VATTEN 63:139–143. Lund 2007

INHIBITION OF THE NITRIFICATION PROCESS OF ACTIVATED SLUDGE MICRO-ORGANISMS BY SCRUBBER WATER FROM AN INDUSTRIAL FLUE GAS CLEANING PROCESS

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Abstract

The microbial transformation of ammonia to nitrate, the nitrification, is a central process in the nitrogen biogeochemical cycle. In a modern wastewater treatment plant, the nitrification process is a key process in the removal of nitrogen and inhibitory compounds in sewage can seriously affect the nitrogen removal. A major sewage cleaning plant in the southern part of Denmark is a recipient of industrial sewage from a major fish meal industry. Severe nitrification inhibition was observed in scrubber water from an incineration of process air, and the processes that lead to the production were stopped. In order to investigate the relation between incineration temperatures and the production of inhibitory compounds, the process air was burned at temperatures from 800°C to 1000°C. The termically affected condensate was collected and the nitrification inhibition effect of the condensate was tested using active sludge from the municipal wastewater cleaning plant. The investigation showed that it is possible to reduce the nitrification inhibition effect considerably by raising the incineration temperature from 800°C to 850°C and in some cases to 900°C. The investigation also showed that a further rise in the temperature beyond 850°C and in some cases 900°C, is unnecessary.

Key words – Inhibition, nitrification, scrubber water, wastewater treatment

Introduction

Biological nitrification and denitrification are key processes in the removal of nitrogen in modern sewage cleaning plants. In sewage cleaning plants receiving both municipal and industrial discharges, the occurrence of toxic compounds in the industrial discharge can inhibit the removal of nitrogen (Grüttner et al., 1994). The first step in the overall nitrogen removal process, the nitrification, is the process that is most sensitive to inhibiting substances, due to the relatively low growth rate of the nitrificating bacteria compared with other main groups of bacteria active in the aerobic metabolic processes in the plant. A main design parameter for the aerobic tank is the volume. The aerobic volume must be sufficient to secure an adequate aerobic sludge age, and, hence a sufficient population of nitrifying bacteria. The required aerobic sludge age can be defined as the inverse value of the difference between the growth rate and the decay rate (Sindkjær et al., 1996).

Since the number of substances with a potential inhibitory effect on the nitrification process can be high in a complex industrial wastewater, and since toxic substances in a mixture may interact, inhibition tests using active sludge in monitoring the load of inhibitory substances in industrial discharges is a realistic way of assessing the potential nitrification inhibition in a sewage cleaning plant.

A classic example of solving one environmental problem and hereby creating a new one is the use of a wet scrubber to clean an industrial flue gas. The often chemically complex scrubber water from the cleaning of industrial flue gas is a result of the complexity of the flue gas cleaned, and if incineration of the flue gas is part of the cleaning process, incomplete combustion can result in added formation of nitrification inhibitors, such as hydrogen cyanide (Daigger and Sadick, 1998).

Scrubber water from the cleaning of sludge incineration flue gas was found to be an important internal inhibition at a major Danish sewage cleaning plant (Sindkjær et al., 1996).

The implementation of the Danish Action Plan on the Aquatic Environment has resulted in a general upgrading of the sewage cleaning in Denmark and the acceptance level of discharges via the outlets from municipal wastewater cleaning plants is low.
Since nitrogen removal can be regarded as a critical factor in the biological wastewater treatment, a focus on industrial wastewater as nitrification inhibitor is necessary in the management of modern biological waste water treatment plants.

The processing of fish into fish meal and oil at a major Danish Fish meal factory results in an associated production of approximately 1 m^3 of sewage per 1 ton of processed fish. A part of this sewage is scrubber water from thermal oxidation of the process air. Preliminary studies (Gram and Rasmussen, 2000) showed that the termically affected part of the scrubber water had a substantial nitrification inhibition effect.

