Key technologies for tannery wastewater treatment

Wolfram Scholz[1]

W_2O Environment Ltd.

+ 43 676 782 9383

wolfram@w2oenvironment.net

Abstract

Tannery wastewater is a complex mixture of organic substances derived from the hide and inorganic substances such as salts and chemicals, which are added during the beamhouse and tanyard processing. Sulphide and chrome bearing streams have to be segregated well from the soak and de-lime effluents and are treated separately in a sulphide oxidation system and chrome precipitation plant. Sulphide oxidation is carried out in batch using blower assisted jetox aeration and achieves a complete oxidation of sulphides to sulphates within 8 hours. The segregated effluents are fine screened at 1 mm to remove coarse solids and mixed and aerated during the balancing stage to provide an uniform effluent for the following Primary treatment. Dissolved Air Flotation removes efficiently suspended solids, as well as fats, surfactants and colour of the wastewater achieving a clear effluent with < 50 mg/l Suspended Solids. The residual soluble COD and BOD is then treated biologically with a combination of anoxic and aerobic treatment to also allow removing nitrogen compounds such as ammonia, nitrate and Kjeldahl nitrogen. Biological denitrification/nitrification in combination with membrane bioreactor technology achieves a high reduction of 92% COD and 99% BOD, with ammonia of less than 2 mg/l achieved in the effluent.

The membrane bioreactor permeate is solids free and can be polished with Nanofiltration to allow for up to 75% high quality water recycling, thus reducing the discharged volume to 25%. The Nanofiltration permeate is completely clear and contains only minor concentrations of salt and has a consistent quality enabling high quality water re-use.

[1] Gymnasiumstr. 6, Top 12, 1180 Vienna, Austria

Keywords: Tannery effluent, sulphide oxidation, nitrogen removal, MBR, membrane bioreactor, NF, nanofiltration, water recycling

Abbreviations

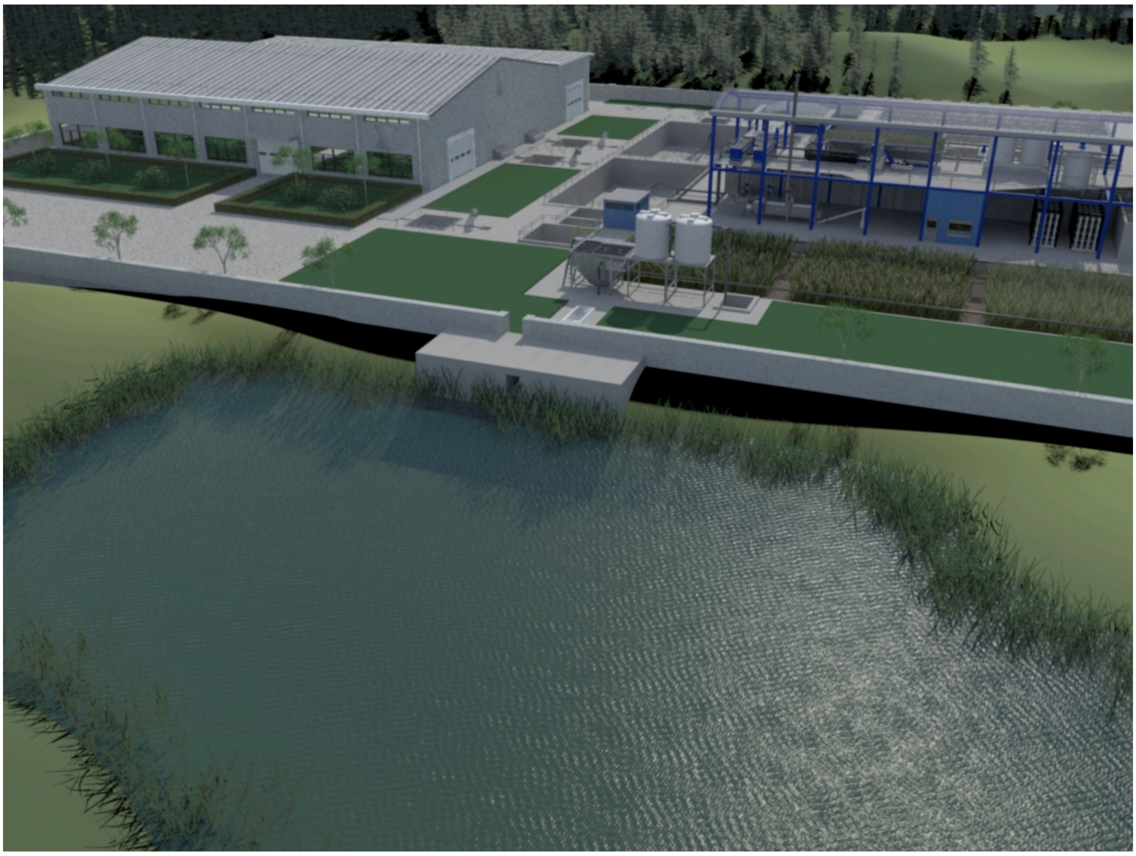
BOD	biological oxygen demand (mg BOD,L^{-1})
COD	chemical oxygen demand (mg COD,L^{-1})
DAF	dissolved air flotation
MBR	membrane bioreactor
MLSS	mixed liquor suspended solids (mg,L^{-1})
N	nitrogen
NF	nanofiltration
P	phosphorus
SS	suspended solids (mg,L^{-1})

