List of publications


**Patent Filed**


**Technical papers presented in the International and National conferences**


3. Boopathy R, Sekaran G. Evaporated residues of RO reject stream management generated from leather industry in the 27th National Convention of Environmental Engineering conducted by The Institution of Engineers (India), Mangalore, Karnataka, India on January 24-25, 2012.
Electrochemical treatment of reverse osmosis concentrate generated by the leather industry using a Cu–graphite electrode†

R. Boopathy and G. Sekaran*

Electrochemical treatment of reverse osmosis concentrate (ROC) generated by the leather industry was evaluated using a copper coated graphite (Cu–graphite) electrode for the elimination of refractory organic pollutants. The effect of dilution of the ROC and applied current density on the performance of electrochemical oxidation was investigated. The presence of chloride ions in the ROC favoured the complete elimination of TKN and COD removal by 98% at optimum conditions: current density, 100 mA cm$^{-2}$ and electrolysis period, 6 h. The increase in ROC dilution slightly decreased the percentage removal of COD from 98% to 96%. The effect of current density on the removal of COD and TKN in raw ROC was found to be lower than in more diluted ROC. It was concluded that electrochemical treatment was more favourable for ROC samples without dilution. The generation of trihalomethanes during the electrochemical oxidation of ROC was effectively removed in an activated carbon packed bed column.

Introduction

Advanced membrane technology has become increasingly attractive for the reclamation of wastewater discharged from various industries compared with conventional technologies. Membrane processes are highly efficient, economical, easy to operate and automate, do not require the intensive use of chemicals used in pre-treatment operations and occupy less space.$^{1-4}$ Moreover, membrane separation techniques combine process stability with an excellent effluent quality. Reverse osmosis treatment imparts water with very high quality for reuse.$^{5-10}$ However, the generation of reverse osmosis concentrate (ROC) in significant quantities and the cost of its disposal or treatment was considered to be one of the main disadvantages.$^{11,12}$ The ROC is characterised by a high concentration of inorganic salts, organic compounds and biological constituents. The concentration of chromium in ROC may vary from 0.84 mg L$^{-1}$ to 1.16 mg L$^{-1}$ in the ROC generated by the leather industry. The salinity of ROC generated from industrial origin was less than that of the ROC discharged from desalination plants. Solley et al.$^{13}$ reported that the contaminants in ROC could be seven times more concentrated than in the feed water. As ROC contains anthropogenic organics,$^{14}$ its release into the environment needs to be managed carefully.$^{15}$ Several methods, such as coagulation and activated carbon adsorption,$^{16}$ ozonation,$^{14}$ combined O$_3$ with biological activated carbon,$^{15}$ photocatalysis and electrochemical oxidation$^{17,12}$ have been investigated for the management of ROC.$^{16,14}$ Among these, electrochemical oxidation has certain advantages for ROC treatment that include effective and robust control of reaction conditions, in situ generation of oxidants and operation at ambient conditions (temperature and pressure). Furthermore, the high salinity of ROC allows a high electrical conductivity, thereby lowering ohmic losses in an electrochemical system and decreasing energy consumption. There are reports on the treatment of ROC by electrochemical oxidation using different electrode materials.$^{12,16,17}$

Electrochemical oxidation can occur both via direct and indirect pathways. Direct oxidation involves only electron transfer at the anodic surface. Typically, the direct oxidation rate exhibits slow kinetics$^{18}$ at higher current densities with diffusion limitations. Therefore, indirect oxidation processes mediated by electro-generated oxidising agents (OCl$^-$ and OH$^-$) from wastewater, and with inorganic mediators (e.g. chloride, bromide) were often targeted to enhance the oxidation performance. Besides process conditions, the choice of anode material is of great importance for the electrochemical oxidation as it affects the performance and selectivity of the process.

Apart from the well-known but expensive boron-doped diamond (BDD) electrode, a number of different anode materials including thin film oxides (e.g. PbO$_2$, SnO$_2$), noble metals (Pt, Pd), and dimensionally stable anodes (DSA) such as Ti-based metal coated with metal oxides (e.g. RuO$_2$, IrO$_2$) or mixed metal oxides (MMOs) such as Ru–IrO$_2$ and Pt–IrO$_2$ have been investigated in recent years for the treatment of tannery wastewater, landfill leachate, petroleum wastewater and other...
bio-refractory organic waste streams. High chloride content in the ROC led to in situ generation of active chlorine species (i.e. Cl₂, HOCI and OCI⁻) for an effective indirect oxidation of organics. However, these potential oxidants led to the formation of chlorinated by-products such as trihalomethanes (THMs) and/or haloacetic acids (HAAs). The possible formation of chloride, chlorate, and perchlorate is of particular concern because of their toxic effects on living organisms. Hence, the effective operating conditions for the degradation of persistent pollutants at controlled by-products generation is important.

