



Biological nitrogen elimination with simultaneous biological sulfide oxidation: a report after 13 years of operating experience

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This paper is dedicated to Mr Rainer Binder (1954–2008)

Cleaning tannery wastewater has never been a trivial task, especially for those leather manufacturers who directly discharge into surface waters. Because of the dramatic savings in water consumption that have been achieved over recent decades by Bader, (*reductions of approximately 80%*), the wastewater is usually highly concentrated, especially with nitrogen compounds. However, a targeted denitrification process combined with simultaneous sulfide oxidation allows the company to eliminate the nitrogen compounds from the wastewater by at least 70% and at a reasonable cost.

Process description

The following description refers to the treatment of an effluent produced from a fully integrated tannery – that is raw material to the finished leather state. Chromium-containing

liquors within the production process are recycled, and this separate operation within the wastewater treatment plant is not described in the following presentation. However, the general process scheme for the complete system is given in *Panel 1*:

With targeted nitrification and denitrification, it is possible to remove most of the nitrogen content from the wastewater using biological processes. This produces gaseous nitrogen that has evolved, but also includes nitrogen removal from the effluent by the bio-mass produced. Ultimately, this forms a sludge that is suitable for agricultural use.

The system will work even in wastewater with a nitrogen content that is very high when compared to municipal wastewater. A description of the basic biochemical processes is summarised in *Panel 2*.

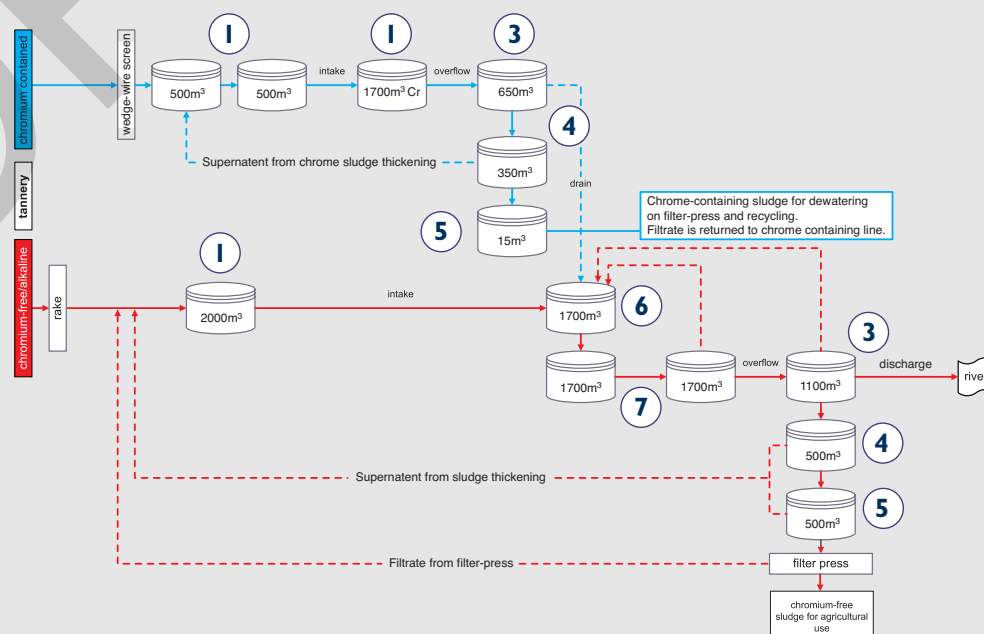
Panel 1: General process scheme for the complete effluent treatment

— Treatment of chromium containing wastewaters

— Treatment of chromium-free wastewaters with nitrification/denitrification edges

KEY:

1. Mix/buffering
2. Precipitation
3. Clarification
4. Sludge thickening
5. Sludge holding
6. Denitrification
7. Nitrification





Panel 2: Basic Biochemical Process

Basic Biochemical Process		
Principle	Process description	
$N \rightarrow \text{biomass}$		Solids from activated sludge treatment
$N_{\text{org}} \rightarrow \text{NH}_3 \text{ or } \text{NH}_4^+$	Ammonification	
$2 \text{NH}_4^+ + 3 \text{O}_2 \rightarrow 2 \text{NO}_2^- + 4\text{H}^+ + 2 \text{H}_2\text{O} + \text{energy}$	Nitrification	Atmosphere
$2 \text{NO}_2^- + \text{O}_2 \rightarrow 2 \text{NO}_3^- + \text{energy}$	Nitrification	
$4 \text{NO}_3^- + 4\text{H}^+ \rightarrow 2\text{N}_2 \uparrow + (5 \text{O}_2) + 2 \text{H}_2\text{O} + \text{energy}$	Denitrification	Atmosphere

THE NITRIFICATION/DENITRIFICATION STAGES

In the period covered by this report (2000 – 2011), the input loads of raw wastewater (from both split flows as illustrated in Panel 1) were calculated as between 460 and 780 kg Total Nitrogen/day, at concentrations between 650 and 780 mg/litre. These values include all of the filtrates that are recycled from sludge treatment and filter press operations.

