

## Integrated mechanical, biological and physico-chemical treatment of liquid manure streams

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**Abstract** The results obtained during the first year of execution of a joint Russian-Dutch project "The development of integrated anaerobic-aerobic treatment of liquid manure streams with maximisation of production of valuable by-products (fertilisers, biogas) and re-utilisation of water" (1999–2001) are discussed. The application of a straw filter was an effective means to separate the solid and liquid fractions of diluted pig manure wastewater and resulted in the removal of a significant part of the dry matter, total nitrogen and phosphorus (65, 27 and 32%, respectively). From the filtrate generated, 60–80 % of the COD was removed in a UASB reactor operating at 20–30°C. Up to 66% of phosphate was precipitated after air stripping of the CO<sub>2</sub> from the anaerobic effluents. Ammonia was efficiently removed (>99%) from the anaerobic effluents using zeolite (Ural laumantite) as an ion exchanger. However, the N-content of the resulting zeolite was too low to be used as a fertiliser. A feasible alternative for nitrogen elimination involved nitrification of the anaerobic effluent followed by denitrification in a UASB reactor using the COD of the filtrated manure wastewater as carbon source.

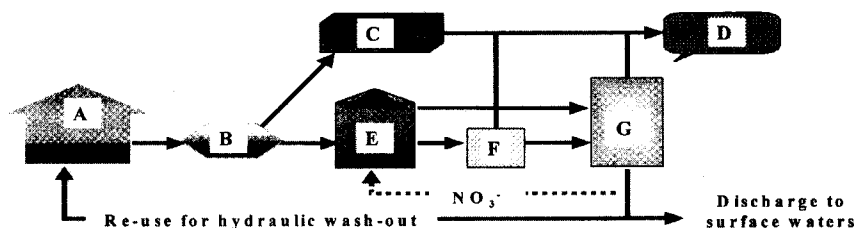
**Keywords** Fertiliser; liquid manure; nitrification; straw filter; struvite; UASB reactor; zeolite

### Introduction

More than 100 million tonnes of manure wastewater containing 2–4% total solids is produced in Russia at big complexes and medium-scale farms due to so-called run-off (flushing) technologies used for cleaning (Kalyuzhnyi *et al.*, 1999). A possible solution for sustainable utilisation and treatment of diluted manure streams is the preliminary mechanical separation of solid and liquid fractions followed by separate biotechnological and physico-chemical treatment of both fractions. Using this approach, treatment can be focused on re-utilisation of fertiliser potential and environmental protection. This approach is the basis of the joint Russian-Dutch project "The development of integrated anaerobic-aerobic treatment of liquid manure streams with maximisation of production of valuable by-products (fertilisers, biogas) and re-utilisation of water" (1999–2001). The ideology and main directions of the research activities within the project are represented in Figure 1.

This paper discusses the results obtained during the first year of the project:

- i. performance of a straw filter for separation of solid and liquid manure fractions (step B);
- ii. COD elimination from filtrate after straw filtering using a UASB reactor (step E1);
- iii. performance of zeolite as a means to remove ammonia from anaerobic effluents (step F1);
- iv. optimisation of nutrient precipitation from anaerobic effluents (step F2);



**Figure 1** Proposed scheme of liquid manure treatment (A – farm (manure production); B – separation of solids/liquid; C – composting of solids; D – final form of fertiliser; E – anaerobic elimination of major part of COD (and nitrate if necessary); F – physico-chemical removal of nutrients; G – biological elimination of resting BOD and nutrients)

- v. start-up of a nitrifying biofilter treating anaerobic effluents (step G1);
- vi. denitrification of aerobic effluent in a UASB reactor (step E2).

## Materials and method

### Manure wastewaters

The raw manure wastewaters (RMW) were taken directly from two pig farms using flushing technologies for cleaning and located in the Moscow and St. Petersburg regions. Some of wastewater characteristics are presented in Tables 1–2.