Besides reducing the airborne emission of nitrogen oxides, trimethylamine (TMA) and ammonia as well as other air pollution elements, the oxidation process and the scrubbing process result in a significant reduction in smell. The process air is burned at a temperature of approx. 800°C, with a capacity of 240.000 m^3 per hour. The total amount of fish processed at the factory during the year 2001 was approx. 0.6 million tons, which equals 56 % of the total Danish industrial catch that year or 44 % of the total Danish catch of fish for consumption and industrial purposes in 2001.

Historically, air from the oxidation process has been scrubbed with water and parts of the condensate produced in the scrubber process has been lead, untreated, to the nearby marine recipient, the Ho Bay, which is a part of the Wadden Sea, and parts have been treated at Esbjerg municipal wastewater treatment plant. The plant has a capacity of treating 290.000 Person Equivalents (PE) with biological nitrogen removal in an activated sludge process.

As a consequence of the Danish Action Plan on the Aquatic Environment, the emission of untreated sewage to the Wadden Sea has ceased. In the future, it is planned that, after a pre-treatment at the factory, the sewage will be lead to a rebuilt municipal sewage cleaning plant with an added cleaning capacity.

The objective of this study has been to investigate the relation between process conditions, especially incineration temperatures, and the nitrification inhibition in scrubbed flue gas. Pilot incineration of process air from the fish meal production plant was carried out and the nitrification inhibition effect of the scrubber water was examined.

Materials and methods

Experimental setup

A schematic diagram of the experimental setup is illustrated in Figure 1. The system consisted of a thermal incinerator with a two-chamber heat regeneration system, a scrubber unit and a stripping column with the purpose of providing the incinerator with a homogeneous flow of polluted air representative of the process air of the fish meal factory. The stripping column and the scrubber were constructed to serve the present study while the pilot incinerator was a commercial type (Recco-Strom). The experimental setup was implemented in situ at the fish meal factory with the approximate dimensions: Height 8m, area covered by the setup 40m^2.

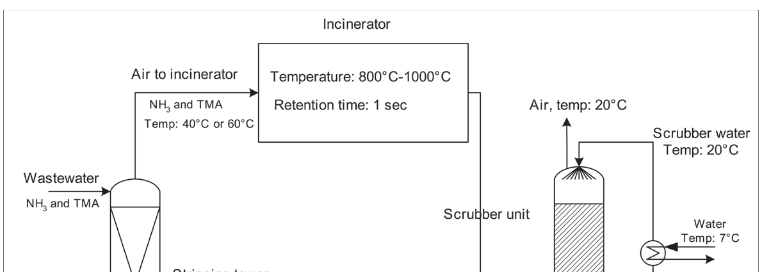

Figure 1. *Schematic diagram of the experimental setup.*

Stripping column

The column had a diameter of 0.4m, a height of 7.2m and a packing height of 5.36m (Mellapack 250Y). The stripping column provided a homogeneous flow of saturated process air to the incinerator. Main components of the process air were ammonia and trimethylamine and small amounts of other volatile amines. The stripping process was carried out with saturated air to ensure isothermal conditions. If dry air had been used, the air would have been saturated in the stripping column when it came into contact with the wastewater. Simultaneously, the wastewater would be cooled and experiments at constant temperatures would be impossible. During the experiments, the stripping temperature was chosen to be constant at either 40°C or 60°C. According to Henry's law a rise in temperature of approximately 20°C will double the ammonia concentration in the air to the incinerator. A stripping temperature of 60°C corresponds to the most polluted air at the fish meal factory. Two different temperatures were chosen in order to investigate possible influence of different ammonia and trimethylamine concentrations in the incoming air on the nitrification inhibition.

Incinerator

The incinerator consists of a cylindrical combustion chamber with a diameter of 0,5m, with two heat regeneration chambers, one at each end, filled with ceramic packings. The flow was reversed periodically during operation of the unit. The nominal flow rate was 250 Nm^3/h with a retention time of approximately 1 sec. Natural gas was used as fuel. During experiments the combustion temperature was varied between 800°C and 1000°C.