This nitrogen originates primarily from the breakdown of skin components from the conversion of raw hides into leather, and from chemicals used in processing. This nitrogen component exists in the waste water offered for treatment partly as organic-nitrogen and partly as ammonium-nitrogen.

With reference to Panel 1, ammonification of the organic-nitrogen starts in an upstream buffer basin. The ammonia-nitrogen that is produced is then oxidised by nitrifying bacteria in the presence of oxygen - via the intermediate nitrite stage - into nitrate.

Effluent is recirculated from this oxidation stage back to an upstream denitrification step that operates intermittently, where the nitrate-nitrogen can be partially converted into gaseous N_2 . In this stage, there is an absence of free oxygen, and in this event the denitrifying bacteria remove oxygen from the nitrate component. In addition to the nitrogen evolved as gas, a part of the nitrogen is also bound in the bio-mass generated in this stage.

REMOVAL OF SULFIDE IN THE DENITRIFICATION STAGE

A carbon source is required for the denitrification phase, and this is provided by the pre-clarified raw wastewater. However, this also contains sulfides, but these are rapidly oxidised into sulfate, and thus completely removed during denitrification stage. Because this oxidation process is carried out at high speed in anoxic conditions, no hydrogen sulfide gas is formed.

The only requirement is to ensure that there are no anaerobic zones in the bioreactor where an evolution of hydrogen sulfides would be possible. This could cause an inhibition of the biological process, but optimum performance is achieved by state of the art management.

The limiting factor for any further reduction of the nitrate that is formed in the nitrification step is the total hydraulic load of the system. In practice, the total nitrogen concentration in the process can be reduced to values of less than 20 mg/l for short time periods when the conditions are optimal. This value is however not relevant for reliable, continuous operation as it cannot be maintained all of the time.

Frequently occurring problems

[1] TEMPERATURE SENSITIVITIES OF NITRIFICATION-DENITRIFICATION

A problem that should be considered is taken into account in German legislation, that is, the metabolism of nitrifying bacteria ceases almost completely if temperatures within the bioreactor drop below 12°C . This means that nitrification, and consequently denitrification, are therefore no longer possible below this temperature.

Contrary to the experience from municipal sewage plants with systems such as described in this report, after a cold period when the temperature has fallen below 12°C , the nitrification processes will return completely when 20°C is reached. In contrast, after a warm period the processes operates efficiently until the temperature drops to 12°C .

Experience so far shows that the start-up phase after cold periods can take significantly longer than six weeks. During these start-up phases, it is possible that accumulations of nitrite may inhibit the nitrification. The reasons for this nitrite-accumulation is not fully understand, and the nitrite can only be reduced by a targeted denitrification after a "jump-starting" of nitrification.

[2] FILAMENTOUS BACTERIA

Aerobic biological treatment of tannery wastewater is usually only possible with comparatively low loads of bio-mass. Depending on the levels of natural fats in the wastewater (a function of the production process and the raw hides) an increased growth of lipophilic filamentous bacteria, such as *Microthrix parvicella*, must be regularly expected, especially in the spring.

This is because these natural fats are not completely eliminatable by grease separators. Accordingly, bulking or floating sludge will increase due to the increase of these bacteria, and this will inhibit settling of the bio-solids. Various measures to address the problems arising from filamentous bacteria are described in professional literature and journals.

Achievable performance

When considering the performance of a wastewater treatment process, a distinction must always be made between the short-term output values that can be achieved under optimum conditions, and a maximum output that can be maintained under all usual operating conditions (supply situation, weather, start-up phases, etc.).

In particular, it is vitally important where such performance data is used to identify the technically feasible limits, and only use standards that can be maintained in the long term. Using short-term values that can be achieved under optimum conditions is only of scientific interest.