### Straw filters

Two experimental installations consisting of tanks with a rack to retain randomly packed straw were constructed. The straw filter in St. Petersburg had the following parameters: straw weight – 15 kg, cross-section – 0.52 m<sup>2</sup>; height – 0.5 m; volume – 0.26 m<sup>3</sup>. The straw filter in Moscow had approximately five times less volume with a similar cross-section/height ratio.

### UASB reactor

Investigations were carried out in a laboratory UASB reactor (diameter – 6.8 cm, height – 85 cm, total working volume – 2.6 l) made from transparent plastic and seeded with floccular anaerobic sludge originating from a previous research study (Kalyuzhnyi *et al.*, 1999). The operating temperatures were 29–30 or 17–20°C. The acetoclastic and denitrifying activities of the anaerobic sludge were determined as described elsewhere (Kalyuzhnyi *et al.*, 1999; Klapwijk and Rensink, 1996).

### Ion-exchanger columns

Ammonia removal from anaerobic effluents was investigated using columns packed with 300 ml of zeolite (Urals laumantite). Hydraulic retention time (HRT) of the anaerobic effluent in the columns was maintained at 4 h throughout all the experiments.

### Nutrient precipitation

The feasibility of simultaneous removal of ammonia and phosphate from anaerobic effluents *via* their precipitation in the form of insoluble minerals was investigated in batch vessels by pH adjustment to the alkali values performed by natural ageing, CO<sub>2</sub> stripping and NaOH dosing. In every run, the solution after precipitation was centrifuged before analysis.

### Nitrifying reactor

An airlift reactor (made from glass and packed with stones) with a working volume of 0.7 l was used for nitrification of the anaerobic effluents under ambient temperatures in the

laboratory (17–20°C). Air at a flow rate of 3 ml/min was continuously pumped through an external loop. In the middle of this loop, an electronic sensor (“Datchik”, Russia) was inserted for on-line monitoring of soluble oxygen. The electric signal from this sensor was transferred to a programmable data logger system. The data were recorded every 2 or 30 s and were averaged (when necessary) over 3-min intervals. A personal computer programmed to function as a terminal emulator was used to communicate with the data logger. Secondary sludge from Kur’yanovskaya municipal aeration station (Moscow) was used as the seed sludge for formation of the attached biofilm. The various respiration rates of the airlift sludge were assessed as described by Klapwijk and Rensink (1996). During the start-up period, a gradual increase of organic loading rate (OLR) was applied by decreasing HRT.

#### Analysis

All analyses were performed using Standard Methods (APHA, 1985) or as described previously (Kalyuzhnyi *et al.*, 1999).

