

# TREATMENT OF PIG FARM EFFLUENTS BY AERATION, STRUVITE PRECIPITATION AND FILTRATION

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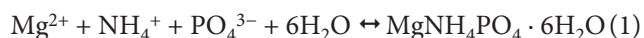
## ABSTRACT

These experiments were performed to verify the potential ways of treating pig farm effluents using aeration, struvite precipitation and filtration. MgCl<sub>2</sub> brine was added as a source of magnesium for struvite precipitation. Following aeration, precipitated struvite was separated from the effluent by filtration through a compressed straw filter. The filter plus struvite can be composted to yield struvite-enriched compost. A series of 5 batch pilot-scale experiments (effluent volumes from 200–400 l) was carried out and laboratory tests on the same effluent were performed to validate the pilot-scale results. Following 24 hours of aeration the pH increased to from 8.5 to 9, providing good conditions for struvite precipitation. Filtration proved to be efficient for separating precipitated struvite and total suspended solids. The efficiency of orthophosphate phosphorus removal in the pilot system varied from 63 to 96%, ammonia nitrogen removal varied from 22 to 79%, but magnesium removal efficiency was low due to the high natural Mg concentration, suggesting that the addition of Mg might not be necessary. Chemical oxidation demand declined significantly as a result of very high bacterial activity and the treated effluent no longer had an unpleasant smell.

**Keywords:** struvite, aeration, piggery effluent, filtration, nutrient recovery

## Introduction

Precipitation of magnesium-ammonium phosphate (MgNH<sub>4</sub>PO<sub>4</sub> · 6H<sub>2</sub>O; MAP; struvite) from wastewater is a recently developed method for sequestering and recycling nutrients (EPA 2013). Struvite is a biogenic mineral that can be directly applied as a slow release fertilizer. Struvite precipitation occurs in water with high concentrations of magnesium (Mg), orthophosphate phosphorus (P<sub>ortho</sub>) and ammonia nitrogen (N<sub>amon</sub>) under alkaline conditions. According to the literature, the apparent pH value of struvite minimum solubility varies from 9 to 11 (Snoeyink and Jenkins 1980; Stumm and Morgan 1996). The basic chemical reaction of struvite precipitation according to Doyle and Parsons (2002) can be described by the following equation (1).



Struvite precipitation for wastewater treatment and phosphorus removal was studied intensively in the past. Information on a wide spectrum of factors influencing the process can be found in the literature e.g. (Snoeyink and Jenkins 1980; Stumm and Morgan 1996; Ohlinger et al. 1998). Munch and Barr (2001) state that the most important factors for struvite precipitation are the Mg:N<sub>amon</sub>:P<sub>ortho</sub> molar ratio and the pH of the solution. A number of pilot-scale wastewater treatment systems utilizing struvite precipitation to remove phos-

phorus were tested recently, e.g. removal from municipal wastewater (Ohlinger et al. 2000), industrial wastewater (Matynia et al. 2013), source-separated urine (Wilsenach et al. 2007), wastewater from agriculture (Liu et al. 2011), etc. Currently, a number of technologies for struvite precipitation from municipal and industrial wastewater are commercially available and several different methods based on struvite precipitation were designed and tested for small wastewater producers in agriculture. However, their use in practice is limited due to low cost effectiveness and lack of relevant legislation. Application to the land is still considered to be the most cost effective and common method for disposing of the majority of agricultural effluents, especially piggery effluents (Münch et al. 2001). But application of piggery effluents to the land results in eutrophication and other environmental problems. Although anaerobic digestion provides an effective solution for the treatment of the majority of agricultural effluents (Holm-Nielsen et al. 2009) it might not be feasible for small producers. A number of studies have recently focused on struvite precipitation from piggery effluents. Utilization of aerated reactors and the addition of a source of magnesium to the effluent proved to be efficient (Suzuki et al. 2005; Shepherd et al. 2009a). However some problems associated with the technology remain unresolved.

Separation of the precipitated struvite from piggery effluents is reported to be a major problem by Shepherd et al. (2009b). The high concentration of total suspended-

ed solids and bacterial biomass in some piggery effluents prevents separation based on a difference in density (e.g. sedimentation or hydrocyclone). The high heterogeneity of the effluent over time causes significant problems for automating treatment systems. For this reason, we performed a series of 5 batch pilot-scale experiments, which were duplicated with the same wastewater in the laboratory. Piggery effluent collected from a concrete storage tank placed under pig stables in central Bohemia was used. The numbers and age of the pigs varied during the study. The pilot-scale reactor used for the experiments was constructed according to the experience gathered during laboratory experiments performed prior to the pilot testing. Aeration of the effluent (CO<sub>2</sub> stripping) was used for effluent alkalization and MgCl<sub>2</sub> brine (used for dust-control on roads) as a source of magnesium. Filtration through compressed straw was used to separate the suspended solids and struvite from the effluent. This material can be composted. The high temperatures reached during the thermophilic phase of composting provide effective sanitation.

## Materials and Methods

### Pilot Scale Treatment System (Layout in Fig. 1)

This system consisted of tank A (1 m<sup>3</sup> plastic IBC container) for fresh effluent, which was pumped into the tank from the underground bunker. Effluent was pumped from tank A into the aerated reactor B (1 m<sup>3</sup> metal IBC container with 3 aeration segments (FORTEX AME-350) connected to aeration pump Secoh EL-S-200) placed on a 2.4 m high frame so that the treated effluent could be drained gravitationally into the filtration vessel C (1 m<sup>3</sup> plastic IBC container filled with compressed straw). The treated effluent was collected in tank D after filtration.

