Membrane based process water recycling and side stream membrane bioreactor treatment for effluents from the beamhouse process.

Track: Innovations on the environmental concern

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Abstract

Leather processing involves a series of water intensive batch processes, which are carried out in drums. The resulting waste streams are in many cases combined and can be characterised as a complex mix of organic and inorganic substances. The application of economic water recycling techniques is therefore limited due to contaminations with salts and soluble substances. A viable treatment option is the segregation of highly contaminated process streams and side stream treatment, which allows then for recycling. The integration of membrane technology into currently practiced beam-house processes rationalizes the leather manufacturing process by enabling water recycling and by recovering process chemicals. The relatively small volume of highly organic loaded concentrates resulting from direct membrane filtration can be further treated in a membrane bioreactor to achieve discharge compliance.

Membrane bioreactors (MBRs) are considered to be the ‘Best Available Technology’ for the treatment of industrial effluents. MBR combine an activated sludge process with membrane ultrafiltration to facilitate complete retention of the biomass. This combination results in high mixed liquor suspended solids (MLSS) concentrations leading to increased levels of COD removal efficiency, low waste sludge volumes and a permeate which is solids free. Large scale industrial MBRs have been proven as a successful technology with numerous applications in various industries. However the operation of cross-flow systems is cost intensive due to high cross-flow velocities and operational pressures (up to 8 bars).

Submerged or integrated membrane systems can be operated at significantly lower pressures and, hence, reduced energy consumption and cost. In this case membranes are submerged into the bioreactor and permeate is pumped under negative pressure of only 0.02-0.4 bars. Coarse bubble aeration is applied to induce the necessary cross-flow and to reduce membrane fouling.

The use of a combined side stream membrane filtration and submerged MBR (SMBR) treatment system for the treatment of segregated beamhouse effluents from a Spanish tannery has been evaluated. Soak, lime, washes and degreasing effluent are concentrated by cross-flow membrane filtration, with a 50-67% recovery rate. Permeate resulting from membrane filtration was re-used for leather processing without causing any detrimental effects on leather quality. The highly contaminated concentrates where treated in a submerged membrane bioreactor and a reduction of average 98% COD, 99% BOD and SS and 95% ammonia was achieved at steady permeate flow rates of 25 LMH. Membrane based side stream and MBR treatment of small volumes of highly concentrated waste streams showed to be a viable option for cost effective tannery waste water treatment.

Keywords

Membrane bioreactor , process water recycling, side stream treatment, tannery effluent, ultrafiltration, water and chemical recovery

Abbreviations

BOD_5	biological oxygen demand (mg BOD_5 mg/ l)
Ca^{2+}	Calcium (mg/l)
Cl^-	Chlorine (mg/l)
COD	chemical oxygen demand (mg COD/l)
LMH	liters per square meter filtration area per hour
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids (mg SS/l)
MLVSS	mixed liquor volatile suspended solids (mg VSS/l)
MWCO	molecular weight cut off (kDa)
NH_4-N	ammonia nitrogen (mg/l)
NO_2-N,	nitrate (mg/l)
NO_3-N	nitrite (mg/l)
ortho-P	ortho phosphate (mg/l)
S^{2-}	Sulphides (mg/l)
SO_4^{-2}	Sulphate (mg/l)
TMP	transmembranal pressure (bar)
UF	ultrafiltration

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, de-liming with ammonium salts, degreasing, especially in ovine processing and pickeling to prepare the hide for tanning. Within these processes organic substances as proteins, fats and hair which account for approximately 80 % of the weight of the salted hides are removed and are being discharged from the process as highly organic loaded effluents [1].
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 [2]. By strictly regarding economical demands an approach of “green-processing” has been developed, that enables the leather industry to reduce environmental and operational costs. A part stream related implementation of processes-integrated measures and recycling technologies using Ultrafiltration and Membrane bioreactor technology was tested and optimised in pilot scale to demonstrate the technical and economical feasibility of recycling and to fulfil the quality criteria for leather processing.