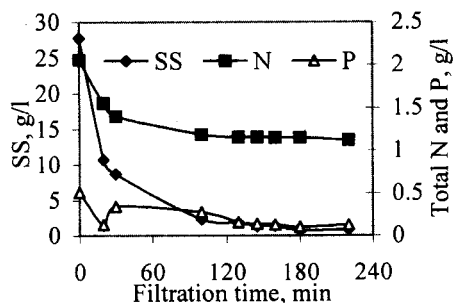
### Results and discussion

#### Straw filter efficiency for separation of solid and liquid manure fraction

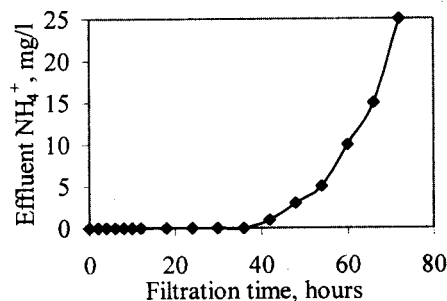
Typical dynamics of filtrate quality during the start-up of the straw filter in St. Petersburg are shown in Figure 2. It is seen that after 4 hours of operation, the straw filter was able to remove from the RMW 97, 45 and 75% of the suspended solids (SS), total nitrogen and phosphorus, respectively. An integrated mass balance of the straw filter system for a working cycle (4 days) is presented in Table 1. From these data, one can conclude that the system ensures a removal of 65, 27 and 32% of dry matter, total nitrogen and phosphorus, respectively. These cumulative figures are inferior to those obtained during the start up period possibly due to the partial solubilization of entrapped matter on the straw filter. Thus, to minimise these unwanted processes, the duration of a working cycle for a straw filter should be decreased (if possible). Testing of the straw filter in Moscow where the RMW was substantially more dilute (see row “RMW” in Table 2) also showed a significant reduction (up to 60%) in SS and colloidal COD in the filtrate (compare rows “RMW” and “FMW” in Table 2). However, straw filtration had a minimal influence (which it is quite obvious) on concentrations of soluble components like volatile fatty acids (VFA), ammonia and phosphate.

#### COD elimination using UASB reactor

The generalised results of the UASB treatment of the RMW originating from the Moscow region and the corresponding straw filter filtrate are presented in Table 2. It can be seen that



**Figure 2** Typical dynamics of filtrate quality during the start-up of straw filter



**Figure 3** Dynamics of NH<sub>4</sub><sup>+</sup> concentration in the effluent of zeolite column (HRT=4 h)

**Table 1** The integrated mass balance of the straw filter system for a working cycle (4 days)

Parameter	Straw	Manure	Straw +entrapped matter	Filtrate
Wet weight, kg	15	520	106	ND
Dry matter, kg	12.84	11.91	20.56	4.19
Total nitrogen, kg	0.06	0.948	0.318	0.69
N-NH <sub>3</sub> , kg	~0	0.424	0.012	ND
Total phosphorus, kg	0.003	0.203	0.067	0.139

ND – not determined

**Table 2** Some characteristics of the raw and treated pig manure wastewaters

	COD <sub>tot</sub> <sup>a</sup> g/l	COD <sub>SS</sub> <sup>a</sup> g/l	COD <sub>Col</sub> <sup>a</sup> g/l	COD <sub>Sol</sub> <sup>a</sup> g/l	VFA, g COD/l	pH	N-NH <sub>3</sub> , mg/l	P-PO <sub>4</sub> <sup>3-</sup> , mg/l
RMW	8.3–10	1.8–2.1	1.9–4.2	4.2–7.2	3.1–4.6	6.6–6.9	187–296	170–209
ATRMW	1.7–2.1	0.2–0.3	0.8–1.3	0.6–0.8	<0.02	7.5–7.6	218–358	170–176
Removal, %	75–85	86–89	60–69	84–86	99		–(17–21)	0–16
FMW	7.1–8.3	0.6–1.3	0.8–1.5	3.3–6.7	3.2–3.4	6.5–7.0	156–311	156–159
Removal, %	15–17	38–67	58–64	7–21	0–26		0–17	8–16
ATFMW	1.1–1.6	0.2–0.3	0.7–0.8	0.5–0.6	<0.01	7.7–8.0	218–391	45–59
Removal, %	60–64	67–77	12–80	57–68	~100		–(26–40)	63–71
Tot.rem.* , %	84–87	86–89	63–81	88–92	100		–(17–32)	68–72

RMW – raw manure wastewater

ATRMW – anaerobically treated RMW (HRT of 1.2–1.4 days, OLR of 4–6 g COD/l/d, 30°C)

FMW – filtrated (through straw filter) manure wastewater

ATFMW – anaerobically treated FMW (HRT of 1.0–1.2 days, OLR of 3–5 g COD/l/d, 30°C)

\*Filtration + anaerobic treatment

the combination of straw filtration and anaerobic treatment led to better COD and phosphate removal compared to the application of the single steps separately. However the ammonia concentrations increased in each step presumably due to anaerobic hydrolysis of proteinaceous substances in the RMW. The concentration of phosphate substantially dropped during the treatment of FMW. This was attributed to partial precipitation as whitish deposits (presumably: calcite, CaCO<sub>3</sub>, hydroxyapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH and struvite, MgNH<sub>4</sub>PO<sub>4</sub>), which were clearly visible on the reactor walls and in the internal gas-sludge separation device. It should be noted that the COD removal was higher compared to available literature data about treatment of pig manure in UASB-like reactors (Lo *et al.*, 1994). However, such exhaustion of easily degradable COD (e.g., VFA) in the anaerobic effluents might create problems for biological post-treatment (e.g., for biological N and P removal).