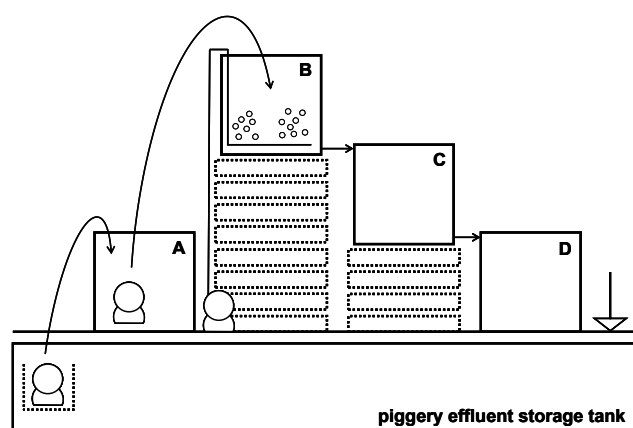


Fig. 1 Pilot system layout.

### Pilot Testing

The tests were performed during the summer of 2013. The effluent was pumped from the concrete storage tank

into tank A by a sludge pump equipped with a protective filter basket wrapped in plastic filter fabric with a mesh size of 1 mm. From tank A, samples of piggery effluent were taken for laboratory tests and for determination of the inlet concentrations of the chemical parameters (*I<sub>n</sub>*). Immediately after filling tank A, test determination of the P<sub>ortho</sub> concentration (hereinafter P<sub>ortho</sub> equals c(H<sub>n</sub>PO<sub>4</sub><sup>n-3</sup>); n = 0; 1; 2; 3) was performed on site using colorimetric kits (Aquaterm, s.r.o.). Dosage of MgCl<sub>2</sub> brine (33% w/w) was calculated according to the test determination of the P<sub>ortho</sub> concentration (see Table 1, the same molar ratio of Mg:N<sub>amon</sub>:P<sub>ortho</sub> was tested in the laboratory the same day). Brine was added to aerated reactor B after filling it with the effluent. The volumes of effluent varied in the tests. Reactor B was aerated (310 l/min.) for 24 hours. Throughout aeration, the effluent physicochemical parameters (pH, oxidation-reduction potential (ORP), electrolytic conductivity and dissolved O<sub>2</sub> concentration) were monitored using a Hanna HI9628 multi-meter. Samples of the treated effluent were taken from reactor B (*R out NF*) after switching off the aeration. The effluent was then drained into filtration vessel C and samples of the output treated effluent (*R out F*) were taken. Identical tests on a small scale were repeated in the laboratory, but the filtration step was excluded.

### Laboratory Tests

Tests were performed on a coagulation bench in 1 l vessels. The vessels filled with 800 ml of the effluent were aerated continuously (2.4 l/min.) for 24 hours. Samples were taken for analysis after switching off the aeration (*L out*). There were three replicates of all the laboratory tests.

### Testing for Microbial Activity during Aeration

This test was performed to determine why there was a decrease in the O<sub>2</sub> concentration during aeration of the effluent and assess microbial activity during aeration. The test was carried out in the laboratory on a coagulation bench using 2.5 l vessels containing 2 l of the effluent in 3 replicates during the winter of 2014. The effluent was aerated continuously (2.4 l/min.) and no Mg source added. 60 ml samples of each effluent replicate were collected during aeration. 10 ml were immediately frozen and analyzed later for chemical oxygen demand (COD) and biochemical oxygen demand after 5 days (BOD<sub>5</sub>). 50 ml were centrifuged and the separated solid was then frozen and analyzed later for phospholipid fatty acids – PLFA. The separated solid samples for PLFA were extracted and analyzed using the method described by Snajdr et al. (2011). Samples were taken after 1, 2, 6, 9, 14, 16, 18, 20 and 24 hours of aeration. Input and output effluent samples were analyzed routinely. The test results are marked as *M* in the figures and tables.

### Effluent Analysis

Before the analysis of the chemical parameters monitored, except for COD, BOD<sub>5</sub> and total suspended sol-

**Table 1** The input information for the pilot tests.

Test No.		1	2	3	4	5
Effluent volume	(l)	200	275	400	400	400
P <sub>ortho</sub> tentative	(mg/l)	500	120	150	300	150
Volume of MgCl <sub>2</sub> brine	(ml/l effluent)	1.0	0.73	0.625	0.625 <sup>b</sup>	x
Calculated ratio Mg:P <sup>a</sup>		1.38 (0.78)	4.41 (2.89)	4.32 (3.08)	1.95 (1.55)	2.38

<sup>a</sup> The ratios were calculated using data obtained from laboratory determinations of the input samples with the source of the Mg being from added MgCl<sub>2</sub> brine. Numbers in brackets are original Mg:P ratios before the addition of the brine.

<sup>b</sup> In case of test 4 in the laboratory two different experiments were performed, one with 0.625 ml of brine added per l of effluent and one without the addition of brine.

x Not analyzed.

ids (TSS), effluent samples were centrifuged to separate the macroscopic TSS and increase the repeatability of the laboratory analysis. *In* and *R out* samples were centrifuged at 4000 rpm at 20 °C for 6 min. *L out* samples were centrifuged at 5000 rpm at 20 °C for 12 min. The *L out* samples were centrifuged to separate all the struvite crystals. Orthophosphates (P<sub>ortho</sub>) were determined using the ammonium molybdate spectrometric method (ISO 2004). The ammonium molybdate solution is characterized by a low pH, which facilitates complete dissolution of residual microscopic struvite crystals. Ammonia nitrogen (N<sub>amon</sub> = c(NH<sub>3+n</sub><sup>+n</sup>); n= 0, 1) was determined using Nessler's reagent spectrophotometry (Greenberg et al. 1992); the concentrations of magnesium (Mg) and calcium (Ca) were determined using emission spectrometry with inductively coupled plasma (ISO 2009). The concentration of chlorides (Cl<sup>-</sup>) and COD values were determined using titration methods (ISO 1989; ISO 2002) and TSS was determined gravimetrically (Kenkel 2013). The ISO method was used to determine BOD<sub>5</sub> (ISO 2003).

