THERMAL HYDROLYSATE AS A CARBON SOURCE FOR DENITRIFICATION

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ABSTRACT

Thermal hydrolysate is the liquid fraction (supernatant) of thermally treated wastewater sludge. The objective of the present study was to investigate the quality of thermal hydrolysate as a carbon source for denitrification. Steady state denitrification experiments in moving bed biofilm reactors are carried out. It was demonstrated that 2/3 of the COD in the thermal hydrolysate was utilised as a carbon source in the post denitrification step, with a retention time of 52 minutes. This degree of utilisation is about the same as reported for biological hydrolysate, which generally has been considered to be of better quality as a carbon source than thermal hydrolysate. The yield of soluble COD in the thermal hydrolysis process (180 °C in 30 minutes) was found to be 28%. Typical COD-yields for biological hydrolysis are around 11%.

KEYWORDS

Carbon source; denitrification; moving bed biofilm reactor; nitrogen removal; thermal hydrolysis.

INTRODUCTION

As a consequence of the North Sea- and the Baltic Sea Treaties as well as the Wastewater Directive of the European Union, several large wastewater treatment plants discharging to sensitive receiving waters, have to include nutrient removal. In most cases a combination of biological and chemical processes is chosen. Phosphate removal by chemical precipitation is mostly used since the efficiency of this process is little influenced by changing characteristics of the incoming wastewater and the efficiency with respect to phosphate removal is high.

Biological nutrient removal, on the other hand, is very dependent upon the characteristics of the raw water, in particular the content of organic matter to the content of nutrients. Very often the content of readily biodegradable organic matter available as carbon source in the raw water, is the limiting factor for the biological nutrient removal process. In many Scandinavian situations, a typical fractionation of the raw water COD is as shown in table 1. In a situation as the one presented in Table 1, it may be more favourable both from an economical as well as an ecological point of view to use a process based on pre-precipitation and post-denitrification, or a combination of pre- and post-denitrification (Ødegaard and Karlsson, 1994; Andersson et al., 1992).
<table>
<thead>
<tr>
<th>Fraction of total COD</th>
<th>%</th>
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<tbody>
<tr>
<td>Soluble, readily biodegradable</td>
<td>10-15</td>
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<tr>
<td>Soluble, slowly biodegradable</td>
<td>15-20</td>
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<tr>
<td>Soluble inert</td>
<td>10-15</td>
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<tr>
<td>Particulate, slowly biodegradable</td>
<td>25-30</td>
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<tr>
<td>Biomass</td>
<td>10-15</td>
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<tr>
<td>Particulate inert</td>
<td>10-20</td>
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In post-denitrification processes a carbon source has to be added. The main disadvantage by the use of an external carbon source (methanol, ethanol etc.) is the extra cost of the chemical, but some extra sludge is produced as well.

An alternative to the addition of an external carbon source, is the addition of an internal one, made from the sludge. The organic matter of the sludge is, however, primarily on a slowly biodegradable form. Biological, thermal or chemical hydrolysis of the sludge may result in solubilization of particulate organic matter that may then be utilised as carbon source.

**THE INVESTIGATED PROCESS**

The basis for the experiments performed in this investigation, is a process (figure 1) described by Ødegaard (1992a). In this process pre-precipitation is used in front of a biological nitrogen removal process based on a combination of pre- and post-denitrification in moving bed biofilm reactors. Carbon source for the post denitrification step is made available by hydrolysis of the sludge produced. The idea is that the particulate organic matter, which in a traditional pre-denitrification step would have to be enzymatically hydrolysed, can be more efficiently hydrolysed in a concentrated sidestream and used in a post-denitrification step. The overall result is that both the nitrification and the denitrification step will be more efficient and compact.