#### Ammonia removal from anaerobic effluents by zeolite

It was found that one volume of Urals laumantite (particle size of 1–2 mm) could treat at least 10 volumes of anaerobic effluent using an HRT of 4 h. Treatment was defined as a decrease of ammonia concentration from 360 to 1–5 mg N/l (Figure 3). However, the chemical analysis showed that 1 kg of completely saturated zeolite contained only 3.6 g of ammonia and 5.3 g total nitrogen. Such a low N-content restricts its application as a fertilizer. A possible solution may be a chemical regeneration of zeolite for multiple (cyclic) uses. Nitric acid has been proposed as a regenerating agent with the aim to produce a liquid fertilizer (ammonia nitrate). The investigations directed towards optimisation of this process are in progress. The other solution can also include a search for the ion-exchangers with

**Table 3** Relative decrease of ammonia and phosphate concentrations in the ATFMW during multi-step base dosage

Step	Change of pH	Decrease of $\text{NH}_4$ , %	Decrease of $\text{PO}_4$ , %
I	7.8 → 9.7	7.75	11.1
II	9.1 → 9.7	4.6*	9.3*
III (+2 mM of $\text{MgSO}_4$ )	9.2 → 9.7	9.8*	12.4*
IV	9.0 → 9.7	17.3*	29.4*
V	8.9 → 9.7	10.5*	11.1*
Total after 5 steps		40.6	55.7

\*Relative decrease in filtrate after the previous step

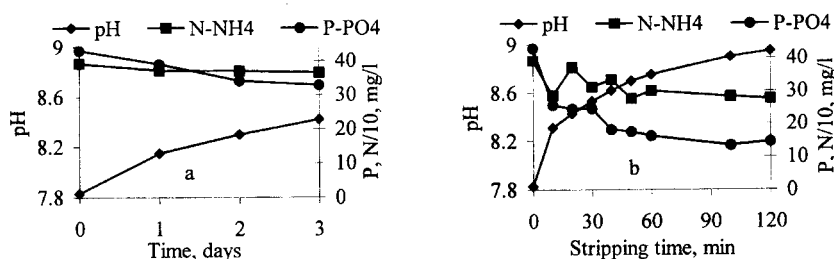
better ammonia adsorbent properties than Ural laumantite. Clinoptilolite and wollastonite (if locally available) are among the candidates to be considered (Lind *et al.*, 2000).