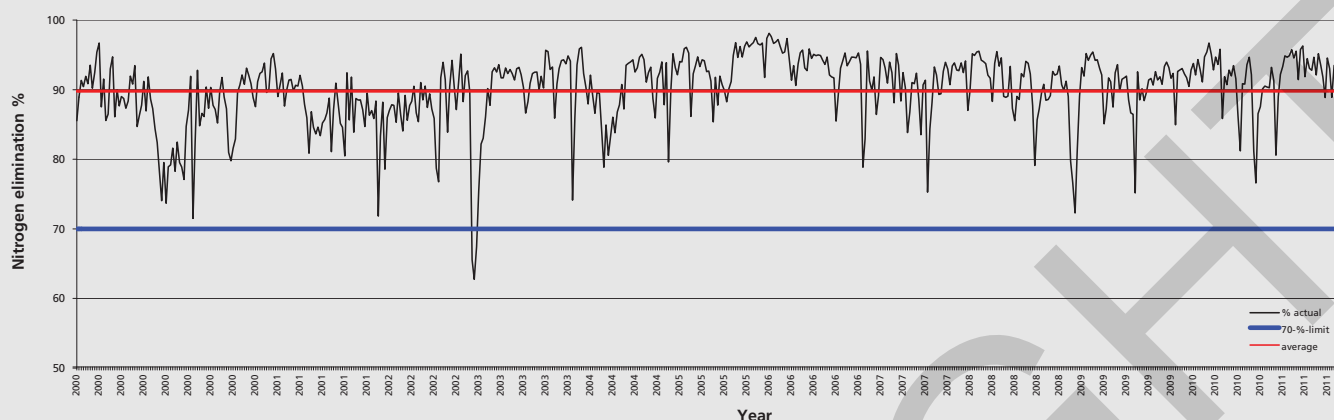
Furthermore, operational disruptions present special challenges to everyone who is in charge of a wastewater treatment plant. These are not covered by this summary of experiences, and they were not taken into account in the following information that is provided.

The combination of the denitrification process with the quasi-simultaneous biological oxidation of sulfides eliminates the need for the widely-used sulfide oxidation processes using manganese sulphate as a catalyst. It thereby avoids:

- further salinification of the wastewater
- additional use of chemicals
- an increase in the quantity of sludge to be disposed of
- a cost increase in terms of equipment and operational costs.



Panel 3: Nitrogen elimination rate (converting in biomass + denitrification)
January 2000 to August 2011 [%]



The aerobic wastewater treatment process is frequently criticised for its high energy input. For good quality equipment, and using the latest techniques (*frequency-controlled air supply, etc.*) and regular professionally skilled maintenance and operation, the overall energy consumption can be reduced to well below 0.7 kWh/kg COD. This includes all split flows, all ancillary facilities including sludge treatment and air purification, and is at least 20% below the guidelines for energy consumption for municipal water treatment plants as defined by the Federal Environment Service (UBA) in Germany.

The biological wastewater treatment method described has ensured a lowering of the total nitrogen content from the year 2000 to 2011. The performance achieved is set down in *Panel 3*.

The values given have been maintained for long-term operation. They do not take into account operational disruptions, but they do include regularly occurring start-up phases. In addition, the values only apply to leather production based on chromium tanning.

Because of the high inflow-load, the limits for nitrogen that are generally stated for effluent concentrations do not apply in this situation. Standard effluent limits must be defined (analogously e.g. to those as per Appendix 25 of the Wastewater Act (AbwV) for COD), by a percentage elimination performance for nitrogen.

This must not be confused with the denitrification rate. This is because a part of the nitrogen is not denitrified - hence evolution as nitrogen - but is incorporated in the sludge produced from activated sludge treatment: after dewatering by filter press this is available for agricultural use. However, when there are no operational disruptions, the following effluent standard values can be maintained in the longer term:

i) $\text{NH}_4\text{-N} < 10 \text{ mg/l}$

ii) $\text{N}_{\text{total}} = \text{N}_{\text{org}} + \text{NH}_4\text{-N} + \text{NO}_2\text{-N} + \text{NO}_3\text{-N} > 70\% \text{ elimination}$

Application and costs

These procedures can be installed in new plants or retro-fitted into most existing plants where nitrification is used. Investment costs for a targeted denitrification operation can be

put at roughly €220,000 for a plant of the size indicated in this report.

The running costs - that also include all partial flows, all sludge treatment, complete exhaust air treatment, costs of personnel, energy, auxiliary materials, sludge disposal fees, depreciation, maintenance, laboratory work and external support - can be put at roughly €4 - 6/m³.

Acknowledgments

The values given are based on the experience of several thousand individual tests carried out on about 1000 investigation days over the course of some 11.5 years. Before this phase there were four extremely busy and nerve wracking years of development in which the process was developed at a pilot scale step by step, installed temporarily into the system, tested and optimised and then finally converted up to full scale. We wish to extend our particular thanks to:

- *the Günzburg District Office and the (former) Krumbach/Schwaben Water Authority (now part of the Donauwörth Water Authority) for the very close and patient cooperation and their always realistic assessments of what was feasible.*
- *Dr. Gerhard Metzner and the Bavarian State Office for Water Management, for the detailed and skilled professional advice and the provision of test facilities on a long loan.*
- *Ms Jutta Knödler (I-T-G GmbH; Association of Engineers for Environmental Technology) for long-standing competent professional expert advice, data analysis and creation and definition of the theoretical conditions for the permits.*
- *Mr Rainer Binder (1954 to 2008) for looking after the experimental systems and for the very practical assistance and support, in particular during the implementation phase and the subsequent operational phase.*
- *Mr Alexander Kunstmann for his long-standing analytical support for all the experiments and for the system itself, and for the responsible management of our system since the tragic death of his predecessor, Mr Rainer Binder.*