NITROGEN REMOVAL IN FIXED-BED SUBMERGED BIOFILTERS WITHOUT BACKWASHING

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ABSTRACT

The paper reports the findings of four years of pilot-scale research on nitrogen removal in fixed-bed biofilters fed on real raw municipal wastewater. The plant was made of two fixed-bed biofilm reactors in series with an intermediate settling tank from which excess biomass from the first stage was discharged. The first filter was used for carbon removal either with oxygen or nitrates. The second filter was used for nitrification. The average nitrification rate at 20°C was 0.84 gNH_4^+-N $m^{-2}d^{-1}$ with 5 mg l^{-1} dissolved oxygen in the bulk liquid. Temperature dependence was calculated ($r_n = r_{n,20°} \, 1.05^{T-20}$). The influent organic load strongly affected ammonia oxidation. If the organic loading exceeded 2.5 gCOD m^{-2} d^{-1} nitrification rate was reduced by 50%. Denitrification was performed by recycling nitrates back from the second filter and by using sewage itself as carbon source. Denitrification rate showed to be strongly dependent on temperature ($r_d = r_{d,20°} \, 1.11^{T-20}$) and on the recycle rate. Hydrolysis of the colloidal COD fraction showed a similar dependence on both temperature and recycle rate. Therefore, it has been concluded that the hydrolysis of finely dispersed COD particles can be the limiting step of denitrification in the biofilter when real sewage is used as carbon source. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Biofilm processes; nitrogen removal; nitrification; denitrification; hydrolysis.

INTRODUCTION

The main objective of the research has been the operational testing of a biofilm process for the biological removal of COD and nitrogen from urban wastewater with reactors that do not require periodical backwashing. The aim of the research was to develop a reliable and robust process which could be easily operated and to provide sound design figures and consistent relationships. The research programme started in 1993 and intermediate results are reported elsewhere (Canziani *et al.*, 1994a, b; Vismara *et al.*, 1996).

METHODS

The pilot plant

The plant used in the experimentation has been fed on real raw sewage (1 to 3 m^3 h^{-1}) coming from a wide mixed urban and industrial area in Northern Italy (100'000 PE) served by a combined sewer system. The plant was made of two fixed-bed biofilm reactors in series with an intermediate settling tank from which excess biomass from the first stage was discharged (Fig. 1). The biofilters were filled with loose Flocor®-

type PVC carriers with specific surface from 140 to 230 m^{-1} in reactor 1 and from 230 to 400 m^{-1} in reactor 2. Operation of the pilot plant started in March 1993 and ended in July 1997. This paper will report the results obtained after December 1995 and the final conclusions of the whole research programme.
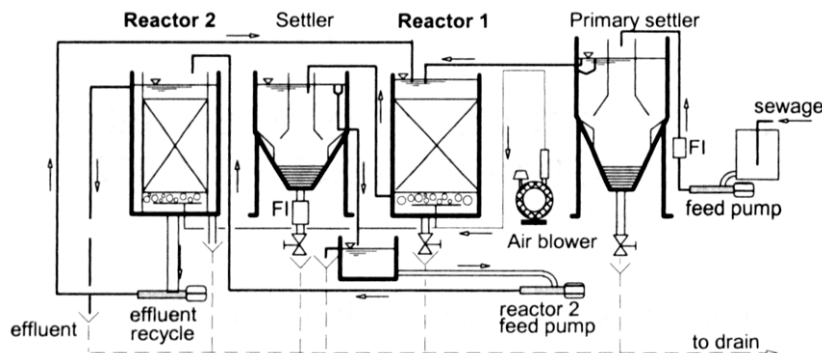

Figure 1. Schematics of the pilot-plant used in the experimental programme.

Sampling and analyses

Monitoring of flow-rates, temperatures, dissolved oxygen concentration and pH were performed three to five times a week. Grab samples were taken between 7:30 and 11:00 a.m., when daily peak concentrations occurred. Suspended solids, total COD (TCOD), 0.45-μm-filtered COD, NH_4^+-N, and NO_3^--N were analysed twice a week on the influent and effluent from both reactors. Analyses of volatile suspended solids and NO_2^--N were performed twice a month. Table 1 shows the characteristics of the influent.