### Analysis of Separated Solids

Separated solids obtained by centrifugation (5000 rpm, 20 °C, 12 min) were dried at laboratory temperature. Separated solids of the samples taken directly from the reactor (*R out* NF) and the separated solids obtained from the laboratory tests were analyzed. The qualitative composition of the crystalline phase of the separated solids was assessed using X-ray powder diffraction (XRD). Measurements were made at 25 °C with a Co anode with a step size of 0.02 [°2Theta]. The obtained diffraction patterns were compared with the results in the literature. The same method has been used by a number of authors e.g. (Ohlinger et al. 1998; Le Corre et al. 2005).

The amount of struvite in the separated solids was estimated by dissolution tests. 100 mg of the separated solids were stirred in 250 ml of mixed (900 rpm) HCl solution (pH 4.5) for 2 hours. All the struvite dissolved under these conditions, which was earlier experimentally verified with chemically pure struvite. The ionic composition of the final solution was then determined.

The concentration of struvite components in the test solution was compared to the theoretical concentration assuming all the separated solids were pure struvite and the fraction of struvite in the separated solids estimated.

## Results and Discussion

### Quality of Input Effluent

Information on the tests is summarized in Table 1. The concentrations of the parameters monitored in the input effluent and its pH and electrolytic conductivity determined in the laboratory are listed in Table 2. High heterogeneity of the concentrations of the struvite components in the effluents tested can be clearly seen. The P<sub>ortho</sub> concentration varied from 211 to 723 mg/l. The N<sub>amon</sub> concentration varied from 1,698 to 2,325 mg/l. N<sub>amon</sub> molar concentrations were significantly higher than the concentrations of the other struvite components; therefore, only the Mg:P<sub>ortho</sub> molar ratio is shown in Table 1. Mg concentrations were high and varied from 143 to 262 mg/l, Ca varied from 77 to 178 mg/l and COD from 2,688 to 11,711 mg/l; high COD correlated with high TSS. Shepherd et al. (2009a) report similar P<sub>ortho</sub> concentrations in two piggery effluents. Liu et al. (2011) record the P<sub>ortho</sub> concentrations in the piggery effluent they used in their tests varied from 76 to 1,862 mg/l and N<sub>amon</sub> varied from 1,562 to 5,336 mg/l. Huang et al. (2011) used effluent with average concentrations of P<sub>ortho</sub> of 555 mg/l, N<sub>amon</sub> of 1,266 mg/l, Ca of 135 mg/l and Mg of 6.7 mg/l. The electrolytic conductivity varied from 12,220 to 15,750 mS/m and the pH was between 7.5 and 7.9. A surprisingly a high Cl<sup>-</sup> concentration (709 mg/l) was recorded in the effluent treated in test 1 together with the highest P<sub>ortho</sub> concentration, although the concentrations of the other struvite components and COD and TSS were lower than in the other tests. We assume that the effluent was somehow altered compared to the other samples. This may be due to the heavy rain in the region before the tests, which might have washed out some fertilizers and other chemicals stored close the effluent storage tank.

**Table 2** Determination of the input parameters of the effluent – *In samples*.

	$P_{ortho}$	$N_{amon}$	Mg	$Cl^-$	COD	Ca	TSS	Elec. Conduct.	pH
test No.	(mg/l)							(mS/m)	-
1	723	1698	143	709	2688	124	1524	12220	7.46
2	211	2204	154	x	6481	151	3125	15140	7.71
3	221	2325	172	92	6196	178	x	15520	7.87
4	670	2298	262	43	10304	77	4420	13500	7.66
5	367	2193	221	x	11711	80	4983	15 750	7.78
<b>M</b>	21	2201	183	x	4160	94	1200	x	8.02

