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BADER®

Industrial area Northwest - Green

Press Release

dedicated to Mr Rainer Binder

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

Cleaning tannery wastewater has never been a trivial task, especially for those who discharge it directly into a waterbody. Because of the dramatic savings in water consumption that have been achieved over recent decades (reductions by approximately 80%), the wastewater is usually highly concentrated and especially high polluted with nitrogen compounds. A targeted denitrification process combined with simultaneous sulphide oxidation allows us to eliminate the nitrogen compounds from the wastewater today by at least 70% at a reasonable cost.

Process description

When interpreting the following statements, it is extremely important to note that the observations and assessments do not include the operational disruptions that are always possible.

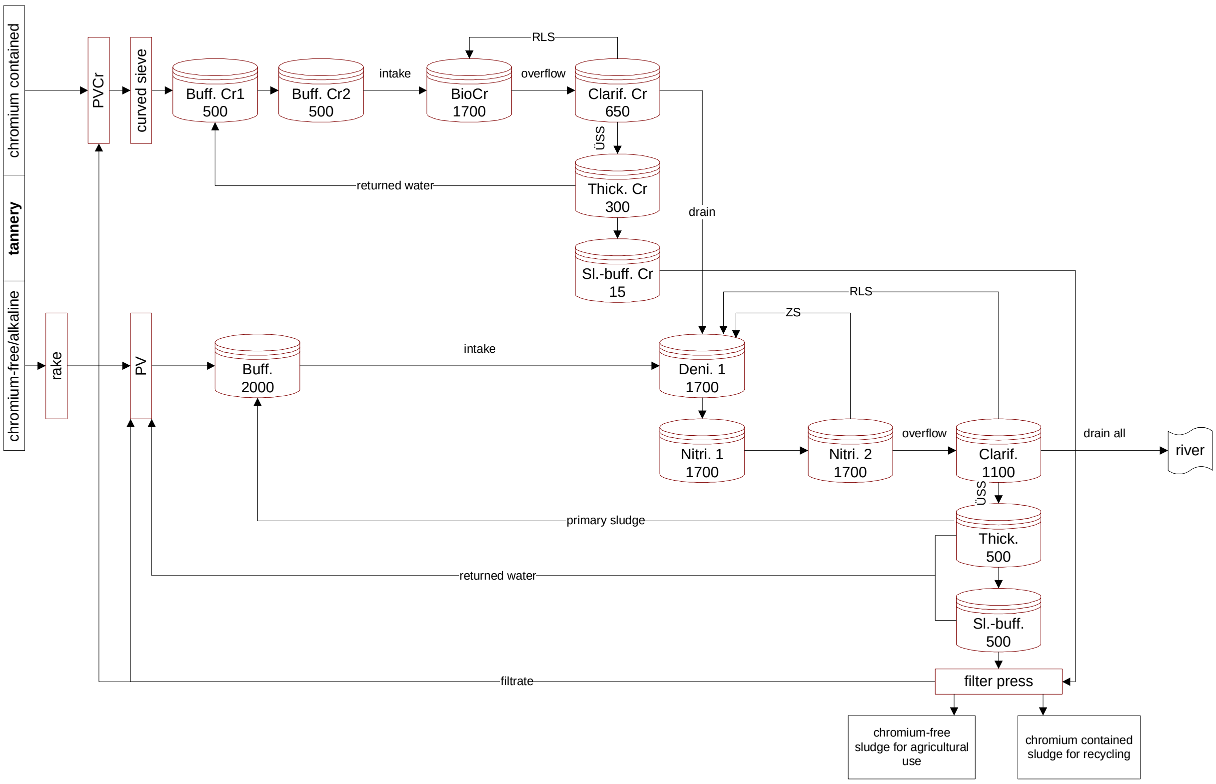

Figure 1: Wastewater treatment unit overview

Furthermore, it should be noted that this refers to the production associated with a fully integrated tannery (raw material to finished leather). The practice of recycling of the chromium-containing liquors within the production process was not considered in the following statements as part of the wastewater treatment plant.

The general process scheme for the complete system is shown in figure 1.

With a targeted nitrification and denitrification it’s possible, to eliminate the nitrogen largely from the wastewater by biological processes, including the elimination by production of biomass. That system will work, even in wastewater with a nitrogen content that is very high compared to municipal wastewater. A description of the basic biochemical processes is summarised in figure 2. The input loads of raw wastewater (both splitflows) in the period considered, were calculated between 460 and 780 kg N_{total}/day, at concentrations between 650 and 780 mg/litre. These figures include all reversals from the sludge treatment.