Table 1. Characteristics of the wastewater used in the experimental runs (n = number of samples)

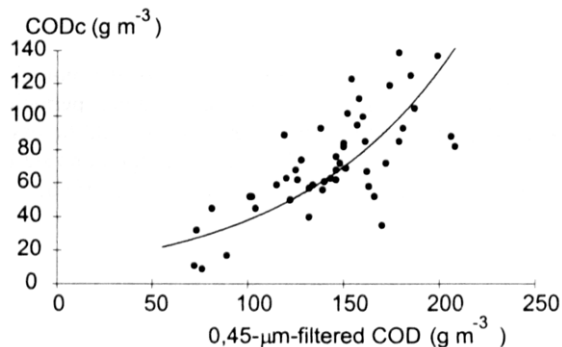| Parameter	Years								
	1994			1995			10/3/96 - 9/5/97		
	Average	St. dev.	n	Average	St. dev.	n	Average	St. dev.	n
SST	140	149	59	570	929	67	377	726	167
Total COD (TCOD)	253	117	58	740	1050	66	586	948	165
0.45-μm-filtered COD	135	49	49	135	46	64	140	45	166
TKN	27.2	9.7	61	26.6	7.1	77	32	9.9	169
NH_4^+-N	24.0	8.5	61	23.6	6.3	77	28	8.8	169

Figure 2. Trend of colloidal COD (CODc) vs. 0,45µm-filtered COD in the influent wastewater.

High suspended solid concentration in the influent wastewater since 1995 was due to excess sludge recycle upstream of the point where sewage was taken for feeding the pilot plant.

Table 2. Influent filtered and colloidal COD fractions of samples with TCOD < 500 g m^{-3} (i.e. not affected by excess sludge recycle)

COD fraction	% of Total COD	n
0.45-μm filtered	34 ± 10%	49
Soluble	25 ± 8%	46

Soluble and colloidal COD (CODs, CODc) for the evaluation of hydrolysis efficiencies were determined with the following procedure: in a 100 ml stirred sample the pH is raised up to 10.5 by adding NaOH (6M);

then, 1ml of a 100 g l^{-1} ZnSO$_4$ solution is added; after stirring for two minutes, the solution is filtered through a 0.45 μm pore-size membrane. COD of the 0.45-μm-filtered liquor was assumed to be the "soluble" COD fraction (CODs), while the "colloidal" COD fraction was defined as the difference between 0.45μm-filtered COD and CODs. In Figure 2 the trend of colloidal COD vs. 0.45μm-filtered COD is shown, while Table 2 shows the percentage of the filtered and soluble COD fraction.

The weight of fixed biomass was determined by removing the biofilm from 20 support media each time and oven drying at 105°C.

RESULTS

Nitrification

Profile samples in reactor "2" showed no concentration gradients, due to intense aeration (45 to 55 m h^{-1}). Therefore, a "complete mix" hydrodynamic model could be assumed. Nitrification rates never exceeded 1.45 gNH$_4^+$-N $m^{-2}d^{-1}$ at summer temperatures (around 25°C) and never fell below 0.4 gNH$_4^+$-N $m^{-2}d^{-1}$ at 12°C (with average values of 0.6 gNH$_4^+$-N $m^{-2}d^{-1}$). The average value at 20°C was 0.84 gNH$_4^+$-N $m^{-2}d^{-1}$ with 5 mg l^{-1} dissolved oxygen in the bulk liquid.
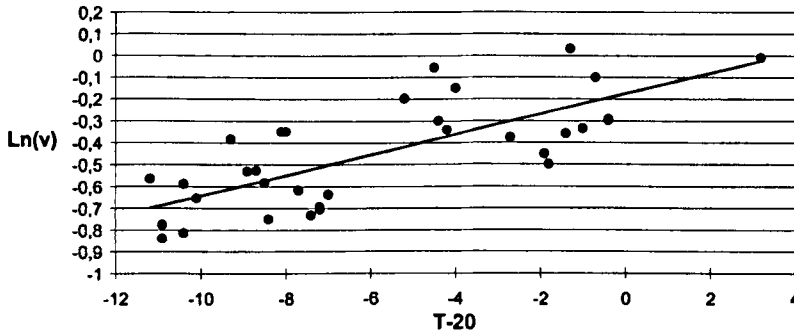

Figure 3. Nitrification rates (ln values) vs. Temperature (T-20°C values). Ammonia limiting conditions have been considered, i.e. dissolved oxygen to effluent NH$_4^+$-N ratio > 3 (Harremoës et al., 1982); rainy periods have not been considered.