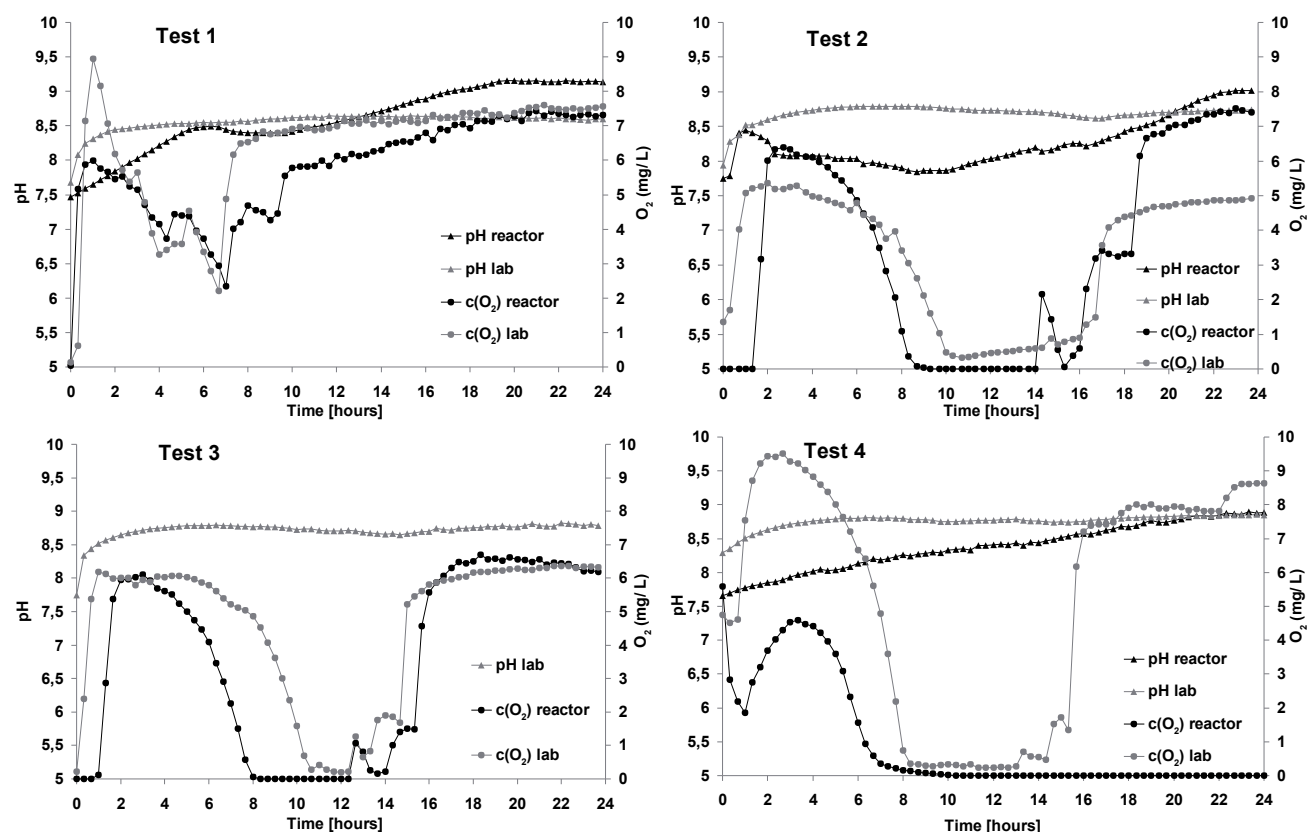
Tentative  $P_{ortho}$  determination enabled relatively accurate, although in all cases underestimated, values of the  $P_{ortho}$  concentration. The heterogeneity of the Mg concentrations leads to difficulties in estimating the ideal amounts of  $MgCl_2$  brine.

### Physicochemical Parameters

The dissolved oxygen concentration and pH measured throughout the tests (in the laboratory and pilot reactor) are shown in Fig. 2. The data were not recorded in test 5 due to failure of the multi-meter. In the pilot reactor, the pH increased gradually throughout the test, reaching values higher than 8.5. In the laboratory, the pH increased rapidly after the start of aeration

and then remained more or less constant, probably due to the higher aeration rates. The pH value of approximately 8.5 is similar to the results published by Korchev et al. (2011) and are high enough for effective struvite precipitation.

The  $O_2$  concentration shows similar trends in the reactor and laboratory; it gradually increased in the first hours of aeration and usually reached full saturation at the prevailing temperatures after a few hours. However, subsequently the  $O_2$  concentration decreased sharply and oxygen was often completely depleted. After about 14 hours of aeration, the  $O_2$  concentration began to increase again and usually reached full saturation at the end of the tests. This phenomenon can be explained



**Fig. 2** Dissolved oxygen concentration and pH measured throughout the test in the laboratory (average values shown) and reactor (in case of test 3 pH data in the reactor were not recorded due to failure of the multi-meter).

by the activity of the microorganisms and is discussed below.

Further data (temperature, electrolytic conductivity and ORP) measured throughout the tests in the pilot reactor are shown in Fig. 3.

The temperature varied throughout the tests as the reactor was placed outdoors and the aeration provides efficient heat exchange. Maximum temperature reached about 30 °C and the minimum temperature was approximately 15 °C.

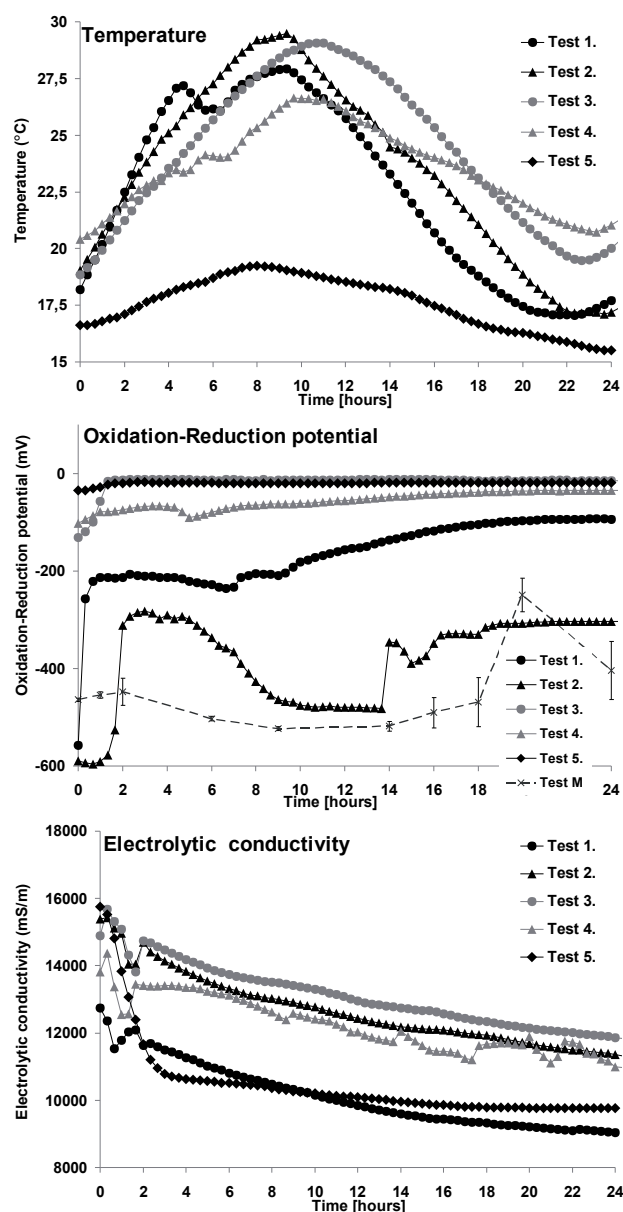
The electrolytic conductivity increased after addition of the  $MgCl_2$  brine at the beginning of the tests. It dropped significantly after approximately one hour of aeration, then increased slightly and then gradually and continually decreased. The differences in the input and output effluent electrolytic conductivities varied from

2,500 to 4,000 mS/m. The decrease in the conductivity is caused mainly by the precipitation of various minerals including struvite.