The application of membrane filtration for process stream recycling does not alter the chemical or biological characteristics of the process streams and enables therefore direct water recycling [3]. The most contaminating processes during leather production are the initial steps of soaking, liming, the following washes and degreasing operations carried out during ovine leather manufacturing. Membrane filtration was

tested for these four process streams and leather processing trials demonstrated the feasibility of direct re-use. Direct membrane filtration produces a clear permeate, due to the retention of particular matter as well as fats and proteins, which derive from the hide during the beam-house processes.
All the substances, which are retained during filtration are concentrated up during the membrane process and have to be treated separately as a small but highly concentrated volume. Concentrate treatment was carried out in a membrane bioreactor which degraded biologically organic compounds and removed as well nitrogen derived from the protein hydrolysis during the treatment process.

Methods

Membrane screening

Preliminary studies were carried out with the aim to select suitable membranes for each part stream filtration plant [5, 13]. During the membrane screening several ultrafiltration membranes with various cut-offs in the range of 20 – 250KDa and as well organic and ceramic materials were tested on effluents, which were directly collected from the tannery drum (Figure 1.1).

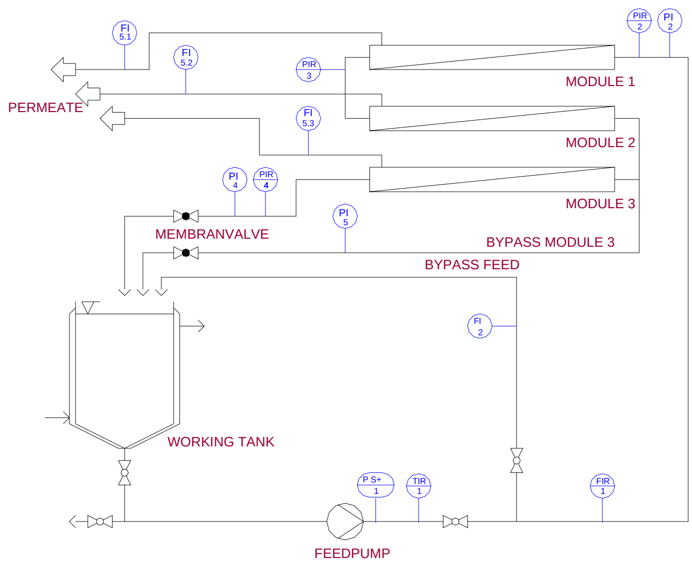

Figure 1.1: Flow diagram of the lab scale membrane testing unit

Adequate membrane modules for each process stream were selected on the basis of retention capacity, permeate flow also under increasing concentration, success of cleaning, regeneration capacity and compatibility to the waste stream and costs [4].
The following three phases were exercised during the membrane screening [5]:

- The re-circulation phase in which wastewater is filtered without any permeate discharge to evaluate the stationary starting condition of the membrane
- The concentration phase, where permeate is discharged continuously to evaluate the effects on permeate flow in the concentration modus
- The regeneration phase, where the efficiency of chemical cleaning to obtain the original permeate flow is evaluated after completion of the filtration test

Clean water tests were conducted before and after the membrane tests to evaluate the membrane performance. Concentrate and permeate samples were taken during the concentration mode were analyzed to evaluate the specific retention capacity of the tested membrane modules.

Table 1.1 gives an overview of the results of the selected membrane modules in respect of the achieved permeate recovery rates, the specific membrane performance and the retention capacity as well as a grading of the cleaning success.

Table1.1: Results of the preliminary membrane screening [5]

part stream	Selected membrane cut-off	achieved concentration rate	flux at min/ max concentration	Retention *[1] at min./ max. concentration (COD)	Filtration performance	Recovery efficiency
		[%]	[lmh]	[%]		
main soak	100 kD/	90 %	130/ 80	89/ 86	++	+
lime	100 kD/	90 %	110/ 40	49/ 6	O	++
washes	20 kD*/	90 %	100/ 60	66/ 28	+	++
degreasing/ tallow recovery	100 kD/	90 %	65/ 50	95/ 93	+	+

*[1] retention related to raw feed concentrations

The results of this initial test showed that the operation in concentration mode up to 90 % permeate recovery was not technical feasible. The membrane performance decreases for most of the part streams when a 70-80% permeate recovery is exceeded during the concentration mode. This which went also along with a decrease of permeate quality.
The results of this preliminary screening served as a basis to design the pilot plants, which were installed at the tanneries to conduct the on-site trials.