The soluble organics, that are not removed in the pre-precipitation step, contains the most readily biodegradable organic matter from the raw wastewater. This fraction can be utilised positively by having a small pre-denitrification step and a corresponding small recirculation flow of nitrified wastewater, removing some nitrate efficiently. The main part of the denitrification is, however, carried out in a post denitrification step with hydrolysate as the carbon source. An additional effect of the pre-denitrification step is that the organic load on the aerobic step is reduced even further than with pre-precipitation as the only preceding step.

The present investigation is a follow-up of the Scandinavian EUREKA-project HYPRO (Henze and Harremoës, 1990), in which the use of hydrolysed sludge as a carbon source for denitrification was investigated. The objective of the study presented in this paper, was to investigate the quality of thermal hydrolysate as carbon source in a high rate biofilm denitrification process.
Pre-precipitation Moving bed biofilm reactors Post-precipitation

Coagulant Polymer

Recirculation, $r = 0.25 Q_{\text{inn}}$

Coagulant

Sludge

Thickener Hydrolysis Hydrolysate

Fig. 1. The NTH-process for nutrient removal (Ødegaard, 1992a).

Thermal conditioning of sludge is a well known process, and in the 60'es and 70'es quite a few wastewater treatment plants used thermal treatment of the sludge. The method gained only limited popularity, however, mainly due to the high organic content of the supernatant, that resulted in a high internal load on the treatment plant. In the proposed process (figure 1) this carbon rich supernatant is considered positive, as a potential carbon source for denitrification.

Thermal hydrolysis (treatment) involves heating of the sludge, usually to a temperature in the range of 150 °C to 200 °C. The pressure adjoining these temperatures are in the range of 6 bar to 25 bar. The yield of organic matter defined as COD$_F$ (sample filtered through a ≈ 1 µm filter) of the supernatant divided by the total COD of the sludge before treatment, is quite linear between these temperatures. At 150 °C the yield will be in the range of 15 to 20 %, while at 200 °C the yield will be around 30% (Barlindhaug, 1995). With biological hydrolysis yields around 11% are obtained (Æsøy and Ødegaard, 1994).

Experiments carried out with biological hydrolysate as carbon source, showed that practically only the volatile fatty acids were utilised for denitrification. The volatile fatty acids constituted around 2/3 of the organic matter in biological hydrolysate (Æsøy and Ødegaard, 1994). It should be noted that the sludge used in these experiments with biological hydrolysate, was from the exact same treatment plant as for the present study. The sludge consisted of about 70% chemical sludge (FeCl$_3$) and 30% biological sludge.

Considering the fact that thermal hydrolysate has a considerably lower fraction of volatile fatty acids than biological hydrolysate, one of the important issues for investigation in this study was whether or not any organic fractions other than volatile fatty acids were utilised.

Thermal hydrolysis can not be considered solely as a method for producing a carbon source. Excellent dewatering properties are obtained, the sludge is hygienised, and a substantial reduction in the sludge production is obtained when comparing to a situation with addition of an external carbon source. The sludge may also be considered as stabilised since most of the easily biodegradable organic matter is removed with the hydrolysate in the dewatering step.
THE PILOT PLANT

The pilot plant configuration was based on the principles of the NTH-process (figure 1). The biological step included one anoxic pre-denitrification reactor (T1), three nitrification reactors (T2-T4), two post-denitrification reactors (T5 and T6), and one final aerobic reactor with only half the volume of the other reactors (T7), in order to remove excess carbon source and increase the effluent oxygen concentration.

The reactors used are so called moving bed biofilm reactors developed in Norway over the last few years (Ødegaard et al., 1994). The biofilm carrier elements are shaped like small cylinders (about 10 mm in diameter and in height), with a cross inside the cylinder and longitudinal fins on the outside. The carrier elements are made of polyethylene with a density of 0.95 g/cm³. Aerobic reactors are stirred by aeration while the anoxic reactors are stirred mechanically.

In the last (T4) nitrification reactor the oxygen concentration is kept low (O₂-concentration of approximately 2 mg/l) in order to minimise the amount of oxygen entering the pre- and post-denitrification steps. In this reactor, the ammonium concentration is designed to be so low that the nitrification rate is not limited by oxygen.