ORP increased swiftly after the beginning of aeration. In tests 3 and 5, ORP reached values of approx. -15 mV and remained constant for the rest of the test. In tests 1 and 4, it continued to gradually increase throughout aeration and reached values of approx. -34 mV (test 4) or -100 mV (test 1). A decrease in ORP was recorded in test 2 following a rapid increase. Later ORP increased again, but the values at the end of test 2 were still approx. -300 mV.

### Chemical Parameters

The chemical parameters of the output effluents from the different tests and the calculated decrease in the parameters compared to the input effluent are summarized in Table 3. The efficiencies of removal of the struvite components in the tests are shown in Fig. 4. Higher rates of aeration in the laboratory compared to the pilot reactor, together with more effective TSS (and struvite) separation via intensive centrifugation, could be one of the reasons for slightly better removal efficiencies recorded in the laboratory. The compressed straw filter was efficient in capturing the TSS including struvite, which is clearly confirmed by the TSS concentrations before and after filtration, as well as the differences in the  $P_{ortho}$  removal efficiencies. This efficiency for the reactor-treated effluent after filtration varied from 63% (test 2) to 96% (test 1) and surprisingly was higher when the Mg:P ratio was lower. The  $N_{amon}$  removal efficiency varied from 22% (test 5) to 79% (test 4). It seems that stripping of  $NH_3$  by aeration and possibly also the nitrification processes played a substantial role in  $N_{amon}$  sequestering. The concentrations of  $N_{amon}$  dropped significantly more than would occur if  $N_{amon}$  was only precipitated in the form of struvite.  $NH_3$  is in equilibrium with the air according to Henry's Law and facilitates air stripping of  $N_{amon}$ .  $NH_3$  is the predominant  $N_{amon}$  form in aqueous solution with a high pH and temperature (Negulescu 1985). The output Mg concentrations were higher than the input ones in tests 2 and 3. Even in test 5 without the addition of a source of Mg, the removal efficiency did not exceed 27%, which indicates that part of the  $P_{ortho}$  was sequestered in a different way than by struvite precipitation. It can be assumed that part of the  $P_{ortho}$  was sequestered through precipitation of other minerals and part through incorporation into the biomass. The Ca concentrations of the output filtered effluents are summarized in Table 4. The removal efficiencies of Ca varied from 25% (test 5) to 79% (test 3). Part of the Ca was precipitated in the form of magnesium calcium carbonate (CCM; (6% Mg, 94%  $CaCO_3$ )) or hydrated calcium carbonate ( $CaCO_3 \cdot nH_2O$ ). It can be assumed that one of the forms in which Ca and  $P_{ortho}$  precipitate was hydroxylapatite ( $Ca_{10}(PO_4)_6(OH)_2$ ) as  $Ca^{2+}$  ions interact effectively with  $P_{ortho}$  to form calcium phosphates in wastewater systems, commonly as poorly crystallized hydroxylapatite



**Fig. 3** Temperature, electrolytic conductivity and oxidation-reduction potential measured throughout the test in the pilot reactor and oxidation-reduction potential of the samples measured during test M.



**Table 3** Chemical parameters monitored in the output effluents from the different tests and calculated removal (or increase marked by minus) of the chemicals compared to those in the input effluent.

Test No.		Portho	Namon	Mg	Cl <sup>-</sup>	COD	TSS
		(mg/l)					
1	<i>R out NF</i>	252	631	163	1250	1870	1172
	Removal	471	1067	-20	-541	818	352
	<i>R out F</i>	32	931	114	1280	1720	779
	Removal	691	767	29	-571	968	745
	<i>L out<sup>a</sup></i>	4.7 ± 0.2	887 ± 69	103 ± 4	x	1458 ± 5	x
	Removal	719	861	40	x	1230	x
2	<i>R out NF</i>	154	1170	284	981	x	2540
	Removal	57	1034	-130	x	x	585
	<i>R out F</i>	78	1160	216	1070	3260	1150
	Removal	133	1044	-62	x	3221	1975
	<i>L out<sup>a</sup></i>	6.5 ± 0.5	1009 ± 64	210 ± 2.6	x	2551 ± 19	x
	Removal	205	1241	-56	x	3930	x
3	<i>R out NF</i>	98	1120	295	1160	4324	x
	Removal	123	1205	-123	-1068	1872	x
	<i>R out F</i>	79	1120	222	1110	3876	x
	Removal	142	1205	-50	-1018	2320	x
	<i>L out<sup>a</sup></i>	6 ± 0.2	869 ± 85	212 ± 5.7	x	2402 ± 63	x
	Removal	214	1414	-40	x	3794	x
4	<i>R out NF</i>	173	359	225	445	4967	4 210
	Removal	497	1939	37	-402	5337	210
	<i>R out F</i>	106	479	192	454	3654	3020
	Removal	564	1819	70	-411	6650	1400
	<i>L out<sup>a</sup></i>	9 ± 1.1	1115 ± 155	193 ± 11	x	3013 ± 246	x
	Removal	660	1185	69	x	7292	x
	<i>L out no Mg<sup>a</sup></i>	10 ± 0	941 ± 125	149 ± 11.5	x	2762 ± 65	x
	Removal	660	1359	113	x	7542	x
5	<i>R out NF</i>	286	1980	164	x	9598	4 231
	Removal	81	214	12	x	2113	752
	<i>R out F</i>	64	1721	161	x	4921	2345
	Removal	303	472	12	x	6790	2638
	<i>L out<sup>a</sup></i>	7.1 ± 0.1	1342 ± 125	156 ± 6	x	3656 ± 469	x
	Removal	360	854	20	x	8055	x
M	<i>M out<sup>a</sup></i>	1.2 ± 1.6	1080 ± 159	197 ± 11	x	3103 ± 138	x
	Removal	19.8	1121	-14	x	1057	x