Dependence of nitrification rates on temperature was calculated from data plotted in Figure 3, obtaining the following relationship: $r_n = r_{n\ 20°}\cdot1.05^{T-20}$. A statistical analysis of variance showed a 1% significance level. Dissolved oxygen concentration was in the range 5 ± 1.1 g m^{-3}, while the organic loading rate was in the range 2.5 ± 1.2 gCOD$\cdot m^{-2}\cdot d^{-1}$. Ammonia limiting conditions were chosen since they are typical of completely mixed reactors with low effluent ammonia concentrations.
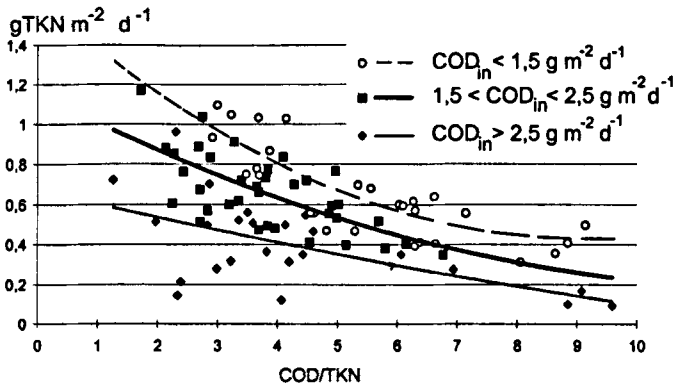

Figure 4. Nitrification rates at 20°C vs. influent COD/TKN ratio, at different influent COD loading rates.
Lines show the average trends of the corresponding points.

It is well known that the organic load strongly affects biological ammonia oxidation (e.g.: Boller *et al.*, 1994). In this experimental programme, it has been observed that maximum nitrification rates are 40 to 60% lower when the organic loading rate exceeds 2.5 gCOD m^{-2} d^{-1} (Figure 4).

Exceptionally high peaks of suspended solids in the effluent were experienced in spring and biomass in the reactor decreased from about 13-14 gSS m^{-2} down to 3-4 gSS m^{-2} (Figure 5). Nitrification rates reduced accordingly, in spite of rising temperatures (Figure 6). First investigations revealed the presence of worms (mainly nematodes) and rotifers: these may have weakened the structure of the biofilm which could be ablated by air bubbles and flushed away with the effluent. Also, predator species may have exerted their action on the nitrifying biofilm, as it has been observed by others (Lee Natuscka *et al.*, 1994). Parker *et al.* (1989) showed that periodical washing in trickling filters may control their growth. Further research is in progress on this aspect.
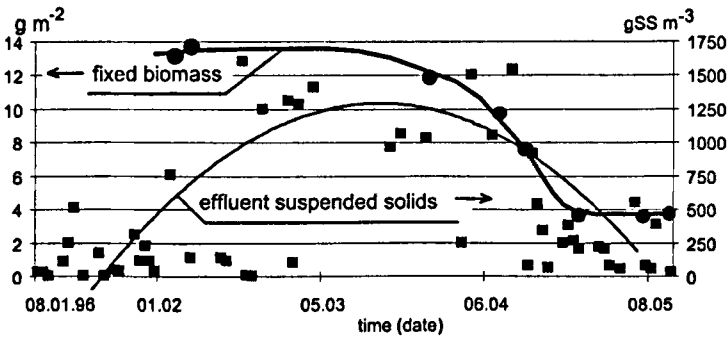

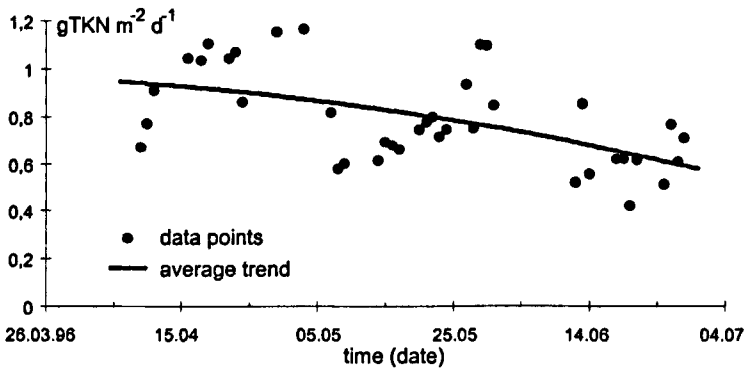Figure 5. Fixed solids on supports (gSS m^{-2}) and effluent suspended solids (gSS m^{-3}).

