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RECOVERY OF BETTER QUALITY REUSABLE SALT FROM SOAK LIQUOR OF TANNERIES IN SOLAR EVAPORATION PANS

Central Pollution Control Board
Ministry of Environment & Forests
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FOREWORD

Tanning an ancient craft in India, a cottage industry for several centuries attained the status of a mature industry significantly contributing in country's economy. The industry imparts export avenues and employment generation for economically weaker sections. The tanning units in India are mainly concentrated in the states like Tamil Nadu, West Bengal, Uttar Pradesh, & Punjab.

The Tanneries are of major concern considering their pollution potential. The tannery effluent is characterized by high dissolved solids due to presence of large amount of salt used for curing/ preservation of hides/ skins. The cured hides/ skins are soaked and washed with water to remove salt and dirt. Evaporating the soak/ wash water (saline liquor) in solar evaporation ponds (SEPs) is generally practiced for recovery of the salt which is not much of reuse due to presence of organic impurities.

The Central Pollution Control Board (CPCB) initiated the efforts on "Removal of Suspended and Organic Impurities in the Saline Soak Water Streams from Tannery to Obtain Better Quality Salt in the Solar Evaporation Pans". In conjunction with this, study was conducted by Central Leather Research Institute, Chennai.

A pilot plant was established in a CETP at Vaniyambadi, Tamil Nadu, for removal of suspended, colloidal & organic impurities from segregated saline soak liquor by physico-chemical and biological treatment followed by membrane process to recover the water and salt. This pilot plant study aimed to assess the performance under field conditions. The findings are enumerated in this report.

The assistance extended by the tannery units and CETP management, Vaniyambadi during this study is gratefully acknowledged. Dr. B. Sengupta, former Member Secretary and Sh. J. S. Kamyotra. Member Secretary lead the team of Shri U. N. Singh, SEE, Shri R. C. Saxena, SEE and Ms. Pavithra L. J. AEE, in preparing this volume.

I hope that this document will be useful to the Industry, Regulatory Authorities, Policy makers and all concerned with environmental management.

Delhi
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1.0 Introduction

1.1 Background

Tannery sector is the significant contributor to the export of Indian economy and provides large scale employment opportunity for people of economically weaker section of the society. Further 93% of the tanneries in organized sector come under the small scale industry category. Besides being important from economic and employment generation consideration, the tannery sector is also important from environment protection point of view, because preservation and processing of raw hides and skins cause severe pollution problem.

The Tanning industry in India is well developed. It has back up of a strong R&D base, modern technology as well as trained manpower. The unique aspect is that it turns out best possible quality leathers from relatively low quality hides. India annually produces around 180 million sq. m of leather, which accounts for about 10% of global production. Goat and buffalo based leathers are India’s major strength.. Major tanning centers in India are shown below. Out of 2500 tanneries in India, Taminadu accounts for 50%, West Bengal 20% and U.P. 15%.

Major tanning centers in India

Sl. No	Region	Area
1	Tamil Nadu	Chennai, Ambur, Ranipet, Vaniyambadi, Erode, Trichy and Dindigul
2	Andhra Pradesh	Hyderabad/Warangal
3	Karnataka	Bangalore
4	Punjab	Jallandhar
6	West Bengal	Kolkata
7	Uttar Pradesh	Kanpur, Unnao and Agra

1.2 Importance of the Project

The segregation, collection and disposal of saline wastewater streams into solar evaporation are practiced in tanneries to minimize the Total Dissolved Solids (TDS) and Chlorides in the treated effluent and to protect the environment. The wastewater generated from the soaking operation contains soluble proteins such as albumin & globulin and suspended matters like dirt dung and blood in addition to salt. In conventional solar evaporation pans there is no physico-chemical treatment provision and the suspended solids settle down in the pans and affect the evaporation rate. In addition to that, the salt obtained in the pans is highly contaminated for reuse and the purpose for which the solar evaporation pans installed are not served fully. In order to obtain better quality salt in solar evaporation pans, the Central Board took up a study on “Removal of Suspended and Organic Impurities in the Saline Soak Water Streams from Tannery to Obtain Better Quality Salt in the Solar Evaporation Pans”.

1.1 Objectives:

The objectives of the present study are:

1. Detailed inventory of existing system
2. Characterization of spent soak liquor
3. Removal of suspended and colloidal impurities from saline soak liquor by physico chemical treatment
4. Removal of organics through biological treatment Process.
5. Design and implementation of pilot scale membrane system for the recovery of water and concentrated saline liquor
6. Reuse of concentrated saline liquor for pickling process
7. Demonstration and dissemination

2.0 SOURCES OF SALINE SOAK LIQUOR

2.1 Preservation

The main problem in handling raw hides/skins is the transport from the slaughterhouse to the tanneries. The slaughterhouses are not well organized, and, situated in remote areas. So transport of the raw skins/ hides to the tanneries takes more time. But during transportation, the raw skin/ hide degrades as a result of variation in temperature and the microbial attack due to the presence of moisture and nutrients. Therefore, the preservation of the raw skins/ hides is necessary.

In India, hides and skins are preserved with common salt at abattoirs or at local collection centers. Hides and skins obtained after flaying contain water to the extent of about two-thirds of their weight. The presence of moisture makes the hides and skins very liable to bacterial attack. Putrefying bacteria degrade the hides and skins causing damage to both grain and flesh side of the pelt and leads to greater degree of degradation**.** To avoid this, generally salt (30 – 40% on raw hide/skin weight basis) is applied on the flesh side of the hides and skins. The salt dehydrates the hides and skins to moisture content insufficient to support the growth of moulds and bacteria.

2.2 Soaking and Washing

Soaking and washing is carried out in the tannery to remove salt, any foreign material such as dirt and manure and to restore the moisture content of hides/ skins. Additives like wetting agents, Surfactants and enzyme preparations are generally used in the soaking operation. Soaking is generally carried out in pit or paddle.

Soaking is normally carried out employing two or three changes of water namely

- Pre or dirt soaking (soaking I)
- Main soaking (soaking II)
- Wash after main soaking (soaking III)

In the first soak, the hides / skins are soaked in water, about 300 to 400% on the raw weight basis, for a period of about 3-4 hrs. After draining the water, the hides and skins are soaked again with 300 to 400% of fresh water with 0.1 to 0.2% of wetting agent and 0.2% of preservative. The hides / skins are left in the bath over night. Next day the skins are piled to drain off and taken for liming. In some tanneries, an intermediate soaking (washing) with about 300% water for a period of about one hour is also carried out.

The efficiency of soaking process depends on the quality of water (water softness and bacterial count), temperature and duration of soaking, nature of raw material (fresh, wet salted, dry, dry salted skins/ hides).

