Final Report 2005

Preliminary investigations
for the Margaretenhöhe MBR demonstration plant

A study subcontracted by the Berlin Centre of Competence for Water for the EU-Life demonstration project ENREM "Enhanced Nutrients Removal in Membrane Bioreactor"

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Abstract

As part of the EU-Life ENREM demonstration project the Department of Chemical Engineering, TU Berlin, was appointed to conduct the preliminary pilot trials in a representative site for verification of basic process design and operation criteria of the full-scale MBR demonstration plant. In addition to conception and construction of the pilot plant, this investigation consisted of two successive trial phases with distinct operation conditions. The first one was dedicated to the assessment of the "irregular sludge removal strategy" (the biomass is accumulating in the reactor, which is partly emptied when the sludge concentration reaches a given value). In the second trials phase normal operation conditions with daily sludge wastage were implemented with 28,5d SRT.

The major outcome of the trials was that COD removal, enhanced biological phosphorus removal and the post-denitrification performed a similar way under both operational conditions. The denitrification rate was approximately 1 mgN/(h goTS). An influence of the anaerobic sludge loading on the post-denitrification rate was observed with higher rates (up to 4 mgN/(h goTS)) corresponding to higher organic loading. An influence of storage compounds built up in the anaerobic phase is assumed.

Nitrification was better in the second phase when 4 mgN/(h goTS) were constantly reached while nitrification was unstable with an average of 2 mgN/(h goTS) in the phase of irregular sludge removal.

The aerobic and anoxic reactors were enlarged during the regular sludge withdrawal phase by 23% resulting in 35d SRT. This led to a better COD removal and slightly better nitrogen removal. The enhanced SRT produced possibly a deterioration of biological P removal due to overloaded poly-P storage. A second possible reason is the massive reproduction of sludge worm *Tubifex tubifex,* which was observed after the plant enlargement. Different strategies to reduce the worm population were attempted. Ammonium dosing had no success. Copper dosing reduced the number of worms significantly but the population grew back after the dosing was stopped.

The prolongation of SRT reduced the sludge yield from 0.23 gTS/gCOD at 28.5d to 0.18 gTS/gCOD at 35d.

Content

Nomenclature

DNR	specific denitrification rate, $\frac{\Delta\ NO_3 - N}{\Delta t \cdot VSS}$ ($mgNO_3$-N/gVS h)
DO	dissolved oxygen (mgO_2/L)
EPS	extracelluar polymeric substances
HCT	hydraulic contact time (h)
HRT	Hydraulic retention time (h)
NR	specific nitrification rate ($mgNH_4$-N/gVS h)
PS	Polysaccharides
SRT	solids retention time
TS	total solids (g/L) = MLSS+ 0.9 g/L salts
VSS	volatile suspended solids (g/L)

1 Introduction

Aiming at the development of a high performance membrane activated sludge system for municipal waste water treatment in decentralized areas, the Berliner Wasserbetriebe (BWB), Veolia Water (VeW) and TU Berlin conducted the three year IMF project in the frame of the Kompetenzzentrum Wasser Berlin (KWB). Results of the IMF project suggest a system which combines enhanced biological phosphorus removal (EBPR) with post-denitrification without additional carbon dosing (Adam (2004), Lesjean et al. (2002), Gnirss et al. (2003)). In October 2003 a proposal was submitted to the EU-Life program named "Enhanced Nutrients Removal in Membrane Bioreactor" (ENREM) in order to construct and operate a demonstration plant with this innovative process. The proposal was accepted by the European Commission in September 2004 with official start in January 2004.

This study is part of the ENREM project. Major goals were the verification of basic process design and operational parameters with a pilot plant erected on a representative site.

In a first trials phase from June 2004 until January 2005 a discontinuous excess sludge withdrawal strategy was tested. These results were discussed in the Progress report (Vocks and Kraume (2004)). Major outcome of the study was, that the discontinuous excess sludge wastage did not impact the specific elimination rates except for the nitrification. Nitrification rates were unsteady and in average at 2 mgN/(h goTS). However, in the studied case the discontinuous sludge management turned out not to be favourable, due to unexpectedly high influent concentrations for COD, nitrogen and phosphate. To have sufficient elimination, a certain amount of biomass concentration was needed, which was only reached at the end of each sludge removal cycle. Especially nitrogen elimination was not satisfying while COD- and P effluent concentration were mostly in the targeted range.

In the second trials phase, described in this report, excess sludge was withdrawn on a daily basis and the plant was operated with a fixed sludge age. Since nitrogen elimination was still not satisfying, the volumes of aerobic and anoxic reactors of the plant were extended. This study led to better appreciation of the process design and plant start up.

2 Material and Methods

2.1 Pilot plant

The used pilot plant was the same as described in the progress report (Vocks and Kraume (2004)) with slight modifications. The ENREM process, combining enhanced biological phosphorus removal with post-denitrification without additional carbon dosing was implemented throughout this study.

Online data of NO_x and phosphate in the effluent were not available anymore since both apparatuses failed. In June 2005 the two aerobic and the two anoxic reactors were enlarged by app. 23 % each (see Table 2-1) resulting in a total pilot plant volume of 167 L. To flatten hydraulic and concentration peaks a storage tank was installed in front of the plant. The volume of the storage tank was 156L. The hydraulic influent profile to the storage tank was simulating typical decentralized inflow characteristics. The throughput of the plant stayed at 13 L/h.

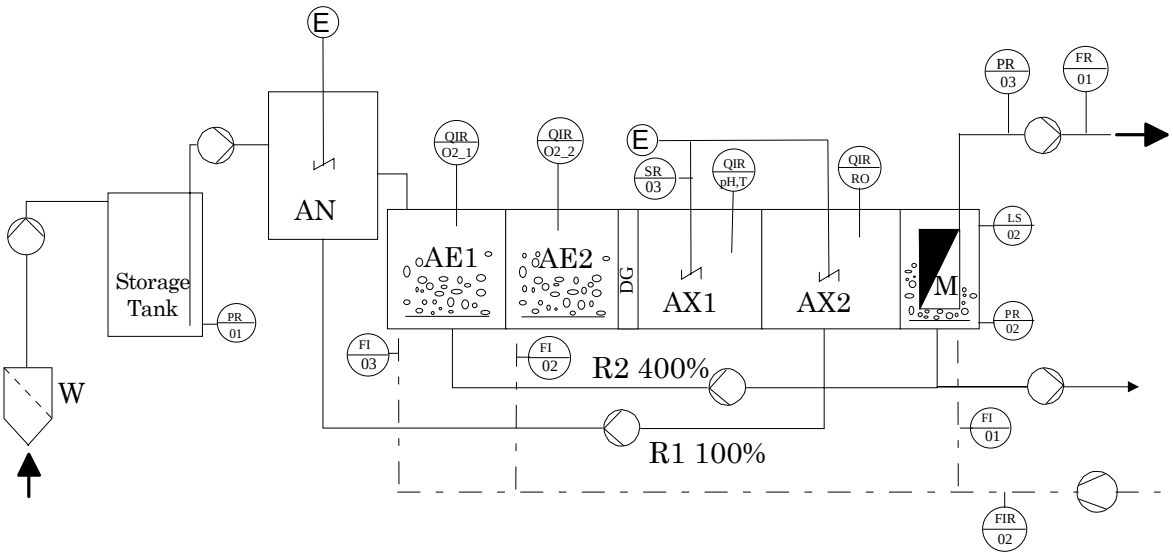

Figure 2-1: Flow sheet of the pilot plant. All pumps are peristaltic pumps. W=wastewater, AN=anaerobic, AE=aerobic, DG=degassing, AX= anoxic, M=membrane

Table 2-1 Volume, hydraulic contact time (HCT) and hydraulic resistance time (HRT) of the pilot plant before and after the extension

	V (L)		HCT (h)		HR T(h)	
	before ext.	after ext.	before ext.	after ext.	before ext.	after ext.
AN	26,3	26,3	1,0	1,0	2,0	2,0
AE1	18,1	23,5	0,2	0,3	1,4	1,8
AE2	17,8	23,1	0,2	0,3	1,4	1,8
DG	5,0	5,0	0,1	0,1	0,4	0,4
AX1	26,7	34,7	0,3	0,4	2,1	2,7
AX2	26,7	34,7	0,3	0,4	2,1	2,7
M	19,5	19,5	0,3	0,3	1,5	1,5
Total	140,0	166,8	2,5	2,9	10,8	12,9

Contrary to the previous period the excess sludge was withdrawn continuously. An additional peristaltic pump was installed which draw with a flow rate of 1L/h, extracting four times a day one litre of sludge from the membrane reactor. This results in a sludge age of 28,5d before and 35d after the plant enlargement.

2.2 Sampling

For the determination of plant performance, space profiles were measured at least once a week. Therefore, microfiltrated grab samples from each compartment of the plant were taken, respecting the contact time of each chamber between sampling. For the influent concentration an unfiltered sample from the storage tank was taken. Hence, this was a 6h to 12h mixed sample, depending on the present level in the tank.

2.3 Batch tests

Several kinds of batch tests were conducted to monitor biological kinetics and to study the influence of different parameters on the kinetics.

Standard Batch Test

Three different environmental conditions were implemented in an 1L batch reactor tempered to 20°C: anaerobic conditions (1h), aerobic conditions (2h), anoxic conditions (1h). During anaerobic and anoxic conditions, the batch reactor was flushed with nitrogen gas. During aerobic conditions the batch reactor was aerated with pressurized air to a minimum concentration of 5mg O_2/L. At the beginning of the anaerobic phase, sodium acetate was dosed to a concentration of 100 mg acetate/L in to the reactor. Ammonium chloride was dosed after starting the aerobic phase to a concentration of 30 mgNH_4-N/L. To avoid nitrate limitations in the anoxic zone a sodium nitrate solution was used to implement at least 50 mg NO_3-N/L.

