



## INNOVATIVE CLEANER PRODUCTION TECHNOLOGIES AND TREATMENT OF SEGREGATED STREAMS FOR RECOVERY OF QUALITY SALT & WATER FOR REUSE

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**Abstract:** *The conventional treatment system adopted by Indian and Global Tanneries consist of (i) Segregation of Spent Chrome Stream and discharge of supernatant for combined treatment along with effluent from all sectional operations starting from soaking to finishing, (ii) Conventional physiochemical and biological treatment for reduction of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), etc., (iii) Ultra-filtration and Reverse Osmosis (RO) system for recovery of water and Multiple Effect Evaporator (MEE) for the evaporation of RO reject stream and generation of mixed salt in case of Zero Liquid Discharge (ZLD) system and (iv) Storage of mixed salt recovered from the MEE system for which no viable disposal system is found.*

*Establishment of treatment system for the mixed stream results in poor performance of biological treatment units, increases the O&M cost, and accumulation of recovered mixed salt in case of ZLD system. It is estimated that, more than 8-10 tons of mixed salt is generated during the treatment of 1.0 MLD effluent under ZLD system. To address this serious environmental problem, an innovative approach of segregation of saline streams such as soak liquor and chrome liquor are planned to be collected separately with the feasibility of recovering reusable quality salt and chromium in the form cake for regeneration and use in the form of Basic Chromium Sulphate (BCS) by the tanneries. This innovative treatment concept has been developed and is being implemented in many CETPs in India. This will become the first of its kind in Global Leather World. This developmental scheme is in accordance with the guidelines and recommendations of UNIDO in terms of sustainability of ZLD system for the leather sector.*

*The technological developments on cleaner productions, centralized chrome recovery reuse system, segregation of saline soak water for separate treatment with recovery of water and quality salt are dealt in this technical paper.*

**Keywords:** *Combined Treatment, Segregation of saline stream, Chromium, Quality water, ZLD.*

### 1. INTRODUCTION

The tanneries in World Leather Sector process about 17million tones of hides & skins per year. Only less than 20% of fresh hides and skins are processed without applying salt and more than 8-10million tones of salt mainly in the form of sodium chloride is applied for curing. They are transported, stored, and processed in a period of 2-6 months. The entire salt applied is discharged as waste in the effluent as dissolved solids, causes environmental challenges due to increase in salinity and depletion of quality water resources, etc.

With a view address the environmental challenges, technological developments such as (i) Segregation of Spent chrome stream and adoption of improved chrome recovery system by recovering chromium in the form of cake, (ii) Advanced process control and cleaner production, (iii) Segregation of saline stream with high TDS around 20000mg/L from soak liquor, separate treatment and recovery of quality salt and water for reuse by adopting ZLD system[1], (iv) Improved biological treatment system with mild chemical usage for reduced sludge generation, (iv) Advanced tertiary treatment systems, etc. for the application of single or multiple stage Reverse Osmosis (RO) system for recovery of water. Recent applied R&D on sustainable development in cleaner leather

production, environmental protection techniques with focus on saving energy and chemical by converting the physiochemical treatment into total biological treatment, water-recovery for reuse, quality salt recovery for reuse, etc. are detailed in this technical paper.