2.3 Soak Liquor

The wastewater generated from the soaking operation i.e., soak liquor, contains salt, soluble proteins such as albumin & globulin and suspended matters like dirt dung & blood. Obnoxious smell and ammonical odour emanating from degraded proteins is also associated with spent soak liquor. Quantity of wastewater discharged from the soaking operation is given in table below.
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Quantity of water used and wastewater discharged from soaking operations

Sl. No	Operation	Float volume in percentage (%)	Quantity per tonne of salted skin soaked in litres
1	Pre or dirt soaking (soaking I)	300 - 400	3000 - 4000
2	Main soaking (soaking II)	300 - 400	3000 - 4000
3	Wash after main soaking (soaking III)	300 - 400	3000 - 4000

Soaking is divided into two parts namely dirt soaking (removal of salt, dirt, dung etc.) and main soaking. Both the dirt soaking and main soaking are discharged directly into the solar evaporation pans. Most of the organic pollutants in the dirt soak are from the raw material. Dung, soluble proteins, hydrolysable fats, soluble salt etc are washed away with water resulting in increase in suspended solids, biodegradable organics and dissolved solids concentration.

2.4 Disposal of Soak Liquor

In Tamil Nadu, according to pollution control regulations, the tanneries are required to segregate the salt laden soak liquor and discharge into solar evaporation pans (SEPs). In Vaniyambadi, wastewater from soaking operations in individual tanneries are segregated and conveyed to common solar evaporation pans at CETP through underground pipeline.

2.5 Evaporation in Solar Evaporation Pans

The annual water evaporation in North Arcot District is about 250 cm per year (i.e. about 6 mm/day). Average evaporation rate for saline soak water was fixed at 4.5 mm per day in solar pans by TNPCB. Accordingly 220 m^2 area of solar evaporation is provided per m^3 of soak liquor.

However in the actual field conditions, mainly due to the presence of high suspended solids concentration and organic matter the evaporation rate has been found to be low. Foul smell due to the biodegradation of suspended organic matter is often observed in most of the pans. Salt obtained from SEP is impure and not reusable.

Organic matter in the soak liquor undergoes anaerobic degradation resulting in the obnoxious odour emission from the pans. This condition facilitates the growth of purple sulphur bacteria and result in the formation of pink coloration to the liquor. The growth of purple bacteria also contributes significant source of suspended solids and reduces the evaporation rate.

The recovered dry salt is about 75% pure and contains more than 20% organic & other impurities rendering it useless. It is therefore necessary to remove the suspended solids from the soak liquor before discharging in to SEP.

3.0 LABORATORY STUDY

Laboratory studies were carried out in CLRI lab at Chennai, which comprised characterization of soak liquor, feasibility of removing the suspended solids and organic impurities form soak liquor in order to obtain better quality salt in the solar evaporation pans.

3.1 Characteristics of Soak Liquor

The segregated soak liquor is conveyed through pipeline from individual units to common solar evaporation pans at CETP in Vaniyambadi. In the present study the soak liquor was collected periodically from the discharge point at the entry of common solar evaporation pans and was analyzed for various parameters. The characteristics of the soak liquor is given in the table below.

Characteristics of soak liquor received in the CETP

Parameter	Value				
pH	7.7	7.2	7.6	7.8	8.0
BOD 5 day at 20^{o}C	1600	3000	1200	1800	2800
COD	3200	5000	2700	3400	4000
Total Solids (TS)	28000	42000	23000	32000	40000
Total Dissolved Solids (TDS)	25000	37000	20500	28800	36000
Suspended Solids (SS)	3000	5000	2500	3200	4000

Chloride as Cl^-	15000	18700	12000	14000	18000
Sulphate as SO_4^{2-}	650	1000	500	750	900

Note : All values except pH are expressed in mg/L.

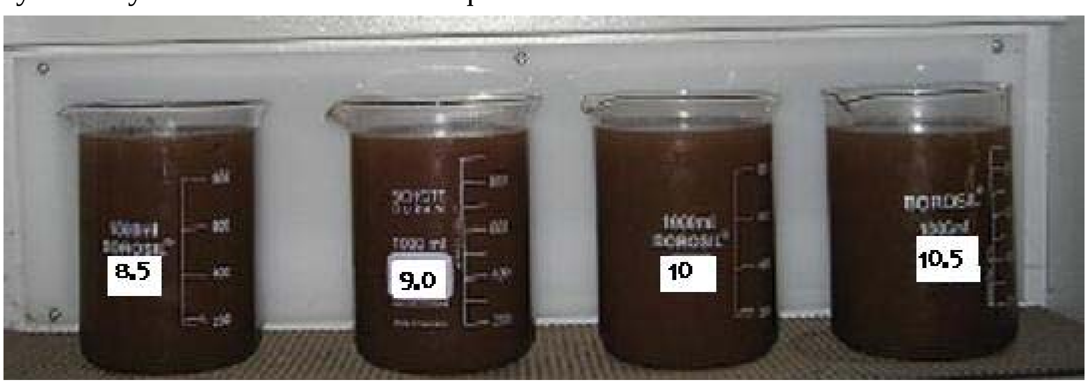
Soak liquor is contaminated with soluble proteins, dung, dirt and other suspended impurities. High concentration of suspended solids (2500-5000 mg/L) and other impurities reduce the evaporation rate. If the soak liquor is discharged to the Solar Evaporation Pans without treatment, the salt obtained is impure and is not fit for reuse. In order to improve the evaporation rate and to improve the quality of the dried, the following study was carried out in laboratory.

- Removal of suspended solids in the soak liquor by simple physico-chemical treatment
- Removal of dissolved organic impurities in the soak liquor by biological treatment process

3.2 Removal of Suspended Impurities by Physico-chemical Treatment

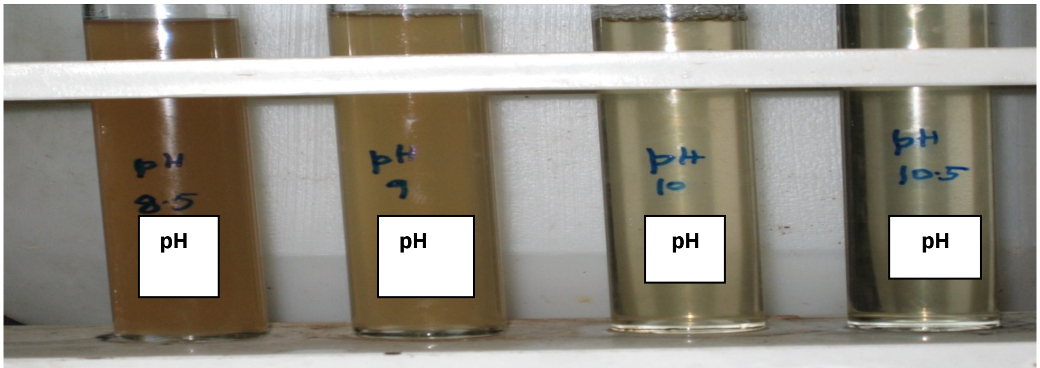
Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Lime, Alum (10%) and Polyelectrolyte (0.01%) were used as coagulants. Rapid mixing of liquid with addition of coagulants leads collision of particles to form larger particles (flocs). Coagulation can effectively reduce the concentration of pollutants in soak wastewater. Batch scale studies were carried out using Jar test apparatus. Coagulation studies were done by increasing the pH from 8.5 to 10.5 using lime and subsequently brought back to pH 7.5 using 10% Alum. 1ml of 0.01% polyelectrolyte was also added.