The flow through the pilot plant (Q) was approximately 1 m³/d resulting in a combined hydraulic retention time for the two post-denitrification reactors of about 50 minutes. The total hydraulic retention time for the biological part of the pilot plant was 2 hours and 40 minutes. The recirculation flow to the pre-denitrification step was 20-30 % of the incoming flow (Q).

The pre-precipitation step consisted of coagulant addition, followed by pipe flocculation and separation in an upflow sludge blanket reactor. A prepolymerized aluminium coagulant (PAX 14) was used as the main coagulant while an anionic polymer (Praestol 2540) was added as flocculation aid.

The wastewater originates from a nearby apartment building complex. The highest NO₃-Nequiv. loads in figure 3 and 4 (>900 g/m³·d), is caused by extra addition of nitrate in order to get data with high loads.

The pilot plant was run more or less continually for a year with thermal hydrolysate as carbon source. Periodically, different programs of analysis were run, resulting in 36 days with reliable steady state data.

THE HYDROLYSATE

The operating conditions for the thermal hydrolysis process was a temperature of 180 ºC and a retention time of 30 minutes. The heating and the cooling of the sludge gave an additional retention time at >100 ºC of approximately 40 minutes. The CODₚ yield of the hydrolysis was approximately 28%. On the average, only 6% of the total COD in the hydrolysate was particulate.

In one period MAP-precipitation was used for removing ammonium from the hydrolysate. The MAP precipitation functioned well, removing most of the ammonium without influencing the organic composition of the hydrolysate.

In another period the hydrolysate (supernatant after the thermal hydrolysis) was subject to controlled biological hydrolysis for 8 hours at 37 ºC in a biofilm reactor, before being used for denitrification. The biological hydrolysis caused the fraction of volatile fatty acids to increase while the fraction of carbohydrates and proteins (nitrogenous organics) decreased.

Variations in the procedure for collecting and hydrolysing sludge, gave varying storage times for the sludge before thermal hydrolysis was carried out, in the range of 1 to 4 days (at approx. 16 ºC). This resulted in different degrees of spontaneous biological hydrolysis before the thermal hydrolysis. The longest storage
times had approximately the same effect on the composition of the thermal hydrolysate as the controlled biological hydrolysis described in the paragraph above.

In table 2 a typical fractionation of the organic content of thermal hydrolysate produced at a temperature of 180 °C is given. The sum of the three organic fractions in table 2 was not always equal the CODF measurements. Hydrolysates high on volatile fatty acids and low on proteins and carbohydrates tended to have some CODF unaccounted for, while hydrolysates with a low fraction of volatile fatty acids tended to be somewhat overestimated, indicating an overestimation of proteins and/or carbohydrates.

| TABLE 2 | ORGANIC CONTENT OF THERMAL HYDROLYSATE PRODUCED AT A TEMPERATURE OF 180 °C |
|---------|----------------------|-----------------|------------------|------------------|
| % of CODF | Volatile fatty acids | Proteins | Carbohydrates | Unknown |
|          | 20-40 %              | 30-60 %    | 10-25 %        | ++10-20 %        |

For a period of three experimental days, the hydrolysate was produced under different conditions from those described above. The temperature was lowered to 160 °C, acid (H₂SO₄) was added to reach a pH of 2, and oxygen (equivalent to 10% of the sludge COD) was added. The CODF yield in this situation was approximately 26%. The composition of the hydrolysate also changed so that only 15% of the CODF was found as volatile fatty acids, 70% was found as proteins, while approximately 20 % was found as carbohydrates.

There seemed to be a linear relationship between the concentration of volatile fatty acids and ammonium in the hydrolysate. For thermal hydrolysate the relationship between the two components was [CODVFA] = 11,0/[NH₄-N], while the corresponding factor for biological hydrolysate was found to be 7,2 (Æsøy, 1993). This indicates that, compared to biological hydrolysate, a larger fraction of the volatile fatty acids in thermal hydrolysate is produced from other constituents than proteins.

