# Sustainable Treatment and Reuse of Diluted Pig Manure Streams in Russia

From Laboratory Trials to Full-Scale Implementation

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#### Abstract

This article summarizes the results obtained during the laboratory and pilot development of integrated biologic and physicochemical treatment and reuse of diluted pig manure streams. The application of a straw filter was an effective means to separate the solid and liquid fractions of raw 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 total chemical oxygen demand (COD) was removed in an upflow anaerobic sludge bed reactor operating at 15-30°C. Ammonia was efficiently eliminated (>99%) from the anaerobic effluents using Ural laumantite as an ion exchanger. However, the nitrogen-content of the zeolite was too low to consider this method of ammonia removal economically feasible. The phosphate precipitation block, consisting of stripper of CO<sub>2</sub> and fluidized-bed crystallizator, was able to decrease the concentration of soluble phosphate in the anaerobic effluents up to 7–15 mg of phosphate/L. The application of aerobic/anoxic biofilter as a sole polishing step was acceptable from an aesthetic point of view (the effluents were transparent

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and almost colorless and odorless) and elimination of biochemical oxygen demand (the resting COD was hardly biodegradable). However, the effluent nutrient concentrations (especially nitrogen) were far from the current standards for direct discharge of treated wastewater. We discuss the approaches for further improvement of effluent quality. Finally, we provide an outline of a full-scale system that partially implements the laboratory- and pilot-scale results obtained.

**Index Entries:** Integrated system; nutrient removal; phosphate precipitation; pig manure wastewater; straw filter; upflow anaerobic sludge bed reactor; zeolite.

#### Introduction

In Russia, according to the available statistics, on January 1, 1999, there were, respectively, 8.575, 17.381, and 210.810 million pigs, cattle, and poultry (Table 1) (1). Taking into account the average figures presented in Table 1, the yearly produced manure can be estimated as 382.7 million t (as concentrated livestock wastes). However, in the Soviet Union, breeding of agricultural animals has been developed on an industrial basis, and Russia has inherited the majority of the facilities. As a result, currently, e.g., almost one quarter of all pigs are handled on huge complexes (in total 33) having a capacity for fattening 54,000–216,000 of the animals. However, as a result of the flushing technology used for cleaning, these complexes produce yearly about 30 million t of pig manure wastewater containing only 2–2.5% total solids. Although these complexes are equipped with aerobic treatment plants, their 30-yr exploitation has demonstrated a complete failure of this technological approach. Often the aerobic systems work (if they do) unsatisfactorily owing to frequent overloading with highstrength manure, and, therefore, the complexes are responsible for the severe pollution of soils, groundwaters, rivers, and lakes in the surrounding areas. In addition, such a practice leads to the loss of manure and its fertilizer potential, a serious problem considering the current lack of organic fertilizers in Russia and an exhaustion of soils in most regions (3).

A possible solution for sustainable utilization and treatment of such diluted manure streams is the preliminary mechanical separation of solid and liquid fractions followed by separate biologic and physicochemical treatment of both fractions. Using this approach, treatment can be focused not only on environmental protection but also on reutilization of the valuable components comprising manure wastewater. This approach is the basis of two consecutive joint Russian-Dutch projects: (1) "the development of biotechnological methods for manure treatment focused on fertiliser production" (1996–1998); and (2) "the development of integrated anaerobic-aerobic treatment of liquid manure streams with maximisation of production of valuable byproducts (fertilizers, biogas) and re-utilisation of water" (1999–2001). The ideology and main directions of the research activities within these projects are represented in Fig. 1. Various steps of

| Table 1                                      |
|----------------------------------------------|
| Livestock and Waste Production in Russia     |
| (without nonmarketable breeding animals) (1) |

| Animals                           | Number of heads<br>(million) | Average production of manure (t/[head·yr]; % humidity) (2) | Estimated yearly<br>manure production<br>(million t) |
|-----------------------------------|------------------------------|------------------------------------------------------------|------------------------------------------------------|
| Pig<br>Cattle<br>Poultry<br>Total | 8.575<br>17.381<br>210.810   | 2.4 (87.5)<br>20 (90)<br>0.069 (73–76)                     | 20.6<br>347.6<br>14.5<br>382.7                       |

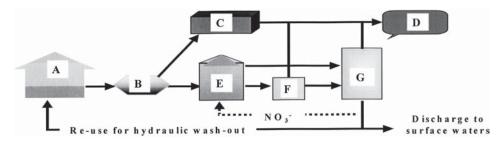


Fig. 1. Proposed scheme of integrated liquid manure treatment/reutilization. A, farm (manure production); B, separation of solids/liquid; C, composting of solids; D, final form of fertilizer; E, anaerobic elimination of major part of chemical oxygen demand (COD) (and nitrate if necessary); F, physicochemical removal of nutrients; G, biologic elimination of resting biochemical oxygen demand (BOD) and nutrients.

this integrated treatment scheme were investigated on laboratory and pilot levels (3–9). This article summarizes the results obtained and gives an outline of a full-scale system that partially implements them.

#### Materials and Methods

#### Wastewater

The raw manure wastewaters (RMWs) were taken directly from the pig farms using flushing technologies for cleaning and located in the Moscow, St. Petersburg, and Vologda regions. Some of the wastewater characteristics are presented in Table 2.