Figure 6. Decreasing nitrification rates due to loss of biological solids.

Hydrolysis of particulate organic matter

Previous investigations have suggested that extracellular enzymes have to be released by the biofilm in order to hydrolyse the particulate organic matter (Larsen *et al.*, 1994; Hu *et al.*, 1996). Subsequent research (Janning *et al.*, 1997; Janning *et al.*, 1998) has shown that the hydrolysis process occurs as the only process with wastewater particulates and that only 10% of the particles accumulated on the biofilm was effectively hydrolysed in 12-hour long experiments. It may be inferred that only the smallest fraction of the organic particulates can actually be hydrolysed within the reactor at usual hydraulic retention times adopted in full scale plants, that is, the colloidal COD fraction. The degree of hydrolysis (DH) of the particulate organic matter can be expressed as follows (Larsen *et al.*, 1994):

$$DH = \frac{1}{1 + b^{-1}\dfrac{Q^2}{AV}} \tag{1}$$

where b^{-1} is a biological parameter accounting for enzyme production and the rate of the hydrolysis process, Q is the flow rate through the reactor, A is the biofilm surface and V is the water volume in the reactor. If Q^2/AV is constant, DH should depend on b^{-1} only, which, in turn, should depend on temperature, as other biological parameters. Therefore, equation 1 can be written as:

$$DH = \frac{1}{1 + \dfrac{b_{20}^{-1}}{\theta^{T-20}}\dfrac{Q^2}{AV}} \tag{2}$$

Processing the experimental data of colloidal COD has lead to a value of $b^{-1} = 0.22$ d^2 m^{-1} and $\theta = 1.11$ (Figures 7 and 8). Experimental data are rather dispersed, due to the extremely variable substrate composition of settled sewage and to the approximation of the very simple experimental method used for the classification of particles as colloidal or soluble. A statistical analysis of variance showed a 5% significance level and the analysis of the residuals showed an equal scattering around zero.
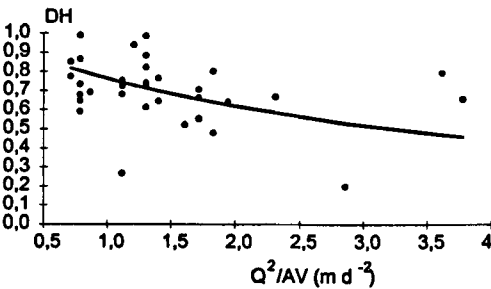

Figure 7. Dependence of the degree of hydrolysis on the combined hydraulic loading (Q^2/AV).
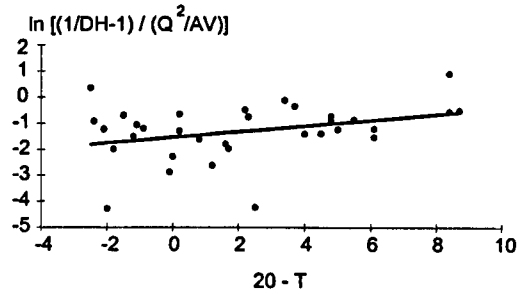

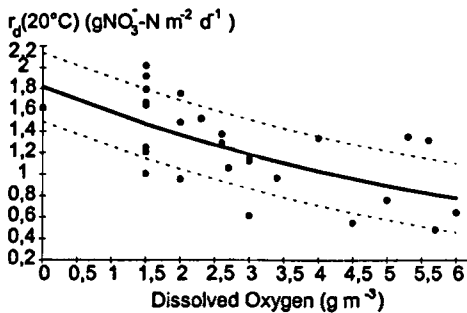Figure 8. Regression of the degree of hydrolysis vs. temperature.

Figure 9. Denitrification rates at 20°C vs. dissolved oxygen concentration in reactor "1". Dotted lines are the 20th and the 80th percentile.
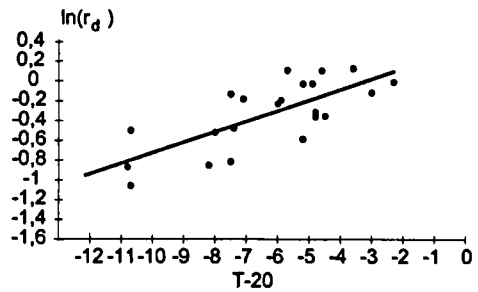

Figure 10. Denitrification rate (ln values) vs. temperature (T-20°C values).