The nitrogen, which originate primarily from skin decomposition as well as from the chemicals input, exists in the raw wastewater partly as organic-N and partly as ammonium-nitrogen. The ammonification of organic nitrogen into ammonium nitrogen starts in the drainage channels and continues in an upstream buffer basin.

The ammonia nitrogen is oxidised by nitrifying bacterias in the presence of oxygen - via the intermediate stage nitrite - into nitrate. In an upstream denitrification step that operates partly intermittently, the nitrate-nitrogen can partially be converted into gaseous N_2. A further part of the nitrogen is bound in the biomass. The nitrate is inhaled by denitrifiers, since oxidised nitrogen compounds can replace oxygen in the system.

Biochemical principle	Process description		Final location of the nitrogen
N → biomass			Activated sludge
N_{org} → NH_3 or NH_4^+	Ammonification		
2 NH_4^+ + 3 O_2 → 2 NO_2^- + 4 H^+ + 2 H_2O + energy	Nitritation	Nitrification	
2 NO_2^- + O_2 → 2 NO_3^- + energy	Nitratation		
4 NO_3^- + 4 H^+ → 2 N_2↑ + (5 O_2) + 2 H_2O + energy	Denitrification		Atmosphere

Figure 2: Biochemical principles

The necessary carbon source for the denitrification phase is provided by the pre-clarified raw wastewater containing the sulphides. The sulphides are rapidly and completely oxidised into sulphate during denitrification. Because the oxidationprocess is carried out in a high speed in anoxic conditions, no hydrogen sulphide gas is formed. It is only necessary to ensure that there are no anaerobic zones in the bioreactor where an involution of sulphides would be possible and which could cause the inhabitation of the biological process. This can be achieved with technical measures, following the state of the art.

The hydraulic load of the system including the final sedimentation tank (return ratio) is the limiting factor for further reduction of the nitrate that is formed in the nitrification step. The total nitrogen concentration in the process can only be reduced for short timeperiods to values of less than 20 mg/l, when the conditions are optimal. This value is however not relevant for reliable, continuous operation as it cannot be maintained safely.

Frequently occurring problems

A consideration that is already in the German legislation should be mentioned at this point: the metabolism of nitrifying bacteria ceases almost completely when temperatures in the bioreactor drop below 12℃. Both nitrification and consequently denitrification are therefore no longer possible for biological or biochemical reasons at temperatures below this limit.

Contrary to the experience from municipal sewage plants, systems such as those described here, the nitrification processes return completely after every start-up phase after a cold period (temperature in the bioreactor less than 12°C) to the initial reaction speed for nitrification, when 20℃ is reached. If the tempera ture in the bioreactor gets down to the 12℃ limit after a warm period, the processes conti nue stably until that temperature is reached. Experience so far shows that the startup phase after cold periods can take significantly longer than 6 weeks.

During these startups, it is possible that accumulations of nitrite may inhibit the nitrification. We do not yet fully understand the reasons for the nitrite-accumulation. This nitrite can only be reduced by a targeted denitrification after “jump-starting” of nitrification.

Aerobic biological treatment of tannery wastewater is usually only possible with comparatively low sludge loads. Depending on the levels of natural fats in the wastewater as a function of the productionprocess and the raw hides, increased growth of lipophilic filamentous bacteria such as *Microthrix parvicella* must be regularly expected, especially in the spring. Such fats are not completely eliminable by grease separators. In order to improve the sludge sedimentation, which will be negatively affected by this bulking or floating sludge, various measures are often described in the 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 value that can be achieved under optimum conditions and a maximum output that can be maintained under all usual operating conditions (supply situation, weather, startup phases, etc.). In particular, it is vitally important where such performance data is used to identify the technically feasible limits, to use only that standards, which can be maintained in the long term. Using the short-term figures that can be achieved under optimum conditions is really 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 survey of experiences nor were they taken into account in the information below.

Compared to the widely-used conventional catalytic sulphide oxidation processes (using iron salts and manganese sulphate as a catalyst), the combination of the denitrification process with the quasi-simultaneous biological oxidation of sulphides avoids further effort that have to be made normally to treat the sulphide. It thereby avoids:

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

The aerobic wastewater treatment process is not infrequently criticised for its high energy input. For technical equipment using the latest techniques (e.g. frequency-controlled air supply etc.) and regular professionally skilled maintenance and operation, the overall energy consumption (all splitflows, all ancillary facilities including sludge treatment and air purification) can be reduced to well below 0.7 kWh/kg COD, which is at least 20% below the indicated energy consumption for municipal water treatment plants defined by the Federal Environment Service (UBA) in Germany.