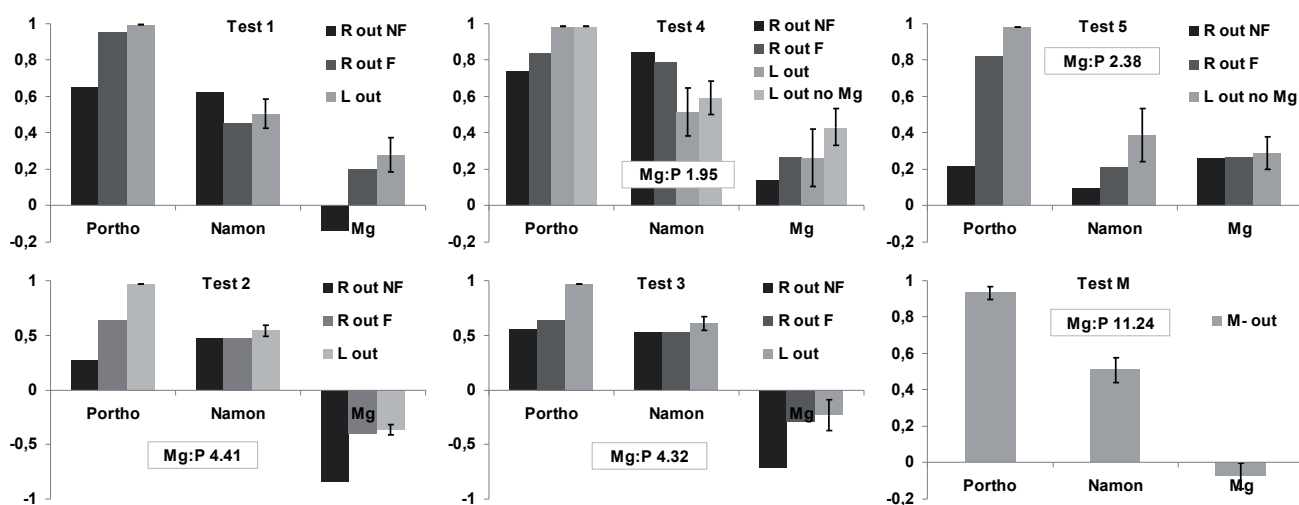
<sup>a</sup> In the laboratory experiments standard deviations of the three parallel tests performed are shown after a ± sign.

**Table 4** Ca concentration in the output effluent from the filtered pilot reactor (R out F) recorded in the different tests and the amount removed compared to that in the input effluent.

Test No.:		1	2	3	4	5
Ca concentration	(mg/l)	52	43	38	38	60
Ca removal	(mg/l)	72	108	140	39	20

**Table 5** Calculated COD and TSS removal (reactor output compared to input).

Test No.:		1	2	3	4	5
COD removal	(%)	36	50	37	65	58
TSS removal	(%)	49	63	x	32	53



**Fig. 4** Removal efficiency of the struvite components in the tests (when negative, an increase in the parameter was recorded) in the pilot reactor before and after filtration and in the laboratory (in the case of test 4 in the laboratory an additional test (*L out no Mg*) without brine was performed; Mg:P ratio in this case was 1.53).

(Le Corre et al. 2005). The removal efficiencies of COD and TSS varied from about 30 to 65% for both parameters (see Table 5). The average removal efficiencies throughout the 8 months operation of the demonstration reactor reported by Suzuki et al. (2005) are 50% for  $P_{ortho}$ , 37.5% or Mg, 20% for Ca and 77% for TSS.

#### Analysis of the Separated Solids

The results of XRD and estimation of the amount of struvite in the separated solids are summarized in Table 6. It is obvious that struvite was present in all the separated solids obtained in the tests, although its concentration varied substantially. In pilot test 1, the input effluent had a high  $P_{ortho}$  concentration and low concentrations of

COD and TSS. In this test, struvite forms about 95% of the crystalline phase and its content in the separated solids was estimated at 68%. In the other pilot tests, struvite forms from 65% (test 5) to 45% (test 3) of the crystalline phase of the separated solids. Magnesium calcium carbonate was the second most abundant mineral in the crystalline phase and it forms from 35 to 45% of the crystalline phase in tests 2 to 4. In test 1, it forms only 5% of the crystals and it was not detected at all in test 5. Hydrated calcium carbonate was present in crystalline form, although it is probable that part of it also precipitated in an amorphous form. Graphite was present in quite a high concentration in test 5. Quartz crystals were also detected, probably due to their flushing into the effluent in the

**Table 6** XRD results – identified minerals and semi-quantitative estimates of their share of the crystalline phase and estimates of the percentage of the struvite in the precipitate based on the dissolution tests.

