Clean Salt recovery and water recycling using Nanofiltration and Reverse Osmosis

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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. In tannery effluent high concentration of Sodium Salts such as Sodium Chloride and Sodium Sulphates are found, which remain in the effluent after Primary and Biological treatment, resulting in high Total Dry Solids (TDS) levels after conventional treatment. Consequently many tanneries and leather business parks had to implement Zero Liquid Discharge systems to achieve strict TDS discharge limits, which comprise of a complex Tertiary treatment with Reverse Osmosis and Evaporators. The evaporation of the Reverse Osmosis concentrate shows difficulties, due to the nature and complex mix of residual salts causing scaling, which goes along with difficult disposal of the waste salts.

Nanofiltration membranes retain bi-valent ions and residual organics and leave salty water containing only Sodium Chloride, permeating the membrane. Nanofiltration is operated at a lower pressure of about 8-10 bars, thus consuming less energy than Reverse Osmosis and achieves higher recovery rates of up to 90%. This membrane technology is a suitable pre-treatment, due to the separation of scaling compounds and can improve the performance of Reverse Osmosis and the following Evaporators. The residual salt, after evaporation is pure Sodium Chloride, which can potentially be re-used for salting or pickling.

This combination of Nanofiltration with Reverse Osmosis and Evaporation can improve the overall performance of Tertiary tannery effluent treatment allowing for clean salt recovery and consistent high quality water re-use.

Keywords: Tannery effluent, Nanofiltration, Reverse Osmosis, salt recovery, water recycling.

Introduction

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 shockloads. Therefore the produced permeate quality is varying little with the feed water quality [2]. 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. [5]

Nanofiltration

Nanofiltration (NF) is a pressure drive membrane process, where hydraulic pressure is used to exceed the osmotic pressure of the wastewater, to filter water (permeate) through a semi-permeable Nanofiltration membrane. The residual feed stream (reject) is concentrated up during the filtration process and retains divalent and multivalent ions such as calcium, magnesium, sulphates and metals, which are to large to filter through the membrane.

Picture: 1: Nanofiltration plant installed in France

Nanofiltration technology is suitable for high quality water recycling and re-use for most leather processes, where the recycled process water may contain minor concentrations of Sodiumchloride [6]. 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 Sodiumchloride. The consistent quality of the NF enables water re-use [4].

Picture: 2: Holding Tank with Nanofiltration permeate for water recycling.

Reverse Osmosis

Reverse Osmosis (RO) plants are using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure.

The desalinated water that is demineralized or deionized, is called permeate (or product) water. The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream.

As the feed water enters the RO membrane under pressure (enough pressure to overcome osmotic pressure) the water molecules pass through the semi-permeable membrane and the salts and other contaminants are not allowed to pass and are discharged through the reject stream (also known as the concentrate or brine stream). The water that makes it through the RO membrane is called permeate or product water and usually has around 95% to 99% of the dissolved salts removed from it.

RO system employs cross-flow filtration, where, the wastewater passes along the membrane filter with the salt-free permeate passing through the membrane and the salt containing concentrate being retained. To avoid build up of contaminants, cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean.

Table 1: Comparison of Nanofiltration and Reverse Osmosis technology

Comparison	Nanofiltration	Reverse Osmosis
Salt retention	Ca^{2+}, SO_4, Cr^{3+}	NaCl
Permeate	NaCl	Salt free
Purpose	Water softening	Desalination
Recovery rate	75 -90 %	65-75%
Operational Pressure	8-12 bars	18-25 bars