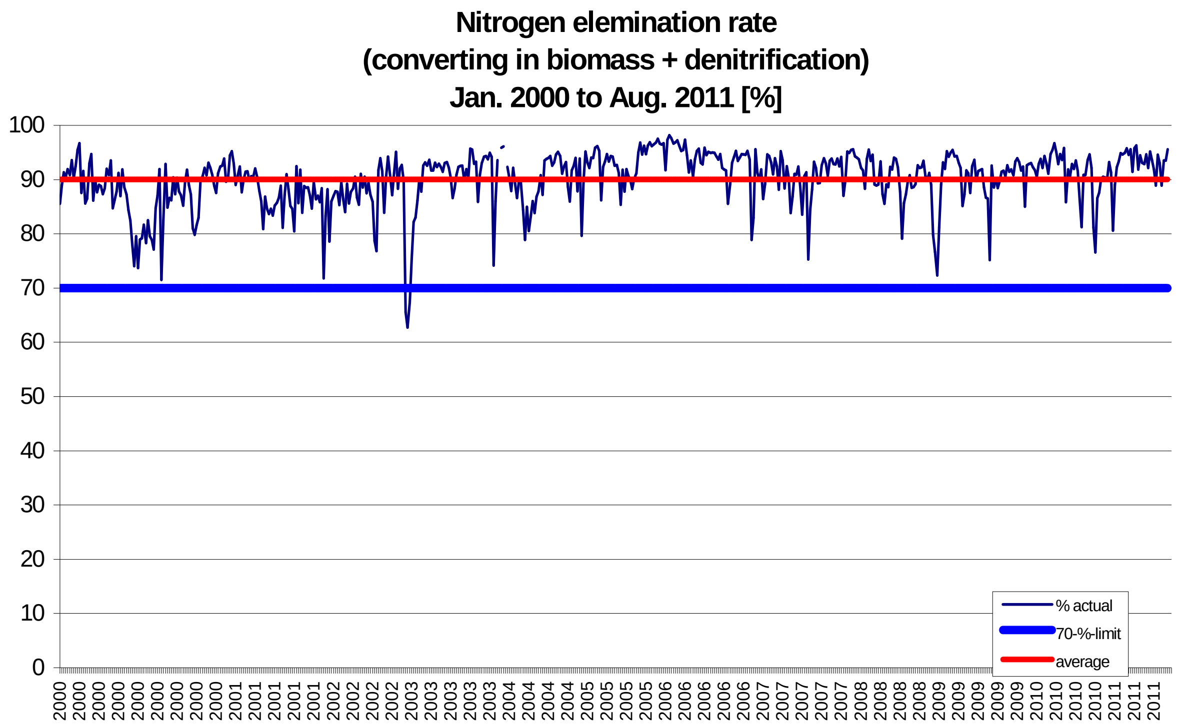

Figure 3: Nitrogen elimination rate

Biological wastewater treatment such as this allows the represented metrics to be achieved (figure 3). The values given are only those that can be maintained for long-term operation without taking account of operational disruptions, but they do include regularly occurring start-up phases. The values apply only for leather production using chromium.

Because of the high inflow-load, the generally used limits on effluent concentrations do not make sense. 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 nitrogen elimination performance. It should be noted that this must not be mixed up with the denitrification rate, because a part of the nitrogen is not denitrified but is instead incorporated in the activated sludge; this is included in the given elimination efficiency figures.

When there are no operational disruptions, the following effluent standard values can certainly be maintained in the longer term:

NH_4-N:	**< 10 mg/l**
$N_{total} = N_{org} + NH_4\text{-}N + NO_2\text{-}N + NO_3\text{-}N$:	**> 70% elimination**

Applicability of the procedure / costs

The procedure can be retrofitted or installed in new and into most existing plants, where nitrification is used. In the share of investment costs for a targeted denitrification operation can be put at roughly 220,000 € for a plant of the size specified above.

The running costs (all partial flows, not only denitrification; including all sludge treatment and complete exhaust air treatment: including costs of personnel, energy, auxiliary material and sludge disposal, fee, depreciation, maintenance, laboratory work and external support) can be put at roughly 4 to 6 €/m³.

Acknowledgment

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 4 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

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