RESULTS FROM THE PILOT EXPERIMENTS

The results presented here are only some of the main conclusions from the present study. More detailed information will be found in Barlindhaug (1995).

Consumption of hydrolysate

The experiments showed that the differences in composition of the hydrolysates, seen in table 2, did not affect the amount of hydrolysate utilised in the denitrification. It may be assumed that most of the proteins and carbohydrates have to be enzymatically hydrolysed before being able to diffuse into the biofilm, while volatile fatty acids are diffusible. When the utilisation is the same regardless of composition, it seems as if organic matter that has not been biologically hydrolysed in advance, will be so in the biofilm reactor.

Figure 3 shows the utilisation of the supplied hydrolysate for all available data. The figure demonstrates that most of the hydrolysate was utilised in the first denitrifying reactor. When only considering the data where CODF was not supplied in excess, 56% of the CODF was removed through the first denitrifying reactor, 67% through both DN-reactors, while 74% was removed altogether, including also the last aerated reactor.

Virtually all the volatile fatty acids was utilised, while the utilisation of carbohydrates was in the same range as the general CODF-removal. The utilisation of proteins was 50-60 % for the hydrolysates produced at 180 °C, while a larger utilisation was recorded for the hydrolysates produced at 160 °C, containing more proteins.
Fig. 2. COD\textsubscript{F} utilised in the first DN-reactor (T5), in both DN-reactors (T5 and T6) and all the last three reactors (T5, T6 and T7), versus COD\textsubscript{F} added as hydrolysate in reactor T5.

Most of the volatile fatty acids were utilised in the first denitrifying reactor, while the utilisation of proteins and carbohydrates were more equally distributed between the two denitrifying reactors. This means that at very short retention times, a high percentage of volatile fatty acids in the hydrolysate is desired.

**Removal of NO\textsubscript{3}-N equivalents**

When investigating the utilisation of carbon sources in denitrification, the characteristics of denitrification should be measured in terms of removed electron- or NO\textsubscript{3}-N equivalents. When using one of these two notions, influence on the results caused by the system dependent oxygen feed to the denitrification reactors is taken care of. In the present study NO\textsubscript{3}-N equivalents are calculated as follows:

\[
[\text{NO}_3^-\text{Nequiv.}] = [\text{NO}_3^-\text{N}] + 0,6[\text{NO}_2^-\text{N}] + 0,35[-\text{O}_2].
\]

Figure 3 shows the removal efficiency of NO\textsubscript{3}-N\textsubscript{equiv.} for all available data, as a function of the C/N-ratio (C/N-ratio = \(g \text{ COD}_{\text{F,added}}/g \text{ NO}_3^-\text{N}_{\text{equiv.inflow}}\)). 6,9 g COD\textsubscript{F} in the form of hydrolysate had to be added to remove 1 g of NO\textsubscript{3}-N\textsubscript{equiv.}. This C/N-ratio held together with 67% utilisation of the hydrolysate in the post denitrification step, gives an average production of biomass of approximately 0,38 g COD\textsubscript{biomass,produced}/g COD\textsubscript{F,utilised}. This biomass-yield was confirmed from both the production of particulate COD and the consumption of NH\textsubscript{4} in the denitrification reactors.

From figure 3 it seems as if the capacity of the denitrification reactors is exceeded at the highest nitrate loads, when hydrolysate is not added in excess. These data-points are, however, from a period with a rapid increase in the load. An alternative explanation could therefore be that the biomass had not yet reached a steady state situation.
The pilot plant was run with COD$_F$ and/or NO$_3$ limitation, so consequently the maximum denitrification rate was not obtained. However, the highest denitrification rates registered were higher than values earlier reported for the same type of reactor with methanol or acetate as the carbon source (Rusten et al., 1994 and 1995).

