

**ECOLOGICAL FRIENDLY PRODUCTION PROCESS AND WASTE
TREATMENT FOR CIRCULAR ECONOMY IN LEATHER
TANNING INDUSTRIES**

SENGODA GOUNDER RAJAMANI¹, ARNOLD MULDER²

¹*Chairman, Asian International Union of Environment (AIUE) Commission,
India, e-mail: dr.s.rajamani@gmail.com, Mobile: +91 9840063210*

²*AMECON, Delft, The Netherlands*

Ecological friendly processes with recovery of salt, chemicals and water for reuse in the tanning process as well as from liquid and solid waste are necessary for the promotion of circular economy. Recent developments in cleaner production and treatment process by reducing volume of effluent and pollution discharges, recovery of quality salt in the segregated streams such as saline soak liquor, spent chrome liquor and adoption of advanced aerobic oxidation process in the treatment system resulted in the recovery of purified salt, quality chromium and water for reuse. The achievements of innovative cleaner production and effluent treatment for promotion of circular economy are: Reduction in water usage in soaking process from 6000-8000 liters to less than 3000 liters/ ton of hides, Separate treatment of saline streams and recovery of quality salt, chromium in the form of cake / powder and Replacement of physiochemical treatment into biological treatment reduction in chemical usage and sludge generation by more than 60%. Viable cleaner production and sustainable treatment technologies had been engineered and are being implemented in many major leather clusters and Common Effluent Treatment Plants.

Keywords: cleaner production, chrome recovery, circular economy

INTRODUCTION

The treatment and disposal of tannery effluent with high salinity and Total Dissolved Solids (TDS) is a major challenge in most of the land locked tannery clusters. This resulted in development of appropriate cleaner production process to reduce the volume of water usage and pollution discharges. The segregation of streams such as saline soak liquor, spent chrome liquor enable to adopt advanced aerobic oxidation process, membrane system, recovery of quality chromium in the form of cake/powder, purified salt (sodium chloride) and water for reuse.

The merits of the developed cleaner production and effluent treatment are: (i) Reduction in water usage in soaking process from 7000 liters to less than 3000 liters/ton of hides (Buljan *et al.*, 1997), (ii) Segregation of high saline streams from soaking operations and spent chrome liquor for separate treatment and recovery of quality salt, chromium in form of cake/powder, water for reuse under Zero Liquid Discharge (ZLD) concept (Buljan and Rajamani, 1997; Schaapman *et al.*, 1990; Rajamani, 2020), (iii) Upgradation of physiochemical treatment into biological treatment process with reduction in chemical usage to reduce sludge generation by 60-70%, (iv) Advanced oxidation treatment using ozone for achieving COD reduction, colour and turbidity removal to the required level in the composite effluent (Rajamani, 2022) and (v) Integration of treated tannery effluent with treated domestic sewage for achieving TDS norms and use of the entire treated effluent for irrigation.

Viable cleaner production and sustainable treatment technologies had been engineered and are being implemented in a Leather Complex with about 200 new tanneries, a Common Effluent Treatment Plant (CETP) with capacity of 20 mld. This is

one of biggest leather cluster with adoption of new and innovative cleaner productions with circular economy.

Sustainable Cleaner Technologies for Circular Economy

The raw hides & skins available in the market for leather tanning contains 30-50% of salt (Sodium Chloride) on total weight basis. These hides & skins are taken for soaking operations without proper salt dusting. The volume of water usage is 6000-8000 liters per ton of hides and TDS concentration ranges from 40000 to 60000 mg/l. The entire soak liquor is mixed with other sectional streams and discharged as a composite stream and the TDS level is in the range of 20000-25000 mg/l. This high TDS level in the effluent affects the performance of biological treatment system and inability to achieve discharge parameters particularly TDS which is being enforced in many Indian States and other countries as well.