Mineral	Struvite	CCMa	Hydrated calcium carbonate <sup>b</sup>	Quartz	Graphite	Calculated average percentage weight of struvite in the precipitate
<b>Test No.</b>	<b>(w % of crystalline phase)</b>					<b>(w % of precipitate ± standard deviation) ± standard deviation)</b>
<b>1</b>	<i>R out NF</i>	95	5	–	–	68 ± 15
	<i>L out</i> <sup>d</sup>	94	6	–	–	–
<b>2</b>	<i>R out NF</i>	60	35	4	1	19 ± 20
	<i>L out</i> <sup>d</sup>	44	49	6	1	–
<b>3</b>	<i>R out NF</i> <sup>d</sup>	45	45	7	–	22 ± 4
<b>4</b>	<i>R out NF</i>	56	38	5	–	24 ± 6
	<i>L out</i>	59	36	4	–	–
	<i>L out no Mg</i>	58	37	4	1	–
<b>5</b>	<i>R out NF</i>	65	–	8	5	19 ± 3
	<i>L out</i>	67	–	9	6	–

<sup>a</sup> CCM – magnesium calcium carbonate – (6% Mg, 94% Ca)(CO<sub>3</sub>)

<sup>b</sup> Hydrated calcium carbonate – CaCO<sub>3</sub> · nH<sub>2</sub>O

<sup>c</sup> Three different estimates were obtained using dissolution tests based on three different chemical parameters ( $P_{ortho}$ ,  $N_{amon}$ , Mg), standard deviations of the results are shown after ± sign

<sup>d</sup> Samples containing this phase, which was not identified.

form of small sand particles. The estimated fraction of struvite in the total separated solids was approximately the same for tests 2 to 5 and varied around 20%.

### Microbial Activity during Aeration

The test was performed with effluent collected during the winter of 2014. The effluent quality was significantly different from that collected during the summer of 2013, as there were fewer pigs stabled and the effluent was not as frequently spread on the fields. The main difference was in the concentration of  $P_{ortho}$ , which was significantly lower than in the effluents collected during summer. The concentrations of the parameters monitored in the input effluent are listed in Table 2 (marked as M).

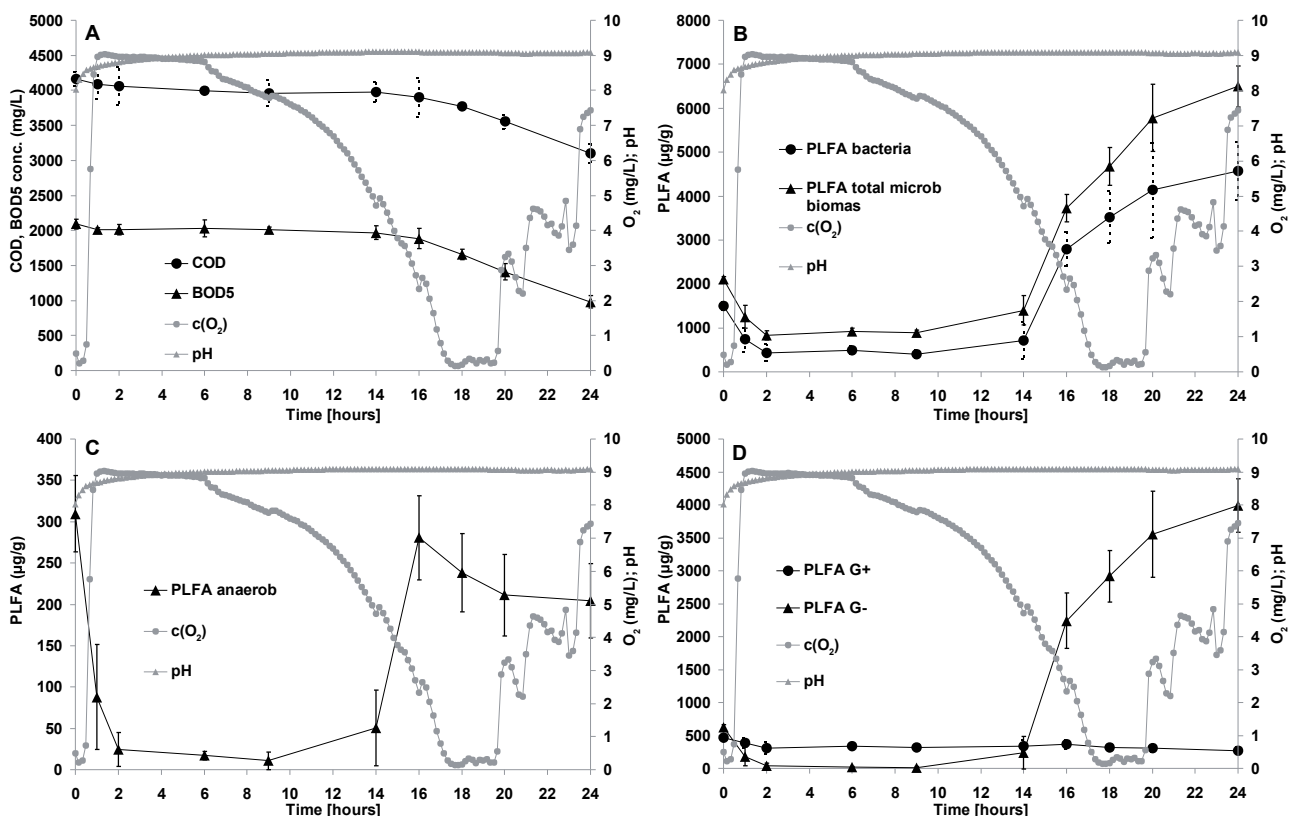
The pH and the  $O_2$  concentration is shown together with the COD,  $BOD_5$  and PLFA results in Fig. 5. The pH gradually increased during aeration from 8.02 at the beginning to 9.10 at the end. The  $O_2$  concentration followed a similar dependence as in the tests performed earlier, both in the laboratory and the pilot reactor, although  $O_2$  depletion occurred somewhat later, around the 18th hour. The ORP values of the samples taken throughout the tests are shown in Fig. 3. It was highly negative around  $-450$  mV at the beginning and increased only to approx.  $-400$  mV at the end of the test.

