Biological treatment of whitewater in a laboratory process in order to determine kinetic parameters for model development

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Abstract Implementation of an in-mill biological treatment plant is one solution to the problems associated with closure of whitewater systems. It is, however, important to operate the treatment with low concentration of nutrients in the effluent. The effect on the COD reduction from decreased additions of NH_4-N and PO_4-P were investigated in three parallel aerobic suspended carrier reactors during treatment at 46 to 48°C of whitewater from a recycled paper mill producing liner and fluting. In the reference reactor, a COD reduction of 89% was achieved and 45.6 mg NH_4-N/(g COD reduced) and 11.6 mg PO_4-P/(g COD reduced) was consumed at an organic load around 20 kg COD/(m^3·d). Reduced additions of NH_4-N decreased the COD reduction. Addition of 56% of the consumption of NH_4-N in the reference reactor resulted in a COD reduction of 80%. The response from decreased addition of PO_4-P was different compared to NH_4-N but it could not be determined if this is due to unsuitable experimental design or a different reaction mechanism. Reducing the addition of PO_4-P to 26% of the consumption of PO_4-P in the reference reactor, decreased the COD reduction to 83%. The main conclusion from the experiment is: biological treatment has the potential of treating whitewater from recycled paper mills with low effluent nutrient concentrations.
Keywords Aerobic degradation; closure; model; nutrients; pulp and paper; whitewater

Water Science and Technology **Vol 50 No 3 pp 195–206**

Introduction

During recent decades, much effort has been aimed at decreasing the amount of fresh water used in paper mills. This has been achieved by increased recycling of the whitewater at different positions in the process. There are several incentives for implementing a closed whitewater system, e.g. less dependency of access to fresh water and decreased impact on the environment (Webb, 1997). The closure is, however, associated with several problems due to the accumulation of organic and inorganic compounds in the whitewater (Berard, 2000). High temperature and high concentrations of salts promote corrosion and scaling whereas other severe effects arise from microorganisms in the whitewater system. Increased concentrations of organic compounds in the whitewater in combination with a warm surrounding create suitable environmental conditions for microorganisms. The microbial growth leads to different problems, such as increased demands for retention aids, odour problem and deteriorated product quality. The possible solutions to these problems can be divided into two different groups according to what principle is used for solving them. Either the microbial growth is suppressed with biocides or the substrate for the microorganisms is removed. Several different techniques, such as evaporation and membrane filtration, can be used to remove organic compounds in the whitewater. Another promising solution is in-mill biological treatment, if necessary complemented by a suitable separation process, e.g. flotation or filtration, and a final polishing step, e.g. ozone treatment.

The biological treatment process requires a balanced composition of the wastewater, in particular with regard to biodegradable organic matter (here quantified as chemical oxygen demand, COD), nitrogen and phosphorus. Normally, the whitewater concentrations of nitrogen and phosphorus are low, especially in the readily available forms of ammonium and orthophosphate. To obtain an efficient biological process, these have to be added. It is important to avoid excess addition of nutrients since this would lead to increased concentrations in the whitewater system, which in turn would have the negative effect of promoting microbial growth (Malmqvist *et al.*, 1999). Consequently, the nutrient addition to the biological treatment process should be carefully controlled to keep the concentrations of nitrogen and phosphorus in the effluent as low as possible. An automatic control system to fulfil these requirements is discussed in Alexandersson *et al.* (2003).

Low concentrations of nutrients in the effluent are of interest not only for in-mill treatment but also for external biological treatment processes where nutrients have to be added. The effluent standards for such plants are usually made more stringent at regular intervals and the amounts of nutrients these types of plants are allowed to release into the environment will probably be further decreased in the future. Consequently, it is important to operate these plants with a minimum of nutrients in the effluent. Since the nutrients are associated with a cost there is also an economic incentive to minimise the use of nutrients.

The possibility to operate a biological treatment plant with low concentrations of nutrients in the effluent cannot be applied to all types of processes. Changing the environmental conditions will affect the composition of the microbial community, which will be reflected in changed process characteristics, for example settling properties. Therefore, nutrient limitation is more suited for biofilm processes than for activated sludge systems since it is well known that nutrient limitation in an activated sludge system can result in a bulking sludge (Jenkins *et al.*, 1993) due to increased growth of filamentous organisms. Although the same filamentous organisms can appear in a biofilm process this would not have such severe negative effects since this process does not rely on the settling properties of the sludge.

The ability to control the process is dependent on fundamental knowledge about the dynamic process response of the biological system during low and changing levels of nutrient concentrations and how the degradation process is affected. Therefore, laboratory experiments were carried out, in which whitewater was treated in biological aerobic suspended carrier reactors. The purpose was to analyse the behaviour of the system and to determine the correlation between the COD reduction and varying concentrations of nutrients.