In order to meet the challenges in achieving the environmental regulations and to improve the in effluent treatment system with recovery of quality chemicals, salt and water for reuse, the following cleaner productions have been developed for implementation:

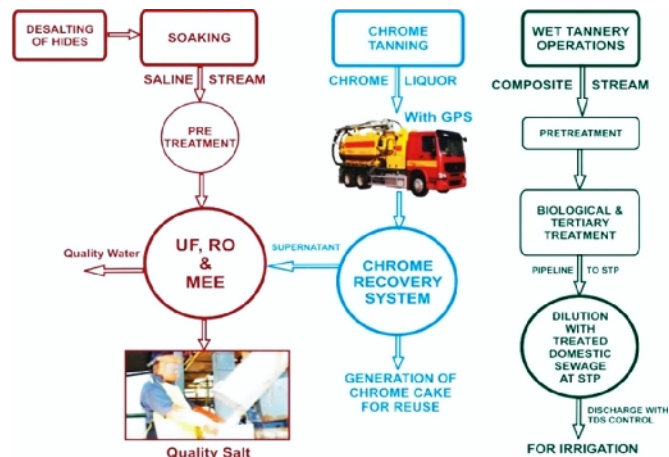
- Improved method for desalting of skins by using simple system such as DODECA by tanneries at source and centralized mechanical desalting of hides by adopting proven equipment which are portable as well.
- Sulphide reduced liming process by the use of suitable enzymes to extent feasible for reduction of sulphide load by 60-70% in the effluent.
- Safe and sustainable disposal of waste fleshing by conversion into fertilizer, composting by using with dewatered bio-sludge and other degradable organic matter (Langerwerf *et al.*, 1997).
- Segregation of chrome stream and adoption of improved Common Chrome Recovery System (CCRS) and recovery of chromium in the form of cake or powder. The supernatant also further processed and converted into reusable chemical and quality water.
- Reduction in sludge generation by biological treatment with minimum chemical usage, anaerobic digestion of sludge with bio-energy generation and conversion into composting (Suthanthararajan *et al.*, 2001).

Segregation of Streams in Tanneries

All the tanneries in addition to the adoption of suitable cleaner productions, the streams are segregated as follows for separate treatment.

- Saline soak liquor from pre-soaking, main soaking and washing.
- Spent chrome liquor from chrome tanning operations.
- All other streams starting from liming, deliming, washing and all remaining wet finishing operations are collected as a composite stream.

The concept of sustainable cleaner production and circular economy is shown in Figure 1.



Ultra Filtration (UF), Reverse Osmosis (RO), Multiple Effect Evaporator (MEE)

Figure 1. Innovative Cleaner Production for Sustainable Treatment with TDS Control

Saline Soak Liquor

Saline Soak Liquor is generated from the three stage operations of namely (i) Pre or Dirt soaking (Soaking I), (ii) Main soaking (Soaking II) and (iii) Wash after main soaking (soaking III). During the conventional three stages of soaking using pits and paddles more than 6-8 m³ of effluent is discharged per ton of raw material process. By the use of drums for soaking after viable desalting and cleaner production process, the volume of water usage and effluent discharge is reduced to less than 4 m³/ton of raw hides and skins.

The saline soak effluent from each tannery is discharged into the exclusive conveyance system to CETP for separate treatment under ZLD concept with recovery of quality water and reusable salt. The treated saline stream is partly reused in pickling / soaking and balance is evaporated for generation of reusable salt (mainly sodium chloride) and water. The salt is having more than 99% purity and has got market demand for industrial and other uses in land locked areas. The overall TDS level in the other composited stream is reduced by about 60% (i.e. from more than 20000 mg/l to less than 10000 mg/l). Due to this reduction, the environmental authorities permit the sustainable option of mixing the treated composite effluent with treated domestic sewage available near the tannery cluster and enable meet all the discharge parameters including TDS.

Sustainable Desalting Process

The tanneries processing salted goat, sheep, cow & buff calf skins in small scale can adopt desalting frames and rotary drums. DODECA (12 frame) wooden frames can be adopted for small size skins weighing up to 4-5 kgs. For medium size hides weighing up to 10 kg can be desalted using rotary drums with perforated holes.

Majority of tanneries in the cluster are in small & medium scale, they are not having the capability and land space to have mechanical desalting system required for big size hides. Hence, it is necessary to adopt mechanical desalting as a centralized facility. It is

proposed to provide two centralized desalting facility for a capacity of about 80-100 tons per day during the implementation. The desalting process, clarification of the dusted salt solution, reuse in pickling, etc. are shown in Figure 2.