#### Removal of ammonia and phosphate from anaerobic effluents via precipitate formation

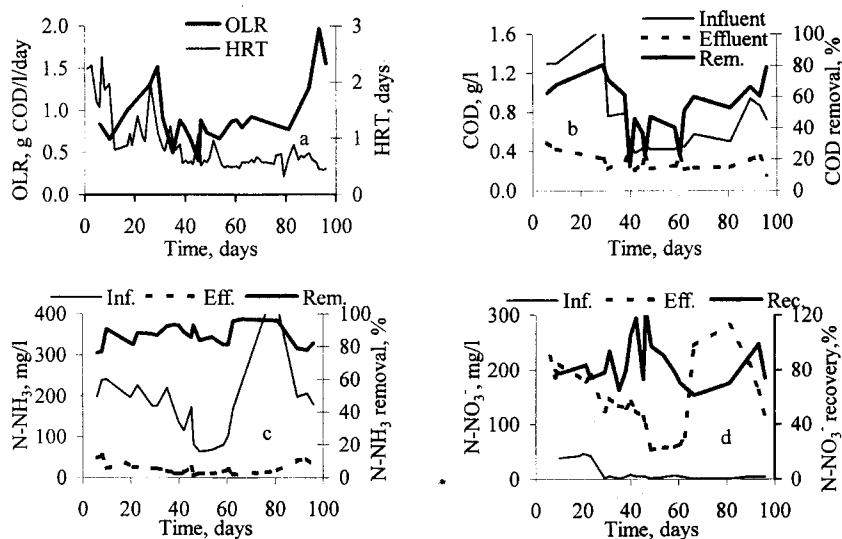
In addition to ammonia and phosphate, the anaerobic effluents contain magnesium and calcium (usually in the concentrations around or higher than 2 mM). So, struvite and hydroxypatite precipitation can be initiated by adjusting the pH to the optimal supersaturating value, which is above 9 (Battistoni *et al.*, 1998a; Momberg and Oellerman, 1992). However, partial precipitation of these minerals likely occurred in a UASB reactor (see paragraph “COD elimination using UASB reactor”) which had an effluent pH around 8 (Table 2). Effluent pH can be further increased by natural ageing, air stripping of  $\text{CO}_2$  or base dosing (Battistoni *et al.*, 1998a). Our experiments with the first two methods (Figure 4) indeed showed a substantial pH increase (especially during air stripping) in the ATFMW accompanied by a noticeable decrease of phosphate and ammonia concentrations – 23 and 7% (natural ageing) and 66 and 29% (air stripping), respectively. Comparable (with air stripping) nutrient removal from the ATFMW was achieved using 5-step base dosage accompanied by addition of magnesium during step III (Table 3). It can be seen that application of mainly struvite precipitation resulted in a decrease in phosphate and ammonia concentrations by 56 and 41%, respectively (some losses of ammonia with all methods probably occurred due to rise in pH). Further, base dosage and batch precipitation is not very convenient from a technological point of view. Thus, attempts are currently being undertaken to develop a continuous reagentless process based on air stripping similar to that described by Battistoni *et al.* (1998b).

#### Nitrification of anaerobic effluents

A successful start-up of the nitrifying airlift was achieved in two months with the ATFMW (characteristics of which are listed in Table 2) using a HRT of 2–3 days and OLR of



**Figure 4** Dynamics of pH, ammonia and phosphate concentrations during natural ageing (a) and air stripping (b) of the ATFMW (without sand addition)



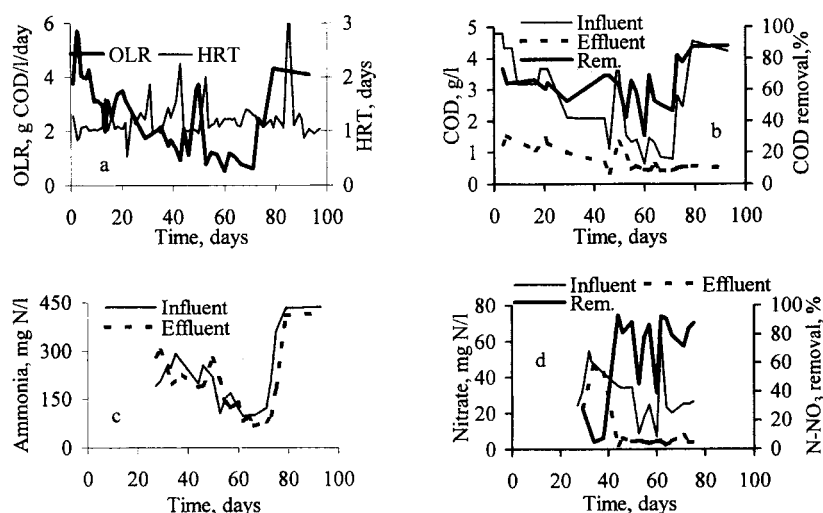
**Figure 5** Operational performance of airlift reactor treating anaerobic effluents from a UASB reactor.