The work was carried out as part of a research project (acronym CLOSEDCYCLE) within the European Union Fifth Framework Programme. The overall objective of the project is to develop knowledge and cost-effective technology for treatment of paper mill process water at the source in the paper mill to replace fresh water with treated water. The project involves specialists in paper making technology, practical operation of paper mills, biological treatment, separation technology, automation and control and analytical chemistry.

Material and methods

Experimental set-up

The experimental study was carried out in three laboratory scale units of an aerobic suspended carrier process. The glass reactors had a volume of 425 ml and they were filled to 50% of the volume with a plastic carrier, Kaldnes, K2 (350 m^2/m^3). Water-saturated air was injected at the bottom of the reactors to provide oxygen and to mix the contents of the reactors. The reactors and the air humidifier vessels were double-walled for the purpose of controlling the temperature by circulating water from a temperature-controlled water bath, which was set to 50°C. Due to heat losses, the temperatures in the reactors were between 46 and 48°C, corresponding well to expected full-scale whitewater temperatures. The pH in the reactors was not controlled. To each reactor both whitewater and nutrient solution were pumped from two separate vessels. Three vessels with whitewater, one for each reactor, were stored at 2–4°C, whereas the three vessels with nutrient solutions were kept in room temperature (20–22°C).

One of the reactors, denoted *Ref*, was used as reference and the load of whitewater and the composition of the added nutrient solution were kept constant for the duration of the experiment. The load of whitewater to the other reactors was also kept constant whereas the compositions of the added nutrient solutions were changed. The amount of nitrogen (ammonium) was varied in the nutrient solution pumped to the reactor denoted *N-lim* and to the reactor denoted *P-lim* the amount of phosphorus (orthophosphate) was changed during the experiment.

Before the experiment was initiated, the three reactors had been operating on identical whitewater for almost 30 days in order to develop a stable biofilm on the carriers. During this start-up period, the load to the different reactors varied somewhat. Therefore, in order to assure all reactors the same initial conditions, the contents of all reactors including the carriers were mixed and evenly distributed among the reactors.

Analyses

Chemical oxygen demand (COD) was determined with the Dr Lange test kit LCK 114. Ammonium nitrogen (NH_4-N) was analysed with the Dr Lange test kits LCK 303 and 304, while total nitrogen was determined with kit LCK 138. Orthophosphate (PO_4-P) and total phosphorus were analysed with the Dr Lange test kit LCK 349. pH was determined with a pH combination electrode. All analyses were carried out on filtered (Schleicher & Schuell, 0.45 μm) grab samples except for the determination of COD, which was also performed on non-filtered grab samples.

Whitewater

In the experiments, a diluted solution of a whitewater was used. Grab samples of whitewater were collected from a paper mill producing testliner and fluting from recycled paper. The products are manufactured in parallel on different paper machines with a combined whitewater system. The whitewater was stored at 2–4°C until it was diluted with two parts tap water and used for the experiment. The diluted whitewater was characterised with regard to COD (total and dissolved), pH, ammonium-nitrogen (NH_4-N), orthophosphate-phosphorus (PO_4-P), total nitrogen (N-tot) and total phosphorus (P-tot). The results are found in Table 1.

Nutrient solution

Two different stock solutions, one consisting of 20 mg/ml NH_4-N and one consisting of 5 mg/ml PO_4-P, were prepared by dissolving 76.36 g NH_4Cl and 21.97 g KH_2PO_4 respectively, in 1,000 ml de-ionised water. Nutrient solutions for the experiments containing both nitrogen and phosphorus were prepared from the stock solutions. The concentrations of the

Table 1 Composition of diluted whitewater used in the experiment

Parameter	Concentration
COD, total (mg/l)	12,500
COD, dissolved (mg/l)	12,400
pH	6.5
NH_4-N, dissolved (mg/l)	< 2
N-tot, dissolved (mg/l)	15
PO_4-P, dissolved (mg/l)	0.1
P-tot, dissolved (mg/l)	0.7

various nutrient solutions used during the test and at what time period they were used for each reactor can be found in Table 2.

Organic load and COD reduction in reference reactor

From day 0 to 8, the concentrations of nitrogen and phosphorus in the nutrient solutions were increased at three occasions to obtain a stable operating point without any limitation with respect to the nutrients. After the increase on day 7, the nutrient concentrations in the effluents were higher than 1 mg/l and the addition corresponded to a COD:N:P ratio of 100:4.2:1.05. According to Jenkins *et al*. (1993), the concentration in an aeration basin of an activated sludge system should not be less than 0.5 to 1.0 mg/l for either orthophosphate or inorganic nitrogen (sum of nitrate-nitrogen and ammonium-nitrogen), to avoid growth limitations. Consequently, sufficient amounts of nutrients were added to the reactors.