Waste water composition, monitoring and analysis

The membrane plant and membrane bioreactor performance was assessed daily for transmembranal pressure, pump rate, permeate flux, pH conductivity, temperature and DO. Samples were taken regularly from the feed, concentrate or mixed reactor liquor and permeate and analysed for COD, BOD, MLSS, MLVSS, ash content, dry matter, organic matter, N- Kjeldahl NO_3-N, NO_2-N, ammonia-N, ortho-P, S2-, Cl^-, SO_4^{-2}, Ca^{2+}, fats and detergents were assessed on a weekly basis according to the Spanish Standards for the Examination of wastewater.

Results and discussion

Soak liquor recycling

Fresh or salted hides are initially soaked in water to clean and re-hydrate them prior to leather processing. Soaking requires large quantities of fresh water. This liquor is characterized as being highly contaminated with suspended and dissolved organic matter, salts, surfactants, proteins and hair removed from the hides and skins. In a very few cases, final soak liquors are recycled for re-use in dirt soak [11]. This is not generally used, because of the bacterial contamination, which damage the hides. Membrane filtration of soak liquors enabled recycling of water and surfactants back into the dirt soak process [8]. Quality assessment, i.e. physical and visual testing of permeate soaked hides/skins were carried out to evaluate the leather quality after process water recovery. As an advantage, the permeate obtained from the membrane filtration was free of bacteria, thus no addition of bactericides was required to disinfect the recycled permeate. Soak effluents were collected from the drum and then transferred via a 200 μm screen to the membrane filtration plant (Figure 1.2).

Table1.2: Overview of average feed waste stream, concentrate and permeate characteristics and elimination rates

Parameters (mg/l)	Feed	Retentate	Permeate	(%)
COD	9,095	16,384	2,758	70
BOD_5	4,618	8,167	1,146	75
TKN	454	673	199	56
Fats	977	1812	N/D	100
MLSS	3,797	7,404	73	98
Dry matter (%)	2	2.5	1.6	20
Organic matter (%)	0.4	0.6	0.1	75

The soak liquors were filtered with the membrane plant at 50 % recovery rate achieving permeate flux rates of 50-60 LMH. The feed concentration of average 9,095 mg/l COD, 3,797mg/l MLSS and 454 mg/l N-Kjeldahl was reduced to 2,758 mg/l COD, 73 mg/l MLSS and 199 mg/l N-Kjeldahl in the permeate (Table 1.2).

Figure 1.2: Membrane pilot-plant for soak liquor recovery

The permeate was collected, diluted 1:1 with tap water and re-used for soaking operations. Sides were processed with permeate and a fresh water control, finished and dyed. In the following the chrome content, physical parameters as crack load distension, burst load distension, tensile strength, percentage elongation at break, tearing load, shrinkage temperature and boiling prove were determined for sides of bovine hides, which were processed with permeate or fresh water as control. The physical parameters of the permeate processed sides gave comparable results with the fresh water control.

Recovery of lime and sulphides from spent un-hairing liquors

Conventional un-hairing/liming processes rely on the application of sodium sulphide or a mixture of sodium sulphide and sodium hydrosulphide to remove the hair. There are essentially two types of process for un-hairing; the more traditional is the 'hair burn' process in which the aim is to degrade all of the hair, the other is the 'hair save' process in which the aim is to degrade the hair root only thus releasing the hair shaft which is removed by screening [9]. Complete removal of hair and hair residue is an important issue for the tanner. Even small amounts of hair root remaining in the hair follicle can result in the downgrading of the leather produced with consequent financial implications for the tanner. There is, consequently, a tendency to 'play safe' and use a slight excess of un-hairing agent. Un-hairing chemicals, which are lost, can be recovered successfully by membrane filtration technologies [7, 8 and 11] The recovery of un-hairing liquors was demonstrated in an on-site pilot membrane filtration plant and optimised for the maximum recovery of chemicals and sufficient retention of protein matter and residual hair and fibres (Figure 1.3).