# Laboratory Installations

Upflow Anaerobic Sludge Bed Reactors

The laboratory reactors (diameter: 6.8 cm; height: 85 cm; total working volume: 2.6 L) were made from transparent plastic and seeded with floccular anaerobic sludge originating from a previous research study (3). The operating temperatures were 29–30 or 17–20°C. The reactors were fed with straw-filtered pig manure wastewater in Moscow.

| Parameters             | Moscow      | St. Petersburg | Vologda     |
|------------------------|-------------|----------------|-------------|
| DM (g/L)               | 10–15       | 12–36          | 15–20       |
| $COD_{tot}(g/L)$       | 11–17       | 15–43          | 15-25       |
| $COD_{cc}$             | 4.8 - 5.9   | ND             | ND          |
| COD <sub>col</sub>     | 1.9 - 4.2   | ND             | ND          |
| COD <sub>sol</sub>     | 4.2 - 7.2   | ND             | ND          |
| Total nitrogen (g/L)   | 0.61 - 0.91 | 1.21-2.20      | 1.0 - 2.0   |
| $N-NH_3(g/L)$          | 0.29 - 0.65 | 0.98 - 1.45    | 0.5 - 0.9   |
| Total phosphorus (g/L) | 0.19 - 0.25 | 0.2 – 0.49     | 0.2 - 0.26  |
| $P-PO_{4}(g/L)$        | 0.17 - 0.21 | 0.19 - 0.23    | 0.15 - 0.18 |
| pH                     | 6.6–7.5     | 6.2-8.5        | 6.5–7.5     |

Table 2
Range of Variation in Some Characteristics of Raw Pig Manure Wastewater<sup>a</sup>

<sup>a</sup>ND, not determined.

#### 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 aging, CO<sub>2</sub> stripping, and NaOH dosing as described in ref. 4. In every run, the solution after precipitation was centrifuged before analysis.

#### **Biofilter**

The reactor was made from glass, packed with road metal (working volume of 0.7 L), and used as a continuous nitrifying reactor as well as an alternating aerobic/anoxic reactor for treatment of the anaerobic effluents at ambient laboratory temperatures (17–20°C). In the latter case, the regime of its operation was as follows: During aerobic phase (duration: 20 or 30 min), the feeding was stopped, while air at a flow rate of 1 L/min was pumped through an external loop of the biofilter. Aeration was switched off during the anoxic phase (duration: 30 or 40 min), while the continuous feeding was restored and the high recycle rate of effluent (20 L/h) was applied to ensure an adequate mixing in the biofilter. A programmable multichannel timer controlled all three pumps used. Additionally, in the middle of the external loop, an electronic sensor (Datchik, Russia) was inserted for online 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.

#### Pilot Installations

#### Straw Filters

Two installations consisting of tanks with a rack to retain a randomly packed wheat straw were constructed. The straw filter in St. Petersburg had the following parameters: 15-kg straw weight, 0.52-m² cross-section, 0.5-m height, 0.26-m³ volume. The straw filter in Moscow had approximately five times less working volume with a similar cross-section/height ratio and straw weight of 3 kg. The other details are given in ref. 9.

### Upflow Anaerobic Sludge Bed Reactor

The upflow anaerobic sludge bed (UASB) reactor was made from transparent plastics and had the following size: 22.6-cm² cross-section (rectangular), 206-cm height, 44.6-L working volume. For experiments in St. Petersburg, it was seeded with 10 L of anaerobic sludge originating from an anaerobic digester treating sewage sludge (Moscow). The RMW was decanted and filtered through a straw filter before being used as an influent for the UASB reactor. After finishing the trials in St. Petersburg, the reactor with the sludge was kept unfed in a cool room for 6 mo. Then it was transferred to the pig complex Nadeyevo (Vologda) to assess its performance for treating a liquid fraction of RMW obtained after separation of solids on vibro sieves.

# Phosphate Precipitation Block

The phosphate precipitation block (PPB) consisted of air stripper (diameter: 20 cm; height: 20 cm; working volume: 6 L) for  $\mathrm{CO_2}$  removal to increase pH and fluidized-bed crystallizator (FBC) 7.8-cm diameter, 105-cm height, 5-L total volume) for crystallization of phosphate minerals such as struvite (MgNH<sub>4</sub>PO<sub>4</sub>) and hydroxyapatite ( $\mathrm{Ca_5[PO_4]_3OH}$ ). Both reactors were made from transparent plastics. The FBC was initially filled with 1 kg of washed sand (0.25- to 0.5-mm fraction) as a source of nuclei to promote phosphate crystallization from supersaturated effluents of the stripper. The fluidization was performed using an airlift loop. This block worked in line with the UASB reactor during pilot trials in St. Petersburg. Other details are given in ref. 5.

#### **Biofilter**

The biofilter was made from transparent plastics and packed with road metal (0.5- to 2-cm fraction). It had the following size: 13-cm diameter, 145-cm height, 19-L working volume) and functioned in alternating aerobic/anoxic regime for treatment of the FBC effluent. During the aerobic phase (duration: 20 or 30 min), the feeding was stopped, while air at a flow rate of 5 L/min was pumped through an external loop of the biofilter.

Aeration was switched off during the anoxic phase (duration: 30 or 40 min), while the feeding was performed for 5 or 10 min, and the high recycle rate of effluent (20 L/h) was applied to ensure an adequate mixing in the biofilter. A programmable multichannel timer (with total time cycle of 1 h) controlled all three pumps used. Secondary (nitrifying) sludge from the wastewater treatment plant of the pig complex Vostochnyi (Leningrad province) was used as seed sludge for formation of the attached biofilm. The excess sludge was periodically withdrawn from the top of the biofilter. It worked in line with the UASB reactor and PPB during pilot trials in St. Petersburg. All other details are given in refs. 4 and 6.

# Analyses

All analyses were performed using standard methods (9) or as described previously (3–8).

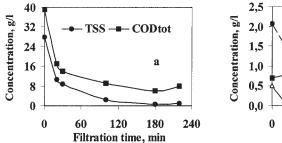
## **Results and Discussion**

Application of Straw Filters for Separation of Manure into Solid and Liquid Fractions (step B)

Separation into solid and liquid fractions is an important element of liquid manure handling in Russia (3). Currently, it is performed by application of sieves and centrifuges. However, both methods are costly, and in Russian agriculture, there is a need to develop less expensive alternatives giving byproducts suitable for reuse. Based on the Flemish experience with a pig slurry separation using straw filters (10), we tested this method under Russian conditions.