The main part of the organic compounds in the water are degraded by different species of bacteria but other organisms, such as ciliates and rotifers, are also important since they, among other things, reduce the amount of sludge produced and keep the water phase clear by preying on free-swimming bacteria. Therefore, in a well-balanced system the major part of the microbial activity is associated with bacteria in the flocs (in an activated sludge system) or in the biofilm (in a biofilm process). Implementation of an in-mill biological treatment process in a closed whitewater system without costly cooling of the whitewater implies operation at temperatures around 50°C, which is above the upper limit for Eukarya (higher-order) organisms. Absence of ciliates and rotifers leads to a biological system with enhanced impact from free-swimming bacteria. Since these are influenced by the hydraulic retention time (HRT), the combined flow rate of whitewater and nutrients have been kept constant, around 750 ml/d, for the duration of the experimental period. However, small variations in the flow rate are unavoidable and this led to an HRT in *P-lim* of 7.5 h, which was somewhat high compared to *Ref* and *N-lim*, where the HRT was 6.5 h. Had not the influent whitewater been diluted the HRT would have been much longer (based on the same influent load of COD). This is a disadvantage, since more time before a response to a change could be observed would be required. The organic load, measured as dissolved COD per reactor volume and day, was fairly constant for all reactors during the experiment and was determined to be between 19 and 22 kg COD/(m^3·d) except for an initial period when the influent load was slightly higher (see Figure 1). This high load was chosen since the objective of an in-mill biological process is to reduce part of the COD in the whitewater to maintain an acceptable level determined by the paper making process rather than to achieve complete degradation of the organic material.

The reduction of dissolved COD varied to some extent for the different reactors during

Table 2 The composition and time interval of nutrient solutions added to each reactor

	Ref		*N-lim*		*P-lim*	
Day	**NH_4-N**	**PO_4-P**	**NH_4-N**	**PO_4-P**	**NH_4-N**	**PO_4-P**
0	354	52	354	52	354	52
5	364	62	364	62	364	62
6	404	82	404	82	404	82
7	520	130	520	130	520	130
12	"	"	390	"	"	97.5
15	"	"	260	"	"	65
22	"	"	0	"	"	32.5
26	"	"	130	"	"	"
35	"	"	260	"	"	"
Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l

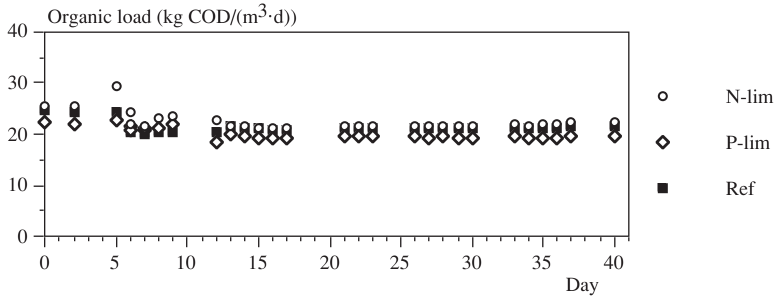

Figure 1 Organic load to the three reactors

the first few days of the experiment but stabilised at a value around 88% at day 8. The reduction of dissolved COD for *Ref* remained high and the average reduction during the entire experimental period was 89%. The nutrient consumption was determined to 45.6 mg NH_4-N/(g COD reduced) (standard deviation = 3.6 mg/g) and 11.6 mg PO_4-P/(g COD reduced) (standard deviation = 0.8 mg/g). When calculating the amount of reduced COD, the particulate fraction in the whitewater was considered to be biologically inert. The impact of this assumption is negligible since more than 99% of the COD in the whitewater originates from the dissolved fraction. Also the reduction of produced biomass is regarded as low and assumed not to influence consumption of nutrients due to the short detention time and the absence of higher organisms.