Introduction

Most of the pollution generated during leather processing evolves from the beamhouse processes, which are the initial steps of leather production. The conventional beamhouse process involves soaking of hides, unhairing with sulphides and lime, following tanyard with de-liming with ammonium salts, degreasing, especially in ovine processing and pickling to prepare the hide for tanning. Within these processes organic substances as proteins, fats and hair, which account for approximately 80 % of the salted weight of the hide are removed and are being discharged from the process as highly organic loaded effluents (IUE 6, 2019).

The raising production and environmental costs urge the leather industry to implement sustainable production schemes with the main objectives of saving resources by process- and production-integrated measures to minimise environmental impacts. By strictly regarding economical demands, an approach of "green-processing" has been developed, that enables the leather industry to reduce environmental and operational costs. The implementation of processes-integrated measures and recycling technologies using Membrane bioreactor technology and Nanofiltration has shown to be technical and economical feasibility for recycling and to fulfil the quality criteria for leather processing.

Picture 1: Wet-blue tannery with effluent treatment plant discharging to a water course



Treatments

Segregation and screening of effluents

A process-controlled drainage from the drums is critical for successful wet-blue tannery effluent treatment to achieve a good segregation of chrome and sulphide bearing effluents without any cross contaminations (TAN, 2011). In wet-blue tanneries this is achieved by draining the lime float and tanning float into separate channels and collection in 3 individual sumps; the lime sump, the chrome sump and the sump for general effluents.

The 3 effluent streams are then fine screened with automated self-cleaning screens (IUE, 2021) to remove all particles > 1 mm. The implementation of fine screening reduces significantly the solids load for the following treatments and the overall treatment costs.

Sulphide Oxidation

The catalytic oxidation by aeration of lime liquors is the most economical and widely used process for sulphide removal. The technique consists of aerating the spent lime liquors for 8 hours. The sodium sulphide present in the spent un-hairing - liming liquors is oxidised by the air oxygen into thiosulphate, and in smaller quantities, into sulphate. The thiosulphate then decomposes into sulphur and sulphite. The amount of oxygen required is estimated at 2 kg per kg of sulphide (S^{2-}). However, the amount of air, which will react in relation to the quantity of air injected, will depend on the aeration device. Therefore, it is necessary to provide for an excess of air to the level of sulphide. Depending on the length of the float used and the volume of wash and rinse waters the lime liquors may contain between 1.5 to 3 g/l of sulphides. After mixing and dilution with the rest of the tannery effluent the sodium sulphide concentration is between 200 - 600 mg/l. Therefore, it is required to separately treat the unhairing-liming floats before they are mixed with other effluent streams. Sulphides can cause inhibitions and reduce the performance of the following biological treatment and have to be reduced to concentrations of <1 mg/l (as S^{2-}), whereas typical sulphide levels in the untreated effluent is of the order of several hundred.

The operation of a sulphide oxidation system is the most cost effective method of oxidising sulphides to sulphates offering advantages compared to other methods such as ferric salt addition which results in high generation of sludge or addition of expensive oxidants such as hydrogen peroxide with high chemical costs. A sulphide oxidation consists of a jetox venturi system connected to a centrifugal pump and an external blower to mix the lime liquors with air (IUE, 2021). Sulphide oxidation systems, operated in batch over 8 hours, have shown to achieve complete oxidation of lime liquors reaching residual levels of < 1 mg/l sulphides (IUE 12, 2019).

Balancing

Balancing of tannery effluent is important to improve the treatment efficiency, and avoid oversize treatment plants, which have to deal with peak effluent flows. A steady uniform effluent flow can be achieved by sizing the equalisation tank to a volume of 70 to 100% of the tannery daily flow. In addition to flow balancing, the equalisation tank provides for neutralisation and precipitation. It is necessary to provide effective mixing by mechanical stirring and air injection to achieve equalisation, prevent anaerobic conditions and settling of suspended solids. The installation of a jetox aerated balancing tank enables complete mixing and aeration of the effluents avoiding re-formation of sulphides (IUE, 2021).

