Nitrogen removal in industrial wastewater by nitration and denitration – 3 years of experience

P. Degn Pedersen*, K. Jensen, P. Lyngsie** and N. Henrik Johansen***

* ENVICARE, Consulting Engineers, Skodshoej 16, DK9530 Stoevring, Denmark
(E-mail: *pdp@envicare.com*)

** CPKelco ApS, Pectin producing factory, Lille Skensved, Denmark

Abstract CPKelco ApS, Denmark is the largest pectin plant in the world and the second largest refined carrageenan plant. The products are used for texturising purposes, primarily within the food industry, but also within the pharmaceutical industry. The products are extracted from imported natural raw materials, like dried citrus peel and special seaweed plants. In the production processes a considerable amount of water and energy are used. The excess water from the production processes is led to CPKelco's own WWTP, which is one of the largest industrial WWTPs in Denmark.

In order to obtain higher process stability and lower energy consumption in the WWTP, CPKelco decided to change the nitrogen removal process from a conventional nitrification/denitrification process to a nitration/denitration process, which comprises an oxidation of ammonium to nitrite and a controlled reduction of nitrite to N_2. Theoretically this process will decrease the oxygen consumption for oxidation by 25% and the use of carbon source for the reduction will be decreased by 40% compared to the conventional process.

This paper presents and discusses the experiences and results from three year's continuous operation of the nitration/denitration process in an activated sludge plant, and the overall performance results are discussed in relation to the previous results. Accordingly the implementation of the nitration/denitration process was done successfully, and today the plant operates with much higher process stability than obtained before, and even the most stringent effluent requirements for nitrogen can be obtained.

Keywords Activated sludge; energy saving process; industrial wastewater treatment; nitration and denitration; process stability

Introduction

In accordance with the Danish Action Plan on the Aquatic Environment, 1987 the discharge of nitrogen should be considerably reduced. This resulted in fixed effluent requirements for municipal WWTPs, but for industrial WWTPs the requirements were related to the best obtainable effluent standards based on the best available technology.

Permission for discharge of wastewater from CPKelco including provisionally effluent requirements was given in 1989 by the authority of Roskilde County. The effluent standards in these requirements were never reached, and in 1996 a revision started and ended in 1999 with final requirements, which are based on maximum daily and yearly discharge of organic matter, nitrogen, phosphorus and suspended solids. Also, the discharges have to comply with guiding concentration requirements, see Table 1.

In August 1998, an action-plan for operation and process control of CPKelco's WWTP was initiated by a project group, consisting of CPKelco's own engineers and Envicare. The main objective was to optimise the plant operation in order to obtain higher process stability and to achieve the best possible effluent standards (in order to negotiate the guiding effluent requirements). This action plan has been running until December 2000 and a number of process initiatives have been carried out. This paper will discuss consequences and results of some of these initiatives.

Water Science and Technology **Vol 47 No 11 pp 181–188** © IWA Publishing 2003

Table 1 Guiding effluent requirements, influent concentrations and removal rates

Parameter	Guiding effluent r equirements mg/l	Actual average influent concentrations mg/l	Required removal rate
COD	500	8,100	93.8
BOD	30		
Total-N	45	1,600	97.2
Inorganic-N	6	1,400	99.6
Total-P	1,5	11	86.4
SS	50	800	93.8

The CPKelco WWTP

The excess water from the production processes is led to the WWTP and in Table 1; the wastewater characteristics of the influent are shown in concentrations. The flow to the plant is relatively stable, 140 m^3/h in average. Of the influent COD, about 90% is dissolved organic matter where off 30 – 40% is easily degradable carbohydrates, and 2–4% is volatile fatty acids, mainly acetate (>75%), lactate and formate (Dueholm, 2000).

The content of NO_x-N (NO_2 + NO_3-N) in the inlet is 800–1,000 mg NO_x-N/l. This is denitrified immediately in the first pre-denitrifying step. Figure 1 shows the schematic process flow sheet of the WWTP (see Figure 1). An external carbon source (additional easy degradable carbohydrates) can be added to the pre-denitrification step if necessary.