Typical dynamics of filtrate quality during the startup of the straw filter in St. Petersburg are shown in Fig. 2. After 3.5 h of operation, the straw filter was able to remove from the RMW 97, 79, 75, and 45% of the total suspended solids (TSS), COD, phosphorus, and nitrogen, respectively. An integrated mass balance of the straw filter for a working cycle (4 d) is presented in Fig. 3. From these data, one can conclude that the system ensures a removal of 83, 32, and 27% of dry matter (DM), total phosphorus, and nitrogen, respectively. These cumulative figures are inferior to those obtained during the startup period, possibly owing to the partial solubilization of entrapped matter on the straw filter (see curve of ammonia in Fig. 2). Thus, to minimize these unwanted processes, the duration of a working cycle for a straw filter should be decreased to 2 to 3 d (if possible). Testing of the straw filter in Moscow where the RMW was more diluted (Table 2) also showed a significant reduction (up to 60%) in TSS and colloidal COD (COD<sub>col</sub>) in the filtrate (4). However, straw filtration had a minimal influence (what it is quite obvious) on concentrations of soluble components such as volatile fatty acids (VFA), ammonia, and phosphate.

Thus, application of straw filter was an effective measure for separation of pig manure into liquid and solid fractions. Moreover, this technique



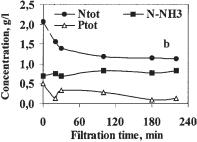


Fig. 2. Typical dynamics of filtrate quality during startup of straw filter.

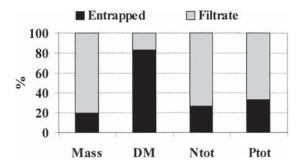


Fig. 3. Distribution of mass, DM, total nitrogen, and phosphorus between entrapped matter in straw filter and filtrate (duration of operation is 4 d).

allowed direct use of straw with entrapped manure matter for composting (discussed next).

# Composting of Straw with Entrapped Manure Matter (steps C and D) and Compost Quality

The straw with the entrapped manure matter was a subject of extensive composting (6-mo duration). The details are given in refs. 7 and 8. The quality of compost obtained was tested with ryegrass in greenhouses using a podsolic soil. The results showed a good efficiency of the composts applied; the crop was increased by 61-95% concerning control without any fertilizers (8).

# Elimination of COD Using UASB Reactor (step E)

# **Laboratory Experiments**

The data for straw-filtered manure wastewater (SFMW) were extensively published (3,4,6). The optimal results are summarized in Table 3. It can be seen that in spite of a  $10^{\circ}$ C drop in temperature, the performance of submesophilic treatment was comparable with mesophilic treatment regarding total COD (COD<sub>tot</sub>) removal under similar HRTs and organic loading rates (OLRs). However, for both regimes, the ammonia concentrations increased in the effluents owing to hydrolysis of proteinaceous sub-

|                         | Performance of              |                                                                       | nd Pilot UASE                                   | Table 3<br>Reactors Tre     | Table 3 Laboratory and Pilot UASB Reactors Treating Filtered Pig Manure Wastewater $(4,5)^{a}$ | g Manure Wast  | tewater $(4,5)^a$         |                        |
|-------------------------|-----------------------------|-----------------------------------------------------------------------|-------------------------------------------------|-----------------------------|------------------------------------------------------------------------------------------------|----------------|---------------------------|------------------------|
|                         | $\mathop{COD}_{tot}(g/L)$   | $\begin{array}{c} \text{COD}_{\text{SS}} \\ \text{(g/L)} \end{array}$ | $\stackrel{COD_{\mathrm{col}}}{(\mathrm{g/L})}$ | $ m COD_{sol} \ (g/L)$      | VFA<br>(g COD/L)                                                                               | Hd             | $N-NH_3 \pmod{L}$         | $P-PO_{4}^{2-}$ (mg/L) |
|                         |                             | Laboratory e                                                          | xperiments (F                                   | HRT: ~1.1 d; O              | Laboratory experiments (HRT: ~1.1 d; OLR: ~4 g COD/[L·d], 30°C)                                | L·d], 30°C)    |                           |                        |
| Influent                | $7.7 \pm 0.6$               | $1.0 \pm 0.4$                                                         | $1.2 \pm 0.4$                                   | $5.0 \pm 1.7$               | $3.3 \pm 0.1$                                                                                  | $6.7 \pm 0.3$  | $232 \pm 76$              | $157 \pm 2$            |
| Effluent<br>Removal (%) | $1.3 \pm 0.3$<br>$83 \pm 2$ | $0.2 \pm 0.1$<br>$72 \pm 5$                                           | $0.7 \pm 0.1$<br>$70 \pm 10$                    | $0.5 \pm 0.1$<br>$88 \pm 3$ | <0.01<br>~100                                                                                  | 7.8 ± 0.2<br>— | $205 \pm 87$<br>-(33 ± 7) | 52 ± 7<br>67 ± 4       |
|                         |                             | Laboratory exj                                                        | periments (HF                                   | RT: ~1 d; OLR:              | aboratory experiments (HRT: ~1 d; OLR: ~4.6 g COD/[L·d], 17-20°C)                              | d], 17–20°C)   |                           |                        |
| Influent                | $4.7 \pm 1.1$               | $0.7 \pm 0.3$                                                         | $0.8 \pm 0.3$                                   | $3.1 \pm 0.6$               | $1.1 \pm 0.1$                                                                                  | $6.7 \pm 0.3$  | 347 ± 88                  | $113 \pm 35$           |
| Effluent                | $0.8 \pm 0.3$               | 2                                                                     | 2                                               | ON !                        | <0.1                                                                                           | $7.9 \pm 0.3$  | $303 \pm 106$             | 78 ± 27                |
| Removal (%)             | 83 <del>+</del> 6           | ND                                                                    | ND                                              | ND                          | 95 ± 4                                                                                         | 1              | $-(24 \pm 8)$             | 33 ± 4                 |
|                         |                             | Pilot experii                                                         | ments (HRT: ~                                   | -3.5 d; OLR: ~              | Pilot experiments (HRT: ~3.5 d; OLR: ~1.7 g COD/[L·d], 15–20°C)                                | , 15–20°C)     |                           |                        |
| Influent                | $6.9 \pm 3.2$               | $1.1 \pm 0.8$                                                         | $1.3 \pm 1.0$                                   | $3.6 \pm 1.0$               | Z                                                                                              | $7.7 \pm 1.0$  | $910 \pm 540$             | $60 \pm 20$            |
| Effluent                | $3.3 \pm 1.1$               | $0.6 \pm 0.5$                                                         | $0.4 \pm 0.2$                                   | $2.1 \pm 1.0$               | N                                                                                              | $7.5 \pm 0.4$  | $905 \pm 355$             | $50 \pm 20$            |
| Removal (%)             | $45 \pm 11$                 | $69 \pm 13$                                                           | $59 \pm 26$                                     | $38 \pm 18$                 | ND                                                                                             |                | $-(3 \pm 17)$             | $36 \pm 31$            |
|                         |                             | Pilot expe                                                            | riments (HRT:                                   | : ~2 d; OLR: ~              | Pilot experiments (HRT: ~2 d; OLR: ~5 g COD/[L·d], 15–20°C)                                    | [5–20°C)       |                           |                        |
| Influent                | $9.2 \pm 3.2$               | $2.5 \pm 2.4$                                                         | $1.4 \pm 0.9$                                   | $6.5 \pm 3.5$               | ND                                                                                             | $6.0 \pm 0.8$  | $810 \pm 290$             | $100 \pm 40$           |
| Effluent                | $3.5 \pm 2.1$               | $1.2 \pm 1.0$                                                         | $0.4 \pm 0.3$                                   | $2.0 \pm 1.2$               | N                                                                                              | $7.2 \pm 0.5$  | $1005 \pm 445$            | $60 \pm 20$            |
| Removal (%)             | $70 \pm 18$                 | $58 \pm 36$                                                           | $74 \pm 15$                                     | $63 \pm 21$                 | ND                                                                                             |                | $-(20 \pm 12)$            | $46 \pm 24$            |
|                         | ,                           | ,                                                                     |                                                 |                             |                                                                                                |                |                           |                        |