Results

Effects of decreased addition of NH_4-N

In *N-lim*, the effects of decreased amounts of added NH_4-N were investigated. The concentration of PO_4-P in the nutrient solution and the flow rate remained equal to those of *Ref*. The influence from varying concentrations of NH_4-N in the nutrient solution on the COD removal can be seen in Figure 2. The added amounts of NH_4-N and PO_4-P to *N-lim* are shown in relation to the amounts of NH_4-N and PO_4-P consumed in *Ref*. The observed small difference in the load between *N-lim* and *Ref* have been considered and compensated for in the calculation. The downward triangles represent added PO_4-P and they clearly indicate that a surplus of orthophosphate has been added during the whole experiment after the increase on day 7. The upward triangles represent added amounts of NH_4-N and on day 12 the concentration (equivalent to the load of ammonium) was decreased to around 83% of what was estimated to be consumed if the degradation in *N-lim* was as high as in *Ref* and if the NH_4-N consumption per (g COD reduced) was the same. Figure 2 shows that the COD reduction was not affected. Instead the reduction was the same as for *Ref*. However, a decrease of the nitrogen addition to 55% lowered the COD reduction to an average value of 83%. When the NH_4-N addition ceased, the COD reduction decreased to zero. Increasing the amount of added nitrogen from 0 to 28% led to a COD reduction of 35%. This partial COD reduction, however, led to a decrease in pH down to pH 4.8 in the reactor although the pH in both the whitewater and the nutrient solution were above pH 6. The reduction in *Ref* did not lower the pH, on the contrary, the pH increased slightly to a value between 6.7 and 7.0. From day 30, the pH in *N-lim* was adjusted to a value between 6.4 and 7.1. This caused the reduction to increase to 59%. The last increase of the concentration of NH_4-N to 57% caused the COD reduction to increase to 78%, which is close to the 83% reduction that was achieved during day 16 to 22 when the NH_4-N concentration was almost identical (55%). The different nutrient concentrations and values of COD reduction together with the number of analyses can be found in Table 3.

The results presented in Figure 2 also indicate a rapid response to the changed nutrient

Table 3 Relative NH_4-N concentrations, percentage COD reduction and the number of analyses for *N-lim*

NH_4-N (%)	COD reduction (%)	Number of analyses
100	86	3
83	89	3
55	83	4
28	35	4
28	59	3
57	78	3

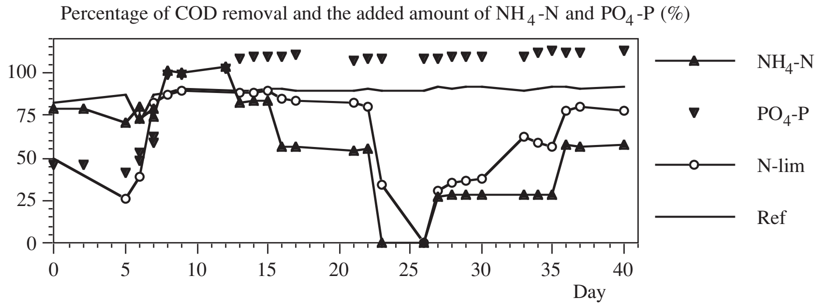

Figure 2 Added amounts of NH_4-N (line with upward triangle) and PO_4-P (downward triangle) in percent of consumed NH_4-N and PO_4-P in *Ref* and the percentage of COD removal in *N-lim* (line with circle) and *Ref* (line without legend)

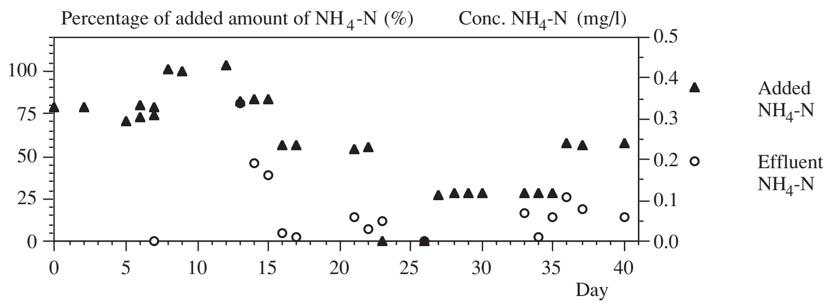

Figure 3 The values for the upward triangles are displayed on the left lateral axis and represent the percentage of the added amounts of NH_4-N to *N-lim* (relative to the consumption of NH_4-N in *Ref*). The concentrations of NH_4-N in grab samples from *N-lim* are indicated with circles and the corresponding values are displayed on the right lateral axis (values for day 5, 6, 8, 9 and 27 to 30 out of range)

composition. The first decrease was probably too small to give any effect on the COD reduction but the decrease on day 15 could be seen in the results from day 16. The other changes during the experiment gave similar results.