A recent review specified that fulvic like material such as hydrophobically charged fractions were removed by membrane separation, whose fluorescence intensity was reduced by an advanced treatment method. Finally, it was shown that oxidants, such as ozone and chlorine could increase or decrease the fluorescence intensity of the effluent. Hence, in this study, the fluorescence spectra of ROC before and after electrochemical oxidation was recorded to identify the effectiveness of the electrochemical oxidation.

In this study Cu-graphite was used as an electrode for the treatment of ROC generated from secondary biologically treated tannery wastewater. The reason for the selection of Cu-graphite as the electrode material was for its dimensional stability in the treatment of ROC and the cost of the material is lower than other oxide coated electrodes. The degree of dilution and current density were varied to evaluate the controlling step for the electrochemical oxidation of organic pollutants in ROC.

Materials and methods

Reverse osmosis concentrate (ROC)

Tannery ROC was collected from a commercial CETP in Rani-pet, Tamil Nadu, India and transported to the laboratory and stored at 25 °C until any further use. The ROC was characterised by following the methodology of APHA (Table 1).

Experimental set-up for the electrolysis of ROC

A rectangular shaped electrochemical cell (length, 15 cm; width, 3.5 cm and height, 15 cm) with a triangular hopper bottom was fabricated using acrylic plastic. Two copper coated cylindrical graphite (diameter, 1 cm and length, 15 cm) rods were used as electrodes (preparation of copper coated graphite is presented in the ESI†); and positioned horizontally with a 1 cm inner electrode spacing between the rods as shown in Fig. 1. The surface area of each electrode was 47 cm². ROC of volume 200 mL was taken into the electrochemical cell and re-circulated through a peristaltic pump, operated at flow rate of 3.3 cm³ min⁻¹. The electrochemically oxidized solution was then applied to a mesoporous activated carbon (surface area, 220 m² g⁻¹) packed bed column. Aliquots of samples were withdrawn from the reactor for the characterisation of parameters such as COD, TOC and TKN.

Analytical methods

Dissolved organic carbon was measured in a Shimadzu TOC-V analyser (Shimadzu, Japan). The samples were filtered through glass microfiber filter paper of pore size 0.45 μm. COD was determined in accordance with the procedure illustrated by Vyrides et al., to overcome the chloride interference. The concentration of TKN, ammonium-nitrogen and chromium(Ⅵ) were determined as per the APHA method.

Total free chlorine generation during the electrolysis process was analysed through color development with DPD (N,N-diethyl-p-phenylene diamine) followed by absorbance measurement in a spectrophotometer at λ₅50 nm. And the concentration of hydrogen peroxide was determined by following the methodology of APHA. The generation of total halomethane (THM) during electrolysis was estimated by eluting it by solvent extraction and detected by gas chromatographic techniques.

The Excitation Emission Matrixes (EEMs) were recorded using a Cary Eclipse fluorescence spectrophotometer. The system comprised of a Xenon arc lamp as a radiation source, excitation and emission gratings, and a sample chamber to hold quartz cuvettes (10 × 10 mm) and a red-sensitive photo-multiplier tube was used as the detector. The EEMs were recorded in the excitation wavelength range of λₑₓ 200–500 nm with a step width of 5 nm and in the emission wavelength range of λₑₓ 350–600 nm with a step width of 5 nm.

Results and discussion

Cyclic voltammetry

The electrochemical behaviour of the graphite and Cu–graphite rods in ROC was studied separately using cyclic voltammetry. Fig. 2 shows the voltammograms obtained in the potential range between 0 and 2 V with a scan rate of 10 mV s⁻¹. An anodic current peak was observed at 1.1 V for the graphite and Cu-coated graphite electrodes. The observed anodic oxidation peak was lower than the reported value of 1.6 V as with a BDD electrode. The decrease in electrode activity with the BDD electrode was due to the formation of oxygen containing functional groups, which act as a barrier for electron transfer. In the graphite electrode system, the electrode surface was regenerated by a quasi-reversible reaction. This is confirmed by the appearance of cathodic current peaks at 0.93 V and 0.85 V.

Table 1 Physico-chemical characteristics of ROC generated by the leather industry

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Parameters</th>
<th>Mean valuea</th>
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<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>6.42</td>
</tr>
<tr>
<td>2</td>
<td>Conductivity (mS cm⁻¹)</td>
<td>34.86</td>
</tr>
<tr>
<td>3</td>
<td>Total dissolved solids</td>
<td>15240</td>
</tr>
<tr>
<td>4</td>
<td>Chemical oxygen demand</td>
<td>640</td>
</tr>
<tr>
<td>5</td>
<td>Total organic carbon</td>
<td>220</td>
</tr>
<tr>
<td>6</td>
<td>Total Kjeldahl nitrogen</td>
<td>46</td>
</tr>
<tr>
<td>7</td>
<td>Ammonia nitrogen</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>Calcium</td>
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</tr>
<tr>
<td>9</td>
<td>Magnesium</td>
<td>13.8</td>
</tr>
<tr>
<td>10</td>
<td>Chloride</td>
<td>9996</td>
</tr>
<tr>
<td>11</td>
<td>Sulphate</td>
<td>3020</td>
</tr>
</tbody>
</table>

a All the values are expressed in mg L⁻¹, except pH and conductivity.
for the graphite and Cu–graphite systems respectively. The result suggested that, the selection of a copper coated graphite electrode was technically feasible for the treatment of ROC generated by the leather industry.