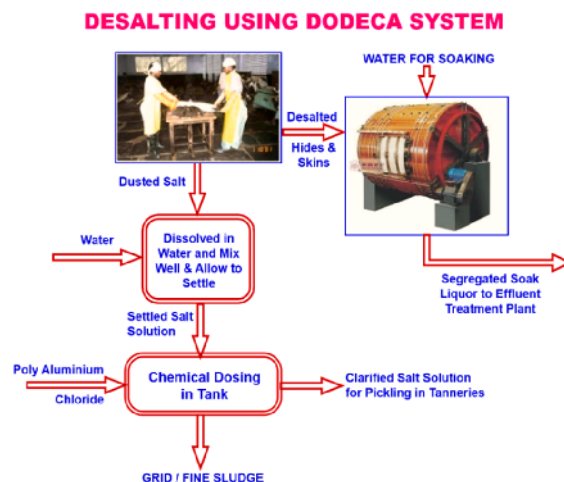


Figure 2. Desalting Process for TDS Management

The salt collected from desalting process would contain grit and organic ingredients. This can be clarified by adding 200 liters of water for 20 kg dusted of salt and grit will settle in bottom of the tank. The supernatant can be collected in a separate tank and added with poly aluminium chloride (PAC) dosing. The suspended and organic settleable matter settles in the bottom as a sludge. This can be disposed in the sludge dewatering system installed in individual tanneries. The clarified supernatant which contains 7-8% salt solution can be used for pickling by adding required balance salt, sulphuric acid and water. The desalting process would reduce the TDS content in the saline soak liquor from the range of 40000-50000 to 20000-30000 mg/l.

Improved Chrome Recovery System

The effluent discharge from chrome tanning operation is about 4-6% of total volume of wastewater from chrome tanneries. Conventionally, the tanneries provide individual chrome recovery system by using MgO (magnesium oxide) as alkali and the recovered chrome slurry is regenerated as basic chromium sulphate (BCS) by mixing with sulphuric acid (H_2SO_4) (Buljan and Rajamani, 1997). BCS is in the form of liquid is reused in the tanning process. In this conventional process, there are limitation and management and reuse of Chromium. The discharge of entire supernatant from chrome system with high TDS (25000-40000 mg/l), Chlorides (8000-15000 mg/l), Sulphate (4000-8000 mg/l), etc. to the CETP along with other streams results in increase of overall TDS in composite stream, constraints in adopting biological treatment system particularly anaerobic system achieving TDS level in the treated effluent is not feasible.

The concept of the improved CCRS (Rajamani, 2018; Rajamani, 2016) (i) Collection of spent chrome liquor from individual tanneries through tankers fitted with

GPS, (ii) Screening, pretreatment, separation of Chromium as a slurry in the reactor by using suitable alkali, (iii) Dewatering of chrome slurry using Chamber Filter Press and recovery of Chromium in the form of cake and (iv) The supernatant with high TDS of more than 30000 mg/l is taken for further treatment integrated with saline soak stream treatment system for recovery of quality salt and water by adopting membrane system.

SUSTAINABLE SOLID WASTE MANAGEMENT FOR CIRCULAR ECONOMY

The tanneries during beam house operation generate large amount of fleshing. It is estimated 20-30 kg of fleshing generated during the process of 1000 kg of hides & skins. Only part of fleshing is taken for commercial process and about 50% of fleshing mainly from skins and small hides are becoming waste.

The following options are proposed for the disposal of fleshing: (i) Conversion into composting using other organic degradable waste and bio-sludge, (ii) Conversion into biological liquefaction and feed to anaerobic reactor for bio-energy generation and bio-sludge (Rajamani, 2021) and (iii) Mixing with dewatered bio-sludge from digester and converting into bio-fertilizer. These solid waste management options have been implemented in a separate industrial type building within the CETP.

COMPOSTING AND GENERATION OF BIO-FERTILIZER

It is estimated that about 5-10 tons of partly dewatered bio-degradable sludge would be generated from soak liquor treatment, composite treatment and anaerobic digester. This bio-degradable sludge can be processed further by adding waste fleshing and degradable organic waste available in the local area. The ratio of the mix would be generally 1:1:1 and the composting process would take about 15-20 days. Proper bio-seeding generated from sewage treatment plant (STP) / bio-spray is being periodically applied for accelerating the composting process.