$$N-NO_3 \text{ recovery} = \frac{([N-NO_3]_{\text{eff}} - [N-NO_3]_{\text{in}})}{([N-NH_3]_{\text{in}} - [N-NH_3]_{\text{eff}})} \cdot 100\%$$

0.4–0.7 g COD/l/day. Ammonia and COD removals at the end of the start-up period were higher than 90 and 65%, respectively (data not shown). The results after the start-up are presented in Fig. 5. During the first 26 days the airlift reactor was fed by the ATFMW and HRT was gradually decreased from two to approximately one day (Figure 5a). This resulted in an increase of the OLR until 1.5 g COD/l/day (Figure 5a) accompanied by ammonia and COD removals around 85 and 65%, respectively (Figures 5b–c). The calculated nitrate recovery from the consumed ammonia was approximately 80% in this period (Figure 5d). The lacking 20% of ammonia can be attributed to consumption for growth of aerobic biomass as well as some losses due to its escape as free ammonia to the gas phase of the airlift as the medium pH was often higher than 8. During days 27–72, the UASB reactor was fed by a mixture of the FMW and the nitrifying effluent from the airlift reactor (see next paragraph), and therefore the characteristics of incoming influent to the aerobic treatment step changed substantially (Figures 5b–d). Due to the more diluted influent, the COD removal dropped on the average to 46% (days 27–72) though the effluent COD concentrations remained almost the same as in the beginning of working period (Figure 5b). However, the ammonia removal increased to 88% (on the average) resulting in an average effluent ammonia concentration of 14 mg N/l during this period (Figure 5c) and approximately 88% of the consumed ammonia was recovered as nitrate (Figure 5d). The actual, basic and nitrifying respiration rates assessed on day 72 were  $49.1 \pm 4.7$ ,  $13.7 \pm 0.2$  and  $34.3 \pm 1.4$  mg O<sub>2</sub>/l/h, respectively. Thus, the respiration rate which for the oxidation of easily biodegradable COD in the anaerobic effluent was accounted for  $14.8 \pm 3.1$  mg O<sub>2</sub>/l/h or  $0.36 \pm 0.07$  g COD/l/day. The latter figure corresponds well to the observed consumption of COD in the airlift reactor during days 27–72 (Figure 5b). After restoration of feeding of nitrifying airlift reactor by the FMW (starting at day 73), the average ammonia and COD removals were 86 and 65%, respectively (Figure 5b–c), i.e. they were practically the same as during the first 26 days of working period. It should be noted that the effluent COD concentrations slightly fluctuated around 0.3 g/l throughout the whole working period of the airlift reactor. It is likely that this concentration represents a hardly biodegradable (neither under anaerobic nor under aerobic conditions) fraction of COD in the pig manure wastewaters.