In physico chemical treatment of soak liquor, first lime was added to increase the pH from 7.5-7.8 range to pH 8.5, 9.0, 10.0 and 10.5. Simultaneously 10% alum solution was added to bring down the pH to about 7.5 followed by 1ml of 0.01% of cationic polyelectrolyte was added. Final pH of the solution after the addition of alum and polyelectrolyte was about 7.5. Soak liquor before chemical treatment is shown below



SOAK LIQUOR BEFORE COAGULATION

After rapid mixing the liquor was allowed to settle for 2 hrs and the supernatant was removed. The supernatant after treatment at different pH are shown below.



SOAK LIQUOR AFTER COAGULATION

Quantity of chemicals used in the chemical treatment is given in table below.

Quantity of the chemicals used for coagulation studies

S.No	Nature of sample	Wt of Lime added for one litre of sample (gm)	Volume of 10% Alum added (mL)	Volume of 0.01% polyelectrolyte added (mL)
1	pH adjusted to 8.5 using lime, alum and polyelectrolyte (pH7.5)	0.05-0.1	2-3	1
2	pH adjusted to 9.0 using lime, alum and polyelectrolyte (pH7.5)	0.12-0.2	4-6	1
3	pH adjusted to 10.0 using lime, alum and polyelectrolyte (pH7.5)	0.5-0.7	10-14	1
4	pH adjusted to 10.5 using lime, alum and polyelectrolyte (pH7.5)	0.7-0.9	14-20	1

After settling, the supernatant was removed for the analysis to find out the percentage removal of the pollutants at various coagulant doses. Characteristics of the supernatant is given in table below.

Characteristics of the supernatant liquor

S.No	Nature of sample	Suspended solids (mg/L)	COD (mg/L)	BOD (mg/L)
1	Raw sample's pH (7.5-7.8)	3000-5000	3000-5000	1000-3000
2	Plain Settling for 30 minutes (pH 7.5-8.0)	2500-4000	2500-4500	900-2500
3	pH adjusted to 8.5 using lime, alum and polyelectrolyte (pH7.5)	1500-2000	2000-3000	700-1800
4	pH adjusted to 9.0 using lime , alum and polyelectrolyte (pH7.5)	1800-1500	1500-2500	500-1200
5	pH adjusted to 10.0 using lime , alum and polyelectrolyte (pH7.5)	400-800	1200-1800	400-800
6	pH adjusted to 10.5 using lime , alum and polyelectrolyte (pH7.5)	200-500	500-1200	300-700

The results clearly indicate that most of the suspended solids are organic in nature, with the removal of suspended solids, the COD & BOD values are decreased. Turbidity of the supernatant was determined for all the samples and the results are given in Table below.

Turbidity of the supernatant after physico chemical treatment

S.No	Nature of sample	Turbidity (NTU)
1	Raw sample's pH (7.5-7.8)	900-1000
2	Plain Settling for 30 minutes (pH 7.5-8.0)	700-900
3	pH adjusted to 8.5 using lime	400-600
4	pH adjusted to 9.0 using lime	100-300
5	pH adjusted to 10.0 using lime	20-50
6	pH adjusted to 10.5 using lime	10-20

The results clearly indicate that physico chemical treatment improves the quality of the wastewater and the subsequently the quality of salt obtained in solar evaporation pans. Based on the results, pH adjustment to 10.5 using lime followed by alum and polyelectrolyte addition removes maximum quantity of pollutants from the soak liquor.

3.3 Observations

- Suspended solids concentration in saline soak liquor is in the range of 3000-5000 mg/l. This reduces the evaporation rate in solar evaporation pans.
- By suitable physico chemical treatment more than 90% reduction in suspended solids was achieved.

- In Physico chemical treatment 0.7-0.9 g of lime, 14-20 ml of 10% alum and 1mL of 0.01% polyelectrolyte per liter of soak liquor are required.
- The variation in quantity of chemicals required depends upon the quality of soak liquor in terms of pH, suspended solids concentration etc.

Supernatant after physico chemical treatment contains dissolved organics and residual suspended solids, and, the salt is not suitable for reuse in pickling. Therefore, further studies were carried out to remove the organics by biological method.

3.4 Removal of Dissolved Organics by Biological Treatment Process

Biological treatment studies were carried out in the laboratory to find out the feasibility of reducing the organics present after physico chemical treatment. The supernatant of soak liquor with pH adjustment to 10.5 followed by alum and polyelectrolyte addition was fed into biological treatment system for the removal of dissolved and residual organics.

Supernatant wastewater flows continuously into an aeration tank where air is injected into the wastewater to mix it with the bio sludge, and also to provide the oxygen needed for the microorganisms to break down the organic pollutants. The mixed liquor flows to a settling compartment, where the bio sludge settles out and part of the settled sludge is returned to the aeration tank to maintain a high population of microbes to break down the organics.

The activated sludge process (ASP) is currently the most widely used biological treatment process. ASP allows microorganisms to adapt to change in wastewater composition with relatively short acclimation time and also allows a greater degree of control over acclimated bacterial population.

3.5 Seeding

Biological treatment of saline wastewater usually results in low *BOD* removal performance because of adverse effects of salt on microbial flora. High salt concentrations cause plasmolysis and/or loss of activity of cells. Rapid changes in salt concentration caused immediate release of cellular constituents and resulting in an increase in soluble *COD*. Due to this, seeding was taken from the settleable sludge in the solar evaporation pans. Acclimatization of soak liquor was done under aerobic condition.

3.6 Feed Characteristics

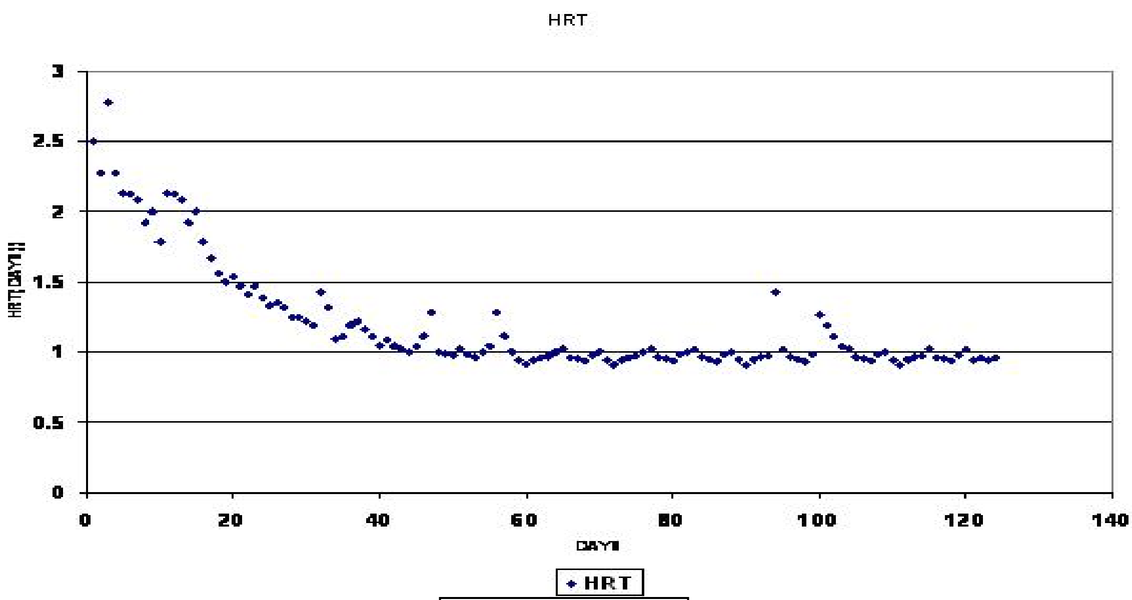
Due to variation in water usage and raw materials, fluctuation in wastewater characteristics was observed. The average feed characteristic during the study period is given in the Table below.