## 2. SEGREGATION OF STREAMS AND SEPARATE TREATMENT FOR RECOVERY OF CHROME, QUALITY SALT AND WATER

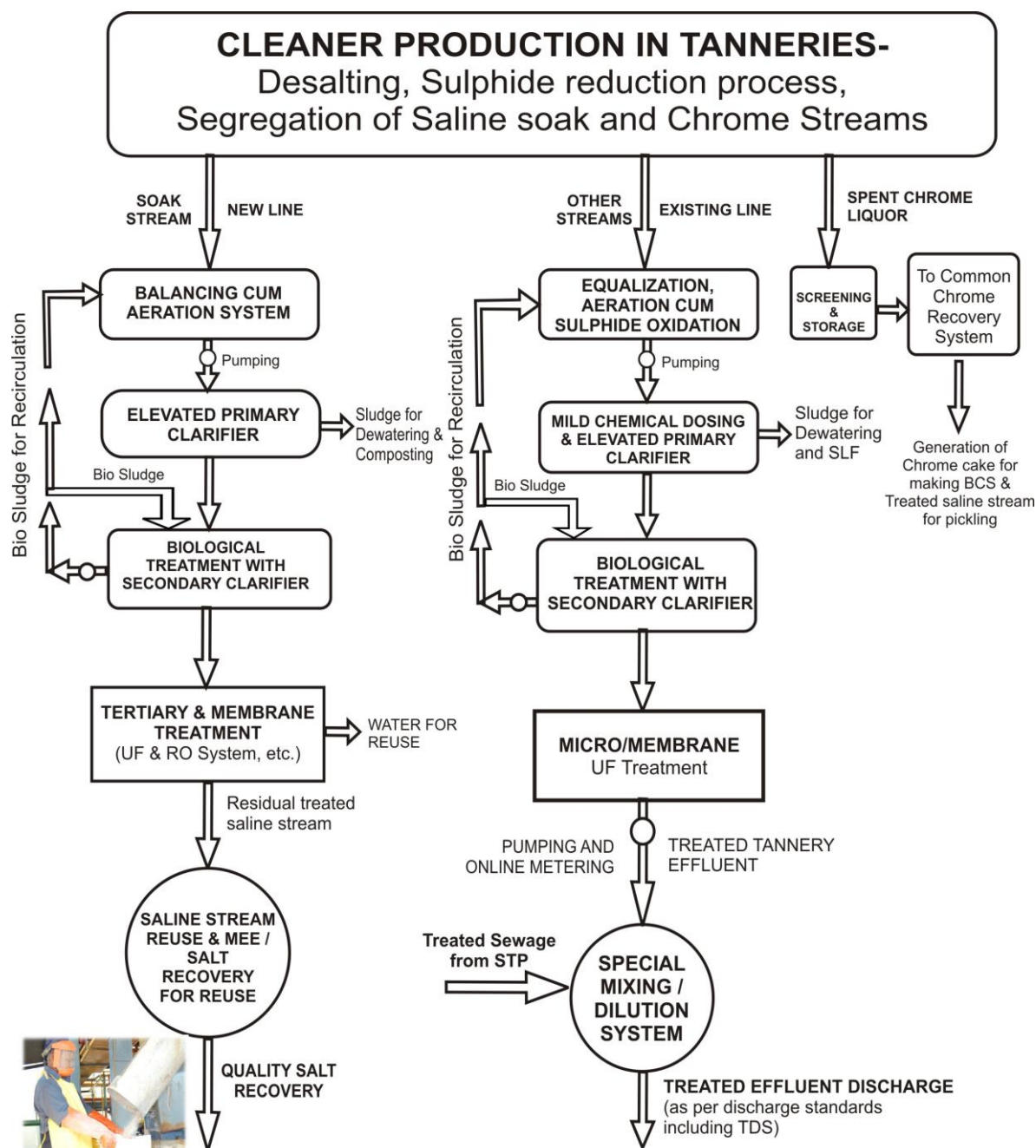
Due to the inherent quality of industrial wastewater such as textile dyeing units, tanneries etc., the conventional treatment plants are unable to meet the prescribed TDS level of 2100 mg/l in the treated effluent. In addition to TDS management the control of volatile solids in hazardous category sludge is also becoming a necessity. For control of salinity, chromium, sludge and viable management of TDS with the recovery of quality water from wastewater, the required treatment steps are (i) Cleaner production and other viable process control in tanneries[2], (ii) Segregation of streams such as saline soak liquor, spent chrome liquor for separate treatment, recovery of chromium, Sodium chloride salt and quality water for reuse, (iii) Upgradation of biological treatment systems with better efficiency in BOD and COD removal, (iv) Minimum usage of chemicals in the treatment process and reduction in sludge generation, (v) Reduction in TDS level in the mixed stream and (vi) Tertiary treatment of the low saline mixed stream and integration of treated tannery effluent with treated domestic sewage wherever feasible for TDS management[3].

The availability of domestic sewage is limited in many locations for dilution/mixing with treated tannery effluent for TDS management. The viable plan of segregation of soak liquor, separate treatment, and recovery of quality salt will be helpful in reduce the TDS level in the mixed stream and scope for adoption of dilution / mixing with available treated domestic sewage.

The segregated soak liquor is taken to the CETPs through separate pipe line and after primary and secondary treatment units, the membrane system is adopted for recovery of water and quality of saline stream for reuse in pickling. The balance treated saline stream is evaporated and quality salt (98% purity) is recovered for reuse without any difficulty. In addition to recovery and reuse of quality water by the industry, the additional benefits are savings in chemical usage in the tanning process and reduction in pollution load in the effluent.

The segregated chrome stream is taken for Centralized Chrome Recovery System (CCRS) for recovery of chromium in the form of chromium cake. In the improved chrome recovery system, the time required in the chrome recovery process is reduced from 16 hrs to less than 8 hrs. By avoiding the soak stream and supernatant from the CCRS to the main composite stream, the TDS level will be reduced from the level of about 15000mg/l to 8000mg/l.

The process flow diagram of segregation and collection of three streams viz. (i) Saline Soak liquor, (ii) Spent Chrome liquor and (ii) Composite stream with low TDS and separate treatment is shown below:



*Fig.1: Segregation and treatment process of Soak saline stream, Spent chrome stream and Composite low saline stream*