**Effect of ROC dilution**

The effect of ROC dilution was studied by performing the electrochemical degradation of ROC at different dilutions such as 1 : 0, 1 : 1, 1 : 2 and 1 : 4 (v/v) (volume of ROC : volume of distilled water). Fig. 3 presents the variation in COD and TKN of ROC with respect to electrolysis time. A regular linear decrease in parameters of ROC with time of electrolysis was observed. Thus, the electrochemical degradation of ROC was controlled by applied current density. The removal of COD and TKN increased with dilution and complete removal was attained at minimum electrolysis time. Complete COD removal was obtained for the dilutions 1 : 1, 1 : 2 and 1 : 4 at 120, 60 and 30 min of electrolysis time respectively. Similarly, complete TKN removal was obtained at 30, 15, 10 and 10 min for 1 : 0, 1 : 1, 1 : 2 and 1 : 4 dilutions of ROC. It is known that the oxidation rate is independent of the organic concentration in kinetically controlled reactions. But, in this study, the change in organic concentration was done by the increase in dilution which caused a significant change in COD and TKN removal (Fig. 3).

The removal of COD from ROC at an electrolysis period of 30 min for all the dilutions is illustrated in Fig. 3a. The percentage of COD removal was found to have decreased from 96.8% to 92.5% with an increase in ROC dilution from 1 : 0 to 1 : 4 respectively. This may be due to the decrease in chloride ion concentration in the ROC by dilution, because the chloride ions were responsible for the removal of TKN and COD in ROC by indirect oxidation through the generation of secondary oxidizing agents (chlorite and hypochlorite ions). The generation of hydrogen peroxide during the electrolysis of ROC was probably due to reducing oxygen at the cathode surface. Thus, the generation of hydrogen peroxide in the Cu–graphite/Cu–graphite system may be attributed to a high active surface area of the electrodes. The solution pH after electrolysis was found to have decreased from 6.4 to 3.2. The generation of hydrogen peroxide under acidic conditions liberates the hydroxyl radicals, which is responsible for the indirect oxidation of organic pollutants in ROC. The concentration of H₂O₂ in the bulk ROC (1 : 0) was found to be 108 mg L⁻¹ and it was 92, 60 and 22 mg L⁻¹ for the dilutions of 1 : 1, 1 : 2, 1 : 4 respectively. These values suggest that the concentration of hydrogen peroxide decreased with increasing dilution of ROC. This may be attributed to the presence of chloride ions, which eased the diffusion of ions for electrolysis and thereby increased the hydrogen peroxide concentration. The appreciable reduction in COD and TKN in diluted ROC that was observed, may be attributed to the generation of secondary oxidizing agents such as hypochlorous acid and OCl⁻ ions during electrolysis. The generation of hypochlorous acid and ionization thereof to OCl⁻ ions were responsible for the elimination of TKN content from the ROC, probably by converting it into chloramines and then into nitrogen.
The generation of hypochlorous acid (HOCl) and hypochlorite ions in the bulk solution from the chlorine gas generated at the anodic surface is indicated in eqn (2) and (3). The algebraic sum of dissolved chlorine gas, hypochlorous acid and hypochlorite is termed as free chlorine. The hypochlorite ion is the major component of the free chlorine in the normal pH range of wastewater.

\[
2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)
\]

\[
Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)
\]

\[
HOCl \rightarrow H^+ + OC\bar{l}^- \quad (3)
\]

The maximum evolution of free chlorine gas was observed as 9, 3.5, 2 and 1 mg L\(^{-1}\) for the ROC dilutions 1 : 0, 1 : 1, 1 : 2 and 1 : 4 respectively (Fig. 4b) at optimum conditions: current density, 50 mA cm\(^{-2}\) and electrolysis time, 120 min. As expected, the increase in dilution decreased the formation of free chlorine in the bulk solution due to the decrease in concentration of chloride ions in ROC.