The evolutions of PO_4-P, NO_2-N, NO_3-N and NH_4-N were measured. With the gained data phosphate uptake rates (PUR), nitrification rates (NR) and denitrification rates (DNR) were computed.

Parallel Batch Test

In order to investigate the influence of special parameters on the biological performance of the sludge, two batch reactors were operated in parallel: one with the standard procedure and one with changed conditions. Studied was the influence of temperature by implementing 15°C and 10°C in the parallel reactor; sludge concentration, by diluting the sludge with permeate; sludge

loading by varying the anaerobic acetate dosage and the kind of carbon source by replacing the acetate with glucose and lactate.

Glycogen and PHB Investigation

Standard batch test and batch test with an extended anoxic period were conducted. Additionally to the anions and cations the course of polyhydroxybutyrate (PHB) and glycogen were measured in order to gain more information about the used C-source for the post-denitrification.

2.4 Chemical analysis

Total nitrogen, total phosphate, total fatty acids and COD were measured with Dr. Lange test kits. Anions (PO_4-P, NO_3-N, NO_2-N) and cations (NH_4-N, C, Ka, Mg) were measured on Dionex DX 100 ion chromatograph.

For the determination of the in-cell stored glycogen the cells were digested with HCl (1ml HCl on 9ml sludge, cooked for 1h at 100°C). Afterwards the pH was adjusted to app. 7. Then the glycogen could be determined enzymatically as glucose with the Humana Liquicolor test kit.

PHB was also measured enzymatically after a digestion with sulphuric acid with a test kit provided by R-Biopharm. Detailed descriptions for the glycogen and PHB measurements can be found in the diploma thesis of Nicke (2005).

Extracellular polymeric substances (EPS) analyses:

Sludge samples were taken in the membrane chamber twice a week. In order to minimize the influence of daily and weekly fluctuations, samples were always taken periodically on the same days and hours. Sludge was separated from the liquid phase containing soluble and colloidal substances by paper filtration (black ribbon, Schleicher & Schuell). Polysaccharide (PS) concentration in the filtrate and in plant permeate was measured according to the photometric method proposed by Dubois et al. (1956) which yields results in glucose equivalents.

Proteins were determined with the method of Lowry et al. (1951) modified according to Frolund et al. (1995).

3 Operation of the pilot plant

Principal Events

In the middle of January 2005 the trials period with continuous excess sludge removal should have started. Unfortunately, operational problems caused a huge sludge loss on January 17th resulting in a TS concentration of 3.2 g/L. Hence, to build up some biomass, the excess sludge withdrawal was started one week later.

From the middle of march a lot more sludge foam was formed than before. This led to sludge losses since the foam swelled sometimes through holes and gaps in the plant cover.

From 1.5.05 until 4.5.05 a serious fire in the neighboured tire storage produced a dramatic change of influent. During these days the influent consisted mainly of the fire fighting water containing fire fighting foam and the burned tire leftovers. The fire department could not provide an accurate composition of the water.

On the 15th of June the aerobic and anoxic reactors were enlarged by 23% each. A few days later a massive reproduction of the sludge worm *Tubifex tubifex* was observed. On the 21.7. and the 28.7. additional ammonium was dosed (30 mg NH_4-N/L in the effluent) to reduce the worm population to a normal amount (Rensink and Rulkens (1997)) without success.

On the 4th of October all worms from the cover and the aerators were removed manually and copper sulphate was dosed for 4 days. The minimum copper concentration was 0.3 mg/L in the plant which should kill all worms according to Rathore and Khangarot (2002). During and right after the copper dosing only pale, dead worms were observed in the sludge. However, within two weeks after the copper dosing the worm population grew back to the starting quantity.

The important events during this trial period are summarized in

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Table 3-1 major events

Date	Event
17.1.05	Serious sludge loss, TS of 2,3 g/L in the pilot plant
from 24.1.05	Start of continuous excess sludge withdrawl (4L/d)
7.2.05	Major break down of several components resulting in a plant operation stop and a temperature decrease down to 4°C in the MBR
from 17.3.05	Begin of massive foam formation

24.3.05	Non-fixable failure of the online P-anlayser
1.5. - 4.5.05	Massive influent of fire water to the plant
15.6.05	Extension of the plant, SRT raise from 28.5d to 35d
27.6.05	First sight of heavy growth of Tubifex worm
21.7. and 28.7.05	Ammonium dosing in order to control Tubifex presence
4.10.05	Copper dosing in order to control Tubifex presence

3.1 Evolution of biomass concentration, loading rates and sludge yield

Biomass evolution (summarised in Figure 3-1). On the 17th of January a huge amount of sludge was lost due to operational problems, therefore this trials period started with a TS concentration of 3.2 g/L. Since part of the lost sludge was collected and reintroduced into the plant, the TS value increased sharply the next day. Afterwards it grew naturally. Even if the sludge age was fixed at 28.5d the TS concentration did not stabilise. It ranged between 10 and 14 g/L due to changing sludge load and sludge reductions caused by operational problems and foaming. From middle of March 2005 heavy foaming was observed which often caused sludge losses due to sludge foam swelling through gaps and holes in the cover of the plant. The fire water entering the plant from 1.5.05 until 4.5.05 contained a lot of fire fighting foam which caused an even heavier foaming.

After the plant enlargement, the TS concentration was stable for the first days but decreased sharply at the 5th of July. This was caused by a massive growth of sludge worm *Tubifex tubifex*. In this phase, sludge flocs were a lot smaller than before and a lot of free swimming bacteria were observed under the microscope. From August onwards the TS concentration raised. Less worms were spotted in the sludge but they were still found attached to probes, walls and the cover and also in the newly developing foam on the anoxic reactors. Microscopic investigations revealed large flocs with filaments and less free bacteria. The decline on the 10.8.05 was due to operational problems and a leaking membrane reactor.

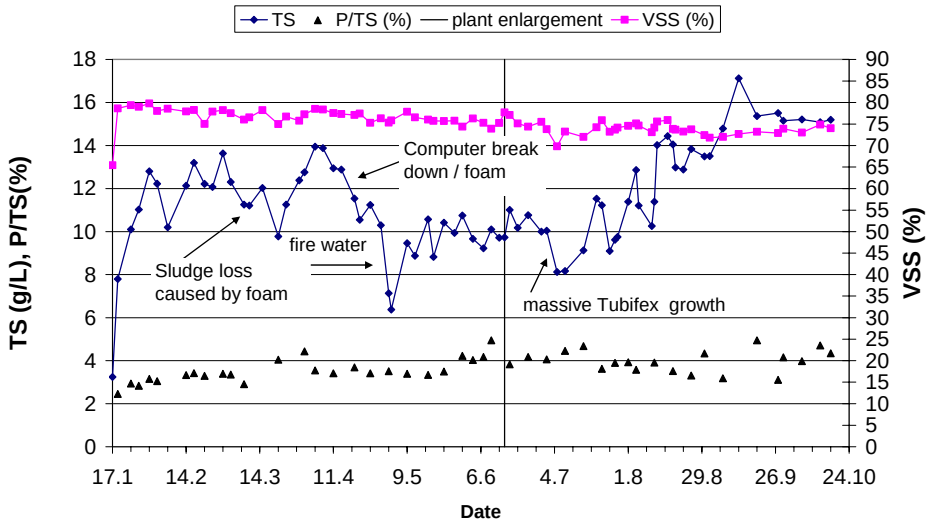

Figure 3-1 Course of biomass concentration, P content in then sludge and sludge loading

VSS was always around 75% of TS, with slightly higher values after the start of this trial phase and slightly lower values in the section with heavy *Tubifex* growth. This might be due to sludge mineralization by the worms and due to higher temperatures in summer.

The P/TS value increased from 2.4% after the sludge loss to about 3.5% in the months January to May. In June the value raised to 4% to 5%. In this phase P-uptake was very effective with PUR of 15 mgP/h gVSS and effluent values below 0.1 mgP/L (see chapter 3.3). This was not the case anymore after the plant extension but the P/TS concentration stayed around 4%. Again an impact of the massive *Tubifex* growth can be assumed.

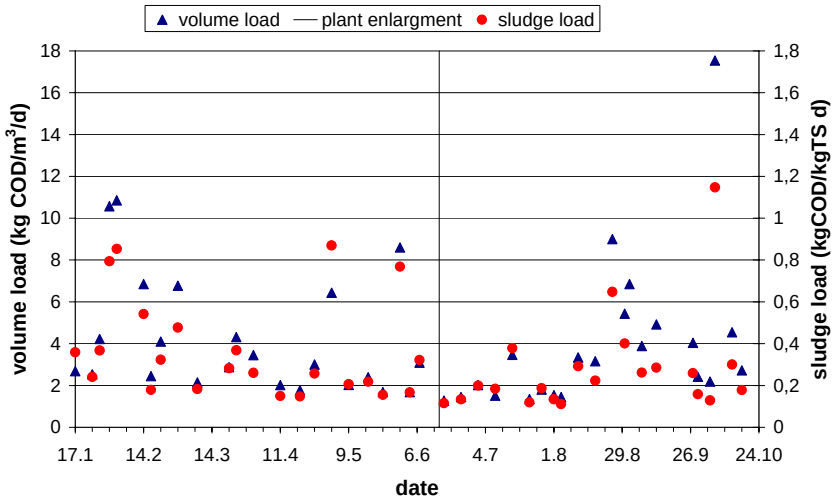

Figure 3-2 Volume and sludge loading from January to October

Loading rates

Due to changing COD influent concentrations and changing TS concentrations, sludge loading was varying between 0.15 and 0.85 kgCOD/kgTS d (mean value 0.369 kg COD/kg TS d) before and between 0.11 and 0.65 (mean value 0.278 kg COD/kg TS d) after the plant enlargement

(Figure 3-2). The volume loading varied between 2 and 18 kg COD/m³/d. A tendency of higher loading rates in winter than in summer can be observed. This effect was even clearer for the phosphate influent concentration and is discussed in chapter 3.3. These lower loading rates in summer also caused lower TS concentration together with the effects discussed above (temperature and worms).