Dissolved Air Flotation

Dissolved Air Flotation (DAF) works on the reverse principle to sedimentation, employing fine air or gas bubbles to lift suspended solids, which were not removed by the prior settlement, to the surface from where they may be removed. Especially fine solids as hair and fibres or fats and proteins can be very efficiently removed by flotation (TAN, 2011)

The flotation process relies on coagulant and flocculent chemical conditioning of the feed stream, as for sedimentation, in order to enhance the solids separation process. The effluent feed is pH adjusted, followed by dosing of a suitable coagulant. A suitable polyelectrolyte flocculant is also required for optimum phase separation, especially of colloidal solids, and will require inline dosing just prior to the effluent entering the flotation tank. After chemical dosing the effluent flows into the flotation tank and is mixed with the rising air bubbles stream. The air-saturated stream is formed by pumping of the treated effluent into a pressurisation chamber along with air, which under pressure, dissolves in the water. The sudden release of pressure in the flotation tank causes the dissolved air to form ‘clouds’ of tiny air bubbles, which come up to the surface carrying the suspended and colloidal solids with it to form a surface sludge ‘blanket’, which is regularly scraped off (IUE, 2021). A DAF system provides higher levels of pollution removal with up to 98% of SS and up to 75% of COD (IUE 5, 2019). A further advantage is that the floated sludge has a higher solids content, up to 10% dry matter, which is much easier and more cost effective to handle than just settling.

Picture 2: Primary effluent treatment plant with screening, balancing, sulphide oxidation and DAF

Biological treatment

Biological processes are based on the fact that micro-organisms can use the organics (BOD) and nutrients (N&P) to build up their cell mass as well as provide their energy requirements. The soluble organics are converted to CO_2 and wasted sludge from the biomass. The biological stage of a waste treatment plant can be either operated under aerobic or anoxic conditions. Aerobic conditions are applied to remove BOD and ammonia of tannery wastewaters, while anoxic conditions are used to convert nitrates to nitrogen in the process of de-nitrification. The activated sludge process is the most common biological treatment method for tannery wastewater treatment. Prolonged aeration time is important for tannery effluents due to the high organic load. De-nitrification loops have been added to biological treatment plants, where low ammoniacal nitrogen discharge limits are imposed (IUE, 2021). The denitrification/ nitrification systems are operated in sequence with effluents recirculating in between the aerated zone and the anoxic zone have shown to consistently reduce ammonia to < 2 mg/l and nitrate to < 5 mg/l (Scholz, 2013).

Membrane Bioreactor (MBR)

Membrane bioreactors (MBRs) combine an activated sludge process with membrane ultrafiltration to facilitate complete retention of the biomass. The process relies on membrane filtration to effectively retain all the biomass in the bioreactor as opposed to conventional treatment, where the biomass is continuously lost during clarification. As a consequence, the MBR process is operated at 3 folds higher mixed liquor concentrations of up to 10 g/l MLSS, than conventional biological treatment. This increase of concentration of wastewater bacteria allows reducing the aerated biological tank dimensions by 55%, compared to conventional biological treatment, which consequently also reduces aeration requirements by 35% (IUE, 2021).

A further benefit of MBR, resulting from increased sludge retention times and operating temperatures, is the reduction of surplus sludge generation. Due to the high sludge retention time and high MLSS, the bioreactor is severely carbon limited and the influent carbon sources are predominantly utilized for metabolic purposes than other cellular growth, e.g., maintenance, thus minimizing biomass production. Large scale MBR plants have shown that only 6.7% of the metabolized COD was incorporated into surplus sludge production, compared to 30-50% in a conventional activated sludge system. This minimizes the surplus sludge and consequently the amount of disposable biological sludge (Scholz, et.al, 2005).

Membrane bioreactor technology is an excellent pre-treatment for nanofiltration or reverse osmosis plants due to the complete elimination of BOD and suspended solids. Small concentrations of BOD after conventional treatment would cause bio-fouling of NF/RO membranes and suspended solids would physically block the spacer of a spiral membrane module. The combination of a Nanofiltration plant applied as a polishing step after MBR treatment allows high quality water recycling back into the tannery process. The advantage of this is a reduction of fresh water and effluent costs. The use of consistent high quality process water will also have a positive influence in regards of saving process chemicals and improving the leather quality. A membrane bioreactor system achieves up to 95% COD, 99% BOD removal and suspended solids free and transparent permeate (IUE 5, 2019).