Scrubber unit

The scrubber unit has a max. capacity of 60 Nm^3/h, and, hence, only part of the incinerator flue gas was scrubbed in the unit. When used for sample preparation the unit was filled with 10 litres of tap water and operated for a period of 30 min. The gas flow rate was 30 Nm^3/h and the liquid rate was approximately 200 l/h. That means that the water was circulated about ten times and the 10 litres of water were in contact with 15 Nm^3 of incinerator flue gas. With the aid of the built-in heat exchanger the gas outlet temperature was maintained at 20°C. A total number of 41 samples were produced.

Inhibition test

Investigation of the nitrification inhibitory effect of the scrubber water from the pilot scrubbing unit was carried out, utilizing activated sludge from the municipal treatment plant that will be the recipient of scrubber water from the factory in the future.

The inhibition of the nitrification process by the activated sludge was carried out in 500 ml conical flasks on a magnetic stirrer to keep the sludge in suspension. The flasks were incubated in diffused light between 20°C and 25°C. Pasteur pipettes were used to ensure sufficient aeration; the concentration of dissolved oxygen was higher than 4 mg/l. To reduce evaporation of possible volatile compounds the test flasks were covered with foil. The activated sludge was used in tests no later than two hours after collection from the sewage treatment plant. Four to six concentrations without duplicates, one control and one reference inhibitor were included in each test setup.

The ISO standard method (ISO 9509, 1989) was used with only one modification. Instead of centrifuging the sludge a third of the sludge volume was decanted after 30 min. of precipitation to reach the approximate sludge concentration. The rates of nitrification in control flasks were between 2 and 6,5 mg N per g suspended solids per hour.

Nitrification rates were determined from the production of oxidized nitrogen-N after 4 hours.

Analytical methods

Ammonium content was determined by the Conway method, described by the Technical Laboratory of the Ministry of Fisheries, Denmark. (Fiskeriministeriets Forsøgslaboratorium, 1989), nitrate and nitrite concentrations were determined using FIA (Flow Injection Analysis) on a FIA Analyzer 5020 from Tecator.

In order to quantify the reduction of organic matter during the incineration process, Total Organic Carbon (TOC) was measured as ppm propane equivalents by using two Total Hydrocarbon Analyzers from Bernath Atomic (model 3006) before and after the incineration.

Results and discussion

The nitrification inhibition at different incineration temperatures is shown in table 1 and table 2. There are two sets of data, one with the temperature of the air to the incinerator at 40°C and one at 60°C. Incineration of natural gas at 800°C, 885°C and 940°C is used as a background inhibition reference. In no cases nitrification inhibition was registered in the scrubber water when only natural gas was incinerated.

With a stripping temperature of 40°C it is possible to reduce the nitrification inhibition effect considerably by increasing the incineration temperature from 800°C to

Table 1. *Nitrification inhibition of scrubber water with incoming air at 40°C.* Results indicated by > means that the highest concentration tested (400 ml/l) did not cause a 50 % nitrification inhibition.

Incineration temperature [°C]	Number of samples	Nitrification inhibition after 4h – EC50 [ml/l]
800	4	57–135
850	3	> 400
900	3	> 400
950	3	> 400
975	1	> 400
1000	2	> 400

Table 2. *Nitrification inhibition of scrubber water with incoming air at 60°C.* The result marked with * at an incineration temperature of 850°C indicates that the test concentration of 400 ml/l caused a 45 % nitrification inhibition.

Incineration temperature [°C]	Number of samples	Nitrification inhibition after 4h – EC50 [ml/l]
800	5	27–50
825	1	200
850	3	> 400*
900	6	> 400
950	3	> 400
1000	4	> 400

850°C. With a stripping temperature of 60°C an incineration temperature of 900°C was found necessary to reduce the nitrification inhibition to an equivalent level.

Figures 2 and 3 show the concentration response curves for two experiments from table 1 and table 2.