Figure 1.3: Membrane pilot-plant for lime liquor recovery

Within the investigation, the potential recovery and re-use of un-hairing liquors was tested and the associated costs of recovery and re-use versus traditional means of discharge calculated. The figures given relate to what might be expected from a medium sized European wet blue operation and have been compiled with the assistance of a Spanish tanner.

The un-hairing liquors, which are the most contaminated liquors from the tanning process, were pre-screened using 200 μm mesh to remove the large amount of hair and fibers. Several batches of spent lime liquors were filtered with the membrane plant at 25, 50 % and 57 % recovery rate. The membrane plant was operated at 2.5 bars inlet pressure and 22m3/hr cross flow velocity and an average permeate flux rate of 40-50 LMH was achieved.

The feed concentration of 25.4 g/l COD, 8.8 g/l MLSS, 1.8 g/l TKN and 0.42 g/l fats was reduced to 10.7 g/l COD, 0 mg/l MLSS, 0.76 g/l TKN and 0 g/l fats in the permeate (Table 1.3). Approximately 90% of sulphides and 50 % of lime were recovered (Table 1.4).

Table1.3: Overview of feed waste stream, concentrate and permeate characteristics and elimination rates

Parameters (mg/l)	Feed	Retentate	Permeate	(%)
COD	25,405	35,122	10,654	58
SS	8,769	14,932	0	100
TKN	1,787	2,384	758	21
Fats	424	792	N/D	100
Ca2+	3,272	4,019	1,477	55
Sulphides	2,571	2,960	2,236	13

The recovered un-hairing liquors were analyzed for lime and sulphides and then adjusted up to the desired concentrations and tested for leather processing (Table 1.2 and 1.3). The permeate was re-used for liming operations in the recirculation stage of the hair save process.

Table1.4: Percentage of un-hairing chemicals recovered from the initial bath concentration

Chemicals	Percentage recovered (%)
Sulphides	49
Lime	25
Volume	90

On semi technical scale (pilot scale) the standard process was compared to a process incorporating recovered liquors and the resultant limed hides were assessed for the degree of hair removal. Standard leather from current production was also taken as a reference. Visual and physical quality assessment of hair removal demonstrated the feasibility of un-hairing liquor recovery.
The results of this case study demonstrate the feasibility of un-hairing liquor recovery by membrane filtration, which can offer significant cost savings due to recycling and to reduction in effluent discharge.

Water recovery from wash liquors

At the end of the conventional unhairing/liming process it is necessary to wash the hides/pelts prior to ‘deliming’. The purpose of this is to remove excess chemicals remaining from the previous stage, both to limit the amount of ‘deliming’ chemicals required and to remove excess sulphide. At high pH conditions sulphide is soluble, as the pH is lowered the solubility decreases and under acidic conditions toxic hydrogen sulphide gas is liberated.
The potential for the re-use of wash liquors exists i.e. for the first wash or for main soak of hides prior to the beamhouse operations, although some pH adjustment may be necessary.

Membrane filtration was applied for the purpose of water recovery. Washes liquors were collected in a sump and transferred like the lime liquors via a screen into the working tank.
Several batches of spent wash liquors were filtered with the membrane plant at 25, 37.5 and 50 % recovery rate. The membrane plant was operated at 2.5 bars inlet pressure and 22m3/hr cross flow velocity and an average permeate flux rate of 50-60 LMH was achieved. The feed concentration of 5.7 g/l COD and 2.6 g/l MLSS was reduced to 2.3 g/l COD and 20 mg/l MLSS in the permeate. The concentration of sulphides and lime were average 0.76 g/l S^{2-} and 0.86 g/l Ca^{2+} (Table 1.5). The permeate was collected, diluted 1:1 with tap water and re-used for washing operations. Sides were processed with permeate and a fresh water control, finished and dyed.