 $^{a}$ Means  $\pm$  SD. ND, not determined.

stances in the SFMW (Table 3). The concentration of phosphate substantially dropped during treatment of SFMW. This was attributed to partial precipitation as whitish deposits (presumably calcite,  $CaCO_3$ ; hydroxyapatite,  $Ca_5[PO_4]_3OH$ ; and struvite,  $MgNH_4PO_4$ ), which were clearly visible on the reactor walls and in the internal gas sludge separation device (4). Note that the COD removal was higher compared to that in the available literature about treatment of pig manure in UASB-like reactors (11). However, such exhaustion of easily degradable COD (e.g., VFA) in the anaerobic effluents might create problems for subsequent biologic nitrogen removal.

#### **Pilot Experiments**

Because the SFMW in St. Petersburg had a higher strength and the seed sludge was poor quality, the pilot trials were started under higher HRT compared to the laboratory experiments (Table 3). When the HRT was on average 3.5 d, resulting in an average OLR of 1.7 g of COD/(L·d), the COD<sub>tot</sub> removal was 45% while removal of suspended solids (SS), and colloidal and soluble COD (COD<sub>sol</sub>) fractions was 69,59, and 38% (on average), respectively (Table 3). In spite of a large fluctuation in influent pH, the effluent pH was rather stable, about 7.5. Specific methane production was also a subject of some variations and accounted (on average) for  $0.23 \,\mathrm{nL/(L \cdot d)}$ . This value is somewhat below the theoretically expected one (0.27 nL/[L·d]) taking into account the observed COD removal (Table 3). The discrepancy can be mainly attributed to entrapment of some part of the undigested SS by the reactor sludge bed. As expected, the ammonia concentrations slightly increased and the concentrations of phosphate substantially dropped during the anaerobic treatment of SFMW (Table 3), for reasons similar to those in laboratory experiments.

After a decrease in HRT to on average 2 d, resulting in an increase in OLR to 5 g of COD/(L·d) (on average; Table 3), the COD to removal stepwise increased to about 70%. This was the result of increased removal of COD and COD fractions (on average 74 and 63%, respectively) compared to the regime with an HRT of 3.5 d (Table 3). By contrast, a slight decrease in SS removal was detected owing to increased washout of sludge and other entrapped particulate matter clearly observed throughout the last period of the pilot trials. In spite of acidic influents fed to the reactor, the effluent pH was stabilized around 7.2 (Table 3) owing to VFA consumption and ammonia production. A phenomenon of substantial total phosphorus and particularly phosphate removals was also observed during this period (Table 3).

The pilot trials in Vologda did not reveal significant differences compared with the trials in St. Petersburg, and all the accumulated data served as a basis for designing a full-scale UASB reactor at pig complex Nadeyevo, Vologda province (discussed later).

Removal of Ammonia from Anaerobic Effluents by Zeolite (step F1)

It was found (4) that 1 vol of Urals laumantite (particle size of 1 to 2 mm) could treat at least 10 vol of anaerobic effluent (HRT of 4 h), reducing

ammonia concentrations from 360 to 1–5 mg of N/L. However, the chemical analysis showed that 1 kg of completely saturated zeolite contained only 3.6 g of ammonia and 5.3 g of total nitrogen. Such a low nitrogen content restricts its application as a fertilizer and this type of zeolite as an economically attractive ammonia adsorbent. One 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 of producing a liquid fertilizer (ammonia nitrate). Another solution could also include a search for ion exchangers with better ammonia adsorption properties than Ural laumantite. Clinoptiolite and wollastonite (if locally available) are among the candidates to be considered (12).