The COD and  $BOD_5$  curves are similar. There was a slight decrease in both curves after one hour of aeration. Later both parameters decreased very slowly. Af-

ter the 14th to 16th hour of aeration, the slopes of the curves changed and both parameters decreased more rapidly.

The PLFA results clearly show that the input effluent is rich in total microbial biomass, consisting mainly of bacteria. After the beginning of aeration, the concentration of specific PLFA representing total microbial biomass and bacterial biomass decreased and remained low until the 14th hour of aeration. From that moment on, the concentration of total microbial biomass and bacteria began to increase and continued to increase until the end of the test, although the slope of the curve was not as sharp after the 20th hour of aeration. A very similar curve was recorded for G- bacteria, although in this case the concentrations after the 2nd hour of aeration were very low. The concentration increased after the 9th hour, but a sharp break in the curve appeared after the 14th hour. It is interesting that the concentrations of G+ bacteria remained more or less stagnant throughout whole test. Anaerobic bacteria were present in the input effluent but the aeration caused a decrease in their concentration. After the 14th hour of aeration and a decrease in the  $O_2$  concentration of the effluent, anaerobic bacteria started to grow once again, reaching a maximum after the 16th hour of aeration. The concentration of anaerobic bacteria decreased from that moment on.

It can be concluded that the increase in  $O_2$  concentration at the beginning of aeration negatively affected



**Fig. 5** Graphs of COD and  $BOD_5$  concentration in aerated effluent (A) and concentration of PLFA specific for bacteria and total microbial biomass (B); anaerobic bacteria (C); G+ and G- bacteria (D) in the solids separated by centrifugation, compared to the  $O_2$  concentration and pH of the effluent.



the microbial biomass adapted to low  $O_2$  concentrations, causing a lag phase after the 2nd hour of aeration. After adaptation of the microbial community to higher oxygen concentrations, the microbial biomass began to grow exponentially. After a certain time microorganisms began to use greater quantities of  $O_2$  than was dissolved in the effluent due to aeration. From that moment on, the  $O_2$  concentration in the effluent decreased, reaching complete oxygen depletion after about 18 hours. All the dissolved  $O_2$  was immediately used by the aerobic microorganisms, giving the anaerobic bacteria an opportunity to grow in the effluent. It seems that after several hours the microbes decomposed the majority of the readily degradable organic compounds and started to utilize more complex compounds in the effluent, resulting in a lower  $O_2$  consumption. Then the  $O_2$  concentration once again increased gradually and the growth in the microbial biomass slowed down slightly. This theory is supported by the significant decrease in COD and  $BOD_5$  values during the low  $O_2$  concentration phase. We think that an analogous phenomenon was responsible for the decrease in the  $O_2$  concentration during tests 1 to 5.

A similar phenomenon is typical for thermophilic aerobic biological wastewater treatment (Lapara and Al-leman 1999). Gehm (1956) report that these processes are characterized by high biodegradation rates, low dissolved oxygen concentrations in the aeration basin resulting from these high biodegradation rates and potential complications associated with poor bacterial settling. Beaudet et al. (1990) studied liquid pig manure treatment at 55 °C and report a COD reduction of approx. 80% after 70 hours of aeration and total elimination of  $N_{ammon}$  by stripping. They report that thermophilic treatment facilitates the rapid stabilization of the effluent and elimination of the unpleasant smell. Although the temperatures reached in our tests did not exceed 30 °C, we assume that the processes in the effluent were similar. Abeynayaka and Visvanathan (2011) report that the half-velocity constant ( $K_s$ ; substrate concentration (COD) at one-half of the maximum growth rate [mass/unit volume]) in aerated wastewater increases with temperature but the  $K_s$  value recorded in their experiments at 30 °C was 30 times higher than the value recorded for domestic wastewater by Metcalf and Eddy (2003). Nevertheless, there were substantial changes in the output effluent as it did not have an unpleasant smell and its colour had changed from black/dark brown to light brown.

## Conclusions

The experiments demonstrated that struvite can be precipitated from piggery effluent by aeration and  $MgCl_2$  brine does not need to be added in the majority of cases. The precipitated struvite and other suspended solids were effectively separated from the treated effluent by filtration through compressed straw. The efficiency of

orthophosphate removal in the pilot system varied from 63 to 96%. Ammonia nitrogen removal was surprisingly high and varied from 22 to 79%, mainly due to ammonia stripping into the air facilitated by the high temperature and the increased pH of the effluent. The original input effluent Mg:P molar ratio varied from 1.55 to 3.08 (except for the effluent in test 1). Surprisingly, a higher molar ratio corresponded to a lower efficiency of the orthophosphate removal. The COD concentration declined significantly (40–65%), probably due to a high biodegradation rate, as did the TSS concentration (32–63%), the colour of the treated effluent changed from black/dark brown to light brown and no longer had an unpleasant smell. Long residence times in the pilot reactor (24 hours) led to a significant increase in the pH and sufficient supply of oxygen for degradation of organic compounds by aerobic bacteria.

Additional testing demonstrated that several hours of aeration caused a significant increase in G- bacteria and total microbial biomass, although the  $O_2$  concentration decreased and the concentration of G+ bacteria remained constant.

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