The effluent concentration of NH_4-N decreased when the addition of NH_4-N was reduced and this can be seen in Figure 3. During the period around day 10 when more than 100% of the estimated consumption of NH_4-N was added the effluent concentration was several mg NH_4-N/l. When the addition was reduced to 83% the effluent concentration started to decrease. Further reduction of the addition lowered the effluent ammonium concentration to values below 0.1 mg NH_4-N/l. During the period from day 27 to day 30 the concentration of NH_4-N in the effluent increased to values between 1 and 1.5 mg NH_4-N/l. This is a clear indication that the biological system was not working at its optimum due to the sudden change in pH. When the pH was corrected, the reduction increased and the effluent concentration of NH_4-N decreased to low values again. The results demonstrate the possibility to operate the biological system with a high reduction of COD while maintaining low levels (< 0.1 mg NH_4-N/l) of NH_4-N in the effluent.

Since most of the COD in the influent whitewater is dissolved, measurements of particulate COD in the reactor originate from produced biomass, either free-swimming bacteria or biofilm detached from the carriers. Microscopic evaluation of the liquid contents in the reactor revealed that free-swimming bacteria represented the major part of the particulate COD. The concentrations of particulate COD, compensated for assumed inert COD in the whitewater, together with percentages of added NH_4-N in *N-lim* can be found in Figure 4.

Effects of decreased addition of PO_4-P

In *P-lim*, the effects on the COD reduction of decreased addition of PO_4-P were investigated. During the experiment the concentration of NH_4-N in the nutrient solution and the flow rate to *P-lim* were the same as to *Ref*. The result from the varying concentrations of PO_4-P in the nutrient solution to *P-lim* can be seen in Figure 5. The upward and downward triangles represent the percentage added NH_4-N and PO_4-P relative to the consumed amounts in *Ref*. The actual organic load to *P-lim* has been taken into account and compensated for in the calculations. The COD reduction in both *P-lim* and *Ref* are also displayed. Reducing the addition of PO_4-P to 79% did not affect the COD reduction, instead the reduction remained the same as in *Ref*. Further decrease of added PO_4-P to 53% did not have any significant influence on the COD reduction. Not until the addition was reduced to 26% an influence on the COD reduction could be observed. The reduction decreased from 89% to 83% where it remained for the duration of the experiment.

It is equally important to maintain low concentrations of PO_4-P in the effluent from the biological treatment as it is for NH_4-N. As can be seen in Figure 6, a considerable amount of

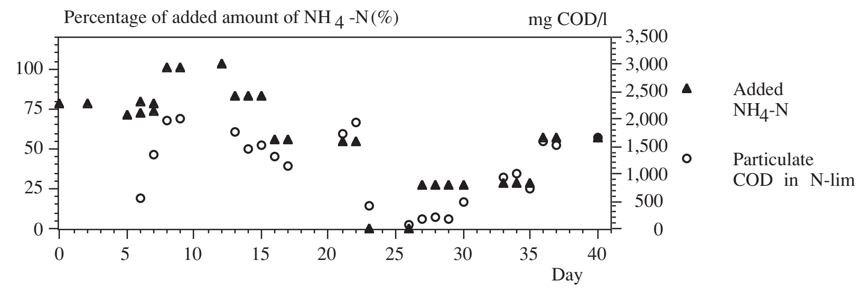

Figure 4 The values for the upward triangles are displayed on the left lateral axis and represent the percentage of the added amounts of NH_4-N to *N-lim* (relative to the consumption of NH_4-N in *Ref*). The concentrations of particulate COD in grab samples from *N-lim* are indicated with circles and the corresponding values are displayed on the right lateral axis

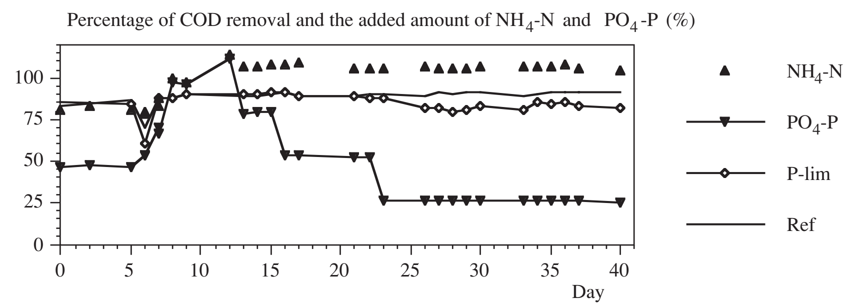

Figure 5 Added amounts of NH_4-N (upward triangle) and PO_4-P (line with downward triangle) in percent of consumed NH_4-N and PO_4-P in *Ref* and the percentage of COD removal in *P-lim* (line with rhombus) and *Ref* (line without legend)