# Removal of Phosphate and Ammonia from Anaerobic Effluents via Precipitation (step F2)

In addition to ammonia and phosphate, the anaerobic effluents contain magnesium and calcium (usually at concentrations  $\geq 2$  mM). Thus, struvite and hydroxyapatite precipitation can be initiated by adjusting the pH to the optimal supersaturating value, which is above 9.0 (13). However, partial precipitation of these minerals likely occurred in the UASB reactor (see step E) that had an effluent pH of about 7.5 (Table 3). Effluent pH can be further increased by natural aging, air stripping of CO<sub>2</sub>, or base dosing (13). Our experiments with the first two methods indeed showed a substantial increase in pH (especially during air stripping) in the anaerobic effluents accompanied by a noticeable decrease in phosphate and ammonia concentrations: 23 and 7% (natural aging) and 66 and 29% (air stripping), respectively (4). Comparable (with air stripping) nutrient removal from the anaerobic effluents was achieved using base dosing accompanied by addition of magnesium (4). However, base/magnesium dosing and batch precipitation are not very convenient from a technological point of view. Thus, we have developed a continuous reagentless process based on air stripping similar to that described by Battistoni et al. (14,15).

The results of continuous, pilot-scale phosphate precipitation promoted by air stripping of  $\mathrm{CO_2}$  to increase pH and crystallization in the FBC are presented in Table 4. The total HRT in the PPB was initially set as ~1 d (~0.6 d in the stripper and ~0.4 d in the FBC). During d 0–32, this block demonstrated a very good efficiency regarding phosphate removal—84% (on average; Table 4)—ensuring effluent phosphate concentration below 10 mg/L. Some drop in ammonia concentrations was also detected. In addition to suspected struvite formation, some losses of ammonia probably occurred owing to its stripping into the gas phase at pH values >8.0, which were usually observed in the precipitation block. Furthermore, biologic nitrification of ammonia was gradually developed in the FBC; the effluents contained 200–300 mg of N-NO $_3$  during d 35–45 (data not shown). Since occurrence of ammonia nitrification, which became almost complete during d 38–45 and led to a drop in pH below 8.0, had a deteriorating impact on the phosphate removal, the total HRT for the precipitation block

Period I (d 0-32) Period II-2 (d 47-75) Parameter HRT (d) 1 0.25  $50 \pm 21$  $57 \pm 11$ Influent P-PO<sub>4</sub> (mg/L) Effluent P-PO<sub>4</sub> (mg/L)  $7 \pm 3$  $15 \pm 4$  $84 \pm 12$ P-PO<sub>4</sub> removal (%)  $73 \pm 10$  $896 \pm 348$  $916 \pm 246$ Influent N-NH<sub>3</sub> (mg/L)  $747 \pm 213$ Effluent N-NH<sub>2</sub> (mg/L)  $560 \pm 217$  $37 \pm 13$ N-NH<sub>3</sub> removal (%)  $32 \pm 9$ 

Table 4 Operational Parameters and Efficiency of PPB Treating Anaerobic Effluents  $(5)^a$ 

was reduced to ~0.25 d at d 47. This resulted in a gradual increase in phosphate removal to the average value of 73%, with the average effluent phosphate concentration of 15 mg/L for period II-2 (Table 4). In addition, ammonia nitrification almost stopped; only negligible concentrations of nitrate and nitrite were observed in the effluent during this period (data not shown). The overall removal of ammonia (presumably owing to struvite precipitation and stripping) was 32% (Table 4).

# Removal of Nutrients from UASB and PPB Effluents Using Aerobic/Anoxic Biofilter (step G)

### **Laboratory Experiments**

Since the PPB effluents were available only during pilot trials, all the laboratory experiments were performed with the anaerobic effluents that were similar to the PPB effluents regarding nitrogen concentrations. Some characteristics of the anaerobic effluents used are listed in Table 3 (under heading "Laboratory experiments") and Table 5. A successful startup of the biofilter in a nitrifying mode was achieved using an HRT of 2 to 3 d and an OLR of 0.4-0.7 g of COD/(L·d). Ammonia and COD removals in the end of startup period were higher than 90 and 65%, respectively (4). Prior to starting an alternating aerobic/anoxic mode of biofilter operation, the actual, basic (endogenous), and nitrifying respiration rates were assessed. They were 49.1  $\pm$  4.7, 13.7  $\pm$  0.2, and 34.3  $\pm$  1.4 mg of  $O_2/(L \cdot h)$ , respectively (4). Thus, the respiration rate for the oxidation of easily biodegradable COD in the anaerobic effluent accounted for  $14.8 \pm 3.1 \text{ mg}$  of  $O_2/(L \cdot h)$  or  $360 \pm 100 \text{ mg}$ 70 mg of COD/(L·d). Taking into account the planned ammonia load on a biofilter (about 300 mg of N-NH,  $^+$ /[L·d]), this quantity of easily biodegradable COD cannot fully fulfill denitrification requirements. In spite of this limitation, the alternating aerobic/anoxic experiment was started in order to assess not only nitrogen but also phosphorous and COD removals in real reactor conditions. Note that the denitrification proceeded almost immediately after switching the biofilter to alternating mode of operation. The typical dynamics of COD, soluble oxygen, nitrate, and ammonia

<sup>&</sup>lt;sup>a</sup>Means ± SD.

