Chapter IX

Summary and conclusions

➢ The residue after evaporation (RAE) generated in leather sector lack reusable characteristics and land co-disposal was also discouraged due to generation of non biodegradable leachates.

➢ At present, the RAE is being packed and stored in the storage yard in all ETPs and common effluent treatment plants (CETPs) of leather sector. The segmentation of new land spaces would be challenging task in the future to store the fresh generation of RAE in proportion to the production capacity.

➢ It is important to find an alternative technique to handle RAE. It has been attempted and proposed to recover sodium chloride and calcium sulphate from RAE by reactive precipitation process.

➢ RAE was collected from an ETP and characterised for physio-chemical properties.

➢ Saturated solution of RAE was prepared and characterised for selective precipitation of NaCl.

➢ Generation of Hydrogen chloride gas was attempted and used for the selective chemical precipitation of NaCl from the saturated RAE solution.

➢ Regeneration of used sulphuric acid from the HCl generation process was studied for reuse application, so that conservation of sulphuric acid was established.
The optimum conditions for the precipitation of sodium chloride from RAE were found to be: HCl gas injection time, 3 min; pH, 8.0; temperature, 40°C, and initial concentration of RAE, 60% (w/v) and the percentage of NaCl recovery was 81%.

Evaporative crystallization (using thermal energy) of acidified RAE solution showed a significant increase in percentage of NaCl recovery from 81% to 98.7%.

The cumulative yield of NaCl by reactive precipitation and evaporative crystallization was 32.5 g/100 mL RAE solution.

The precipitation of NaCl from RAE solution followed the pseudo first order rate kinetics.

Synthetic RAE solution was prepared using catechol and pyrogallol as model organic compounds to study the influence of organic compounds on NaCl precipitation.

The increase in concentration of organic compounds in the saturated RAE solution significantly increased the recovery of NaCl.

Mathematical modelling on NaCl precipitation from RAE solution was developed for the change in sodium ion concentration profile and particle count in the precipitation reactor.

Recovered NaCl was purified and characterised by SEM, EDX, XRD and CV analyses. The analyses evidenced that recovered salt was NaCl and it was relatively equivalent in purity to that of standard NaCl.
Cost analysis on NaCl precipitation was evaluated and compared with cost on landfill disposal.

The net expenditure on processing one kg of RAE by the proposed process was 0.04 USD. The cost towards disposal onto secure landfill (inclusive of transportation cost and handling cost at secure landfill) is 0.11USD per Kg of RAE.

The sulphate ion in residual acidified supernatant (RAS) solution was separated by the addition of various neutralizing agents. Among the neutralizing agents Ca(OH)$_2$ and MgO, the Ca(OH)$_2$ was effective on the separation of sulphate ions from RAS solution.

The optimized conditions for the recovery of sulphate ion as calcium sulphate were pH, 3.0 and temperature, 40°C.

The precipitated calcium sulphate was purified by calcination at 700°C under air atmosphere for 1 h. The surface area of the calcium sulphate$_{(rec)}$ was found to be increased by 5 fold than the surface area of calcium sulphate$_{(std)}$. Thus, the calcium sulphate$_{(rec)}$ could be used as an adsorbent for the adsorption of aqueous dye.

The calcium sulphate$_{(rec)}$ was analyzed using XRD, SEM, EDX, and TGA, and it was confirmed that the precipitated calcium sulphate after calcination was 99.9 % equivalently pure as that of standard calcium sulphate.

The net profit envisaged by the proposed process was 0.076 USD/kg RAE by finding a market for the recovered by products of NaCl and calcium sulphate.
The neutralised RAS solution was subjected to removal of organic compounds by adsorption technique and advanced oxidation processes.

In order, to understand the adsorption of nitrogen containing organic pollutants from neutralised RAS solution, synthetic solution of ammonium ion was prepared and used for the adsorption process.

The optimised conditions for the ammonium ion adsorption were pH, 8.0; temperature, 25°C and contact time, 150 min.

The adsorption of ammonium ion followed second order rate kinetic model and the adsorption isotherm model was obeyed by Freundlich equilibrium model.

The thermodynamic parameters for ammonium ion adsorption concluded that the adsorption of ammonium ions was spontaneous and favourable to CSAC.

The adsorption of ammonium ions was confirmed through SEM and XRD analyses.

However, the adsorption capacity of ammonium ion in neutralized RAS solution decreased steadily with number of cycles.

The adsorption process was not good enough for the removal of organic pollutant from neutralised RAE solution.

Hence, electro chemical oxidation of neutralised RAS solution was studied using graphite/graphite and SS304/graphite systems.

Graphite/Graphite electrode system was found to be an ideal system than the SS304/graphite system for the removal of organic pollutants under studied conditions.
The electro chemical oxidation of neutralised RAS was optimised by RSM tool for graphite/graphite system were found to be: TDS of RAS solution, 45 % (w/v); current density, 50 mA/cm$^2$ and electrochemical oxidation time, 120 min.

The mass transport coefficient ($k_m$) for the electro chemical oxidation of RAS solution was calculated based on pseudo-first order rate constant.

The thermodynamic analysis on electro chemical oxidation of RAS was exothermic in reaction and non-spontaneous in nature.

The calculated specific energy consumption at the optimum current density of 50 mA/cm$^2$ was found to be 0.41 kWh m$^{-3}$ for the removal of COD and 2.57 kWh m$^{-3}$ for the removal of TKN.

Electrolysed RAS solution was thermal evaporated to recover water and residual salt.

The increase in surface area of solution on thermal evaporation significantly increased the rate of evaporation of electrolysed RAS solution.

The optimum roof angle on the thermal evaporator was 30° to 45° for the effective collection of water condensate.

An alternative process for the neutralisation of RAS solution was studied using graphite/graphite electrode system.

The electro neutralisation of RAS solution was effectively carried out by change in the inter electrode space and the applied current.

The decrease in inner electrode space and increase in current density decreased the time of electrolysis for the electro neutralisation of RAS solution.
➢ The actual electrical energy (6 A/h) required for the electro neutralization of 1 litre of RAS solution was higher than the theoretically calculated amount (4.3A /h). The increase in actual electrical energy consumption was 1.4 times higher than the theoretical energy requirement.

➢ The cost towards the electrical energy in electro neutralization (0.0068 USD) was found to be significantly lower than the expenditure on chemical neutralisation (0.047 USD).

➢ Also, there is a scope for the conversion of hydrogen and chlorine gas (if separated) back into hydrogen chlorine gas and thus can be reused in the Sodium chloride recovery process.