Sludge yield

Before the enlargement the sludge yield was 0.23 gTS/gCOD in average which fits well with the 0.21 gTS/gCOD observed in the previous period (Progress Report, 2004) and the ATV values for a sludge age of 25d to 30d.

After the enlargement, the sludge yield was changeful. Taking out the negative values caused by worm growth, an average yield of 0.28 gTS/gCOD occurred. Since the sludge age increased from 28.5 to 35 days due to the plant enlargement, a lower or steady yield was expected but not a higher. However, one has to consider the unstable conditions caused by the worms after the enlargement. Taking into account only the data from 18th of August onwards when the TS concentration was more stable, a yield of 0.18 gTS/gCOD can be computed.

3.2 COD elimination

Figure 3-3 shows the evolution of COD elimination from middle of January. During the whole period the COD elimination was between 90% and 99%. The influent concentration varied in a big range between 500 and 4000 mg/L. In samples with more than 1000mgCOD/L a bigger fraction of suspended solids was observed causing these very high values. This is also demonstrated by the dissolved COD influent concentration measured from the 24.6.05 onwards. The dissolved COD was constantly between 300 and 400 mg/L while the total COD varied between 500 and 1600 mg/L in the same section.

The effluent concentration ranged between 35 and 70 mg/L under stable operational conditions. In the period of the fire water inflow the effluent concentration raised to 166 mgCOD /L. This shows, that the influent was completely modified by the fire water and a significant fraction of hardly degradable COD reached the plant.

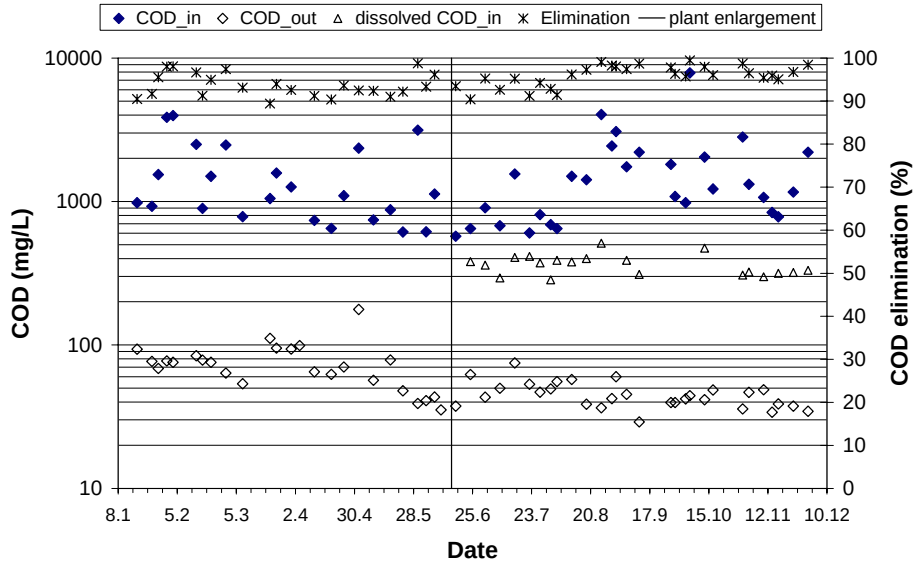

Figure 3-3 evolution of COD elimination and influent and effluent concentration

From the 10.6.05 to the 13.6.05 (Friday to Monday) a time profile of influent and effluent were measured taking samples every four hours. The effluent samples were drawn 2.5h after the influent sample respecting the contact time of the plant. Figure 3-4 shows the course of the COD influent and the corresponding effluent concentration. The influent concentration varied between 1540 mg/L and 671 mg/L while the effluent concentration was independent from the influent and stable between 50 and 70 mg/L. This shows that the hardly degradable COD fraction was relatively constant. So was the dissolved COD concentration which ranged between 300 mg/L and 400 mg/L. The results from the time profile confirms the results obtained from the weekly measurements shown in Figure 3-3.

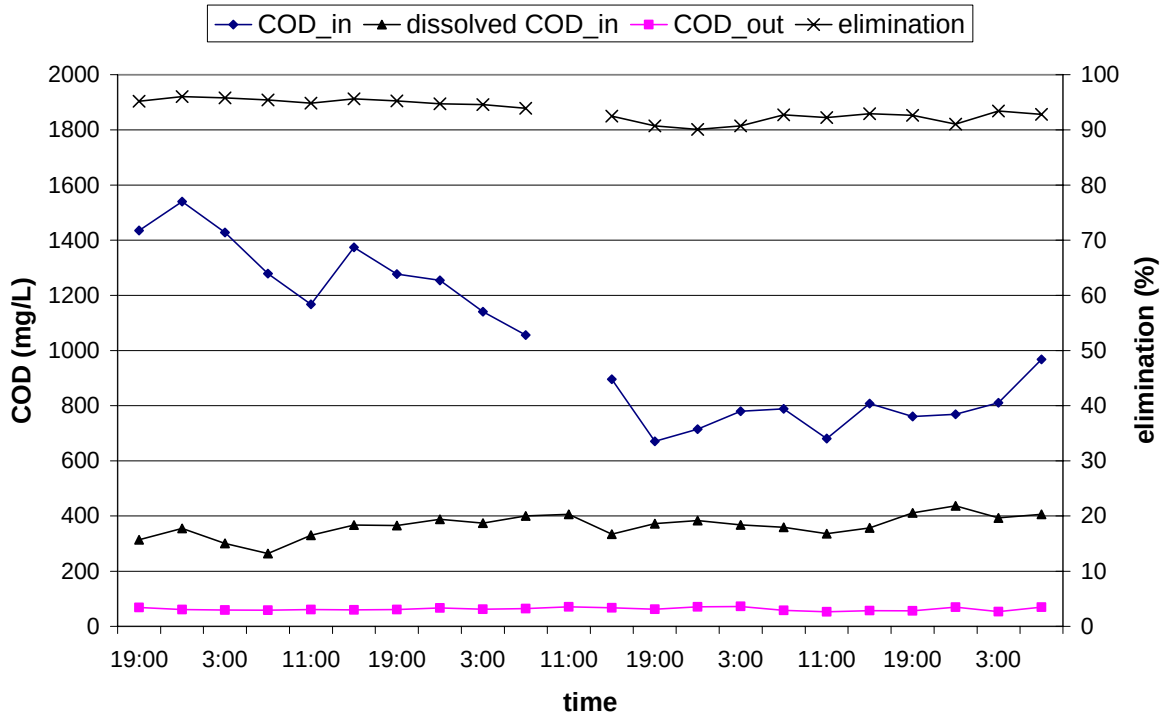

Figure 3-4 Time profile of COD influent and effluent concentration from 10.6.05 until 13.6.05.

Compared to the previous operational period with discontinuous excess sludge wastage, the COD elimination and effluent concentration did not change. Hence, it can be concluded, that the excess sludge management had no impact on the COD degradation.

After the plant enlargement, the COD concentration in the effluent decreased. Regarding the more stable period, starting middle of August, when the TS concentration stabilized in the plant, the effluent COD concentration was between 29 mg/L and 45 mg/L. This shows, that with the longer aerobic contact time, more hardly degradable COD was eliminated. From Figure 3-3 it is apparent that the COD elimination was stable between 95% and 99% during that period.

3.3 Phosphorus elimination

Figure 3-5 shows phosphorus influent and effluent concentration. The TP influent concentration shows a clear season dependency with higher values in winter (up to 45 mg/L) and autumn and declining concentration in summer (down to 12 mg/L). Ortho-P followed slightly that tendency but did not exceed 20 mg/L. High TP influent concentration came together with more solids in the influent. A reason for this behaviour could not be found. One possible explanation is the presents of boat houses in the catchment area. They are mainly used in summer. This might increase the fraction of shower water in the waste water, diluting it. On the other hand this would mean that the "normal" TP concentration in the waste water of this area is around 35 mg/L, which seems to be unrealistic.

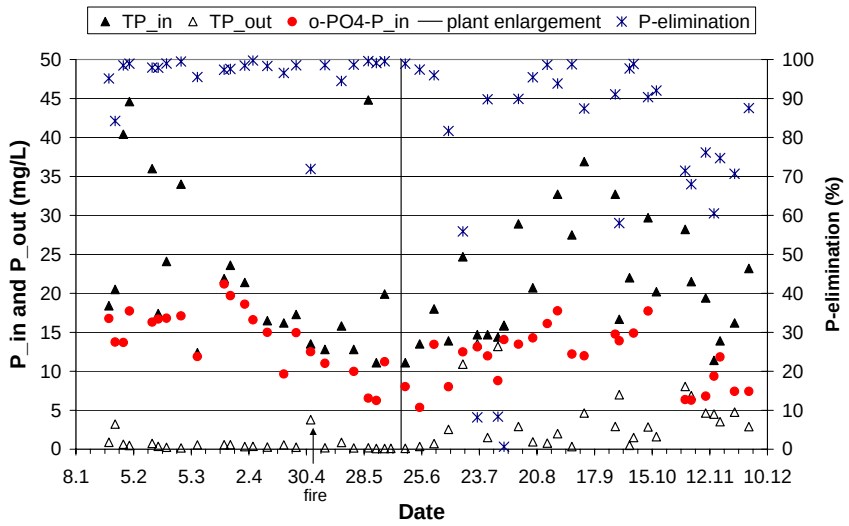

Figure 3-5 Course of Phosphate influent and effluent concentration and P-elimination

Excluding data points under unstable/untypical operational conditions, the TP effluents concentration was always between 0.1 and 0.5 mg/L before the plant enlargement. Higher influent concentration did not lead to higher effluent concentration. P-elimination was above 95% for that period. Figure 3-6 shows phosphate uptake rates (PUR) measured in standard batch tests. It can be seen that the PUR was very constant between 12 and 16 mgP/h/gVSS excluding the period of the fire water inflow.