After the primary settler, the flow is divided into 2 lines: one is the by-pass line to the intermediate settler in front of the activated sludgeplant, the second line is an anaerobic pre-treatment, which takes place in 3 digesters. After digestion and settling in the lamella separator, this line is led to the intermediate settler as well.

All the pre-treated water is now led from the intermediate settler to an activated sludge plant, built up as a 2-step re-circulation plant. The activated sludge plant consists of two parallel lines in the first step (DN/N 1 A and B) and then 1 line in the post step (DN/N 2). Selected plant key data is shown in Table 2.

Plant investigations – problems

In the following the focus is on nitrogen removal in the activated sludge plant. The presented data covers a period from Jan 1996 to Dec 2001. The load data to the activated sludge plant is shown in Figure 2.

The flow and the ammonium load has been relatively stable during the period. It seems as the COD load has slightly decreased. Figure 3 shows the effluent concentrations during the same period.

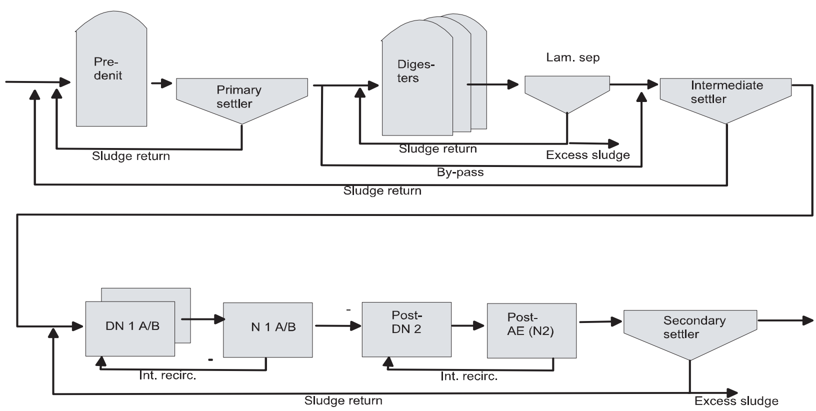

Figure 1 Schematic flow sheet of CPKelco WWTP principle

Table 2 Selected key data of CP Kelco WWTP

Load to the WWTP		
Flow, average m^3/d	3,400	
COD, average	kg/d	27,500
Tot-N, average	kg/d	5,400
Inlet temperature	°C	30–32
Anoxic pre-treatment		
1 – Anoxic tank	m^3	1,500
Temperature	°C	40
Anaerobic treatment		
3 – digester total	m^3	6,500
Temperature	°C	36
Activated sludge plant		
COD, average	kg/d	7,000
NH_4-N, average	kg/d	1,300
Total volume, aeration tanks	m^3	4,050
Total volume, anoxic tanks	m^3	1,750
Temperature	°C	38–40

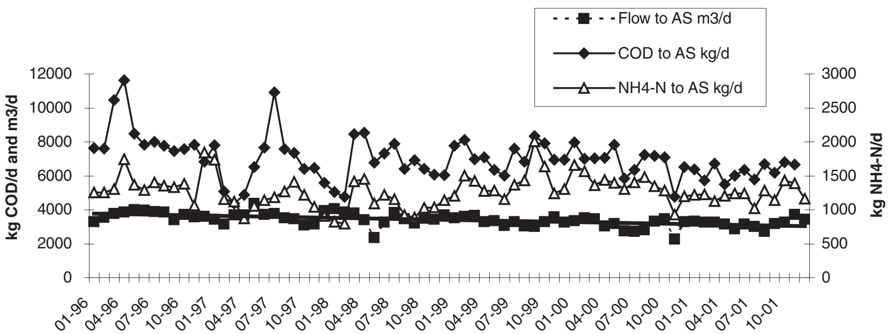

Figure 2 Load to activated sludge plant 1996–2001. Based on monthly average values