Figure 4 shows the combined denitrification rates for the two post-denitrification reactors. The data has not been compensated for changing temperatures due to the fact that most of the data are strongly limited by COD$_F$ or NO$_3$. The COD$_F$ limitation is seen by the horizontal lines indicating maximum NO$_3$-N$_{equiv.}$ removal for different hydrolysate loads. With a few exceptions (the same data-points as the ones deviating in figure 3), the data in figure 4 show that expected removal efficiencies are reached.

The highest DN-rate measured was 1400 g NO$_3$-N$_{equiv.}$ per m$^3$ reactor volume and day (g NO$_3$-N$_{equiv.}$/m$^3$·d). This DN-rate was reached at a concentration of 1,8 mg NO$_X$-N/l in the effluent from reactor T6, at a water temperature of 20 °C and a C/N-ratio of 8.

When considering reactor 5 separately the same day, the DN-rate was 2300 g NO$_3$-N$_{equiv.}$/m$^3$·d at an effluent concentration of 12,6 mg NO$_X$-l from reactor 5. For this particular day, denitrification in reactor 5 alone was not limited by neither the COD$_F$- nor the NO$_3$- concentration. When adjusting to a temperature of 15 °C, the rate is found to be 1700 g NO$_3$-N$_{equiv.}$/m$^3$·d (R$_{T2}$ = R$_{T1}$ · 1,059(T$_2$-T$_1$)).

On one day (indicated on figure 4) the biomass in the pilot plant was measured. The combined DN-rate for the two denitrification reactors calculated on the basis of biomass was 11,9 mg NO$_3$-N$_{equiv.}$/g VS·h, while the DN-rate found for reactor 5 alone was 15,9 mg NO$_3$-N$_{equiv.}$/g VS·h. The water temperature this particular day was 16 °C. In activated sludge systems, DN-rates as high as this can only be reached with ethanol as carbon source, while DN-rates with methanol is usually no higher than 5 mg NO$_3$-N$_{equiv.}$/g VS·h at this temperature (Andersson et al., 1995).

The amount of volatile solids (VS) in reactor 5 and 6 was 2,91 and 2,24 kg/m$^3$ only. This is quite close to common values for activated sludge, and shows that it is not necessarily the amount of biomass, but rather the viability of specialised biomass that is the advantage of biofilm reactors.
Fig. 4. Combined denitrification rates for reactor 5 and 6. The data are categorised after hydrolysate load.

\[(\text{g CODF-added/m}^3\text{d})\]

**THE LIMITATIONS AND POSSIBILITIES OF THE PROCESS.**

One of the drawbacks with the use of hydrolysed sludge as carbon source is that the hydrolysate in itself contains nitrogen in the form of ammonium and organic nitrogen. When used in a post-denitrification process, this nitrogen deteriorates the effluent quality to a certain extent if not removed. The nitrogen content of the hydrolysate can be reduced by removing ammonium through stripping or magnesium-ammonium-phosphate (MAP) precipitation.

The content of COD in the effluent will also increase when hydrolysate is used. This increase is, however, caused by heavily biodegradable COD that causes only minor oxygen demand in the receiving water.

The removal efficiency of Tot-N_{NF} (total nitrogen concentration of samples that has not been filtered) is a function of the nitrogen removed with the sludge (particulate and colloidal bound nitrogen) in the pre-precipitation step and the final sedimentation step, nitrogen added with the carbon source, and nitrogen denitrified in the pre- and post-denitrification step.

In order to estimate the achievable nitrogen removal for a process as the one analysed in this study (fig. 1.), mass balance calculations are carried out. The mass balances are based on the findings of this pilot plant investigation, and a raw wastewater with a total COD value of 350 mg/l is used. Other important assumptions is that the hydrolysis yield of COD_f and Tot-N is 28% and 85%, and that the removal efficiency in the pre-precipitation step is 70% for COD and 20% for Tot-N. The last two assumptions are common values for treatment plants with primary precipitation (Ødegaard, 1992b).