After the plant enlargement on the 15th of June, P-elimination began to decrease and TP effluent concentration raised. Also the PUR began to decrease. On the 5th of July a PUR of only 4 mgP/h/gVSS was measured. That day also a clear decrease of the TS concentration was observed. Hence, an influence of the *Tubifex* worms is assumed. It seems that the worms reduced the PAO population. Concerning the 12 to 16 mgP/h/gVSS under normal conditions, this would mean a decrease of 75% of the PAOs. This also results in an raise of P-load on PAOs by 400%. When the TS concentration began to stabilize in middle of August, also the PUR increased and the TP effluent concentration declined. However, in September the P elimination started to be unstable again. In the months September and October the TP influent concentration was constantly very high. This could be a reason for unsatisfying TP effluent concentration between 1 and 7 mg/L which came along with still good TP-elimination above 90%. Comparable high influent concentration were measured also in January and February but in these months the P/TS content was always clearly below 4 % while it was always above 4 % in September and October (Figure 3-1). Maybe the maximal P-uptake capacity of the sludge was reached with the higher SRT. Therefore an SRT below 30d is recommended for the demonstration plant in order to remove always enough phosphate from the system. On the other hand *Tubifex* could not be reduced to a low amount and an influence of the worm activity could be possible (Rensink and Rulkens (1997)).

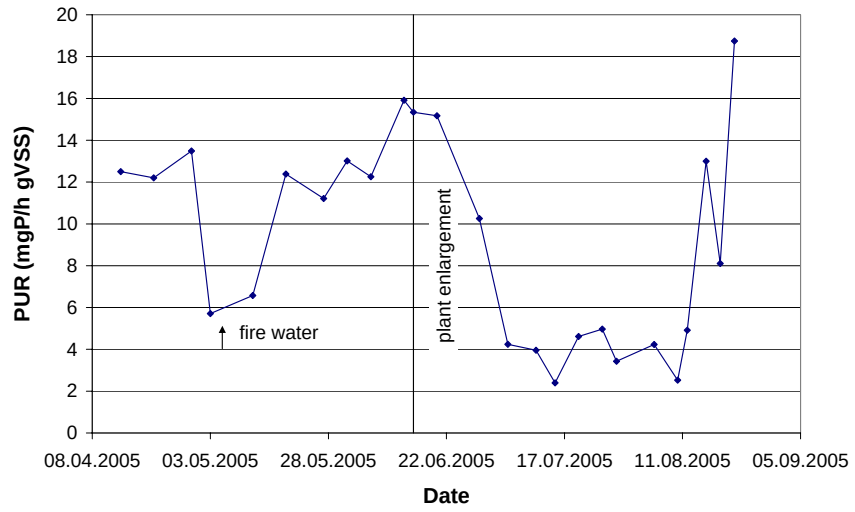

Figure 3-6 Phosphate uptake rates measured in standard batch tests

3.3.1 P-mass balance and P/TS measurement difficulty

A P-mass balance was conducted based on influent and effluent concentrations measured in profile measurements as follows:

$$\frac{dm_{P,TS}}{dt} = \dot{m}_{P,in} - (\dot{m}_{P,Permeate} + \dot{m}_{P,Excess\ sludge})$$

Setting the accumulation term to zero and with $\dot{V}_{in} = \dot{V}_{permeate}$ the phosphorus concentration in the excess sludge, which equals the concentration in the membrane chamber and hence, appr. the whole plant (based on P/TS), can be expressed by

$$c_{P,excess\ sludge} = \frac{\dot{V}_{in}(c_{P,in} - c_{P,permeate})}{\dot{V}_{excess\ sludge}}.$$

As can be seen in Figure 3-7 the calculated P/TS concentration is higher in most cases than the measured. In average, it is two times higher, at 8%, than the measured average. Really high values, above 10%, and really low values, below 2 %, are unrealistic and result from the use of point data and the discarding of the accumulation term. 6% to 10% P/TS are quite often observed with Bio-P sludge (e.g. Barak and van Rijn (2000), , Okunuki et al. (2004)). Regarding the high P-loading during these trials, a P/TS content around 8% seems more realistic than 4%. A failure of the P in sludge determination method is assumed. In fact, digesting the sludge with hypochloric acid or sluforic acid before measuring with the Dr. Lange test kit delivered up to 100% higher values, than measuring only with Dr. Lange (Figure 3-8). A determination after German standard methods (DIN 38405/11) did not lead to higher values than with HCL digestion. Hence, the following method is recommended: 1ml 6M HCL or 1 ml concentrated H_2SO_4 is dosed to 9 ml sludge and then cooked at 100°C for 1h. After adjusting the pH above 2 the Dr. Lange test kit for TP determination is used.

From Figure 3-8 it can be seen that in the 46th week of the year the measured P/TS concentration was close to 5%. This matches well with the average mass balance value of 5.5% during that period.

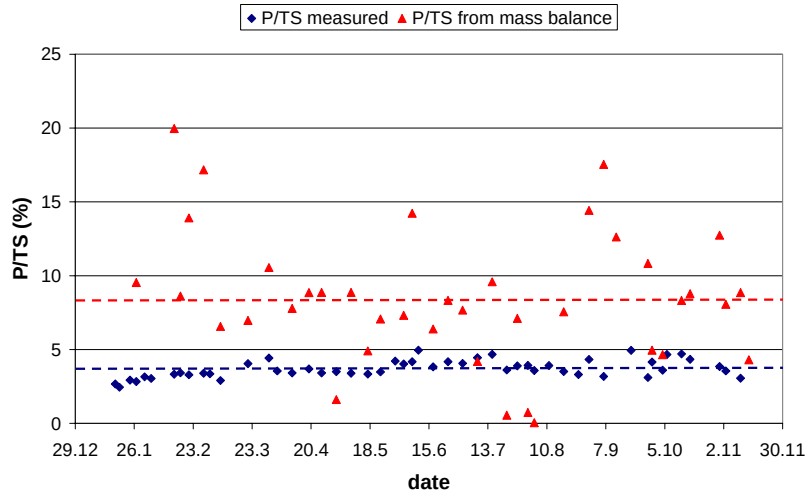

Figure 3-7 Measured P/TS concentration and calculated P/TS concentration from mass balance

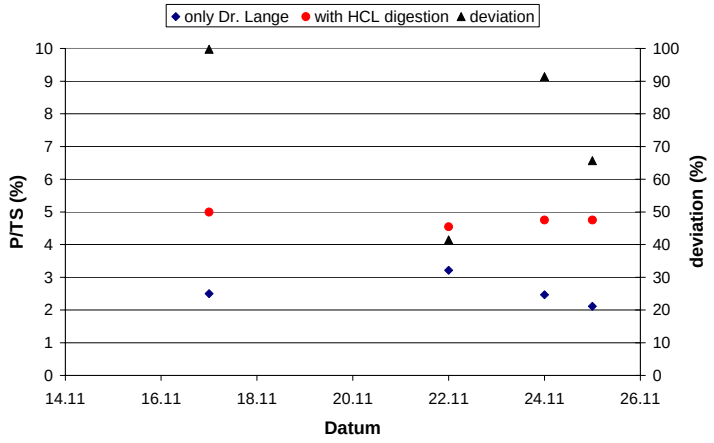

Figure 3-8 The deviation of the two different measurement methods for the P/TS content

3.4 Nitrogen elimination

3.4.1 Standard investigations

Figure 3-9 shows influent and effluent concentration for total nitrogen (TN) and ammonium. The TN influent concentration shows a comparable but not as dramatic evolution as TP with higher values in winter and a decline in summer. Ammonium influent concentration were on a high level in the range of 70mg NH_4-N/L to 113 mg NH_4-N/L.

After the accident in January, where a lot of sludge was lost, nitrification did not perform well and 67 mg NH_4-N/L were measured in the permeate. Nitrification became better in the

following days but stayed on a low level. Nitrification was never complete until May besides two days where the plant throughput was below 13L/h. Nitrification rates measured in standard batch test were between 0.5 and 1.5 mg NO_3-N/h/gVSS. In the batch tests and in the plant a nitrite build up during nitrification could be observed. Nitritation was around two times faster than nitratation. The bad nitrification in the months January to May can be explained by a combination of three effects: nitrifier wash out, low temperatures and high inhibitory concentrations of ammonia. After the sludge loss, most nitrifiers were washed out. The temperature in the plant in this period was low, between 10°C and 15°C during the day and often below 10°C during the night. The optimum temperature for growth of nitrifying bacteria is according to Halling-Sørensen and Jørgensen (1993) between 28°C and 36°C. They state that below 15°C nitrification drops sharply. Hence, the build up of nitrifying bacteria after the sludge loss was inhibited due to the cold climate. End of April the temperature in the plant was constantly above 15°C and full nitrification recovered. The inflow of the fire water together with temperatures around 12°C deteriorated again the nitrifying activity. In June always complete nitrification was reached, but it has to be mentioned that always 1 to 3 mgNH_4-N/L reached the membrane reactor and were degraded there.

The occurrence of nitrite can additionally be explained with high ammonium, and hence, high ammonia concentration. Anthonisen et al. (1976) found nitratation inhibition for ammonia concentration above 0.3 mgNH_3-N/L. This value was exceeded often in the aerobic zones in the plant. Therefore, the growth of nitrite oxidizing bacteria was hindered.