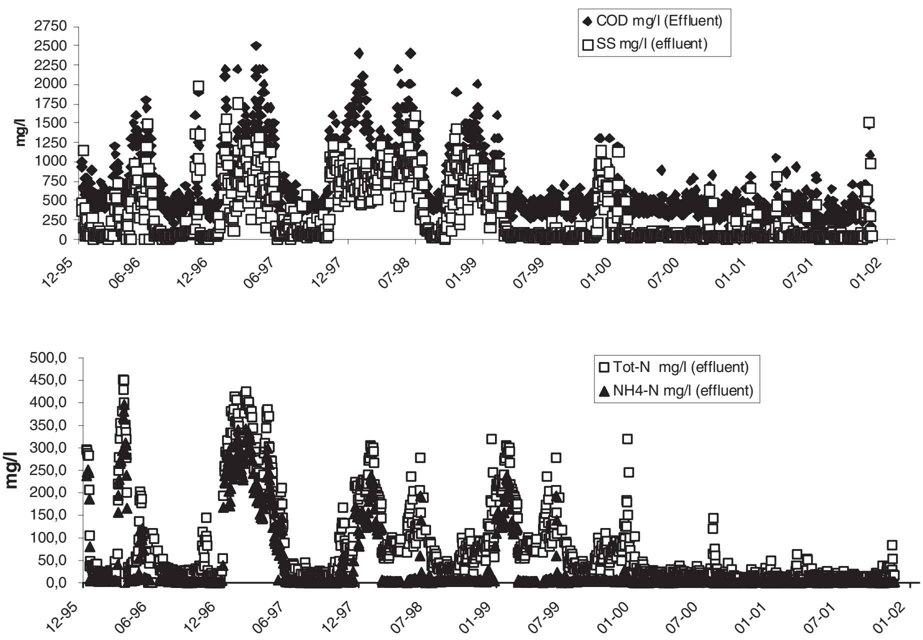

Figure 3 Tot-N, NH_4-N , COD and SS in the effluent, based on daily flow proportional samples

It is quite clear that, before the implementation of the action-plan in middle of 1999 the plant had serious problems in maintaining nitrification. All peaks of tot-N in the outlet are due to high ammonium concentrations (Figure 3). The effluent concentrations of COD and SS show the same pattern, and the conclusion is quite clear. The plant loses sludge in the effluent, which leads to decreased sludge concentration and thereby low sludge age and no nitrification as a result. The plant could actually be operating with nitrification for a couple of months, and then suddenly lose the nitrification for a longer period, up to half a year.

The question was then what causes the problems. This was the main key to obtain a stable plant operation, and was of course the primary problem to solve in the action-plan.

Sludge settling

As was well known, that the sludge very quickly could change settling characteristics, an investigation of the sludge was carried out, considering the following:

- filamentous micro-organisms
- using chemicals (organic flocculants) for increasing the sludge settling characteristics
- physical modifications of the plant for increasing the settling capacity.

Figure 4 shows the key-problem of the plant. The sludge volume index (SVI) is compared to the sludge concentration in the activated sludge process tanks. Before the middle of 1999, the picture was that a high SVI results in sludge escape to the effluent and the sludge concentration in the process reactors decreased.

The sludge investigations resulted in a change of external carbon source from a source based on sugar to alcohol. This decreased the growth of at least one of 3 identified types of filamentous micro-organisms, a *Nostocoida limicola*- type, which seemed very dominant.

Organic polymers were tested and the sludge characteristics could be changed by dosing before settling.This is now used as an emergency solution and are added when the sludge carpet in the clarifier reaches a high limit.

The physical changes were made by using an old lamella separator for settling parallel to the clarifier. This nearly doubled the settling capacity.

Nitrogen removal

In April 1999 it was discovered that the ammonium during nitrification was oxidised to NO_2-N instead of NO_3-N. As the NO_3-N analysis include NO_2-N this was never taken into consideration. During the planning of building the plant in 1987–88, pilot trials showed that nitrite could occur, but it was considered to give bad performance, and should thus be avoided.