Characteristics of soak liquor after physico chemical treatment

S.NO	PARAMETER	UNIT	VALUE
1	pH		7.3-7.8
2	COD	mg/L	500-1200
3	BOD	mg/L	300-700
4	Chlorides as Cl^-	mg/L	12000-19000
5	Suspended solids	mg/L	200-500

3.7 HRT

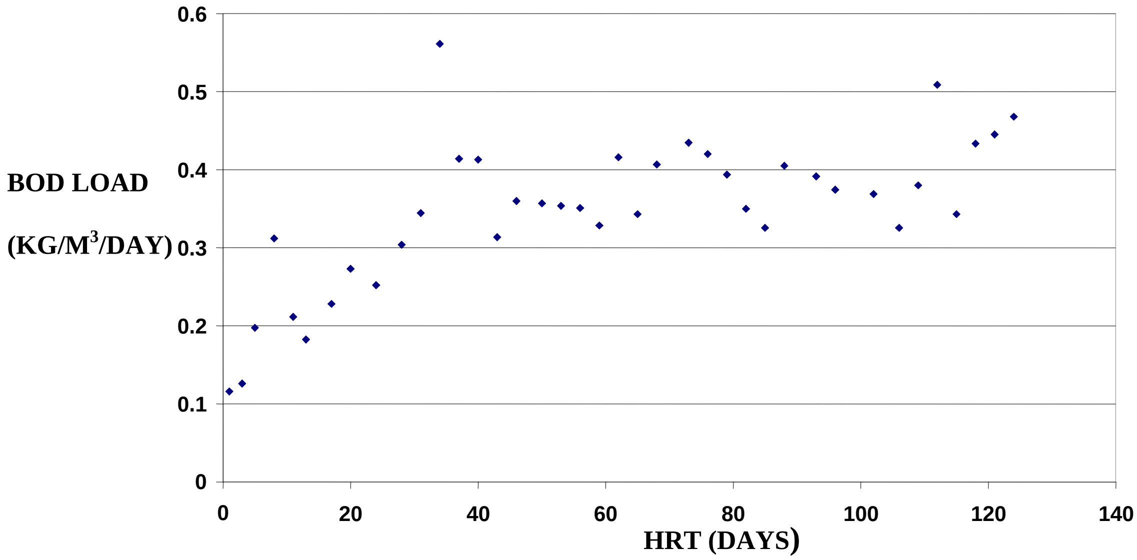
During the acclimatization period, HRT was about 2.5 days and it gradually brought down to one day in about 40 days time. Fluctuation in HRT was due to clogging in feed inlet and intermittent power cut. HRT during the study period is shown in graph.



HRT

3.8 BOD Load

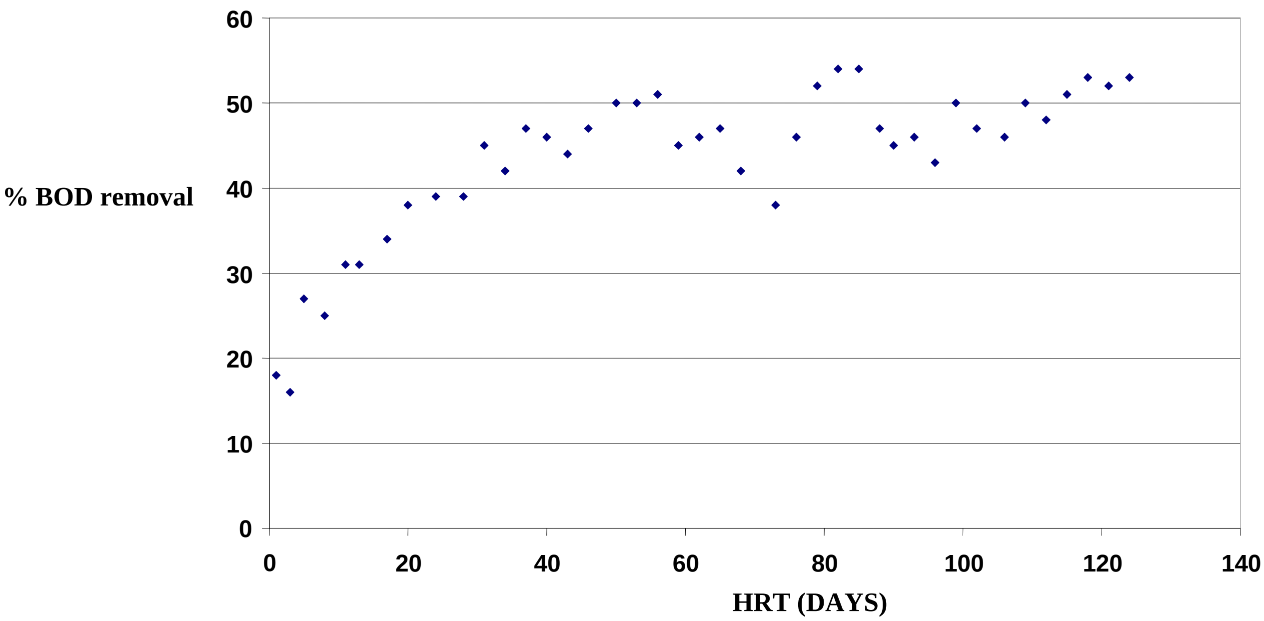
The performance of ASP in treating soak liquor was investigated in different loading rate. The fluctuation in load is due to the change in the feed characteristics. During the acclimatization period, it was started with BOD load of 0.1kg/m^3.day and gradually increased to about 0.3kg/m^3.day. The BOD removal efficiency was observed low. During the study period BOD load was maintained between 0.35kg/m^3.day to 0.45kg/m^3.day. Most of the settlable organic matter present in the soak liquor is removed during the physicochemical treatment. BOD load during the study period is shown in graph.