| Parameter   | COD                                                                                                   | Ammonia   | Nitrate                           | Phosphate |  |
|-------------|-------------------------------------------------------------------------------------------------------|-----------|-----------------------------------|-----------|--|
|             | (g/L)                                                                                                 | (mg N/L)  | (mg N/L)                          | (mg P/L)  |  |
|             | HRT: $1.0 \pm 0.1$ d; C aerobic phase: 30                                                             |           |                                   |           |  |
| Influent    | $0.869 \pm 0.097$                                                                                     | 336 ± 53  | $0 \\ 175 \pm 29 \\ 25 \pm 3^{b}$ | 70 ± 10   |  |
| Effluent    | $0.353 \pm 0.057$                                                                                     | 77 ± 18   |                                   | 30 ± 9    |  |
| Removal (%) | $66 \pm 7$                                                                                            | 77 ± 5    |                                   | 57 ± 17   |  |
|             | HRT: $1.01 \pm 0.04$ d; OLR: $0.75 \pm 0.04$ g COD/(L·d); aerobic phase: 20 min; anoxic phase: 40 min |           |                                   |           |  |
| Influent    | $0.741 \pm 0.026$                                                                                     | 246 ± 110 | $0$ $128 \pm 6$ $31 \pm 5^{b}$    | 40 ± 1    |  |
| Effluent    | $0.301 \pm 0.021$                                                                                     | 42 ± 1    |                                   | 21 ± 1    |  |
| Removal (%) | $70 \pm 1$                                                                                            | 81 ± 8    |                                   | 48 ± 2    |  |

Table 5
Performance of Laboratory Biofilter Treating UASB Reactor Effluents (6)<sup>a</sup>

<sup>&</sup>lt;sup>b</sup>Total nitrogen removal

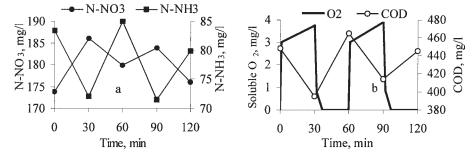


Fig. 4. Dynamics of soluble oxygen, COD, nitrate, and ammonia concentrations during alternating operation of biofilter (influent  $COD_{tot}$ : 790 mg/L; influent ammonia: 344 mg of N/L; HRT: 1.13 d).

concentrations during several aerobic/anoxic phases are shown in Fig. 4. Some results of laboratory biofilter performance are presented in Table 5. Surprisingly, the biofilter showed good removal of phosphate—about 50%. It is likely that some chemical precipitation of phosphate minerals occurred because the sludge had an increased mineral content (data not shown). Nitrification of ammonia was about 80%, while denitrification owing to shortage of easily biodegradable COD was rather poor, resulting in total nitrogen removal of only 25–30% (Table 5). The effluent COD concentrations slightly fluctuated around 0.3 g/L throughout the entire experiment. It is likely that this concentration represents a hardly biodegradable (under neither anaerobic nor aerobic conditions) fraction of COD in the pig manure wastewater.

<sup>&</sup>lt;sup>a</sup>Means ± SD.

Table 6 Operational Parameters and Efficiency of Biofilter Treating Effluents from PPB<sup>a</sup>

| Parameter                                  | Period I<br>(d 0–32) | Period II-1<br>(d 33–46) | Period II-2<br>(d 47–87) |
|--------------------------------------------|----------------------|--------------------------|--------------------------|
| Aerobic phase (min)                        | 30                   | 20                       | 30                       |
| Anoxic phase (min)                         | 30                   | 40                       | 30                       |
| HRT (d)                                    | $3.3 \pm 0.6$        | $3.3 \pm 0.1$            | $2.0 \pm 0.4$            |
| $OLR (g COD/[L \cdot d])$                  | $0.86 \pm 0.48$      | $1.04 \pm 0.16$          | $1.39 \pm 0.22$          |
| ALR (mg N-NH $_3$ /[L·d]) <sup>b</sup>     | $168 \pm 118$        | $28 \pm 22$              | $365 \pm 62$             |
| Influent $COD_{tot} (g/L)$                 | $2.93 \pm 0.7$       | $3.55 \pm 0.29$          | $3.15 \pm 0.55$          |
| Effluent COD <sub>tot</sub> (g/L)          | $0.72 \pm 0.17$      | $0.45 \pm 0.05$          | $0.82 \pm 0.12$          |
| Total COD removal (%)                      | $74 \pm 11$          | $85 \pm 5$               | $71 \pm 7$               |
| Influent $COD_{SS}(g/L)$                   | $0.52 \pm 0.33$      | $1.74 \pm 1.34$          | $0.54 \pm 0.44$          |
| Effluent $COD_{ss}^{(g)}(g/L)$             | $0.05 \pm 0.01$      | $0.02 \pm 0.01$          | $0.12 \pm 0.09$          |
| COD <sub>ss</sub> removal (%)              | $84 \pm 11$          | $99 \pm 1$               | $79 \pm 11$              |
| Influent COD <sub>col</sub> (g/L)          | $0.31 \pm 0.21$      | $0.45 \pm 0.31$          | $0.70 \pm 0.60$          |
| Effluent $COD_{col}(g/L)$                  | $0.23 \pm 0.15$      | $0.04 \pm 0.03$          | $0.15 \pm 0.10$          |
| COD removal (%)                            | $40 \pm 33$          | $86 \pm 11$              | $63 \pm 20$              |
| Influent $COD_{sol}(g/L)$                  | $2.10 \pm 0.96$      | $2.36 \pm 0.22$          | $1.89 \pm 0.96$          |
| Effluent $COD_{sol}(g/L)$                  | $0.43 \pm 0.19$      | $0.39 \pm 0.04$          | $0.56 \pm 0.11$          |
| COD <sub>sol</sub> removal (%)             | $79 \pm 10$          | $83 \pm 2$               | $68 \pm 13$              |
| Influent pH                                | $8.5 \pm 0.5$        | $7.8 \pm 0.6$            | $7.9 \pm 0.2$            |
| Effluent pH                                | $8.2 \pm 0.5$        | $8.2 \pm 0.3$            | $7.9 \pm 0.2$            |
| Influent $N-NH_3$ (mg/L)                   | $560 \pm 217$        | $94 \pm 34$              | $738 \pm 97$             |
| Effluent N-NH <sub>3</sub> (mg/L)          | $134 \pm 79$         | $14 \pm 10$              | $448 \pm 115$            |
| N-NH <sub>3</sub> removal (%)              | $75 \pm 8$           | $84 \pm 10$              | $39 \pm 10$              |
| Effluent N-NO <sub>3</sub> (mg/L)          | $140 \pm 115$        | $195 \pm 130$            | $17 \pm 14$              |
| N-NO <sub>3</sub> removal (%) <sup>c</sup> | $65 \pm 24$          | $45 \pm 31$              | $94 \pm 5$               |
| Total nitrogen removal (%) <sup>d</sup>    | $49 \pm 21$          | $42 \pm 28$              | $37 \pm 12$              |
| Effluent total P (mg/L)                    | $31 \pm 11$          | $31 \pm 11$              | $21 \pm 10$              |
| Effluent P-PO <sub>4</sub> (mg/L)          | $18 \pm 2$           | $20 \pm 2$               | $18 \pm 6$               |