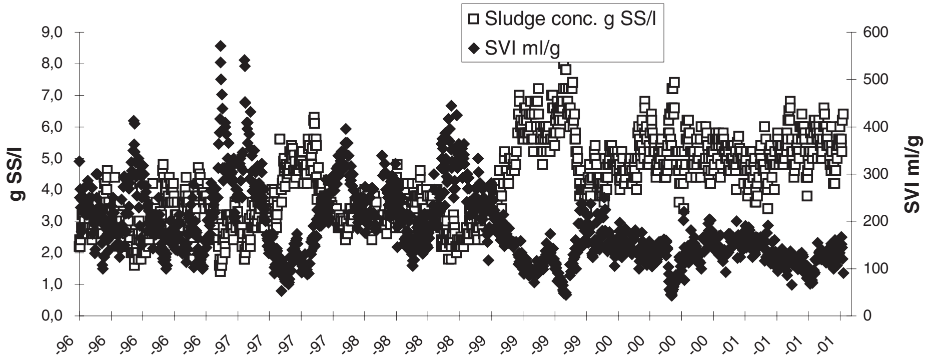

 Figure 4 SVI compared to sludge concentration

The ammonium oxidation is the first step in the full nitrification process, and is called the nitritation-process (Beier *et al.*, 1998).

$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$ (nitritation)
$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$

The oxygen demand for the nitritation process is 75% of that for the total nitrification process.

There are two different approaches to avoid complete oxidation of ammonium to nitrate and to stop the conversion at the level of nitrite.

- High temperature and low residence time in a reactor without biomass retention enable ammonium oxidisers to grow faster than nitrite oxidisers. Nitrite oxidisers are washed out due to their lower growth rate under these conditions. A process of this kind is SHARON and has been tested in laboratory scale, and the first full-scale plant following the SHARON-principle was operating in 1998. (Hellinga *et al.*, 1998). This plant operates on supernatant from digesters on a municipal plant.
- The method for systems with biomass retention like the CPKelco WWTP is the effective inhibition of the nitrite oxidation. Applicability in full-scale has been demonstrated for wastewaters of the starch industry (Abeling *et al.*, 1992). According to the present status of research, effective inhibition of nitrite oxidation depends on the concentration of NH_4^+/NH_3, NO_2^-/HNO_2 and/or pH, oxygen and temperature. However some questions still remain unclear. In particular it could be shown that organisms can adapt to initially inhibiting conditions (Abeling *et al.*, 1992; Antonisen *et al.*, 1976).

The CP Kelco WWTP is considered ideal for nitritation due to the high temperature, high alkalinity, which results in a stable pH on 7,6 to 8 in the aeration tanks. The addition of external carbonsource was controlled according to the NO_2-N content in N1 A/B and N2. The NO_2-N concentration may not exceed 70–100 mg NO_2-N/l. Figure 5. shows the content NO_2-N compared to total NO_x-N.

A close study of the NO_x-N content in the aeration tanks shows that, in some cases, it seems to be a high concentration of NO_x-N just before the sludge characteristics change to high SVI and the nitrification stops. This could indicate that the nitrite inhibition causes the changes in SVI. This needs a proper investigation.

The nitrification rates (or more accurately ammonium conversion rates) are shown in Figure 6.

As the sludge concentration and the stability of the process in the plant increase, Figure 4, the nitrification rate gets lower, as the amount of ammonium nitrified gets more stable. The highest nitrification rates are in 1996 on about 0.25 g N/g VSS*d. Today the total ammonium conversion rate is approximately 0.08 g N/g VSS*d as an average