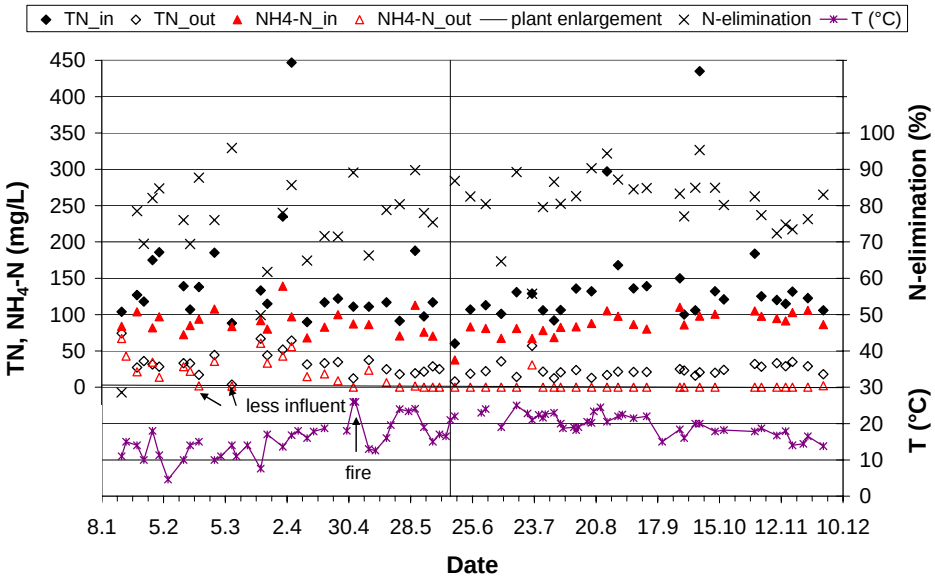

Figure 3-9 Course of influent and effluent concentration of total nitrogen and ammonium, nitrogen elimination rate and the temperature in the plant

TN elimination varied between 50% and 90% in the period before plant enlargement. In May and June, when complete nitrification was achieved, TN elimination was more stable between

75% and 80%. TN effluent concentration was in a range of 20 mg/L to 30 mg/L these days. This was above the targeted 10 mgN/L. Therefore the aerobic and anoxic zones were enlarged by 23% each.

After the plant enlargement nitrification was always complete in the aerobic reactors, with exclusion of one day, were additional ammonium was dosed. The TN elimination slightly increased and was under proper operational conditions above 80%. The limit of 10mg/L was reached at some days but could not be reliably achieved. The potential of the process is apparent in Figure 3-10. Influent and effluent concentration for total nitrogen, ammonium and nitrate taken every 4 hours from 30.8.05 to 1.9.05 are shown. The effluent samples were taken 2.5h after the influent samples, which represents the contact time in the plant. Visible is an enhancement of the process during the sampling period. On 1.9.05 TN-elimination was always above 90% and TN effluent concentrations down to 6 mg/L were reached. The minimum nitrate concentration was 3 mgNO_3-N/L in the permeate. However, it also demonstrates that the process was not stable. Again, an influence of the *Tubifex* worms is assumed. Rensink and Rulkens (1997) also found reduced N-elimination due to sludge mineralization of *Tubifex* worms.

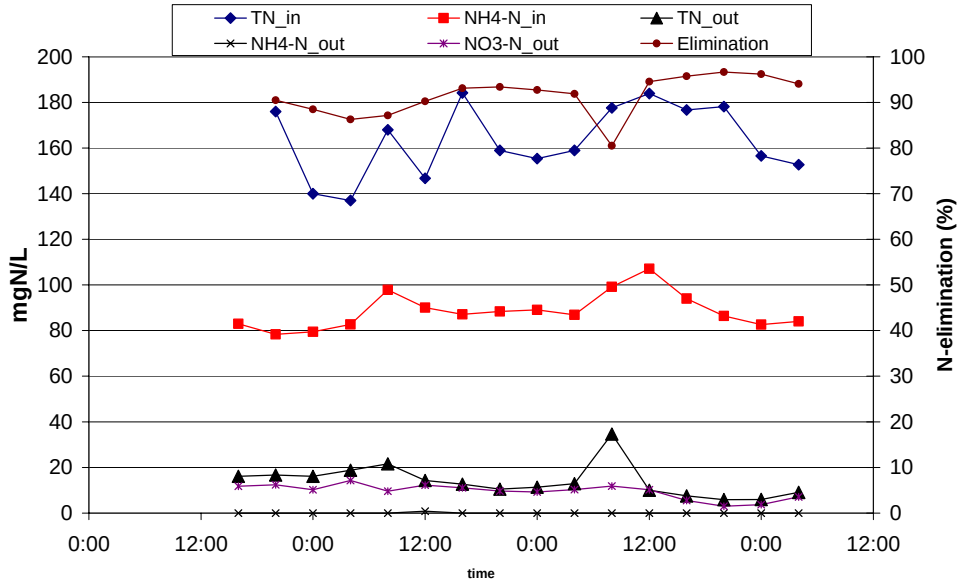

Figure 3-10 Influent and effluent concentrations of different nitrogen compounds taken every 4 h from 30.8.2005 until 1.9.2005. Effluent samples were taken respecting the plant's contact time of 2.5h.

Nitrification and denitrification rates measured in standard batch test are presented in Figure 3-11. In April the nitrification rate was rising slowly from 2 mgN/h/gVSS to 3 mgN/h/gVSS. Since 20°C and a minimum of 5 mgO_2/L are always implemented in standard batch tests, this would mean a slowly growing nitrifyer population. The fire water reduced the amount of nitrifying bacteria dramatically but nitrification came back quickly and was afterwards always above 4 mgN/h/gVSS. This also shows, that the cold temperatures in the period until May hindered the growth of nitrifyers significantly. With conditions constantly above 15°C a quick

build up of sufficient nitrifying bacteria was possible. Hence, a start up of the process should always be done under warm or moderate temperatures.

Denitrification rates were normally 1 to 1.5 mgN/h/gVSS. A maximum of 2.3 mgN/h/gVSS was measured on a day where nearly no nitrification occurred. Therefore, no nitrate was present within the anoxic zones of the plant. As discusses in Vocks et al. (2005) an influence of storage compounds on the denitrification is assumed. If no nitrate is present in the plant, the micro organisms do not use their carbon storage for denitrification. Hence, an unusual high amount of stored carbon can be used in the batch test for denitrification, resulting in higher rates. More hints on storage compounds effecting the DNR are discussed in the following chapter 3.4.2 .

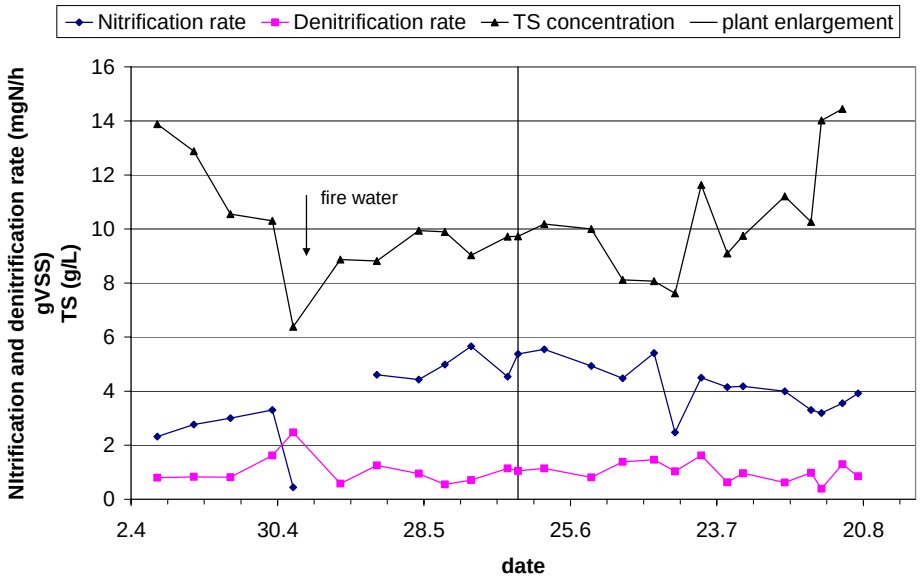

Figure 3-11 Nitrification and denitrification rates measured in standard batch test

3.4.2 Parallel batch tests

As already mentioned in the progress report, Stumpf (2005) found a dependency of the DNR on the sludge concentration. A closer investigation of these data revealed a clear correlation between the DNR and the anaerobic acetate loading (Figure 3-12). Higher anaerobic loading led to better denitrification.

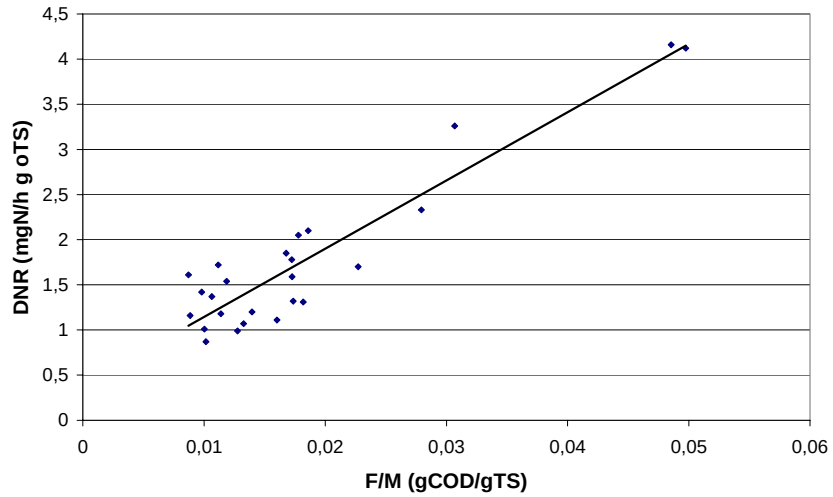

Figure 3-12 Dependency of the DNR from the anaerobic acetate loading. Recoded during irregular sludge removal period.