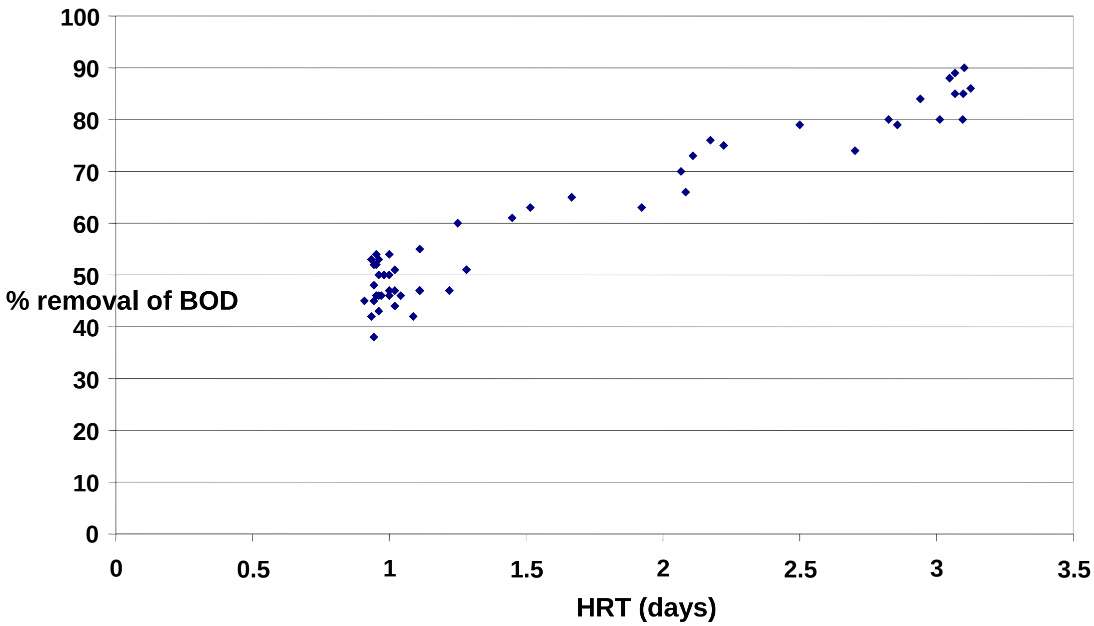
BOD load Variation

3.9 BOD removal efficiency

Performance of ASP in removing the organics in terms of BOD removal during the study period is given below. During the acclimatization period, removal efficiency of about 30% was observed. Average percentage removal of BOD during the study period was about 45-50%.



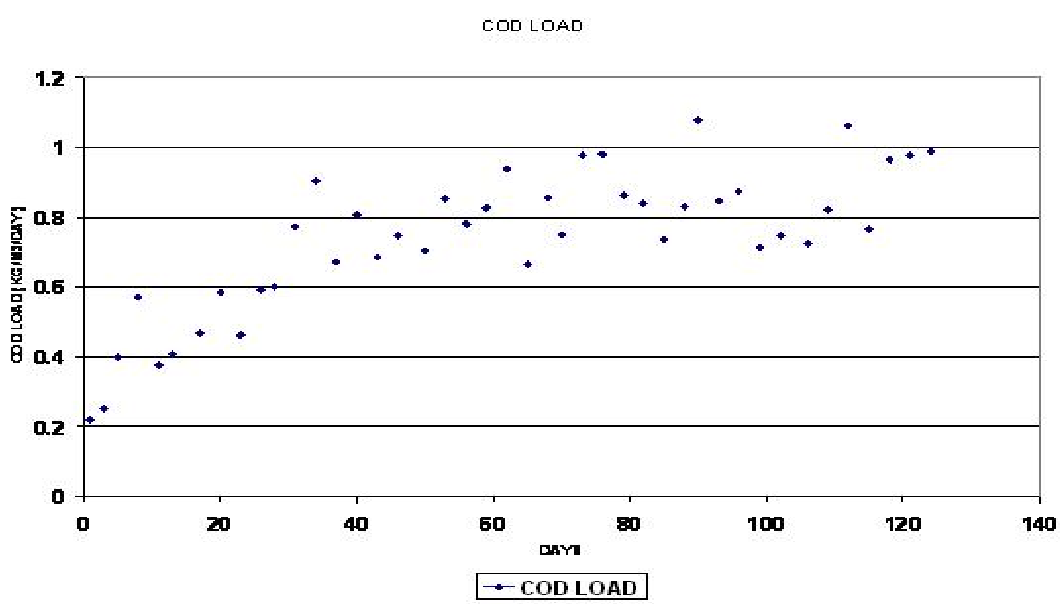
To improve the quality of treated effluent the HRT was increased upto 3 days. BOD removal efficiency of 90% was observed at higher HRT and the results are given below.



Effect of HRT on BOD removal efficiency

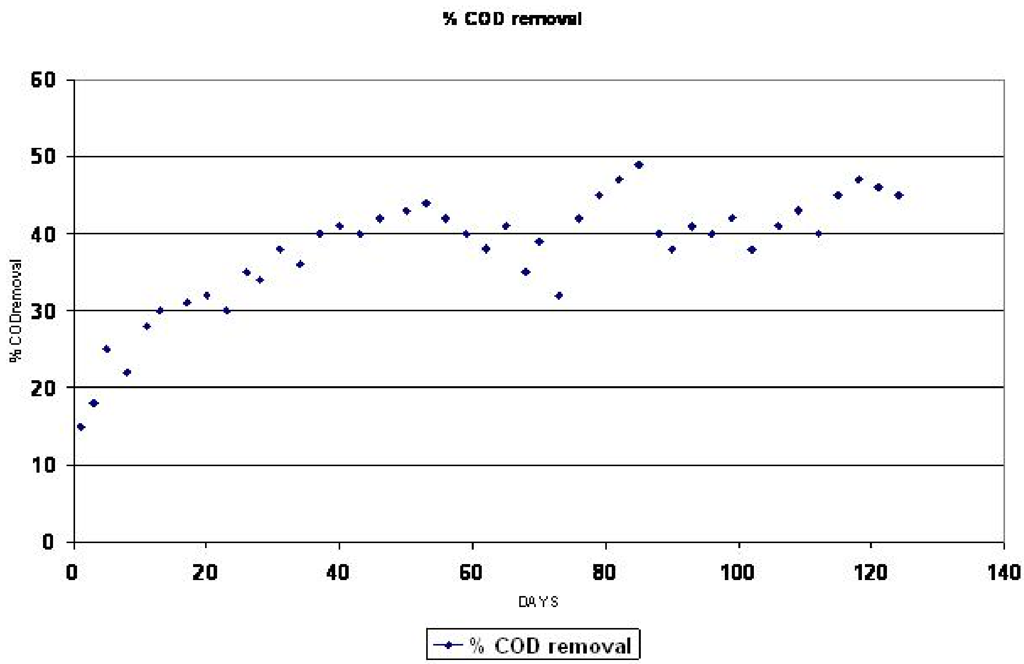
3.10 COD Load

During the acclimatization period the COD removal efficiency was low. Acclimatization of feed at high salt concentration was started with 0.2kg/m^3.day and gradually increased to about 0.8kg/m^3.day in 40 days time. COD load to the reactor was about 0.8kg/m^3.day to 1.0kg/m^3.day during the study period. COD load over a period of time is shown in graph.