In figure 5 the nitrogen removal efficiencies calculated from the mass balances are given, versus the readily biodegradable COD in the raw wastewater that will not be removed during precipitation and consequently is available for the pre-denitrification step. Calculations are carried out for two different C/N-ratios in the raw waste water and for a situation with and without removal of ammonium from the hydrolysate. It is assumed that 45% of the Tot-N is removed from the hydrolysate when ammonium is removed (45% was the average NH_{4}-N/Tot-N ratio for the hydrolysates used in the present study). These calculations are marked (*).
The characteristics of the raw wastewater is very important for the nitrogen removal efficiency in the described process, as demonstrated in figure 5. The C/N-ratio and the distribution of COD (i.e. content of soluble, easily biodegradable COD as compared to particulate and colloidal COD) are the most important factors. To increase the nitrogen removal efficiencies, an external carbon source may be added to the post-denitrification step in addition to the hydrolysate produced from the sludge.

Another important factor is the control of oxygen inputs to the denitrification steps. If the denitrification reactors are supplied with more oxygen than necessary, more carbon source has to be supplied as well, in order to maintain the desired denitrification. When an external carbon sources like methanol is used, the consequences of using more carbon source than necessary are increased costs and increased sludge production. When hydrolysate is used as carbon source in post denitrification, the nitrogen supplied with the carbon source reduces the obtainable nitrogen removal as well. It is particularly important, therefore, to control the input of oxygen to the denitrification steps when hydrolysate is used.

CONCLUSIONS

Generally a carbon source made by biological hydrolysis of sludge is considered to be of better quality as carbon source than that made by thermal hydrolysis. This is true in the sense that the biodegradable fraction of biological hydrolysate consists of VFA only, hence a higher denitrification rate can be obtained than with the more complex thermal hydrolysate. Still the denitrification rates obtained with thermal hydrolysate in this investigation are high. The highest combined denitrification rate recorded for the two post-denitrification moving bed biofilm reactors was 1400 g NO₃-Nequiv. per m³ reactor volume and day. This denitrification rate was reached at a concentration of 1,8 mg NOX-N/l in the effluent from the last DN-reactor (T6), at a water temperature of 20 °C, and a C/N-ratio of 8. A denitrification rate at this level is higher than values reported for the same type of reactor with methanol or acetate as the carbon source (Rusten et al., 1994 and 1995)

It was earlier assumed that a considerable lower fraction of the thermal hydrolysate as compared to biological hydrolysate, would be utilised during denitrification. The results of this investigation show, however, that with a hydraulic retention time of 50 minutes in anoxic moving bed KMT-reactors, 2/3 of the added CODF was utilised. The same fraction was found for biological hydrolysate (Æsøy and Ødegaard, 1994).
Thermal hydrolysis at 180 °C has a CODF yield of around 28% with the type of sludge used for this study, while biological hydrolysis has a typical yield around 11% (Æsøy and Ødegaard, 1994). This makes thermal hydrolysis an interesting alternative.

A simplified mass balance show that the characteristics of the wastewater is important for the total nitrogen removal efficiency of the proposed process. With a favourable composition of the wastewater, high removal efficiencies of nitrogen can be obtained. With an unfavourable composition of the wastewater, an external carbon source can be used as a supplement to hydrolysate, to improve the removal efficiency.

When using an external carbon source like methanol, the consequences of using more carbon source than necessary, are increased costs and increased sludge production. When using hydrolysate as the carbon source in post denitrification, the nitrogen supplied with the carbon source reduces the obtainable nitrogen removal as well. It is therefore particularly important to control the input of oxygen to the denitrification steps when hydrolysate is used.

Thermal hydrolysis should not be considered solely as a method for producing a carbon source. Excellent dewatering properties are obtained, the sludge is hygienised, the sludge may be considered as stabilised, and a substantial reduction in the sludge production is obtained when compared to a situation with addition of an external carbon source.

REFERENCES