Table1.5: Overview of feed waste stream, concentrate and permeate characteristics and elimination rates

Parameters (mg/l)	Feed	Retentate	Permeate	(%)
COD	5,770	9,152	2,439	58
MLSS	1,739	2,786	20	99
TKN	819	1,378	379	54
Fats	280	340	N/D	100
Ca^{2+}	1,205	1,266	860	29
Sulphides	875	853	758	13

Degreasing liquor recycling

There is a growing interest of tanneries to replace conventional degreasing using solvents with a more environmental friendly aqueous degreasing applying surfactants. One disadvantage of aqueous degreasing is the accumulation of emulsified fats, which are insufficiently removed by conventional methods like oil separators. There are various membrane applications to treat oil/water emulsions, which enable an efficient retention of oils and recovery of water [7].

Spent ovine degreasing liquors were collected and screened from the drum, transferred to the membrane filtration plant (Figure 1.4) and filtered at 50 % recovery rate, achieving an average permeate flux rate of 120 LMH. The feed concentration of average 16.8g/l COD, 0.3 g/l MLSS, 6.23 g/l fats and 4 g/l detergents was reduced to 0.95 g/l COD, 0.01 g/l MLSS, 0.2 g/l fats and 0.36 g/l detergents in the permeate. (Table 1.6)

The permeate was collected, diluted 1:1 with tap water and re-used for degreasing operations. Sides of sheep skins were processed with permeate or fresh water as a control and then finished and dyed. In the following the chrome content, physical parameters as crack load distension, burst load distension, tearing load, shrinkage temperature and boiling prove were determined for the permeate and control processed skins. The physical parameters are comparable and the processed skins are suitable for garment leather. The fat content of the concentrate was 9,5 g/l and can be recovered as natural oil in a tallow recovery plant.

Figure 1.4: Membrane pilot-plant for degreasing liquor recovery

Table1.6: Overview of feed waste stream, concentrate and permeate characteristics and elimination rates

Parameters (mg/l)	Feed	Retentate	Permeate	(%)
COD	16,847	25,308	950	94
BOD_5	5,119	6,704	386	92
MLSS	317	427	10	97
TKN	97	120	41	58
Fats	6,235	9,473	197	97
Detergents	3,994	6,967	361	91
Organic matter (%)	1.3	1.8	0.1	92

Submerged membrane bioreactors for beamhouse liquor side stream treatment

Membrane bioreactors (MBR) are an emerging technology of major potential in wastewater treatment. They provide a relatively compact alternative to conventional biological treatment options, producing a 'guaranteed' high quality effluent even at high and varying organic loading rates [10]. The process relies on membrane filtration to effectively retain all the biomass in the bioreactor as opposed to conventional treatment, where the biomass is wasted. As a consequence, the MBR process is operated at much higher mixed liquor concentrations, up to 20 g/l MLSS, than conventional biological treatment [6]. A major benefit of MBR, resulting from increased sludge retention times and operating temperatures, is the reduction of surplus sludge generation [15]. A relatively low cost MBR, developed specifically for the treatment of tannery effluent, was reported to effectively treat difficult tannery effluent streams and enable water re-use in the leather manufacturing process [14]. The MBR process is well suited for tannery effluents which generally require long retention times for the effective biological treatment of the less degradable organic pollutants present. MBR would, therefore, be expected to provide an adequate pretreatment to prevent fouling by residual organics of RO membranes, during the polishing of tannery effluents.