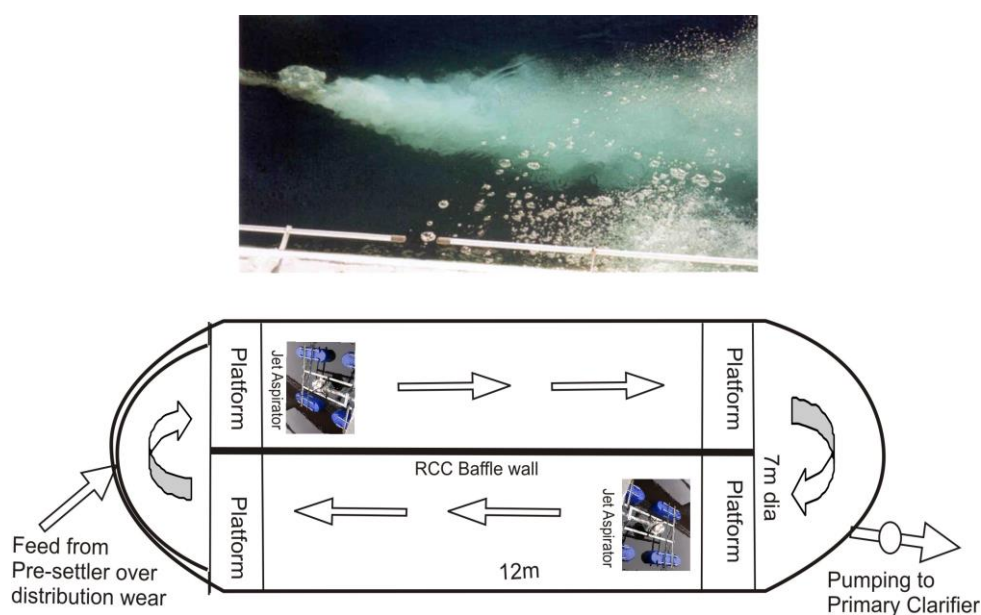
### 3. SUSTAINABLE CLEANER PRODUCTION AND EFFLUENT TREATMENT

Due to the segregation of soak liquor and chrome stream for separate treatment and reuse, the TDS level in the main combined stream taken to the CETP is reduced by 50% and it has become viable to convert the entire CETP to the total biological treatment system and scope for mixing the treated effluent with treated domestic sewage for overall TDS management and disposal by meeting all the discharge parameters without the necessity of multiple stage evaporator for the mixed stream with low TDS.

### 4. INTEGRATION OF EQUALIZATION CUM MIXING SYSTEM WITH BIOLOGICAL TREATMENT FOR SULPHIDE OXIDATION

The effluent is collected in equalization cum mixing system, pumped to the primary clarifier, mixed with high dosing of chemicals such as lime alum, etc. The conventional system adopted in most of the CETPs in India could not reduce the sulphide level in the physiochemical treatment and the sludge accumulation in the equalization tank is one of the major problems. The COD reduction to the prescribed level (i.e. 250mg/l) in the final treated effluent could not be met by some of the CETPs adopting conventional physicochemical and biological treatment. The performances of the aerobic biological treatment system with limited detention time are not satisfactory and unable to produce the required quality effluent.

With a view to oxidize the sulphide present in the effluent, control the sludge settling in the equalization tank and to minimize the chemical usage the equalization system has been upgraded with increased detention time, increased depth and usage of new type of aspirators integrated with a compressor. The residual excess biosludge from the secondary clarifier is pumped to the equalization tank which is helpful in biological oxidation process and to reduce the chemical dosage in the first stage clarifier [4]. The upgradation of equalization cum mixing system into aerobic biological oxidation using residual/excess biosludge and adopted in one of the CETPs in India is shown below:



*Fig.2: Improved Collection cum Equalization cum Sulphide Oxidation System*



The primary clarifier units are also upgraded by providing elevated clarifiers with minimum required chemical dosing. This improved system is performing better in terms of sludge settling, withdrawal, and dewatering.

The improved aeration system with jet aspirator has been successfully adopted in many CETPs in Tamilnadu and proposed to be implemented in more CETPs. The sustainable alternatives to the total ZLD system for a single combined stream have been developed and are being introduced in upgradation of CETPs in Uttar Pradesh and other States[5]. It is also estimated that nearly 80% capacity of the wastewater from the Indian Leather Sector will be treated by adopting cleaner technologies, segregation of streams and separate treatment, integration with treated domestic sewage, etc. In this circumstance for long term sustainability of the CETPs which adopted ZLD for single combined streams, the concept of separate treatment of saline streams with recovery of quality reusable salt, cleaner productions, etc. may have to be followed. UNIDO in its recent technical publications on environment and effluent treatment for the World Leather sector clarifies the limitations of ZLD system and emphasizes the segregated stream treatment aspects[6].

## **5. CONCLUSION**

The conventional effluent treatment systems are being upgraded by segregating the saline soak stream with separate treatment, adoption of UF & RO, and Multiple Effect Evaporators (MEE) with recovery of quality salt for reuse. About 200kg of quality salt (sodium chloride) is recovered from the effluent discharged during the process of each & every tone of hides & skins. The physiochemical treatment is converted into a total biological treatment system to reduce sludge generation by 50%, achieving the pollution control discharge standards and clarity in treated effluent. Upgradation of CETPs with Improved Cleaner Production Process, Centralized Chrome Recovery and Reuse systems, Integrated treatment with treated domestic sewage for sustainable TDS management with financial support from National and International organizations in India and other countries. These technological developments and upgradation of CETPs are being implemented in many locations covering more than 700 tanneries in India with a financial outlay of more than 150 million US dollars.

## **ACKNOWLEDGEMENT**

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