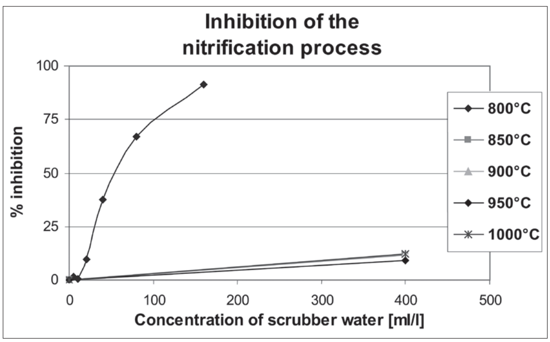

Figure 2. *Concentration response curve from a nitrification inhibition test with scrubber water from an incineration plant with incoming air at 40°C.*

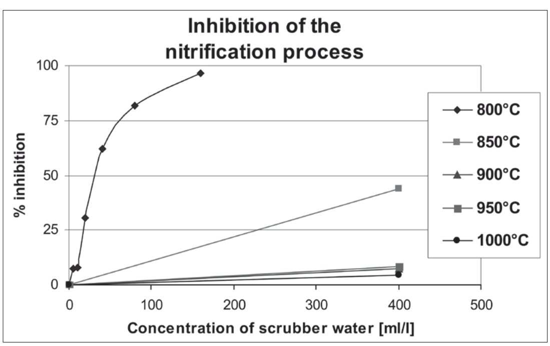

Figure 3. *Concentration response curve from a nitrification inhibition test with scrubber water from an incineration plant with incoming air at 60°C.*

Combustion efficiency

In selected experiments the amount of TOC (Total Organic Carbon) in the air before and after the incinerator was measured. As shown in figure 4 the incinerator caused at least a 95 % reduction of TOC (measured as ppm propane equivalents) in the incineration flue gas, independent of the incineration temperature.

Probable causes of the nitrification inhibition

In order to identify organic components responsible for nitrification inhibition a chemical screening (GC-MS and LC-MS) of the washing water from the production plant (800°C) and from the pilot plant run at different temperatures (800°C–1000 °C) was undertaken by the National Environmental Research Institute of Denmark. The chemical screenings did not reveal a single compound or group of compounds which could be the cause of the observed inhibition of nitrification. (DMU, 2003).

Conclusions

Pilot plant incineration of polluted air, representative of process air from a fish meal factory showed, that by raising the temperature from 800°C to 850°C, and in some cases to 900 °C, the severe nitrification inhibition effect by the scrubber water was reduced significantly from a level of inhibition close to 100 % to a level of inhibition of 10 % or less. With an inhibition effect close to 100 %, scrubber water would seriously affect the biological process, especially the nitrogen removal process in a receiving biological, municipal waste water plant. By significantly reducing inhibitory substances in the scrubber water, a final treatment of the waste water in a biological waste water plant is a possibility.

It has not been possible to identify a specific substance or group of substances which could be the cause of the observed nitrification inhibition. Since the number of

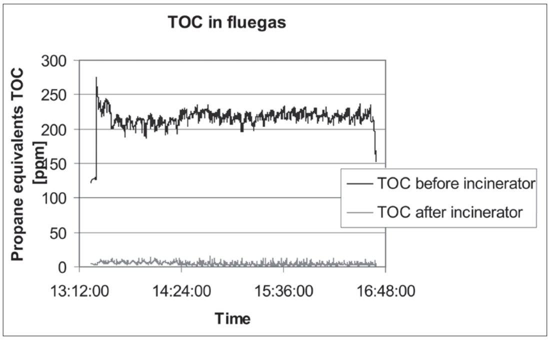

Figure 4. *The content of TOC in incinerator flue gas.*

substances with a potential inhibitory effect must be assumed to be high in the complex waste water produced during the incineration process, the possibility of identifying, with any certainty, specific substances causing the inhibition is limited. The interaction of toxic and inhibitory substances in a complex mixture could play a major role in the problems of assessing effects of specific substances.

Although the identification of specific inhibitory substances would be an asset and could be valuable in relation to adjusting processes in order to minimize toxic and inhibitory effects, the knowledge of the relation between incineration temperature and inhibitory effect of the scrubber water is useful in predicting temperatures that must be reached to prevent unacceptable inhibitory effects in the cleaning process. By knowing the sufficient temperature necessary to reduce the inhibitory effects to an acceptable level, the energy requirements for the incineration can be minimized.

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