of unspiked urine (composition as for spiked urine, but only 1.2 gNH₄-N and 1.2 gNO₃-N) have ammonium nitrate contents (as N) of 24% and 16%, respectively. The solid residue of undiluted stored urine without ammonia loss (composition according to Udert et al., 2006, all nitrogen hydrolyzed to ammonium, 50% ammonium oxidized to nitrate, no carbonate) would have an ammonium nitrate content (as N) of 24% per mass. All these products have an ammonium nitrate content (as N) below 28%, but concentrations in urine vary widely and it is possible that this limit could be exceeded. In this case, the fertilizer will have to conform to the more stringent provisions of the European Regulation (EC) No. 2003/2003 (EU, 2003). Three of them will be critical: first, the content of combustible components (measured as C) should not exceed 0.4% by mass: the solid residue of spiked urine given in Table 3 has a DOC content of 0.35%, which is only slightly below this limit. Therefore, TOC removal from nitrified urine (e.g. adsorption on activated carbon) should be considered as an additional treatment step. Second, a solution of 10 g of fertilizer in 100 mL of water must have a pH of at least 4.5. We measured a pH value of 3.84, when diluting the solid residue of the spiked nitrified urine (about 28 g) in 1 L of nanopure water. Since the pH value in a mixture with less water is presumably even lower, a pH correction with alkaline minerals (e.g. calcite or dolomite) has to be considered. The third provision specifies a maximum chlorine (Cl) content of 0.02% by mass. This is the most critical provision, since the chlorine content (as chloride) in the solid residues was much higher (e.g. 11% in the solid residue of spiked nitrified urine). To the best of our knowledge, it will not be possible to push the chloride content of our products below this limit without removing significant amounts of nutrients. To comply with the EU regulations, the best approach will be to add fillers such as calcite, ground limestone or ground dolomite to the solid residue. Such an addition will reduce the ammonium nitrate content per gram of product, so that the strict rules for high-strength ammonium nitrate fertilizers will not be applicable. The addition of such fillers will also help to stabilize the fertilizer by raising the pH value. Nevertheless, even if the ammonium nitrate content is below 28% (as N), national regulations will require that special precautionary measures are taken for the handling of the ammonium nitrate containing fertilizer (see e.g. TRGS 511, 2008). Another approach to stabilize the solid residue of our process is to remove sodium chloride. Since sodium chloride has a comparatively low solubility, this mineral could be removed by sequential distillation or in an industrial post-treatment process.

6 CONCLUSIONS

- Our study has shown that biological nitrification with consecutive distillation of the effluent can be a stable and efficient process for the concentration and recovery of nutrients from urine. The solid residue contains high amounts of nutrients, such as ammonium nitrate, potassium, sulfate and phosphate, which makes it an interesting product for use in

agriculture.

- Controlling the pH in the reactor via the inflow pump can prevent instabilities of the biological transformation processes. This control mechanism also allows for the control of the nitrification rate. MABRs are prone to strong biofilm growth, which can result in nitrogen loss by denitrification. A biofilm reactor with frequent biofilm erosion, such as an MBBR is supposedly more suitable for complete nitrogen recovery.
- We estimate that a very simple nitrification/distillation setup for urine treatment needs about four to five times the primary energy that is required to remove the same amount of nitrogen and phosphorus in a conventional WWTP and produce equivalent amounts of synthetic phosphorus and nitrogen fertilizers. However, the energy demand can be significantly reduced by using vapor compression and reverse osmosis for water removal. An important advantage of a simple distillation process is the possibility to use solar energy for water heating. This is especially interesting for regions with high solar irradiation.
- The product of our process can be thermally instable, because of its high ammonium nitrate content. The ammonium nitrate content of the solid residues is below the limit for stringent EU regulations (28% N). Nevertheless, measures should be explored that render the product more stable, so that the process can also be used in small facilities, which might not be able to conform to the strict safety rules. Possible measures are adsorptive removal of organics before distillation or the addition of stabilizing fillers such as limestone, dolomite or pure calcite.
- An alternative process to ammonium nitrate production is the complete nitrification to nitrate, which requires an increase of the alkalinity by adding a base. The disadvantage of chemical dosage would be compensated by obtaining a thermally stable product. A possible setup for the nitrification reactor is the use of limestone granules or other alkaline particles as biofilm carriers.

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APPENDIX. SUPPLEMENTARY MATERIAL

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.11.020.

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