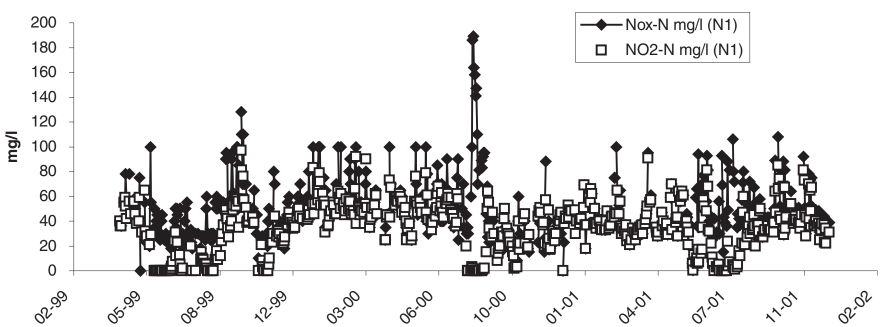

Figure 5 NO_2-N compared to NO_x-N content in aeration tanks

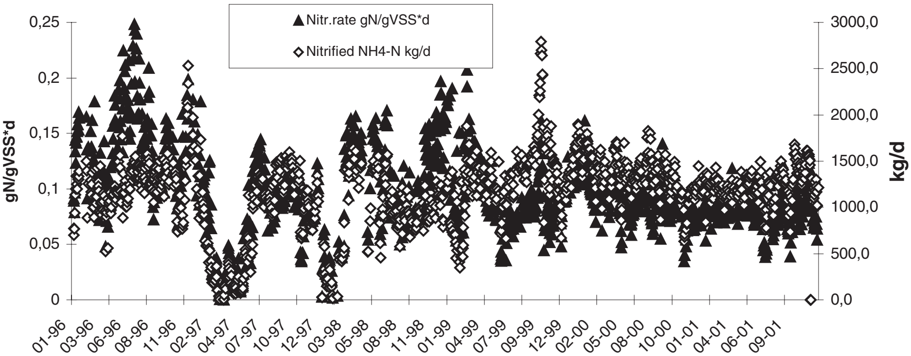

Figure 6 Nitrification rates and amount of nitrified NH_4-N

value. Laboratory investigations in batch tests shows a nitritation rate on 0.07 g N/g VSS*d.

Figure 7 shows the energy consumption for aeration and the actual oxygen requirement (AOR) is shown as a relative value (100% is related to the key data in Table 2).

The AOR is increasing due to the fact that more NH_4-N is converted and the sludge concentration has been high for the last 3 years. The calculation is based on the ammonium conversion is nitrification. Thus, if all the converted ammonium should have been nitrified,

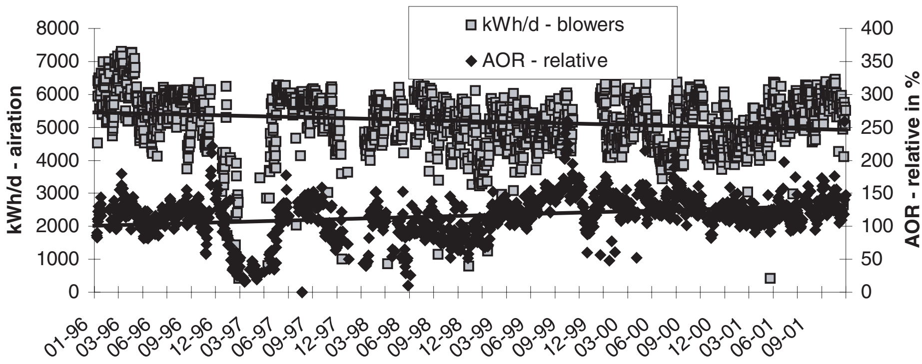

Figure 7 Energy consumption for aeration and relative AOR

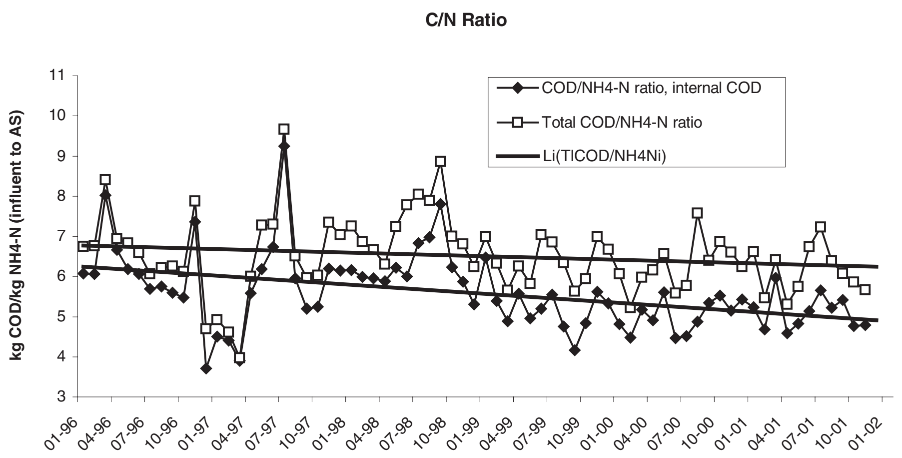

Figure 8 C/N ratios with and without external carbon source

the oxygen requirement would have been 35–40% higher today than in 1996, but the energy consumption for aeration is slightly decreasing, or at least on the same level.