Denitrification

According to the theory of substrate diffusion and reaction in biofilm and to previous experiences (Hagedorn-Olsen et al., 1994), denitrification occurred even at relatively high concentration of dissolved oxygen in the bulk liquid and the following relationship was worked out from the experimental data (Fig. 9): $r_d(20°C) = 1.82 \cdot e^{(-0.14 \, DO)}$, where r_d is the superficial rate (in gNO_3-N m^{-2} d^{-1}) and DO is the concentration of

dissolved oxygen in the bulk liquid (in mg l^{-1}). Opposite to nitrification, denitrification rates were strongly affected by temperature ($r_d = r_{d,20°} 1.11^{T-20}$; Figure 10).

In Table 3 data used for the elaboration of Figure 9 are reported.

Table 3. Average and standard deviation of data used in Figure 9

Parameter	Avg. ± St. dev.	Unit
no. of data (n)	28	
influent NO_3-N loading rate	1.10 ± 0.44	$gN\ m^{-2}\ d^{-1}$
effluent NO_3-N concentration	3.2 ± 1.5	$GN\ m^{-3}$
influent filtered COD loading rate	1.64 ± 0.42	$kg\ COD\ m^{-3}\ d^{-1}$

Data used for the elaboration of Figure 10 are different, since only data with similar oxygen concentration were used, in order to account for temperature dependency only.

Table 3. Average and standard deviation of data used in Figure 10

Parameter	Avg. ± St. dev.	Unit
no. of data (n)	22	
influent NO_3-N loading rate	1.19 ± 0.44	$gN\ m^{-2}\ d^{-1}$
effluent NO_3-N concentration	3.05 ± 1.71	$gN\ m^{-3}$
influent filtered COD loading rate	1.62 ± 0.38	$kg\ COD\ m^{-3}\ d^{-1}$
dissolved oxygen concentration	2.15 ± 0.97	$g\ O_2\ m^{-3}$

In experiments carried in a dynamic sand-bed filter fed on methanol and acetate, reported elsewhere (Canziani and Bonomo, 1998), the dependence of denitrification rates on temperature was much less pronounced ($r_d = r_{d,20°} 1.05^{T-20}$). Since 1.11 was the same factor found for the hydrolysis process, it has been thought that hydrolysis of non soluble organic matter was the limiting step of the denitrification process. If this was true, a clear dependency of denitrification kinetics on the hydraulic combined loading (Q^2/AV) should also be observed. Figure 11 seems to support this hypothesis.
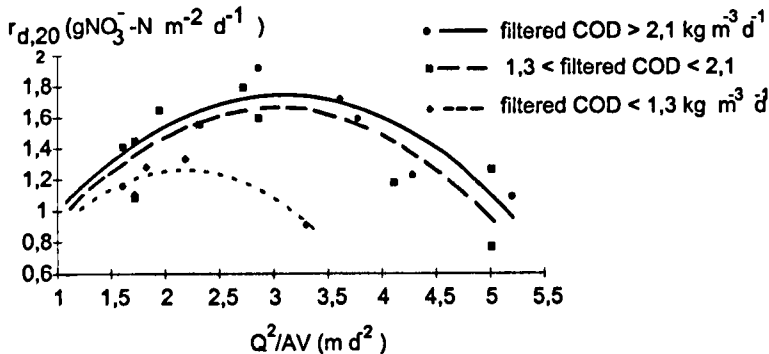

Figure 11. High flow rates in the first reactor cause a decrease in the denitrification efficiency, mainly due to insufficient hydrolysis of non-soluble degradable organic matter.

In Table 5 data used for the elaboration of Figure 11 are reported.

Table 5. Average and standard deviation of data used in Figure 11

Parameter	Avg. ± St. dev.	Unit
no. of data (n)	19	
influent NO_3-N loading rate	1.52 ± 0.46	$gN\ m^{-2}\ d^{-1}$
effluent NO_3-N concentration	3.97 ± 2.26	$gN\ m^{-3}$
dissolved oxygen	1.76 ± 0.41	$g\ O_2\ m^{-3}$

From Figure 11 it can also be observed that a higher $0.45\mu m$-filtered COD concentration corresponds with higher denitrification efficiency. Hydrolysis of colloidal organic substrate really looks essential in order to achieve acceptable denitrification rates even by using sewage organics as carbon source.