3.11 COD removal efficiency

The COD removal rate was low during the acclimatization period. COD removal efficiency of about 20% was observed during the start up and it gradually increased to about 40%. During the study period an average removal of about 40-45% was observed. COD removal efficiency during the study period is shown in graph



Effect of HRT on COD removal efficiency

3.12 Observations on the removal of organics through biological treatment process

- In biological treatment system with HRT of one day, BOD and COD removal efficiency of about 45-50% and 40-45% respectively was observed.
- With a HRT of 2-3 days, BOD removal efficiency of more than 90% was observed.

4.0 PILOT PLANT STUDY

4.1 Location of the Pilot Plant

CETP at Vaniyambadi was chosen for the location of the pilot plant. Vaniyambadi is a municipal town with a population of about 100,000 and located in the western part of North Arcot District in Tamil Nadu. Tanneries in Vaniyambadi are located on the south of Palar river and processing about 100 tonnes of raw materials per day. Vaniyambadi is about 200 km from Chennai.

Vaniyambadi is one of the oldest tanning centers in India. The tanneries are small scale in nature with processing capacity of 0.5 to 2 tonnes per day. In Vaniyambadi mainly wet salted sheep and goat skins are processed adopting chrome tanning.

Vaniyambadi was selected for the present study because of the existing centralized solar evaporation system catering to the need of the 110 tanneries connected to the CETP and there is a scope for implementation of full scale system based on the demonstration plant. Vaniyambadi CETP is first of its kind in India and is in operation from 1992.

In general practice, the tanneries connected to CETP, Vaniyambadi, segregate soak liquor and convey it to common solar evaporation pans. The quality of salt obtained after evaporation from SEP is only 75% pure, containing organic and other impurities rendering it useless.

4.2 Pilot Plant

A pilot scale treatment unit including membrane system for recovery of water and concentrated saline liquor from soak effluent is designed and installed for a capacity of 250 L/hour (saline liquor) at CETP, Vaniyambadi.

Segregated saline streams from Soaking operation (pre-soak, main soak and wash after main soak) is collected and treated to remove suspended / colloidal organics by adopting physico-chemical followed by biological process.

The pilot scale demonstration system consist of the following units

- Settling Tank
- Sequential Batch Reactor
- Activated Carbon Filter
- Ultra Filtration unit
- Nano Filtration unit
- Reverse Osmosis (RO) system

4.2.1 Settling Tank

Soak liquor from tanneries is collected and allowed for settling after the chemical dosing in a settling tank to remove suspended solids. The results are as follows

- More than 90% reduction in suspended solids was observed by physico-chemical treatment.
- Supernatant after physico chemical treatment was evaporated in solar evaporation pans. The rate of evaporation increased by 15-30% which reduces considerable pan area requirement.

The evaporation rate increase in the solar evaporation pan is due to the following reasons

- Removal of suspended and colloidal impurities in the soak liquor which resulted in better sunlight penetration
- Reduction in organic content in the sediment at the bottom of pan
- Improved quality of salt and periodical removal of crystalline salt from the pan

The purity of salt obtained from the solar evaporation pan after physico chemical treatment was about 95%.

SETTLING TANK

SUPERNATANT FROM SETTLING TANK

4.2.2 Sequential Batch Reactor (Biological Treatment)

Though there is improvement in the evaporation rate and quality of salt recovered after physico chemical treatment, the recovered salt contains residual organics and other impurities. The salt could not be reused in pickling due the presence of residual impurities. Therefore, further studies were carried out adopting sequential batch Reactor (SBR) to obtain reusable form of salt. Supernatant from the settling tank flows to a sequential batch reactor. Diffused aeration system is provided in the reactor for supply of oxygen to microbes. Filtration is necessary after biological treatment.

More than 90% removal of organic matter was observed after biological treatment. Treated saline liquor was evaporated and the recovered salt (dry salt) was reused in pickling without any problem.

Purple Phototrophic bacterial species are extremely halophilic (salt loving) and found in most of the solar evaporation pans constructed for evaporation of spent saline soak liquor discharged from tanneries. Presence of purple bacteria in SEP reduces the rate of evaporation and contaminate the recovered salt. Evaporation of soak liquor after treatment completely eliminates growth of purple bacteria.

4.2.3 Membrane System

Need for Membrane Process

Evaporation of water in solar evaporation pan is a time consuming process. Therefore, additional studies were carried out adopting membrane process for better quality and direct reuse of part of concentrated saline liquor (RO reject) without evaporation in pickling process. Normally, pickling operation is carried out in drums with a float volume of 70-100% water. Salt is added in the range of 6.5-10%. During the study, recovered salt was used instead of fresh salt in pickling process. Though the recovered salt from SEP can be reused in pickling, the dried salt is again dissolved in water with a float volume of 70-100%. Membrane process is useful in recovering the water and RO reject can be directly used in pickling process without additional use of water and salt.

Characteristics of treated composite soak liquor prior to membrane system is given in Table below.

Characteristics of treated soak liquor prior to membrane system

S. No	Parameters	Unit	Value
	Volume per tonne of salted skins soaked	L/tonne	9000 – 12000
	pH		7.3-7.8
	COD	mg/L	500-1200
	BOD 5 days @ 20°C	mg/L	300-700
	Total dissolved solids	mg/L	20000-32000

	Chloride as Cl^-	mg/L	12000-19000

Note: All values except pH are expressed in mg/L

Ultra Filtration (UF)

Ultra filtration a low pressure membrane system and is one of the essential pretreatment requirements for treated effluent prior to Reverse Osmosis (RO) system. Ultra filtration system removes the following impurities

- Particulate matter, suspended solids, bacteria and viruses.
- Colloidal materials (non-reactive silica, iron, aluminium, silt etc.,)
- High molecular weight organic compounds

This minimizes RO cleaning protocols and reduces operating pressures and enhances membrane life.

Ultra Filtration is basically provided to protect the RO membrane from pre-treatment slip due to any biological, chemical or physical fouling / scaling that might happen in the membrane surfaces. Traces of BOD and COD that might slip through the entire system, is also taken care by ultra filtration. Hence to safeguard the RO membranes, this system is required. Ultra filtration membrane system is provided with auto back flush and chemical cleaning system.

Nano Filtration

The permeate from the ultra filtration membrane is stored in a permeate storage tank and pumped into a Nano filtration system using high pressure pump through micron filter. Ultra filtration partly removes color. Small organics are not removed in UF. Therefore, Nano filtration membrane system is provided to remove residual organics and divalent ions (hardness) present in the soak liquor.

Reverse Osmosis System

Reverse osmosis (RO), also known as hyperfiltration, is the finest filtration known. This high pressure membrane process will allow the removal of particles as small as ions from a solution. Reverse osmosis is used to purify water and remove salts and other impurities in order to improve the color, taste or properties of the fluid. The most common use for reverse osmosis is in purifying water from salinity.

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 daltons. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics. The larger the charge and the larger the particle, the more likely it will be rejected.