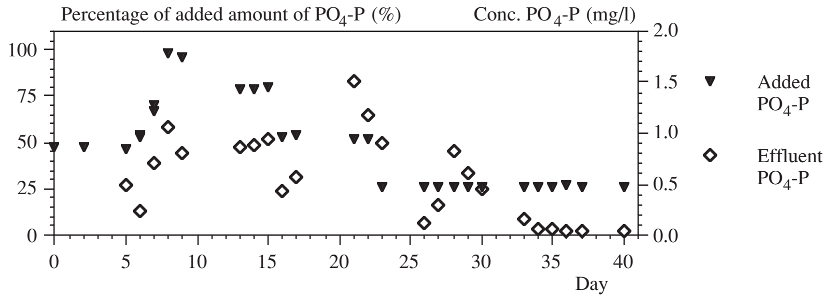

Figure 6 The values for the downward triangles are displayed on the left lateral axis and represent the percentage of the added amounts of PO_4-P to *P-lim* (relative to the consumption of PO_4-P in *Ref*). The concentrations of PO_4-P in grab samples from *P-lim* are indicated with rhombuses and the corresponding values are displayed on the right lateral axis

time elapsed before the effluent concentration decreased to values below 0.1 mg PO_4-P /l although the influent amount of PO_4-P to *P-lim* was significantly decreased. The reason for the concentration increase around day 28 is not known but stable and low effluent values did not appear until day 34. From day 34 and onwards it was possible to operate the reactor with a high COD reduction of 83% and with an addition of only 26% of PO_4-P.

Microscopic evaluation of the liquid contents in *P-lim* revealed that free-swimming bacteria represented the major part of the particulate COD. The concentrations of particulate COD, compensated for assumed inert COD, in the whitewater together with percentage of added PO_4-P can be found in Figure 7.

Other observations

During the experiment it was observed that the water phase as well as the pellets formed by centrifugation of grab samples from the different reactors had developed slightly different colours. The *N-lim* was more or less beige whereas *P-lim* and *Ref* had for some time a more yellowish tone, which towards the end changed into the colour of burnt brick for *P-lim* and pink beige for *Ref*. This would indicate the development of somewhat different microbial systems in the reactors.

Discussion

The characteristics of the microbial community may change during the types of experiments discussed in this paper and this makes results difficult to interpret. However, to draw relevant conclusions it is essential that the experimental systems are operating in

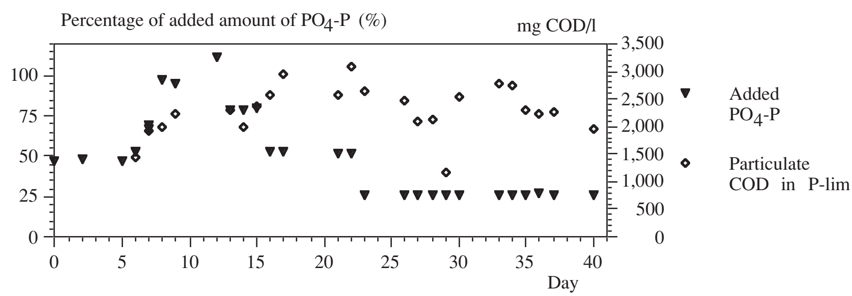

Figure 7 The values for the downward triangles are displayed on the left lateral axis and represent the percentage of the added amounts of PO_4-P to *P-lim* (relative to the consumption of PO_4-P in *Ref*). The concentrations of particulate COD in grab samples from *P-lim* are indicated with rhombuses and the corresponding values are displayed on the right lateral axis

steady-state conditions before any dynamic disturbances are imposed. In this case, the reactors had been in operation for a period of 30–35 days, using the same whitewater as influent and high levels of added nutrients. For this type of high-loaded system operating at high temperatures, experience has shown that 30 days is ample time for the development of a stable biofilm on the suspended carriers (Malmqvist, 2003). Moreover, the effluent concentrations of particulate COD (mostly microorganisms) from *Ref* were stable for the whole duration of the experiment (around 3,000 mg COD/l), which would also indicate steady-state conditions.

In this experiment, it is clear that the microbial activity was related to a combination of organisms in the biofilm and free-swimming bacteria. In Figure 4, it is evident how the effluent particulate COD concentration approaches zero as the COD reduction stops (around day 23). As the HRT in the reactor is only 6.5 hours, free-swimming bacteria are rapidly washed out of the system. However, as the addition of nitrogen is reinitiated (day 26) the COD reduction immediately starts again (Figure 2). This is a result of the activity of microorganisms in the biofilm and several days are required to re-establish a community of free-swimming bacteria. Unfortunately, a pH disturbance occurs around day 27 so any detailed conclusions cannot be drawn. Otherwise it would be expected that the recovery would be associated with a time constant reflecting the exponential growth phase of free-swimming bacteria. In *P-lim* (Figure 7), any similar drastic effects on effluent particulate COD cannot be detected as the COD reduction is high during the entire experimental period and free-swimming bacteria are always present.