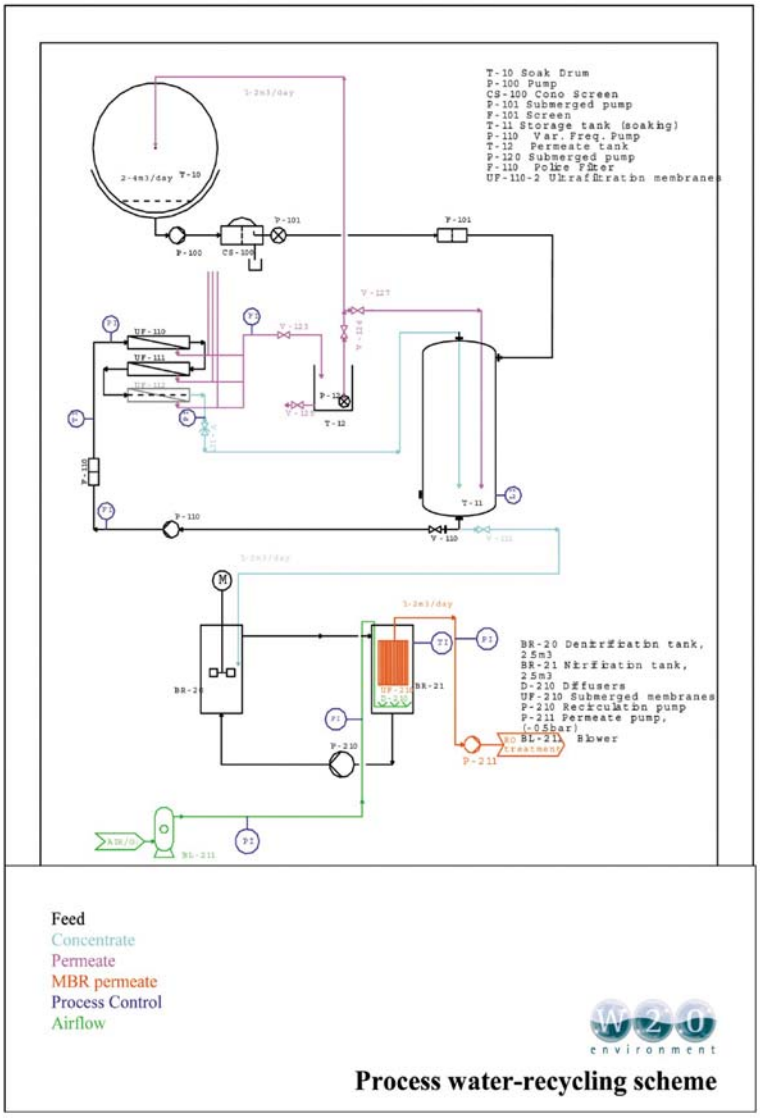

Figure 1.5: Process Flow Diagram of the Soak recovery and MBR process

Membrane bioreactors (MBR's) are nowadays considered as 'Best available Technology' for industrial effluent treatment. Large scale industrial cross-flow MBR's have been proven as a successful technology with numerous applications in various industries [10, 12]. Currently two cross-flow MBR's with external ultrafiltration membrane units are in operation in European tanneries [16, 17]. However the operation of cross-flow systems is highly cost intensive due to high cross flow velocities of 3.5-5 m/sec and to operational pressures of up to 8 bars applied. Approximately 5-8 kWh electricity are consumed to produce 1 m3 of clean and suspended solid free effluent. Submerged or integrated membrane systems can be operated at significantly lower pressures and hence energy consumption. In this case membranes are submerged into the bioreactor and permeate is pumped under negative pressure of only 0.2-0.4 bars. Coarse bubble aeration is applied to achieve the necessary cross-flow and to avoid membrane fouling,. The energy requirements of submerged membranes are significantly lower with 0.5 kWh per $1m^3$ of permeate produced.

The aim of this research was to evaluate a novel combined treatment process with part stream treatment and recycling by membrane filtration and advanced biological MBR treatment of beamhouse concentrates in a continuous on-site pilot trial. (Figure 1.6). Beamhouse liquor concentrates were collected from the membrane filtration plants and mixed according to the volume percentages as discharged from the beamhouse operations. The waste concentrate mix of 53% soak, 10% lime, 21% washes and 16% degreasing was transferred to an aerated balancing tank and was fed continuously to the MBR for advanced biological treatment (Figure 1.5).

The MBR consisted of a $5m^3$ nitrification, which is aerated with fine bubble diffusers. The nitrification is connected via an overflow with a two-chambered agitated $5m^3$ denitrification tank, where nitrates are reduced to molecular nitrogen and are therefore completely eliminated. A framed 20 m^2 plate membrane rig is submerged (Figure 1.6) into the nitrification tank and permeate is drained via a suction pump. To start up the MBR process, the MBR plant was inoculated with 10 m^3 activated sludge from a municipal waste water treatment plant and fed with $2m^3$ concentrate per day.