<sup>&</sup>lt;sup>a</sup>Means ± SD.

# Pilot Experiments

The results obtained with the PPB effluents are presented in Table 6. During period I (d 0–32), when duration of anoxic and aerobic phases was 30 min each, the average HRT was 3.3 d while the average OLR was 0.86 g of COD/(L·d) (Table 6). The average COD<sub>tot</sub> removal was 74%, although the removal of individual COD fractions was not uniform—84, 40, and 79% (on average) for SS, colloidal, and soluble matter, respectively. In spite of significant variations in the influent concentrations, the COD to effluent concentrations were fairly stable, slightly oscillating around 0.72 g of COD/L (Table 6). The efficiencies of nitrification and denitrification were 75 and 65% (on average), resulting in average inorganic nitrogen removal

<sup>&</sup>lt;sup>b</sup>ALR, ammonia loading rate.

 $<sup>^{</sup>c} Calculated as follows: \{1 - [N-NO_{_{3}}]_{_{ef}}/([N-NO_{_{3}}]_{_{in}} + [N-NH_{_{3}}]_{_{in}} - [N-NH_{_{3}}]_{_{ef}})\} \times 100.$   $^{d} Calculated as follows: \{1 - ([N-NO_{_{3}}]_{_{ef}} + [N-NH_{_{3}}]_{_{ef}})/([N-NO_{_{3}}]_{_{in}} + [N-NH_{_{3}}]_{_{in}})\} \times 100.$ 

of 49%. A more than double increase in phosphate concentrations in the biofilter effluents compared with those of PPB (see Tables 4 and 6) was likely owing to the dissolution of the small phosphate precipitates entering the biofilter with the influents (these small precipitates were not accounted for during soluble phosphate analysis because the samples were centrifuged before analysis).

Because of the occurrence of ammonia nitrification in the PPB resulting in the low influent ammonia concentrations entering the biofilter, the duration of anoxic phase of biofilter operation was increased to 40 min and that of aerobic phase was decreased to 20 min, keeping the average HRT on the same level of 3.3 d during period II-1 (d 33–46; Table 6). In spite of an increase in the average OLR to 1.04 g of COD/(L·d), the COD tot removal as well as COD removal of individual COD fractions also increased (compared to period I), resulting in average effluent concentrations of total and COD to food 0.45 and 0.39 g/L, respectively, approaching the biodegradability limit of the pig manure wastewater. Although the effluent ammonia concentrations were relatively low, about 14 mg of N/L, the total nitrogen removal was on average 42% (period II-1; Table 6) owing to insufficient development of the denitrification process (lack of biodegradable COD), which resulted in high effluent nitrate concentrations (195 mg of N/L on average).

To improve nitrate removal, the HRT was decreased to about 2 d (period II-2; Table 6) while duration of anoxic and aerobic phases was equalized to 30 min each. As a result, the average OLR increased to 1.39 g of COD/(L·d), but the COD tot removal and COD removal of individual COD fractions decreased with respect to period II-1, being comparable with those for period 1 (Table 6). The better availability of easily biodegradable COD immediately resulted in an almost complete nitrate removal, and the average effluent nitrate concentration accounted for 17 mg of N/L during this period. However, this operation regime had a detrimental effect on nitrification—the average ammonia concentration accounted for 448 mg of N/L. Besides the higher ammonia loading rate applied (less ammonia stripping in the PPB), this was probably owing to a decrease in concentration of the autotrophic nitrifying bacteria in the biofilter, which were outcompeted by heterotrophic microflora under the elevated OLR imposed on the system during period II-2.

#### Conclusion

The application of a straw filter was an effective means of separating the solid and liquid fractions of diluted pig manure wastewater and resulted in the significant removal of  $COD_{tot}$ , nitrogen, and phosphorus (in our experiments 80, 27, and 32%, respectively). The compost obtained from the straw-entrapped DM was an effective fertilizer, increasing the crop of ryegrass in greenhouses by 61–95%.

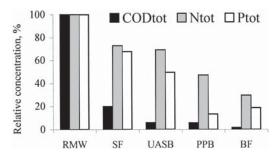


Fig. 5. Relative decrease in  $COD_{tot}$ , nitrogen, and phosphorous concentrations after each treatment step. SF, straw filter; BF, biofilter.

From the filtrate generated, up to 70–80% of the COD could be removed in the UASB reactor operating even under submesophilic conditions (15–20°C). Ammonia was efficiently removed (>99%) from the anaerobic effluents using Ural laumantite as an ion exchanger. However, the nitrogen content of the zeolite was too low to consider this method of ammonia removal economically feasible.

The PPB was able to decrease the concentration of soluble phosphate in the anaerobic effluents up to 7–15 mg of phosphorus/L, but measures should be taken to prevent entrance of small phosphate precipitates into the biofilter, where they can dissolve, increasing soluble phosphate concentrations in the final effluents.