Nitrogen limitation

The experiments with the NH_4-N limited reactor showed that a sufficiently large change in the added amount of nutrient affected the COD removal the following day. The initial decrease in nitrogen load to 83% of the consumption in *Ref* did not affect the COD reduction at all. The effluent NH_4-N concentrations were reduced to below 0.3 mg NH_4-N/l, which indicates that this dosage of nitrogen is close to the actual consumption in *N-lim*. The period at 83% dosage is too short to draw any stronger conclusions whether this dosage is optimal or not. It is, however, clear that further reduction of the dosage (to 55%) affects the COD reduction by a decrease to 83% reduction but also results in low (< 0.1 mg NH_4-N/l) effluent nitrogen concentrations. For nitrogen limited conditions, the balancing point between full COD reduction capacity and low effluent concentrations seems to be between 83 and 55% of the estimated non-limiting nitrogen consumption. This would result in a C:N ratio of 100:3.8 to 100:2.5 in terms of g COD reduced and g nitrogen required for the reduction. When the nitrogen load is further reduced the system behaves in a predictable way, i.e. the COD reduction decreases rapidly. The recovery of the system also demonstrates a strong correlation between the available nitrogen and the reduced COD, which indicates that in terms of control the nitrogen addition allows for good operability.

Phosphorus limitation

In the PO_4-P limited reactor, the reduction of dosage to first 79 and then 53% of the PO_4-P consumption in *Ref* had no or little effect on the COD reduction. Neither did the reduction affect the effluent phosphorus concentration considerably. Not until the dosage was 26% the COD reduction was affected (reduction from 89 to 83%). After some initial disturbance, this dosage level also yielded low (< 0.01 mg PO_4-P/l) effluent PO_4-P concentrations. Analogous to the nitrogen limited case, the balancing point between full COD reduction capacity and low effluent concentrations seems to be between 53 and 26%, resulting in a C:P ratio of 100:0.6 to 100:0.3 in terms of g COD reduced and g phosphorus required for the reduction. Unfortunately there were not made any further decreases in dosage, which could have provided more information. The fact that a reduction was not observed until the dosage was decreased to 26% could be explained by earlier overdosage of PO_4-P. This is somewhat puzzling as the consumption of PO_4-P in *Ref* remained high and in comparison to *Ref*, the consumption of PO_4-P in *P-lim* is significantly lower. Some possible hypotheses for this behaviour will be discussed in the next subsection.

Overdosing of nutrients

It seems as especially phosphorus has been overdosed in the experiment. It is not clear why this is the case, as the consumption in *Ref* indicated that the C:N:P consumption ratio would be close to 100:4.6:1.2. In the nitrogen-limited case, the overestimation of the consumption is less severe but in the phosphorus-limited case the actual consumption was at the most 53% of the expected amounts. The slightly different colours observed could indicate different microbial compositions in the different reactors, which might be expected as they are operated differently. Certainly, low concentrations of PO_4-P will, for example, promote growth of some organisms whereas this situation is devastating for others. Another possible problem is the difficulty of determining the balancing point between reduced COD and added nutrients. If this point is overestimated for a high-loaded system, any small change in the biodegradability of the influent or variations of the nutrient addition will show up as significant changes as the effluent soluble COD and phosphate only represents a small fraction of what is consumed within the reactor. On the contrary, if the point is underestimated, the correlation between nutrient addition and reduction of COD is significantly more evident. The determination of the balancing point is further obstructed if mechanisms such as accumulation and "luxury" consumption of PO_4-P are involved. Also, as a third hypothesis, the increase in phosphorus addition in the initial phase (days 5–7, see Table 2) of the experiment should perhaps have been less aggressive to allow the process to stabilise. It is possible that the phosphorus consumption would stabilise at a slightly lower level had sufficient time been given.

Model development

Mathematical models like the activated sludge model no. 1 (ASM1) (Henze *et al.*, 2000) are used to describe and simulate the behaviour of a biological treatment process and in these models the bacterial growth rate is characterised by a Monod equation $\mu = \mu_{max} \cdot S/(K_S+S)$, where μ_{max} is the maximum specific growth rate and S represents the substrate concentration. With this expression the growth rate is only limited by the substrate. The last parameter K_S, is the half-saturation constant. When the concentration S is equal to K_S the growth rate is half of μ_{max}. ASM1 has been developed for municipal wastewater treatment and in this type of wastewater there is usually a surplus of nitrogen and phosphorus. When a process with limiting amounts of nutrients is described the model must be extended. This can be done by the addition of a term describing the influence of nutrients on the growth rate. If the effects of nutrient limitations on the growth rate were described using the same principle as for substrate limitation, this would lead to the equation:

$$\mu = \mu_{max} \cdot \frac{S}{K_S + S} \cdot \frac{S_{NH4\text{-}N}}{K_{NH4\text{-}N} + S_{NH4\text{-}N}} \cdot \frac{S_{PO4\text{-}P}}{K_{PO4\text{-}P} + S_{PO4\text{-}P}}$$