This result motivated tests to corroborate the influence of the anaerobic acetate dosing. Parallel batch tests were conducted. One batch tests was a standard tests with an acetate starting concentration of 100mgAC/L. In a second batch reactor, only 50mgAC/L were dosed at the beginning of the anaerobic phase. The results are presented in Figure 3-13. It is clearly apparent, that with half of the acetate dosing, only 40% to 60% of the denitrification rate was achieved, which supports the theory of the anaerobic stored carbon source.

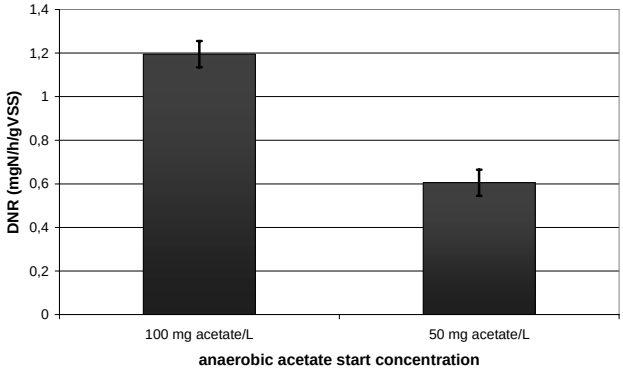

Figure 3-13 DNR in parallel batch tests with half anaerobic acetate dosing. Recoded during continuous excess sludge removal period.

Also investigated with parallel batch tests was the effect of temperature on the nitrification and denitrification rate. Therefore, a standard batch test with 20°C and a parallel batch reactor with 15°C respectively 10°C were conducted at the same time. The results are summarized in Figure 3-14. For nitrification a clear tendency was observed with lower rates at lower temperatures. A temperature shift of 5°C decreased the nitrification rate by 50%, 10°C temperature difference led to a 70% lower nitrification rate. Inexplicably is the behaviour of the denitrification rate. No clear tendency was observed. It was either slightly higher or clearly lower at lower temperatures. Other factors but the temperature seem to affect the denitrification significantly.

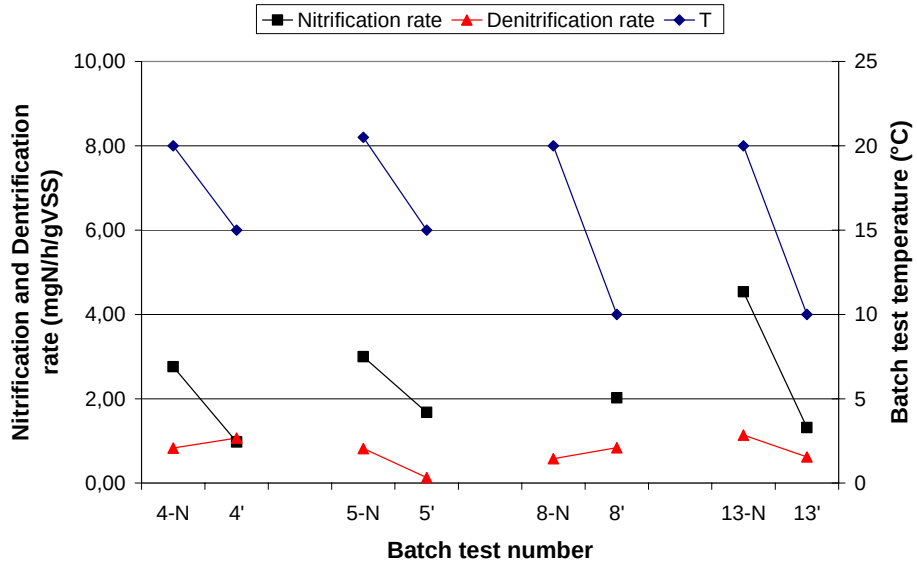

Figure 3-14 Influence of temperature on the nitrification and denitrification rate. Standard batch test (N) with 20°C and parallel batch tests with 15°C and 10°C (').

3.4.3 Glycogen and PHB investigations

A hypothesis for the used carbon source for denitrification in the ENREM process was formulated. From the EBPR process two major carbon storages are known: PHB and glycogen. Since PHB is degraded and glycogen is formed under aerobic conditions, glycogen was assumed to be a possible carbon source. Therefore, standard batch test with enlarged anoxic phases were conducted and the evolution of PHB and glycogen was monitored. PHB was formed under anaerobic conditions and degraded under aerobic conditions (Figure 3-15) as expected from the EBPR metabolism theory. The evolution of glycogen was also according to the theory with a decline in the anaerobic phase and a build up in the aerobic. Under anoxic conditions, the PHB concentration was constant and a use as carbon source for denitrification can be discarded. This was also assumed in the formulated hypothesis. Glycogen showed an unsteady behaviour in the anoxic phase with raises and falls. This shows that glycogen might be involved into some metabolic activity but could not be linked directly to denitrification. A different kind of carbon source must be stored in the process. Jeon and Park (2000) had hints that lactic acid can play a role in the EBPR metabolism. Therefore, first orientating batch tests were conducted supplying lactate in the anaerobic phase. The post-denitrification was slightly increased compared to a parallel standard batch test with acetate dosing. But no final conclusion could be drawn so far and further research is necessary.

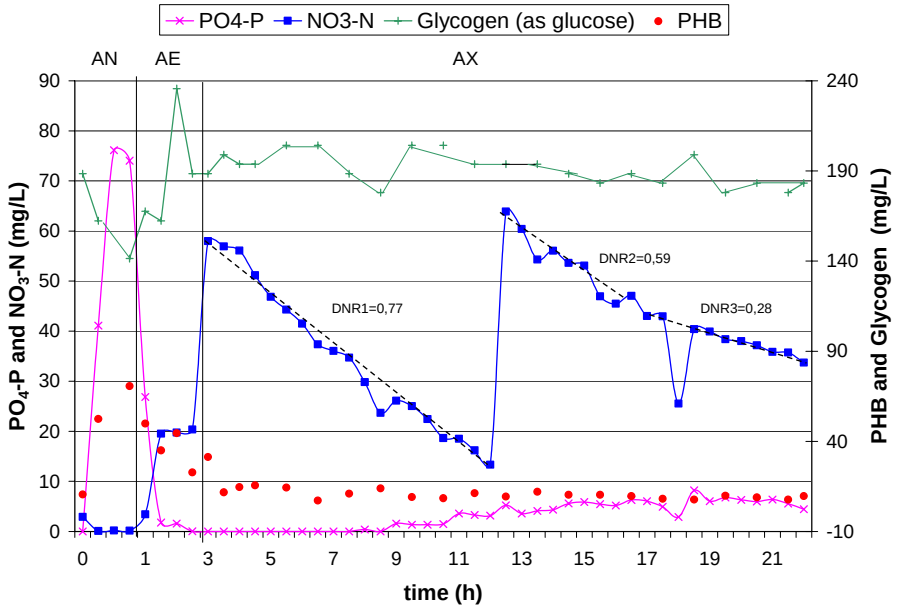

Figure 3-15 Batch test with PHB and glycogen measurements and extended anoxic zone

3.5 EPS measurements

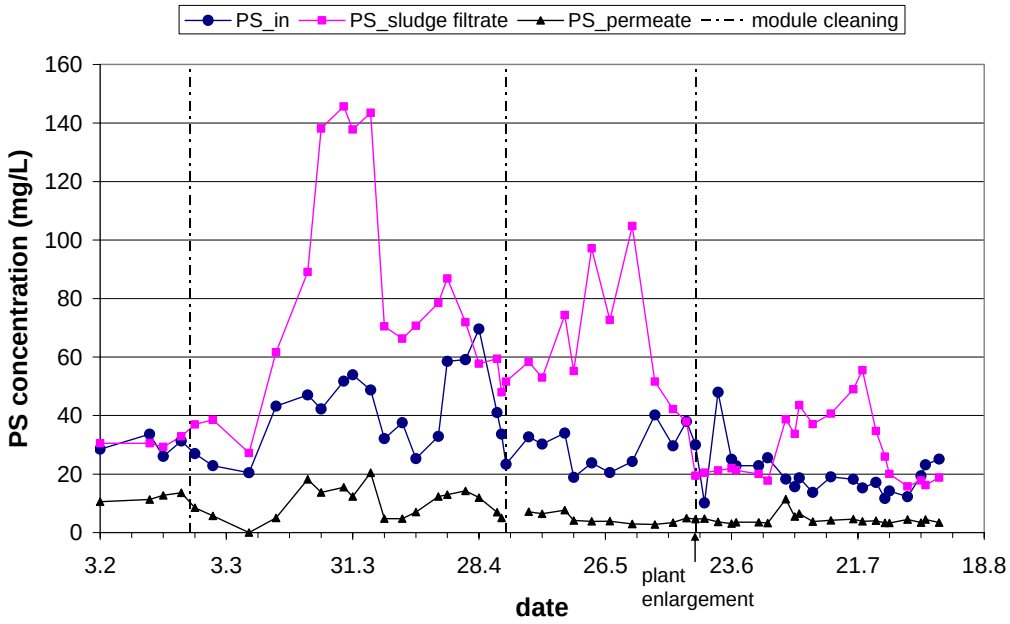

Figure 3-16 Course of PS concentration in the influent, sludge filtrate and permeate.

The polysaccharide concentration in the influent ranged mostly between 11 and 30 mg glucose/L. This was in the same range as observed in 2004 (progress report, Vocks and Kraume (2004)). In March and April higher influent concentrations of up to 70 mg glucose /L were measured. This raise could not be linked to any other changes in the influent.