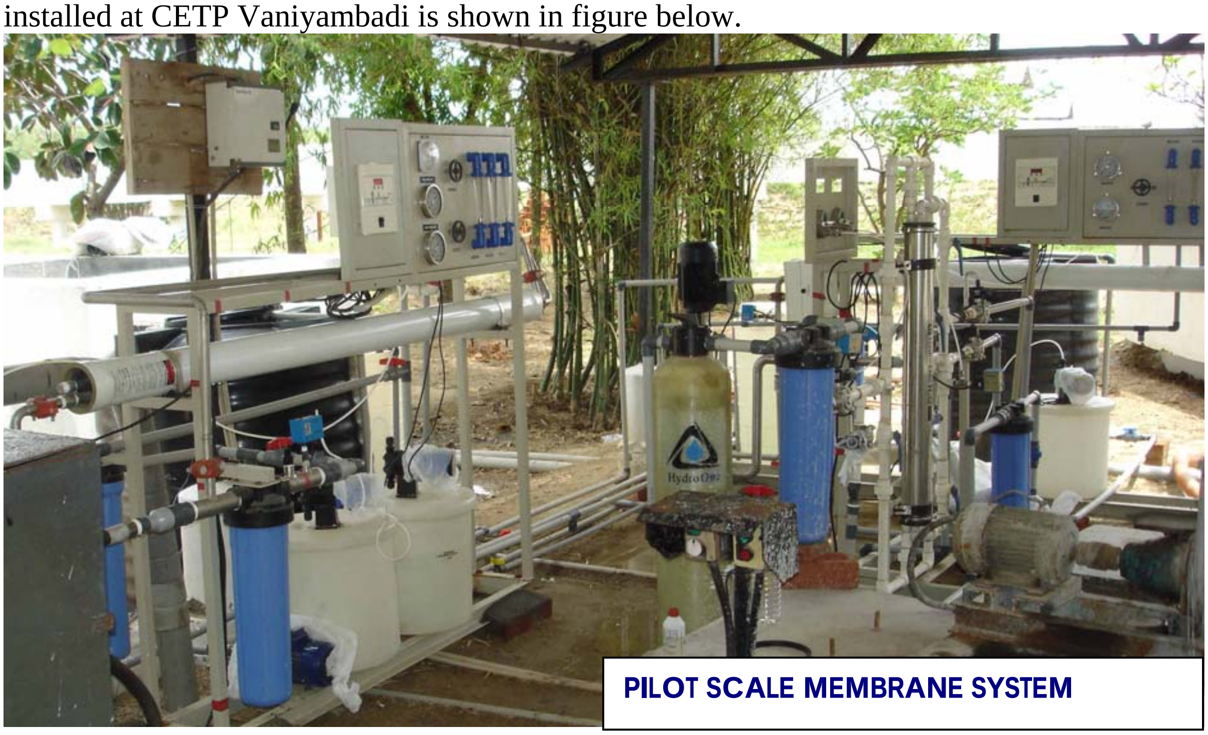
Membranes form the barrier for the ionic separation. This separates the water into two streams. A product stream with low ionic impurities and a reject stream with high ionic impurities.

The RO membranes are sensitive to various types of fouling & scaling factors. Hence a proper pretreatment is necessary as discussed in preceding section.

Membrane Configuration of RO System

Spiral wound, Polyamide, thin film composite (TFC) membrane is provided for recovery of water and to concentrate saline from soak liquor.

The process flow diagram of pilot scale water and saline liquor recovery system installed at CETP Vaniyambadi is shown in figure below.



4.3 Recovery of Water from Soak Liquor using RO System

Water with low dissolved solids content is recovered from treated saline soak liquor by adopting reverse osmosis membrane system. The effluent with dissolved solids are separated into two streams. Recovered water with TDS less than 750 mg/L is collected in a recovered water storage tank. The second stream (Reject stream) with high concentration of salt (40 to 70 g/L) is collected in a reject storage tank. Based on the feed conditions, and controlling parameters, a recovery ratio can be adjusted. The permeate recovery rate from the RO system was found around 60%. The recovery rate vary depending upon the feed TDS level. Permeate (recovered water) from RO system is reused in the leather manufacturing process especially for finishing operations which requires high purity water. The quality of water recovered from the reverse osmosis system for reuse in the process is given in Table below.

Quality of water recovered from soak liquor adopting membrane system for reuse

Sl.No	**Parameters**	**Value**
1	pH	6.5-7
2	Total Dissolved Solids	< 750 mg/ L
3	Suspended Solids	Nil
4	Chloride	< 450 mg/ L
5	Sodium	< 300 mg/ L
6	Permeate Recovery rate	55-70 %

*Except pH, all parameters are expressed in mg/L

4.4 Recovery of Saline Liquor (Reject) from RO System for Reuse

Quantity of reject generated from the membrane system was found around 40%. A storage tank is provided to collect the reject from the membrane system. The quality of reject (saline liquor) generated from the reverse osmosis (RO) system for reuse in pickling process is given in Table below.

Quality of saline reject from RO for reuse in pickling process

Sl.No	**Parameters**	**Value**
1	pH	6 - 7
2	Total Dissolved Solids	60000-70000 mg/ L
3	Suspended Solids	Nil
4	Chloride	36500-42500 mg/ L
5	Sodium	23500-27500 mg/ L
6	Reject volume	30-45%