### Denitrification of aerobic effluent in a UASB reactor

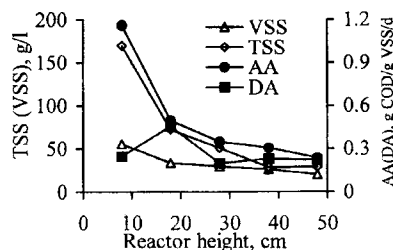
Since the anaerobic effluents contain not enough easily biodegradable COD to fulfil the denitrification requirements, the feasibility of denitrification of nitrifying effluent from the airlift reactor was investigated in the UASB reactor by using COD from the FMW. The results of the UASB reactor performance are presented in Figure 6. During the first 26 days, when the UASB reactor was fed by the FMW solely, an average OLR was 3.6 g COD/l/day using an average HRT of 1.1 days (Figure 6a) and operating temperature of 30°C. The COD removal was 66%, i.e. close to the range listed in Table 2. During days 27–72 (Figure 6), a mixture of the FMW and the nitrifying effluent from the airlift reactor was fed to the UASB reactor (a proportion of both wastewaters was gradually increased from 2:1 to 1:1). It is seen (Figure 6d) that the denitrification efficiency was low (14% on the average) during the first two weeks of this period but then sharply increased to around 90% indicating an achievement of the necessary level of denitrifiers in the UASB reactor. In order to reduce the operational costs of the process in practice, the UASB reactor was operated from day 45 at ambient temperature of laboratory (17–21°C). This change practically did not influence the denitrification efficiency, which was 78% (on the average) with a fairly constant effluent nitrate concentration of about 4 mg N/l during days 45–72 (Figure 6d). The presence of nitrate led to 3–4 times reduction of biogas production with substantial decrease of methane concentration in it – from 75–80 to 30–40% (data not shown). The COD removal efficiency also dropped to 56% (on the average) but it was mainly due to more diluted influent concentration applied because the COD effluent concentration slightly fluctuated around 0.6 g/l (Figure 6b). The formation of whitish precipitates inside the UASB reactor continued to occur and the overall mineralisation of the sludge was quite high especially in the bottom part of the UASB reactor (Figure 7). The acetoclastic sludge activity was maximal in the reactor bottom and, in general, was higher than the denitrifying sludge activity along the entire reactor height. Due to this high acetoclastic activity of the sludge, the COD removal quickly increased to the values higher than 80% (Figure 6b) after restoration of reactor feeding by the sole FMW (day 73 onwards). The influent and effluent concentrations of ammonia were similar throughout the entire experimental period (Figure 6c) likely because its release from organic nitrogen of the FMW was compensated by its consumption for bacterial growth and struvite precipitation.



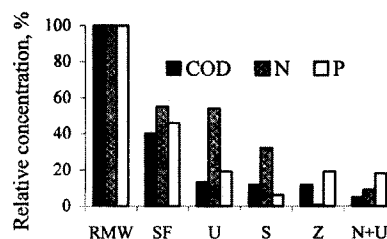
**Figure 6** Operational performance of UASB reactor treating FMW and nitrifying effluent from airlift reactor

## Conclusions

From the numerous experiments presented in this paper the following conclusions can be drawn. The application of a straw filter was an effective means to separate the solid and liquid fractions of diluted pig manure wastewater and resulted in the significant removal of dry matter, total nitrogen and phosphorus (in our experiments – 65, 27 and 32%, respectively). From the filtrate generated, 60–80% of the COD was removed in a UASB reactor operating at 20–30°C. Up to 66% of phosphate was precipitated from the anaerobic effluents through air stripping. Ammonia was efficiently removed (> 99%) from the anaerobic effluents using Ural laumantite as an ion exchanger. However, the N-content of the zeolite was too low to be considered as a fertiliser. The economical feasibility of ammonia removal with this method may only occur with the development of a proper method for zeolite regeneration. The nitrification of anaerobic effluents followed by denitrification in a UASB reactor using the COD of the FMW was shown to be a feasible alternative for nitrogen elimination. Figure 8 summarises the average data showing the decrease in total COD, nitrogen and phosphorus concentrations for the raw pig manure wastewaters after each treatment step. It can be seen that only a combination of these treatment steps followed by biological N and P removal (future research) opens some possibilities of re-use of treated wastewater for flushing or discharge to open water surfaces.



**Figure 7** Distribution of TSS, VSS, aceticlastic (AA) and denitrifying (DA) sludge activities (30°C) along the UASB reactor height at day 72



**Figure 8** Relative decrease in total COD, N and P concentrations after each treatment step (SF – straw filter; U – UASB; S – struvite Z – zeolite (after U); N+U – nitrification + denitrification in UASB)

## Acknowledgements

The financial support of NWO (grant No. 299175) is gratefully acknowledged. We also would like to thank Dr. John Copp for revision of English.

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