Zero Liquid discharge treatment for tannery CETPs

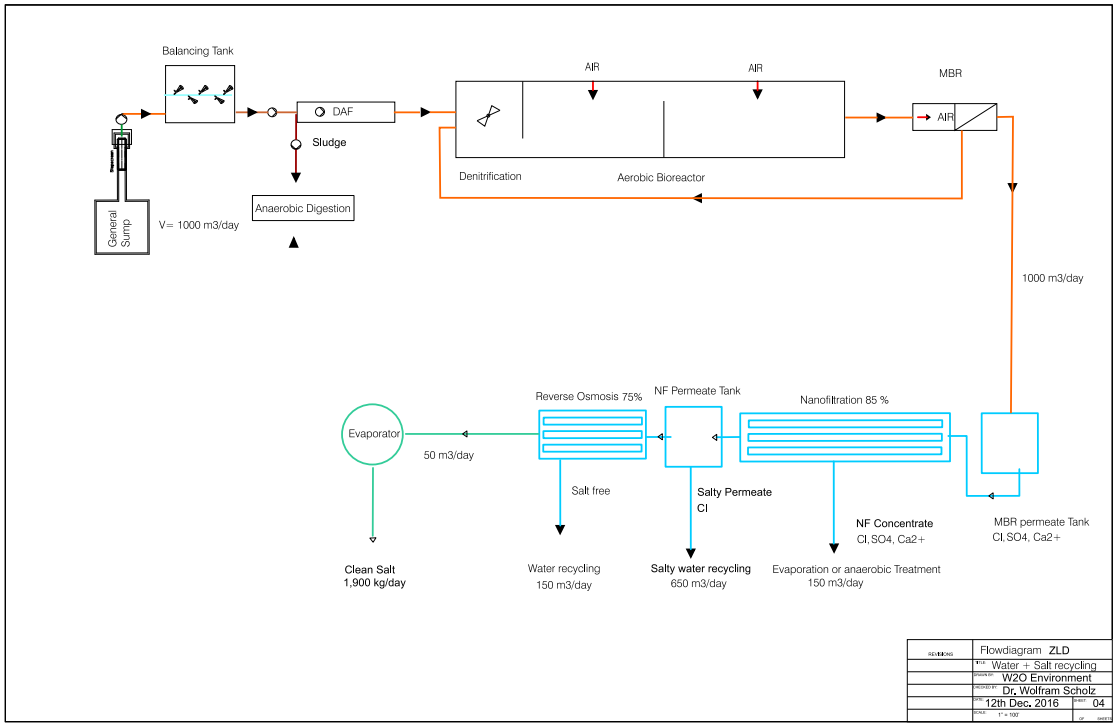
Many tannery business parks, particularly in India and Tamil Nadu, are operating Zero Liquid Discharge ZDL systems to comply with strict environmental regulations in respect of Total Dissolved Solids, TDS [3]. ZDL effluent treatment systems comprise of Primary and Biological Treatments, using Reverse Osmosis for tertiary Treatment to allow for full water recycling for leather processing. The saline reject derived from Reverse Osmosis is then evaporated in Multiple Effect Evaporators (MEE), with the condensate transferred back for leather processing together with the Reverse Osmosis permeate. The salt residue collected from Evaporation is a mix of mono and multivalent salts, organics and chemicals, which consequently make disposal impossible [1].

The concept of integrating Nanofiltration

A Nanofiltration (NF) plant consists of a pre-pressure pump that transfers the effluents via a cartridge filter to the high-pressure pump. The NF plant has several streets of membrane modules containing 7 membranes each assembled in series and is operated at a pressure between 8-12 bars. Nanofiltration requires less energy than equivalent Reverse Osmosis systems for a similar Feed quality.

The slightly salted permeate is collected in a holding tank and can be either recycled back for leather processing or transferred to the following Reverse Osmosis treatment. The plant is fully automatic and shuts down at low level or with changes of the operational pressure. Then the membranes are automatically flushed out with permeate. Compared to Reverse Osmosis higher recovery rates of 75% - 90% can be achieved, which results in a much smaller volume of concentrated brine.

The application of Nanofiltration has shown to completely retain contaminations of larger organic molecules and bi- and multi valent salts, allowing only minor concentrations of Sodium Chloride to filter through the membrane. Nanofiltration treatment is suitable to be integrated into ZLD systems as an ideal pre-treatment before Reverse Osmosis (RO). The slightly salted Permeate contains only Sodium Chloride and can be either re-used for leather processing or diverted for further concentration to the Reverse Osmosis plant. Following Nanofiltration, the performance of the RO plant can improve considerably due to reduced scaling effects, thus achieving higher recovery rates. The concentrate salt brine of the Reverse Osmosis retentate can be evaporated with the multi stage Evaporators achieving a highly clean salt residue, which can be re-used in the tanneries for re-salting or Pickle.



Picture 3: Concept of integration of Nanofiltration into Zero Liquid Discharge treatments

Conclusions

The integration of Nanofiltration into a ZLD systems can achieve between 75 and 90% of water recovery The high quality permeate, containing only reduced concentrations of Sodium Chloride, can be either re-used for leather processing or be further treated with Reverse Osmosis.

The concentrate of the reverse Osmosis contains only Sodium Chloride, which improves the process of evaporation and reduces scaling of the evaporators. Pure Sodium Chloride salt is achieved, with the following crystallization, which can be re-used for re-salting hides or for Pickle. Nanofiltration produces a considerably reduced volume of retentate with a significantly lower TDS compared to Reverse Osmosis.

This combination of Nanofiltration and Reverse Osmosis membrane technologies offers a route of treatment and recovery of high quality water and salt at lower treatment costs. Where appropriate, the quantity of recycled water and salt can be carefully managed to achieve a cost-effective recycling solution.

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