In the above equation, $S_{NH4\text{-}N}$ and $S_{PO4\text{-}P}$ refer to the available concentrations of ammonium and phosphate, respectively, and $K_{NH4\text{-}N}$ and $K_{PO4\text{-}P}$ are the associated half-saturation constants. When the addition of nutrients is lowered the available concentration in the effluent will decrease and the growth rate of the microorganisms will also decrease. The rate of change depends on the half-saturation constants and the nutrient concentrations. A decreased microbial growth rate leads to a decreased degradation of organic material.

From the experimental results it is not possible to determine the half-saturation constants but it is possible to establish their order of magnitude. The five last measurements in *P-lim* lead to an average effluent concentration of 0.05 mg PO_4-P/l (standard deviation = 0.01 mg/l). Since there was only a minor decrease in the reduction capacity and the amount of biomass, measured as particulate COD, did not vary significantly this indicates that the half-saturation constant for orthophosphate is not larger than 0.05 mg PO_4-P/l. There is a slightly larger variation in the effluent concentration of NH_4-N from *N-lim* but all measurements are below 0.1 mg NH_4-N/l when the NH_4-N addition was 55 and 57%. The resulting decrease in COD reduction depends both on decreased amount of biomass in the system and reduced availability of NH_4-N. However, since there is only a minor decrease in COD reduction, the magnitude of the half-saturation constant for NH_4-N is probably not higher than 0.1 mg NH_4-N/l.

Future work

To acquire more accurate determinations of the kinetic parameters for the aerobic suspended carrier process, a new experiment will be designed and carried out. In this experiment, experience from the experiment presented here will serve as a basis. In particular, effort will be spent in the design to assure full excitation of the process in PO_4-P limiting conditions combined with more extensive monitoring using on-line sensors rather than manual laboratory analyses. Continuous measurements are required to capture the detailed dynamics of the process. Also the combination of anaerobic and aerobic processes will be investigated. Another important aspect is how the system will react to both nitrogen and phosphorus being close to limitation. As discussed in Alexandersson *et al*. (2003), operational considerations may have to be considered in choosing between nitrogen or phosphorus limited systems, but more knowledge is needed and this aspect will be considered in the next phase of experiments.

Conclusions

The experimental results show that it is possible to reduce the major part of the soluble COD in the whitewater from a recycled paper mill with an aerobic suspended carrier process. It was demonstrated that it is possible to obtain either low concentration of NH_4-N or low concentration of PO_4-P and yet have high COD reduction. When nutrients (NH_4-N and PO_4-P) were dosed in excess a COD reduction of 89% was achieved for a system with an organic load of around 20 kg COD/(m^3·d). During these conditions, the biological system consumed 45.6 mg NH_4-N/(g COD reduced) (standard deviation = 3.6 mg/g) and 11.6 mg PO_4-P/(g COD reduced) (standard deviation = 0.8 mg/g).

Reduction of the added amount of NH_4-N resulted in a reduction of the COD removal. When the addition of NH_4-N was returned to the initial setting, the COD reduction reverted. It was possible to operate the biological process with high COD reduction (80%) and an NH_4-N addition of only 55% of what was consumed in the reference reactor for the same organic load (around 20 kg COD/(m^3d)). The same effect could not be observed in the COD reduction when the added amount of PO_4-P was reduced. Although the amount of PO_4-P was reduced to 26% of what was consumed in the reference reactor, the COD reduction remained high (83%). However, the possibility to operate the biological system with low effluent concentrations of PO_4-P while maintaining a high reduction capacity was demonstrated.

Although the half-saturation coefficients for ammonium and phosphate could not be determined exactly, the experiments indicate that the half-saturation constant for NH_4-N is not higher than 0.1 mg NH_4-N/l and the half-saturation constant for orthophosphate is not larger than 0.05 mg PO_4-P/l. The established C:N:P ratios for the different systems are also reasonable.

Acknowledgements

The project is financially supported by the European Commission, Research DG, FP5 Programme on Energy, Environment and Sustainable Development under contract number EVK1-CT-2000-00068, CLOSEDCYCLE. The authors are solely responsible for the content herein and this does not represent the opinion of the Commission.

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