Denitrification is a reduction toward N_2. Facultative anaerobic micro organisms will, during anoxic conditions, use the nitrite or nitrate as oxygen source and the process requires an electron donor, normally reduced compounds of organic material (carbon source).

$$2NO_3^- + 10H^+ + 10\,e^- \rightarrow 2OH^- + 4H_2O + N_2$$
$$2NO_2^- + 6H^+ + 6\,e^- \rightarrow 2OH^- + 2H_2O + N_2 \text{ (denitration)}$$

The calculated carbon demands for denitration amounts to 60% of that for complete denitrification.

The C/N ratio for the internal COD and NH_4-N and the ratio for the total COD (including external carbon) and NH_4-N are shown in Figure 8.

The total COD/NH_4-N ratio is relatively stable from 1999 onwards and is slightly decreasing. The ratio based on internal COD is decreasing considerable, which requires more external carbon source (the difference between the curves).

Conclusion

It can be concluded that it is possible to run a nitration/denitration process with high process stability, in an activated sludge plant treating industrial wastewater.

At the CPKelco WWTP it is possible to control the nitrite concentration in the aeration tanks because of pre and post anoxic reactors, where controlled denitritation can take place, based on external carbon source. By controlling the maximum nitrite concentration to approximately 70 mg/l in the aeration tank, problems caused by loss of sludge, due to bad settling, only appeared occasionally. In these cases, the settling characteristics of the sludge has been recovered after dosing organic polymers, which changes the SVI immediately. For a period over 2.5 year nitration/nitrification has never been lost, even though mechanical faults in a couple of cases have caused increasing ammonium content in the effluent.

The WWTP shows a much better performance in a controlled nitration/denitration process, without having increased the energy consumption.

However, a couple of questions have not been answered yet. Is it the nitrite production that caused the sludge problems due to inhibition (maybe even conservation) or is it perhaps COD or lack of phosphorus (even though phosphoric acid can be added)? Why can the micro-organisms switch between nitration and nitrification, when the load on the plant decreases (Figure 5, summer 2000)? Due to the temperature conditions the ammonium oxidisers grows faster than the nitrite oxidisers, but both conversions takes place. Does it mean that the conditions leave space for both types of micro-organisms or can one type do both oxidation steps?

These questions are being properly investigated during a research project started up in the summer of 2001. The main objective in this project is in pilot scale to develop and test the deammonification process, which consist of a combination of nitration and anaerobic ammonium oxidation (ANAMMOX). This research is supported by the Danish Energy Agency, and the project group members are from CPKelco, Herning Municipality (Denmark), Hannover University (ISAH), Aalborg University (Denmark) and Envicare.

References

Abeling, U. and Seyfried, C.F. (1992). Anaerobic-aerobic treatment of high-strength ammonium wastewater – nitrogen removal via nitrite. *Wat. Sci. Tech.*, **26**(5–6), 1007.

Anthonisen, A.C., Loehr, R.C., Prakasam, T.B.S. and Srinatu, E.G. (1976). Inhibition of nitrification by ammonia and nitrous acid. *J. Wat. Pollut. Control. Fed.*, **48**, 835–852.

Beier, M., Hippen, A., Seyfried, C.F., Rosenwinkel, K.-H. and Johansson, P. (1998). Comparison of Different Biological Treatment Methods for Nitrogen-Rich Wastewaters: (De)Nitrification – (De)Nitritation – Deammonification. *Treatment Innovation for the Next Century INNOVATION 2000*, Cambridge, UK, 7–10 July, 1998.

Dueholm, Thomas Ernst (2000). Wastewater Characterization, Copenhagen Pectin A/S (Today: CPKelco ApS). Carried out at Aalborg University, Denmark.

Hellinga, C., Schellen, A.A.J.C., Mulder, J.W., van Loosdrecht, M.C.M. and Heijnen, J.J. (1998). The Sharon process: an innovative method for nitrogen removal from ammonium-rich waste water. *Wat. Sci. Tech.*, **37**(9), 135–142.