Significant reductions in the organic content of the mixed effluent were achieved during the MBR trials (Table 1.7). The effluent was treated at a retention time of 2.5 days with submerged microfiltration membranes, achieving reductions in COD of 98 % and in BOD_5 of up to 100%. A high rate of nitrification (99%) was also achieved. The during the nitrification generated nitrate was de-nitrified to molecular nitrogen gas achieving reduction of ammonia, nitrate and Kjeldahl nitrogen of up to 95%.

Table 1.7: MBR efficiency for concentrate treatment achieved in COD, BOD_5, N-Kjeldahl and NH_4-N reduction . Average of n samples taken over a period of 6 months

Parameter (mg/l)	Number of samples (n)	Influent Range (mg/l)	Average (mg/l)	Permeate Range (mg/l)	Average (mg/l)	Mean removal (%)
COD	38	5,412-58,770	24,792	46-1,552	495	98
BOD_5	38	2,630-22,560	9,599	<5 - 30	6	100
N-Kjeldahl	38	239-2,641	1,031	<5 - 174	80	92
NH_4-N	38	175-1,161	497	<5-139	25	95

The trials demonstrated the successful long term application of MBR technology for the treatment of tannery effluents with large reductions in COD, BOD_5, ammonia and nitrate achieved. Although the COD feed concentrations changed in the course of the trials in the range from 5,412-58,770 mg/l, the COD concentration of the permeate was maintained at an average of 495 mg/l, demonstrating the robustness of the MBR to variations in COD loads.

The results showed an excellent performance of the MBR plant. A permeate flow of average $0.5m^3/hr$ was achieved at < 0.35 bars differential pressure. The extended on-site trials using submerged plate membranes gave good results with high and stable flux rates. The average flux rates achieved were 25 LMH. The bioreactor showed to be very suitable to treat highly concentrated waste streams. The feed concentrations were considerably higher due to increasing concentrations during membrane filtration. In the course of the trials a COD and nitrogen reduction of up to 99 % were achieved. MBR permeate was used for leather processing trials and showed to be of a sufficient quality to be re-used for beamhouse processing. In the future development of the research program a subsequent Reverse Osmosis treatment will be applied to enable upstream recycling of high quality salt free water.

Figure 1.6.. Submerged plate membranes in a Membrane Bioreactor

Conclusions

In order to reduce pollution and simplify water purification a modern strategy is the recovery and recycling of chemicals that are not consumed during leather processing. Membrane filtration was tested in the range of Micro- and Ultrafiltration to purify four selected part streams of beamhouse processing. The results demonstrate membrane filtration to be a valid approach for the recovery of primary resources and for separation, purification and concentration of products used in leather processing.

The recovery of soaking liquors using ultrafiltration demonstrated the feasibility of membrane treatment achieving high permeate flux rates of 50-60 LMH. The operation of ultrafiltration membranes demonstrated to remove proteins and fibers, thus enabling 50 % liquor recovery for re-use in dirt soak.

The recovery of un-hairing liquors demonstrated at high recovery rates (90 % the original volume), reasonable flux rates of 40-50 LMH and by achieving significant savings of 50 % sulphides and 25 % lime the feasibility of recycling.

Membrane filtration for spent degreasing liquors showed an excellent reduction of COD, fats and proteins, achieving high permeate flux rates of 120 LMH and demonstrated the feasibility of process water recovery. The concentrate contains natural fats which can be recovered in a subsequent tallow recovery plant.

The investigated 'clean technology' application of membranes brings the possibility of zero pollutant discharge closer to reality. The investigations carried out demonstrated clearly the benefits and economical feasibility of membrane applications for chemical recovery in the leather industry.

The application of submerged membrane bioreactor technology for the treatment of highly contaminated part stream concentrates showed to be a technical and economical feasible option for efficient side stream treatment. During the membrane bioreactor treatment an average reduction of 98% COD and 99% BOD and SS and a stable membrane performance was achieved. The MBR treated effluent can be therefore discharged to sewer complying with European discharge consents for tannery effluents.

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