*Except pH, all parameters are expressed in mg /L

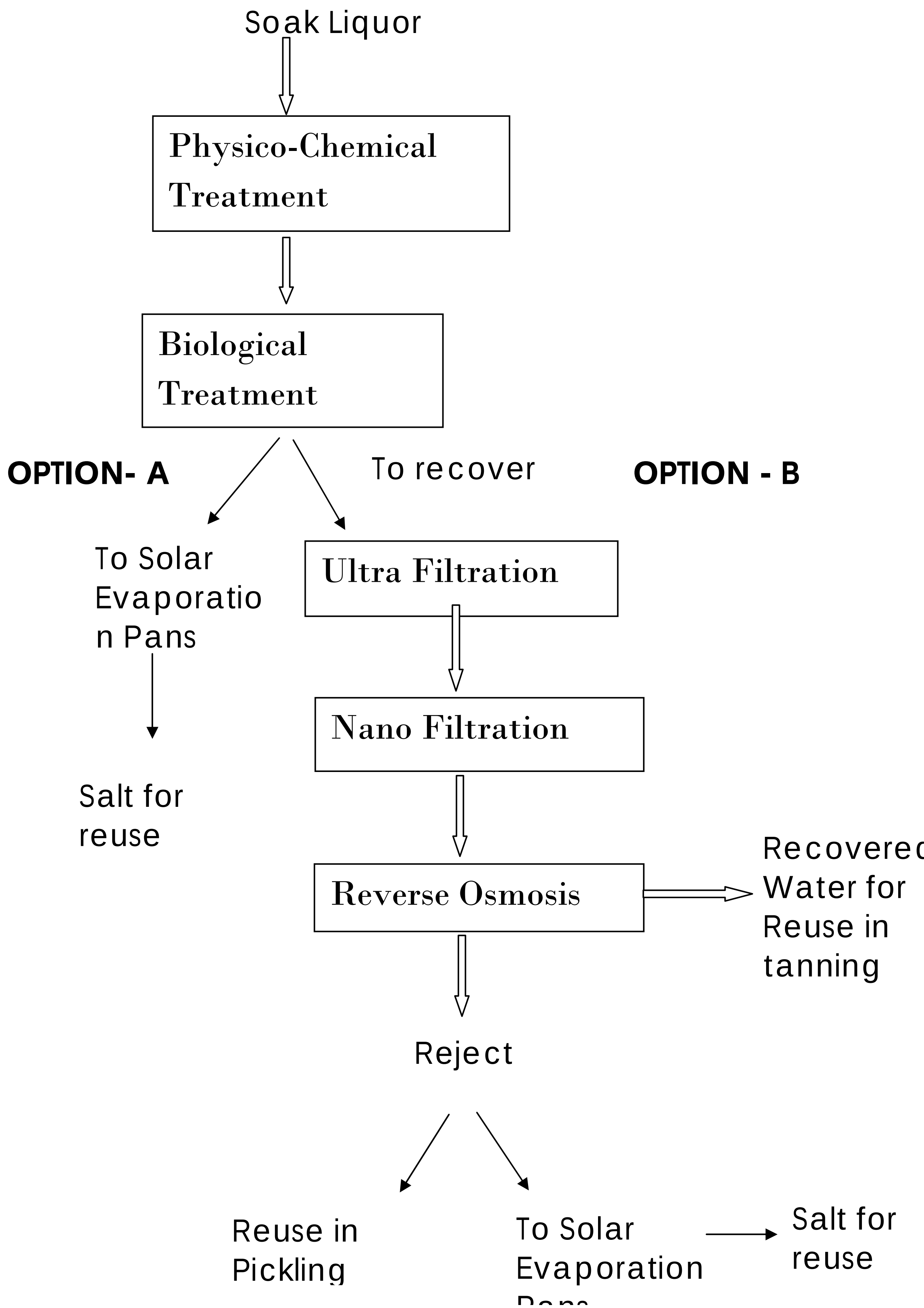
Pickling is the process of acidification of delimed and bated pelts and considered to be highly important preparatory operation before tanning, especially chrome tanning. pH of the pelts are brought down to 2.0-3.0 using sulfuric acid, hydrochloric acid, formic acid singly or in combination. In order to prevent acid swelling, salt is added in the range of 6.5-10% calculated on the volume of the water taken for pickling. The water requirement in pickling process is about 70-100% of hides/ skins. The characteristics of pickle liquor collected from tanneries in Vaniyambadi are given in table below.

Required Characteristics of the pickle liquor

Sl. No.	**Parameters**	**Units**	**Sample A**	**Sample B**	**Sample C**	**Sample D**
1	pH		3.0	2.12	2.8	2.45
2	**BOD (5 day @ 20^{o}C)**	mg/L	285	430	250	400
3	**COD**	mg/L	1470	3000	1100	2500
4	Chloride as Cl^-	mg/L	29800	40080	31000	34700
5	Total Dissolved Solids (TDS)	mg/L	58340	77020	60400	66500

Tanneries have to purchase quality salt required for the pickling process. Therefore, part of the saline reject stream from membrane system can be directly reused in pickling process. Based on the salt concentration required, volume of saline liquor is added followed by the addition of acid. Fungicide has been added for mould protection. Saline liquor reuse process requires only simple analytical control. No negative effect on the quality of leather processed with recovered saline liquor from soak liquor is observed. This leads to saving in the cost of purchase of fresh salt for pickling, as well as environmental problem of disposal of contaminated salt will also be reduced. By adopting this recovery and reuse process about 750-1000 L of water and 50-80 kg of fresh salt to be added in the pickling process can be saved per tonne of raw material. The cost of common salt used in the pickling process is in the range of Rs. 2.0-3.0 per kg. Cost of tanker water is Rs. 30-40/KL. Resulting advantages are saving of salt and water use in pickling process along with a good solution of solid waste disposal.

About 60 – 80% of RO reject is reused in the pickling process, which reduces both salt and water consumption & subsequently the volume of effluent generation.



POCESS FLOW DIAGRAM FOR PURIFICATION RECOVERY AND REUSE OF SALT FROM SOAK LIQUOR

Comparative performance analysis of the pilot plant studies for saline liquor

	Scheme/ Units	Purity of salt recovered	Suitability for reuse/ recycling
	Direct evaporation in SEP	75 %	Odor problem due to the degradation of organic matter. Low evaporation rate due to suspended and colloidal impurities. Salt is removed from the solar evaporation pan only after complete drying. Recovered salt is impure and disposal is a major problem.
	Physico chemical treatment followed by SEP	>95 %	Rate of evaporation is more (15-30%) due to the removal of suspended and colloidal impurities. The crystallized salt from the solar pans are removed periodically and the salt is relatively pure.
	Physico chemical treatment+ biological treatment followed by SEP	>97 %	The salt obtained is almost free from organic impurities and the salt recovered is suitable for reuse in pickling. Precautions should be taken during evaporation of saline liquor to avoid any contamination. Filtration is necessary after biological treatment.
	Physico chemical treatment+ Biological treatment+ membrane	>99.5 % (liquor quality)	High purity salt/saline liquor can be recovered and is almost free from organic and inorganic impurities. The reject from RO system can be directly reused in pickling process based on the requirement without evaporation in solar evaporation pans. Direct reuse of reject reduces solar pan area requirement and considerable level of time Permeate water from RO can be reused in leather manufacturing process which reduces considerable usage of fresh water. The saline reject and recovered salt is free from microbial contamination.

5. CONCLUSIONS

The present laboratory and pilot scale study at a CETP in Vaniymabdi to remove suspended, colloidal and organic impurities from the saline soak liquor generated from tanneries can be concluded as follows:

- Simple phsico-chemical treatment of soak liquor using lime, alum and poly electrolyte results in 90% reduction of suspended solids.
- More than 90% BOD reduction achieved in biological treatment of soak liquor.
- Evaporation of concentrated soak liquor after treatment completely eliminates growth of purple bacteria.
- Treatment of soak liquor followed by continuous removal of crystalline salt from the pans increase the evaporation rate by 15-30%.
- Salt obtained from the system is more than 99% pure and there is scope for reuse in other applications also.
- 25-30 % reduction in volume of saline effluent to be treated in main treatment was observed due to the segregation of spent saline soak liquors
- TDS reduction in the main effluent stream improves the performance of the treatment system (biological and membrane)
- Membrane treatment of soak liquor after physic-chemical and biological treatment results in recovery of water and saline reject for reuse in the process.
- Reuse of saline reject from RO membrane in pickling process eliminates use of fresh salt in the process
- Reduce in usage of water for pickling process
- Minimize the storage and disposal problem of salt generated in SEP
- 30 - 35% reduction in pollution load in the main stream.
- 15 – 20% reduction in fresh water addition in the tanneries.
- 30 – 40% reduction in solar pan area requirement for disposal of saline stream.
- No odour in SEP's.

The overall study shows that the segregation of saline soak liquor followed by physico-chemical and biological treatment removes 90% of suspended and dissolved organic impurities from the liquor, which results in better quality salt in solar evaporation pans. Also, through membrane process there is scope for recovery of both salt and water from spent soak saline liquor for reuse in the process. The overall process will benefit the industry in conservation, minimizing the disposal problem of salt and also protecting the environment.

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