In the progress report it was found that PS concentration in the sludge filtrate is of the same range as the influent concentration under optimized and stable operational conditions. This was also the case here but three periods with significant higher PS concentrations in the sludge filtrate

were spotted: end of March, Mai and July. The highest values of 140 mg/L were measured end of March. In this period a nearly complete break down of nitrification was assessed with up to 70 mgNH_4-N/L in the effluent. An impact of the high ammonia concentration can be assumed here. For the month of May, two things have to be considered to explain the higher values: first the influent of the fire water from 1.5.05 until 4.5.05 with unknown impact on the biomass. Furthermore, temperature was very changeful in Mai with values between 12°C and 30 °C measured in the plant with daily variations of up to 7 °C.

The raise of PS concentration in the sludge filtrate in July may be linked to the intense growth of *Tubifex* worms. Indeed, the first value in the sludge filtrate above the influent concentration was measured on the 5th of July and went along with a deterioration of 2 g/L TS (see Figure 3-1). Beginning of August, the phase of higher PS concentration in the sludge filtrate ended when TS concentration began to rise again.

The PS effluent was unconstant in March and Mai and ranged between 0 and 20 mg/L. There was no dependency of the course of effluent concentration with module cleaning, hence a higher PS retention due to fouling can be neglected. However, the higher effluent concentrations were observed in a period with high and changeful influent concentrations. It must be said that the measured value is a sum parameter and gives no information about the composition of the polysaccharides. Maybe a different type of PS, which could better pass the membrane led to the higher effluent concentrations. From mid of May, PS concentrations were lower and ranged between 2 and 6 mg glucose/L in the permeate. A small peak was observed on the 5th of July, when PS in the sludge filtrate started to rise again.

The enlargement of the plant had neither an effect on PS concentration in the sludge filtrate nor on the PS permeate concentration.

Compared to the operational period with discontinuous excess sludge wastage the PS concentration in the sludge was neither lower nor more stable. It can be concluded that other factors but the excess sludge removal strategy effected more the PS concentration. Of importance were the PS influent concentration and stable operational conditions such as sufficient oxygen supply, moderate temperature shifts, good nitrification and moderate metazoa growth.

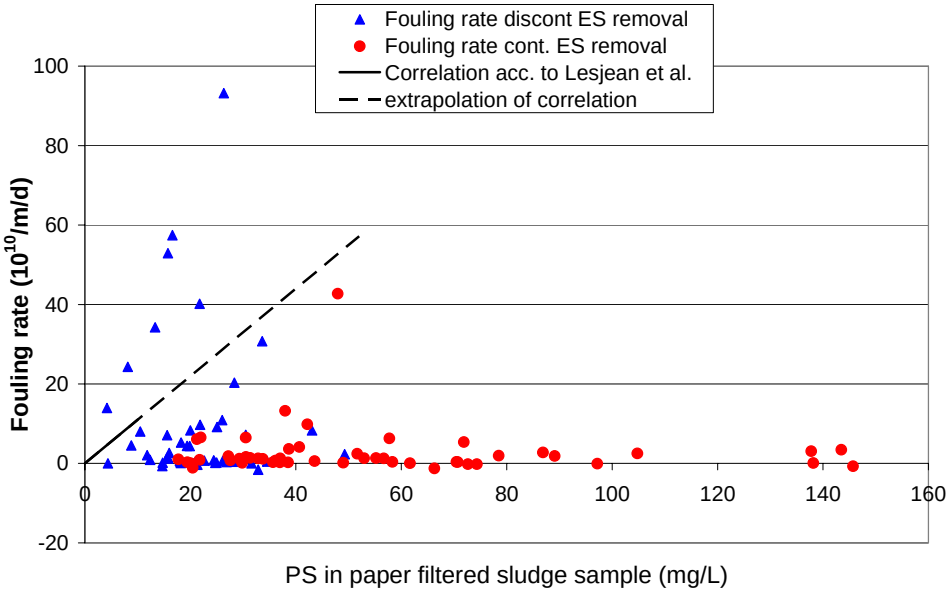

Figure 3-17 Fouling rates for both trail periods and comparison with the correlation according to Lesjean et al. (2004)

A correlation between PS concentration in the plant and fouling rate as mentioned by Lesjean et al. (2004) could not be found for both trial phases (Figure 3-17). However, although the PS concentration was not influenced by the excess sludge removal strategy, the fouling rate was. During the discontinuous excess sludge removal phase the fouling rate scattered a lot with very high values above the correlation according to Lesjean et al. (2004) but also very low values clearly below the correlation. In the phase of continuous excess sludge removal the fouling rate was most of the time on a very low level below $5*10^{10}$/m/d. The PS concentration had clearly no influence on the fouling rate.

The course of proteins (Figure 3-18) shows similar high concentrations in March, May and June as PS. But unlike the polysaccharides the protein concentration in the sludge supernatant was effected by the plant enlargement. After the enlargement, protein concentration was always below 50 mg/L despite the period of the worm bloom. The longer aerobic contact time is assumed to cause more protein degradation. Similar results were found by Iversen (2005) in small scale stirred reactor tests.

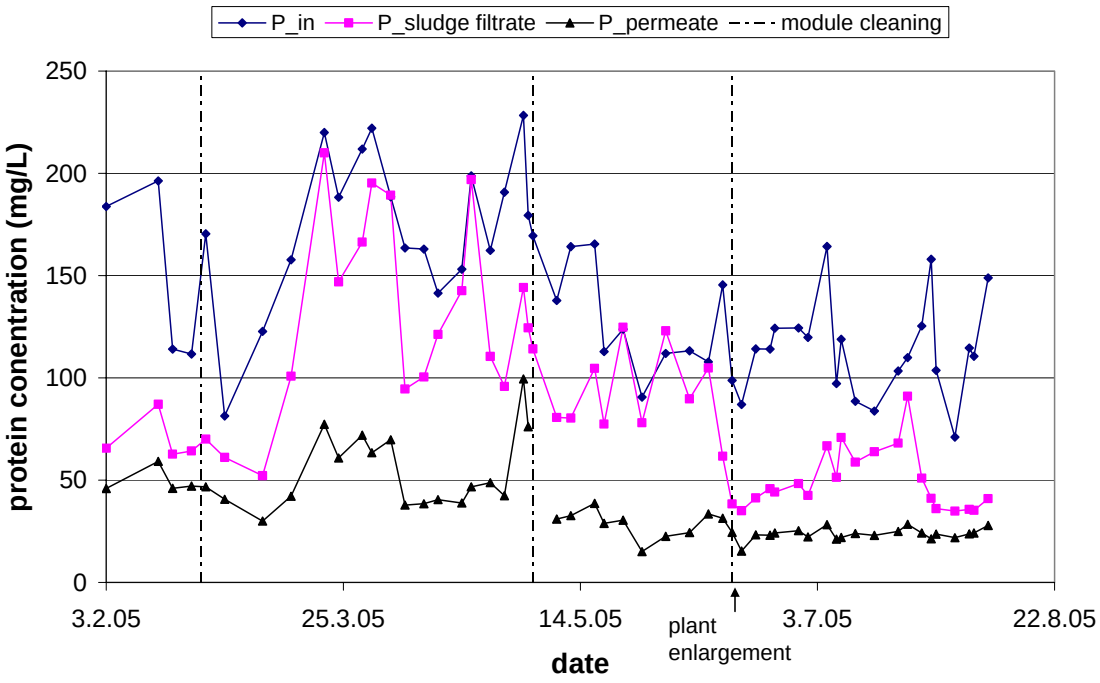

Figure 3-18 Course of proteins in the influent, sludge filtrate and permeate.

3.6 Tested Tubifex Tubifex elimination strategies

Tubifex worms (Figure 3-19) were often observed during the whole operational period. This caused never any problems until July 2005. Just a few days after the plant enlargement the worms were heavily growing. This resulted in a decreasing TS concentration and low elimination rates, especially for phosphorus. Together with the plant enlargement a constantly higher temperature above 20°C came along. This might be one reason for the sudden increase in worm number. They accumulated heavily on the aerators and formed large colonies. This also reduced the efficiency of the aerators. They also were found attached to other surfaces as walls, covers and probes. A minor part of the population was swimming in the sludge. Also found attached to surfaces but also in large numbers in the sludge were the cocoons with eggs of the worms (Figure 3-20). Hence different strategies were tested to reduce the number of tubifex worms.

After a literature review ammonium was identified as a possibility to harm the worms (Rensink and Rulkens (1997)) but would not harm most other organisms in the sludge. Additional ammonium was dosed two times for 3 to 4 days with a minimum effluent concentration of 30 mgNH_4-N/L. However, it had no success and the number of worms stayed high.

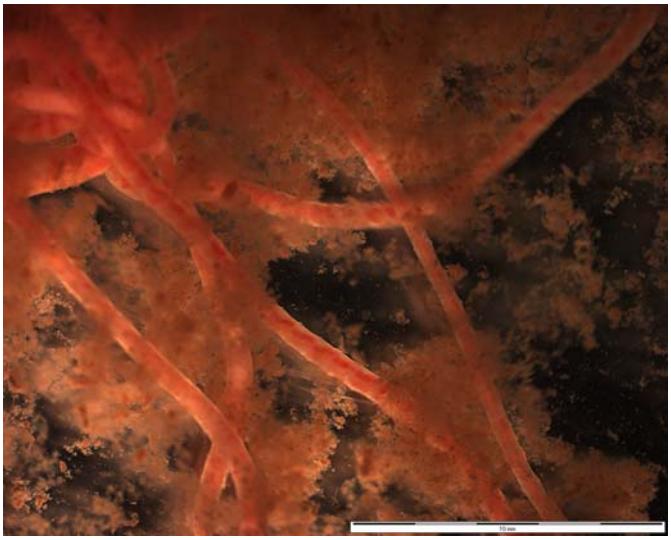

Figure 3-19 Tubifex worms

Rathore and Khangarot (2002) found a mortality of 100% of the Tubifex worms for 0.18mg/l copper at 20°C after 96h. Since this copper concentration is not critical for the rest of the biology, it was attempted to eliminate the worms with copper. Starting the copper dosing also all visible worms were removed manually from the aerators, walls and probes. During the copper dosing dead pale worms were found in the sludge while there was no change for the rest of the microbiology observed. But within one week, the worm population grew back. A second attempt dosing copper for a longer period (2 weeks) showed the same result. The problem might have been the large number of eggs. These were not harmed by the copper and hence, the worm population could grow back fast.