As the soluble fraction in the sewage is low (about 25% of total COD), it is very important to assure suitable conditions for hydrolysis of non directly diffusible organic matter and obtain better efficiency of denitrification.

Aeration should be provided in a denitrification reactor fed on sewage as carbon source for several reasons:

1) aeration keeps good mixing conditions in the reactors and favours substrate diffusion too;
2) aeration will also prevent excess COD loading rates being carried to the nitrification reactor;

If dissolved oxygen is kept around $1,5\ g\ m^{-3}$, experimental data may be statistically elaborated to give a link between the probability of not exceeding a defined value of the denitrification rate. Temperature constant 1,11 has been used to reduce all denitrification rates at 12°C, since above this temperature nitrogen removal is required by Directive 271/91/EEC in sensitive areas (Table 6).

Table 6. Denitrification rates ($gN\ m^{-2}\ d^{-1}$) at 12°C and 1.5 $gO_2\ m^{-3}$ and corresponding probability (elaboration on 22 experimental data)

Probability that denitrification rates are < r_d	r_d at 12°C and 1,5 $gO_2\ m^{-3}$ ($gN\ m^{-2}\ d^{-1}$)
50%	0.65
20%	0.54
10%	0.48
5%	0.45

Sludge settleability

The excess sludge from the secondary settler was always very good (SVI = 57 ± 14 ml g^{-1}) and this allows a design hydraulic retention time lower than one hour. Solids from the nitrifying reactor were very heavy and settled in less than 15 minutes. Before and after "worm bloom" observed during springtime, solids never exceeded $30\ g\ m^{-3}$. In general a final sedimentation, after the nitrifying biofilter, could be avoided and effectively replaced by microstrainers or rapid filtration.

CONCLUSIONS

The proposed process could be applied to real scale and design parameters have been evaluated. The average nitrification rate at 20°C was 0.84 gNH_4^+-N $m^{-2}d^{-1}$ with 5 mg l^{-1} dissolved oxygen in the bulk liquid. Temperature dependence was calculated ($r_n = r_{n,20°}\ 1.05^{T-20}$). The influent organic load strongly affected ammonia oxidation. If the organic loading exceeded 2.5 $gCOD\ m^{-2}\ d^{-1}$ nitrification rate was reduced by 50%. Yet, the development of an excessive predation activity and other disturbs related to spring blooms of

organisms such as worms and rotifers on the nitrifying biofilm are not fully understood. Further research is required in order to prevent excessive biomass losses.

Influence of temperature and dissolved oxygen on denitrification rates was also determined, giving the following expressions: $r_d = r_{d,20°} \, 1.11^{T-20}$ and $r_{d,20°} = 1.82 \cdot e^{(-0.14 \, DO)}$.

When denitrification is performed exploiting sewage organic matter as the carbon source, it is necessary to assure a good degree of hydrolysis of the particulate organic matter. The design must take into account the proportion between soluble and particulate degradable organic matter as a key factor for the entire nitrogen removal process. Low degree of hydrolysis led to poor dissolution efficiency and most of the particulate organic matter leaves the reactor without having being degraded. This may lead to an organic overload in the subsequent nitrifying reactor and to low nitrification efficiency.

The combined hydraulic loading Q^2/AV appeared to be a valuable tool in order to evaluate the optimum recycle rate. It should not exceed 3 $m \cdot d^{-2}$ in order to hydrolyse a significant portion of colloidal COD and yield enough soluble substrate for nitrate removal. It seems reasonable to keep the ratio of 0.45μm-filtered COD to NO_3-N loading rates between 5 and 7, as long as dissolved oxygen is kept below 2 $g \, m^{-3}$.

The excellent settleability of the cast-off biomass permits us to obtain low concentrations of suspended solids in the effluent, avoiding the typical phenomenon of bulking of an active sludge system, in presence of short hydraulic retention times. Yet, the secondary settler has to treat the influent flow as the recycled one: if nitrogen concentration in the sewage is high, recycling ratio increases so that the volume of the intermediate settler may become bigger than the secondary one of a suspended biomass plant.

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