RESULTS AND DISCUSSION

- Improved desalting using DODECA method removes the salt content from 60% to 30% on weight basis.
- Modified and improved soaking process reduces the water usage and effluent discharge from the level of 600-800% to 300-400%.
- Improved chrome recovery system generates chromium in the form of cake / powder.
- Entire supernatant is further process and recovered in the form of quality salt and water for reuse.
- Segregation & treatment of saline soak liquor under ZLD system generates quality water and salt.
- TDS level in the composite stream reduced from about 20000 mg/l to less than 10000 mg/l.
- Improved cleaner production and segregated treatment enable to comply the environmental regulations and discharge norms.
- Scope for replicability in many tannery clusters.

CONCLUSION

This unique and sustainable technological developments in cleaner production aiming at circular economy will reduce the level of TDS in the effluent discharge by 50%, hazardous category sludge generation by 60% and meets the environmental norms. Many full-scale systems are being implemented in India and other countries.

Acknowledgment

Contributions of Department for Promotion of Industry and Internal Trade (DPIIT)-Govt. of India, Indian Leather Technology Association (ILTA), IAFLI, UNIDO, National Mission for Clean Ganga (NMCG), National Green Tribunal (NGT), Mega Leather Cluster (MLC)-Kanpur, Schoolnet India Limited, Asian International Union Environment (AIUE) Commission, Asian International Forum and others commission members from various countries, AMECON & TNO Netherlands, Central Leather Research Institute (CSIR-CLRI), European Union including Italy and Spain, The Netherlands and other Countries such as China, Japan, Romania, Turkey, Taiwan and Russian Federation, New Zealand are acknowledged. Leather Industry Associations and Common Effluent Treatment Plants (CETPs) in India are acknowledged.

REFERENCES

- Buljan, J. and Rajamani, S. (1996), "Technology Package – A System for Recovery and Reuse of Chromium from Spent Tanning Liquor Using Magnesium Oxide and Sulphuric Acid", *TECHPACK / UNIDO / RePO / 1*.
- Buljan, J., Reich, G. and Ludvik, J. (1997), "Mass Balance in Leather Processing", Paper presented in IULTCS Congress, London, UK.
- Langerwerf, J.S.A., Rajamani, S., Ramasami, T., Raghavan, K.V., Van Groenestijn, J.W. and Mulder, A. (1995), "Implementation and Dissemination of the Results of the TNO-CLRI Co-operation Programme", Paper presented in XXIII IULTCS Congress, Friedrichshafen, Germany.
- Rajamani, S. (2016), "Innovative Environmental Technologies including Water Recovery for Reuse from Tannery and Industrial Wastewater – Indian and Asian Scenario", Proceedings of the 6th International Conference on Advanced Materials and Systems (ICAMS 2016), Bucharest, Romania, 513-518, <https://doi.org/10.24264/icams-2016.IV.13>.
- Rajamani, S. (2018), "Sustainable Environmental Technologies Integrated with Cleaner Production – Recent Developments in World Leather Sector", Paper presented in XIVth International Scientific-Practical Conference, Ulan-Ude, Russia.
- Rajamani, S. (2020), "Sustainable ZLD System by Adopting Centralized Treatment of Segregated Streams for Recovery of Reusable Quality Chemical, Salt & Water – First of its kind in India & Asia", *Leather News India Journal*.
- Rajamani, S. (2021), "Biological Liquefaction and Anaerobic Digestion of Waste Fleshing's Integrated with Sludge and Bio-Energy Generation – A Novel and Sustainable Development", Paper presented in XXXVI IULTCS Congress 2021, Addis Ababa, Ethiopia.
- Rajamani, S. (2022), "State-of-the-Art Technology of Advanced Oxidation Process Using Ozone in Water and Industrial Wastewater Treatment – A First of Its Kind Treatment System in India", Paper presented International Workshop organized by CSIR-CSMCRI, Gujarat & NAM S&T Centre, New Delhi.
- Schaapman, J.E., Rajamani, S., Gupta, S.N., Mitra, R.B. and Pelckmans, H.H.A. (1990), "Cleaner Technology in the Leather Industry – Chrome Recovery and Reuse", Paper presented in Water Pollutional Control Federation 63rd Annual Conference, Washington DC, USA.
- Suthanthararajan, Rajamani, S., Kalyanaraman, C., Umamaheswari, B. and Ravindranath, E. (2001), "Anaerobic Digestion of Sludge from Highly Saline Wastewater Streams from Tanneries with Special Anaerobic Sludge Digester with Liquid Separator (ASDLS) System and Generation of Bio-Energy", Paper presented in the 2001 IULTCS Congress held at Cape Town, South Africa.