The application of aerobic/anoxic biofilter as a sole polishing step was acceptable from an aesthetic point of view (the effluents were transparent and almost colorless and odorless) and BOD elimination (the resting COD was hardly biodegradable). However, the effluent nutrient concentrations (especially nitrogen) were far from the current standards for direct discharge of treated wastewater. Possible remedies include usage of some part of the nontreated liquid fraction of RMW to fulfill the denitrification requirements in biodegradable COD or application of posttreatment steps such as constructed wetlands.

Figure 5 summarizes the average data showing decreases in COD<sub>tot</sub> nitrogen, and phosphorous concentrations for the RMW after each treatment step in pilot investigations. It is interesting to analyze the possibility of phosphorous recovery in the proposed scheme of RMW. Approximately one third of phosphorus is retained with solid fraction after straw filter filtration and can be reused in the form of compost. An additional 18% is precipitated inside the UASB reactor while 36% can be recovered from anaerobic effluents using the PPB. The phosphate minerals (presumably struvite and hydroxyapatite) formed have a prospective use as fertilizers or as raw material for the phosphate industry (e.g., the price of magnesium-ammonia phosphate in Russia is \$100–150/t). Based on the data of pilot-scale trials presented in this article, the potential of phosphate recovery

from overall flow of manure wastewater from Russian pig complexes can be estimated as 4.3 thousand tons (as phosphorus) per year.

# Outline of Full-Scale Implementation

The developed technology is in the implementation stage now at pig complex Nadeyevo (Vologda province). This complex, fattening 54,000 pigs per year, produces daily 1600–1700 m<sup>3</sup> of RMW. The wastewater treatment plant was constructed 20 yr ago and includes two-step aeration tanks (not designed for nutrient removal). It stopped operation in the mid-1990s because of enormous energy expenses for aeration as well as the amortization of pumping equipment and other infrastructure. Since that time, the RMW after separation of solid fraction on vibro sieves was directly discharged into sewerage of the city of Vologda. However, as the result of overloading of this municipal treatment plant, such a discharge of the FMW without substantial reduction of COD tot, nitrogen, and phosphorous concentrations will be banned at the end of 2002. To solve this problem, the management of complex Nadeyevo together with the governmental authorities of Vologda province have decided to reconstruct the wastewater treatment plant with partial implementation of the scheme depicted in Fig. 1.

According to the reconstruction plan (the overall investments are estimated as \$1,000,000), a full-scale UASB reactor (working volume of 1000 m³) has already been designed and will be commissioned in 2002. This reactor will be inserted after installment of vibro sieves and primary settlers (which will be optimized) and will treat ~70% of settled SFMW. The anaerobic effluents will be then treated in the PPB (this block is scheduled to be built in 2003) in order to reduce the phosphorous content in them and mitigate scaling problems caused by spontaneous precipitation of phosphate minerals in the pipelines (this is a continuing problem for wastewater treatment plants on such complexes). The PPB effluents together with 30% of settled SFMW (source of biodegradable COD to fulfill denitrification requirements) will then be treated in the existing air tanks. The latter, however, will be renovated (new pumping equipment and so on) and tuned for not only BOD but also nitrogen removal.

Some important parameters of old and new technological schemes for treatment of the RMW are shown in Table 7. The new technological scheme undoubtedly has advantages compared with the old one. Namely, it reduces electric energy consumption and sludge production, guarantees a much better quality of treated water (especially regarding nutrient concentrations), and provides the possibility of energy (biogas) and phosphorous recovery.

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Table 7
Basic Parameters of Old and New Technological Schemes for Treatment of RMW at Complex Nadeyevo (Vologda province)

| Parameter                              | Old technology <sup>a</sup>                        | Proposed technology <sup>b</sup>                   |
|----------------------------------------|----------------------------------------------------|----------------------------------------------------|
| Quality of treated water               |                                                    |                                                    |
| COD (mg/L)                             | $500-600^{\circ}$                                  | 100–300                                            |
| SS (mg/L)                              | 25–30                                              | 25–30                                              |
| Total nitrogen (mg/L)                  | 300-350                                            | 35–50                                              |
| Total phosphorus (mg/L)                | 80                                                 | 30–35                                              |
| Energy consumption/recovery (kWh/d)    |                                                    |                                                    |
| Aeration: air flow (m <sup>3</sup> /h) | 17,860                                             | 5920                                               |
| Energy consumption                     | 11,424                                             | $7584^{d}$                                         |
| Sludge recirculation and mixing        | 1390                                               | 1720                                               |
| Energy production (as heat)            | 0                                                  | 27,300                                             |
|                                        |                                                    | $(CH_4: -4750 \text{ m}^3/\text{d})$               |
| Energy balance                         | -12,814                                            | +18,266                                            |
| Sludge production                      |                                                    |                                                    |
| Primary sludge                         | $9.05 \text{ t/d}$ , or $180 \text{ m}^3/\text{d}$ | $10.2 \text{ t/d}$ , or $204 \text{ m}^3/\text{d}$ |
| Aerobic sludge                         | 5.42 t/d, or 542 m <sup>3</sup> /d                 | 2.94 t/d, or 294 m³/d                              |
| Anaerobic sludge                       | 0                                                  | $0.98 \text{ t/d}$ , or $20 \text{ m}^3/\text{d}$  |
| Total                                  | $14.5 \text{ t/d}$ , or $720 \text{ m}^3/\text{d}$ | $14.1 \text{ t/d}$ , or $520 \text{ m}^3/\text{d}$ |
| Phosphate recovery (t/d)               | 0                                                  | 0.5                                                |

<sup>&</sup>lt;sup>a</sup>Not in operation now; calculations are made on the basis of data from the mid-1990s. <sup>b</sup>Designed to fulfill the limits for direct discharge into sewerage of the city of Vologda.

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<sup>&</sup>lt;sup>c</sup>Without excess sludge (ideal case, almost never fulfilled).

<sup>&</sup>lt;sup>d</sup>Together with mechanical mixing.

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