Picture 3: Biological effluent treatment plant with anoxic and aerobic biological MBR treatment

Nanofiltration

The application of recycling normally relies on suitable process technology for water purification. The wide fluctuation in tannery effluent quality coupled with the requirements for process water of reliable quality tend to favour the application of membrane processes. Membrane filtration processes inevitably play nowadays a key role in modern water recycling since they can produce a water of consistent and reliably high quality. Membranes form a highly selective barrier and are tolerant to shock-loads. Therefore the produced permeate quality is varying little with the feed water quality (Judd S. and Bennett, 2004). The main advantage of a membrane-based process is that the concentration and separation is achieved without a change of state and without use of chemicals or thermal energy, thus making the process energy efficient and ideally suitable for recycling (IUE, 2021).

Nanofiltration technology is a suitable, where a final polishing of effluents, without complete salt retention is required. The Nanofiltration membrane offers a small pore size of 400 – 600 Dalton, which retains efficiently multivalent ion such as total hardness and certain charged or polar molecules. However, sodium chloride a mono-valent salt passes the membrane. The spiral-wound modules are densely packed offering a high membrane surface and therefore require only minimum of space. High reductions of COD, BOD and colour are achieved, due to the fact that the Nanofiltration membrane retains organic fractions. The produced permeate is reduced in COD, completely clear and contains minor concentrations of salt (Scholz, 2017). The consistent quality of the NF enables high quality water.

Results

The segregation and fine-screening of sulphide and chrome bearing effluents and separate treatment with sulphide oxidation and chrome precipitation is essential for wet-blue tannery effluent treatment.

The sulphide oxidation using blower assisted jetox venturi aeration has shown to remove efficiently sulphides with average concentration of 0.19 ppm achieved with the completion of an 8 hr oxidation cycle.

Dissolved Air Flotation has shown to remove 75 % of COD, achieving a clear and transparent effluent with < 50 mg/l SS. DAF treatment achieves a high Primary sludge dryness of up to 10% and therefore reduces considerably the volumes of sludge for de-watering.

Biological treatment with anoxic pre-denitrification followed by aerobic treatment has shown to reduce ammonia to < 2 mg/l and total nitrogen to < 5 mg/l.

The activated sludge is then filtered with submerged membranes resulting in a membrane bioreactor permeate, achieving 92% COD removal with a residual BOD of < 20 mg/l.

Nanofiltration has shown to remove residual organics and colour, achieving water recovery rates of up to 75% of a clear and soft effluent, which is ideal for process water recycling.

Conclusions

The combination of Membrane Bioreactors (MBR) with Nanofiltration (NF) for water recycling is a new strategy to reduce the environmental impact of tannery, reaching steadily the stringent discharge compliance and to provide for high quality process water recycling. With proven economical and technical feasibility, this novel technology has shown reductions of 92 % in COD, 98 % in BOD and complete removal of suspended solids. The high-quality effluent after MBR treatment, allows for cost-effective polishing through NF treatment and high quality water recycling. Full-scale applications of MBR and NF treatment have demonstrated 75 % water recovery.

References

[1] IUE Tannery effluent treatment videos: Animations of treatment technologies (2021): https://iultcs.org/tannery-effluent-treatment-videos/

[2] Environmental Document of the IULTCS. IUE 5 - Typical performance for tannery wastewater treatment (2019): https://iultcs.org/wp-content/uploads/2020/07/IUE_5.pdf

[3]Environmental Document of the IULTCS, IUE 6 - Typical pollution values related to conventional tannery processes, (2019): https://iultcs.org/wp-content/uploads/2020/07/IUE_6.pdf

[4] Environmental Document of the IULTCS, IUE 12 (2019): https://iultcs.org/wp-content/uploads/2020/07/IUE_12.pdf

[5] TAN (2011) - Best Available Techniques for the Tanning of Hides and Skins, chapter 4 p. 183

[6] Scholz W., (2013): Membrane bioreactor treatment of tannery effluents with nitrogen removal and low cost sludge drying. Proceedings for the XXXII Congress of the IULTCS, Istanbul, Turkey

[7] Scholz W., Rougé P., Bodalo A. and Leitz U. (2005) Desalination of mixed tannery effluent with Membrane Bioreactor and Reverse Osmosis Treatment. Journal of Environmental Science & Technology. p. 39:21, 8505 – 8511

[8] Judd S. and Bennett, (2004): A. Membrane Technology recovers water for industrial reuse. Industrial water and wastewater treatment, p.13-14

[9] Scholz W., (2017) Clean Salt Recovery using Nanofiltration. Proceedings for the XXXIV Congress of the IULTCS. Chennai, India