Additionally is must be stated that in the pilot plant ideal conditions for Tubifex worms were prevalent (Ellissen (2005)): high sludge age, complete sludge retention, good aeration and high surface to volume ratio. Surface is important because Tubifex develop and lay eggs on supporting medias.

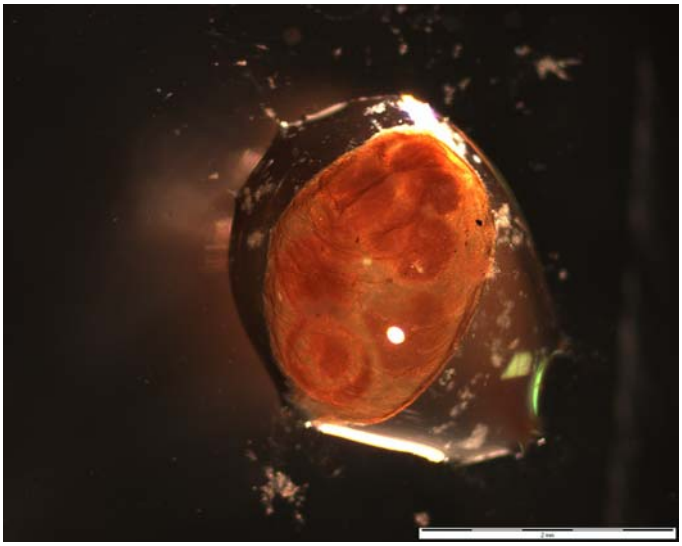

Figure 3-20 Eggs and larva in a cocoon.

4 Recommendations for design, start-up and operation

The plant should be seeded with recirculation sludge from another plant with a TS concentration of 8 – 10 g/L to prevent an intense fouling of the membrane during start-up. It will also ensure sufficient COD elimination directly from the start.

The start-up of the demonstration plant should be done with in-plant-temperatures above 15°C to enhance the growth of nitifiers. In case this is not possible, the throughput of the plant should be reduced by 30% of the targeted average flow in order to prevent inhibitory ammonia concentration in the plant and nitrite build up. When the nitrification rate is reaching values above 4 mgN/h/gVSS in standard batch test, full throughput can be implemented.

To build up biomass no excess sludge should be drawn in the first days. Depending on growth, excess sludge removal can start after 1 to 2 weeks. 2 weeks shall no be exceeded in order not to overload the sludge with phosphorus.

Table 4-1: Comparison of biological performance during the two different periods

	Irregular excess sludge removal	Continuous excess sludge removal
P-effluent concentration	0.1-0.5 mg/L	0.1-0.5 mg/L
Denitrification rate	1-1.5 mgN/h/gVSS	1-1.5 mgN/h/gVSS
Nitrification rate	unsteady, Ø 2 mgN/h/gVSS	stable 4 mgN/h/gVSS
Complete nitrification	Often not before membrane chamber	In aerobic zone

For excess sludge removal strategy a continuous withdrawal is recommended for several reasons. As can be seen from Table 4-1 most biological kinetics were not affected by the excess sludge removal strategy, but nitrification was, and the aerobic zone would have to be build two times larger with irregular removal. Secondly, fouling was lower in the period with regular excess sludge removal. Due to the high influent concentrations for all parameters, always a high TS concentration is needed for good nitrogen elimination. In Berlin, the possible savings while discarding the extra tank for excess sludge storage are small. And finally, the extra tank can be used as a storage in a emergency.

An SRT of 25d to 30d is recommended to achieve both, good nitrification and good P-removal. Recommended hydraulic contact times are at least 30 min for the anaerobic zone, 15 min to 20 min for each of the two aerobic zones and 30 min to 40 min for each of the two anoxic zones. Concerning the recirculations in the plant, this would lead to an overall hydraulic retention time of 14h to 15h. These calculations are based on an average ammonium inflow concentration of 90 mg/L.

Oxygen concentrations in the first aerobic reactor should be controlled to 2 to 3 mg/l and in the second aerobic reactor to 1 to 2 mg/L.
Between the aerobic and anoxic zones a degassing chamber should be installed. The design of this chamber should avoid sludge accumulation by e.g. a stirrer or top-to bottom through flow.
Because of possible foam formation the walls should exceed the water surface by 50 cm. Very big anaerobic foam layers can cause P-release and therefore reduce the effluent quality. Foam destroyers should therefore be mounted on the stirrers of the anoxic zones.
No clear strategy could be developed to prevent worm blooms, but it is recommended to observe metazoa growth and fight worms directly from the start. Otherwise the risk of massive accumulation of worm eggs in plant exists which makes it difficult to fight the worms afterwards.

5 Conclusions

An MBR pilot plant was operated for 16 months. Different operational parameters were implemented for verification of basic process design and operational conditions of the full-scale MBR demonstration plant in Berlin-Margartenhöhe.
Different excess sludge removal strategies were investigated: discontinuous removal every 1 to 4 weeks, and continuous removal. A negative impact of the discontinuous removal strategy could not be stated for COD removal, enhanced biological phosphorus removal or the impelented post-denitrification process (ENREM process). Solely the nitrification rate was unsteady and in average only at 2 mgN/h/gVSS while it was steady and at 4 mgN/h/gVSS with continuous excess sludge removal. The EPS concentration in the plant was not effected by the excess sludge removal strategy but fouling was, showing a higher fouling potential with discontinuous removal.
The biological phosphate removal was satisfying. With influent concentration between 15 mgTP/L and 40 mgTP/L an effluent quality of 0.1 to 0.5 mgTP/L (>95% P-elimination) was constantly possible. This is close to the target of 0.1 mgTP/L. As recommended in the progress report, the demonstration plant is designed with a longer HRT. Therefore, this target might be reachable by pure biological P-removal. In case of unfulfilled quality only a small amount of precipitation chemicals has to be dosed.
P-removal became problematic when an infestation of *Tubifex tubifex* occurred. The PUR dropped from 15 mgP/h/gVSS to 3 mgP/h/gVSS and P-effluent concentration was beyond 1 mg/L. Therefore, worm removal strategies were tested. Additional ammonium dosing had no success. Copper killed the worms, but the population grew back within 2 weeks. Also destabilising for the EBPR process were TP influent concentration constantly above 30 mg/L combined with P/TS concentration above 4%. The demonstration plant should therefore be operated with an SRT below 30d.

Due to high TN influent concentration the N-removal was insufficient. Complete nitrification was only achieved in the membrane reactor and TN effluent concentration was 20 to 30 mg/L (80% TN-elimination). This was clearly above the targeted 10 mgTN/L. Hence, the aerobic and anoxic zones were enlarged. After the enlargement nitrification was completed always in the aerobic zones and TN effluent concentration of 6 mg/L were possible. But the process was unsteady due the *Tubifex* infestation and the targeted quality could not be reliably reached.

From the trials it can be concluded that the demonstration plant should be started in warm or moderate conditions. Temperature below 15°C clearly inhibited the quick build up of nitrifying bacteria. Combined with the high ammonium influent concentration especially the growth of nitrite oxidizers was weak and nitrite accumulated in the system.

6 Student activities

Seven students conducted different projects for this study.

Daniel Stumpf: Auswirkungen der diskontinuierlichen Überschussschlammentnahme auf die vermehrte Nährstoffelimination in einer Membranbelebung.

Vera Iversen: Einfluss instationärer Betriebsbedingungen auf die EPS-Konzentration in einem Membranbelebungsreaktor.

Jörn Villwock: Auslegung und Optimierung eines Speichertanks für eine Membranbelebungsanlage.

Thomas Nicke: Nutzung zellinterner Speicherstoffe als Kohlenstoffquelle bei der nachgeschalteten Denitrifikation ohne Zugabe einer externen Kohlenstoffquelle.

Anne-Cécile Le Coz: Kinetic study about Enhanced Nutrients Removal in Membrane Bioreactor.

Karine Grataloup: Kinetic study about Enhanced Nutrients Removal in Membrane Bioreactor.

Jan Mante: Einflüsse auf die EPS Konzentration in Membranbelebungsanlagen, in progress

7 Publications

Following publications arose from this study:

Vocks, M., Gnirss, R., Lesjean, B., Villwock, J. and Kraume, M. (2005) Membrane Bioreactor system coupled with Low-Pressure Sewer for Decentralized Wastewater Treatment. in *1. ZERO-M Conference on Sustainable Water Management* Instanbul, Turkey

Vocks, M., Lesjean, B., Gnirss, R., Stumpf, D. and Kraume, M. (2005) Auswirkungen der diskontinuierlichen Überschussschlammentnahme auf die vermehrte biologische Nährstoffelimination in einer Membranbelebung. in *6. Aachener Tagung Siedlungswasserwirschaft und Verfahrenstechnik* Aachen, Germany

Vocks, M., Stumpf, D., Lesjean, B., Gnirss, R. and Kraume, M. (2005) Effect of irregular sludge wastage on enhanced biological nitrogen removal in a membrane activated sludge system. in *IWA Specialized Conference Nutrient Management in Wastewater Treatment Processes and Recycle Streams* Krakow, Poland

Drews, A., Vocks, M., Iversen, V., Lesjean, B. and Kraume, M. (2005) Fouling in Membranbelebungsreaktoren: Erfahrungen beim Betrieb mit diskontinuierlichem Schlammabzug *Chemie Ingenieur Technik* **77** (5) pp593-599

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