The results presented in Fig. 4a indicate that the electrochemical oxidation was limited by mass transfer control in diluted ROC. To verify this phenomenon, ROC of dilution 1 : 2 was selected and operated at different current densities and their critical COD (COD\(_{cr}\)) was determined. According to basic principles of electrochemistry, if the limiting step in the electrochemical oxidation process is the organic pollutant transfer from the bulk to the anode surface, the change in the current density would not affect the COD and TKN removal rate. Thus, the calculated COD\(_{cr}\) may be regarded as the COD below which organics present in the solution are oxidised with mass transfer limitation. The calculated COD\(_{cr}\) was found to be 104 mg L\(^{-1}\) at 50 mA cm\(^{-2}\) at a dilution of 1 : 4 which is mainly under mass transport control in the electrochemical oxidation of ROC.

The limiting current density, \(j_{lim}\) predicts the stoichiometric requirement of current density for the electrochemical oxidation of ROC and it was calculated using the following equation

\[
\frac{[\text{COD}]}{[\text{COD}]_{lim}} = \exp \left[-\left(\frac{A_{km}}{V}\right)I\right] \quad (4)
\]

The mass transport coefficient obtained from eqn (4) was used to calculate the critical COD (COD\(_{cr}\)).

\[
\text{COD}_{cr} = \frac{1}{4AF_{km}} \quad (5)
\]

The specific energy consumption, \(E_{sp}\), in W h (g COD\(^{-1}\)) for the electrochemical oxidation of ROC was calculated using eqn (7)

\[
E_{sp} = \frac{UI\Delta t}{3600I\Delta \text{COD}} \quad (7)
\]

where \(U\) is the cell voltage, in V; \(I\) the applied current density, expressed in A; \(\Delta t\) is the duration of electrolysis, in s; \(V\) is volume of solution, in L and \(\Delta \text{COD}\) is the removed COD, in mg L\(^{-1}\). Fig. 4c shows that the increased dilution of ROC and current density significantly increased the energy consumption.
be $2.15 \times 10^{-3}$ and $2.8 \times 10^{-5}$ W h (g COD)$^{-1}$ respectively. The ratio of $E_{sp}$ value to the lowest $E_{sp}$ value (the lowest $E_{sp}$ value was obtained for ROC of dilution 1 : 4) signifies an index to characterise the energy efficiency of electrochemical oxidation. In the present study it was observed that $E_{sp}$ at 1 : 0 dilution/$E_{sp}$ at 1 : 4 dilution was 76.78, which indicates that the electrochemical oxidation of ROC at 1 : 0 dilution was more energy efficient over other dilutions. This was expected, that consumption of energy was minimal for the process operated under kinetic control.

**Effect of current density**

The effect of current density on COD and TKN removal was carried out by varying the current density from 5 to 100 mA cm$^{-2}$. Fig. 5a and b show the kinetic data of COD and TKN removal for the selected current density values. In all cases, a
decrease in COD and TKN was observed with an increase in applied current density in electrochemical oxidation. The maximum COD and TKN reduction of 98.1% and 100% respectively at 100 mA cm\(^{-2}\) was achieved with an electrolysis time of 6 h. The COD was removed by 96.8, 90.6, 78.8, 62.5% with an applied current density of 50, 20, 10, 5 mA cm\(^{-2}\) respectively. An applied current density of 100 mA cm\(^{-2}\) eliminated TKN by 100% after 20 min of electrolysis time, while 100% removal of TKN was achieved at current densities of 50, 20, 10, 5 mA cm\(^{-2}\) after 30, 40, 90, 180 min of electrolysis time respectively. This may be due to the generation of secondary oxidizing agents such as HOCl and OCl\(^{-}\) which were responsible for the oxidation of TKN. This corroborates with the observations recorded by Vijayaraghavan et al. using a graphite electrode.\(^{40}\) The generation of hydrogen peroxide was also responsible for the removal of organic content from the ROC.

![Fig. 6 Total halomethane concentration profile in electrochemical oxidation of ROC at different current densities.](image)

![Fig. 7 Excitation and emission matrix of (a) ROC and (b) ROC after electrochemical oxidation.](image)
Generation of by-products during electrochemical treatment of ROC

During the electrochemical oxidation of ROC, the formation of chloro and bromo organic compounds was more probable due to the generated free chlorine gas.\textsuperscript{41,42} This was confirmed from the selective elution of the electrolysed ROC solution (dialysed) after adsorption onto a C18 column using n-hexane and ethanol as eluting solvents. The compounds extracted with solvents (before and after electrochemical oxidation) were analysed by gas chromatography. The results (Fig. 6) depict that low or nil formation of organic halide was identified at low applied current densities (5, 10 and 20 mA cm\textsuperscript{2}). But, there was a considerable amount of total halomethane (THM) concentration (Fig. 6) detected at applied current densities above 50 mA cm\textsuperscript{2}. Still, the detected concentration of THMs was within the permissible concentration standard for drinking water (100 µg L\textsuperscript{-1}). Hence, it is very important to optimize the current density to be applied in order to increase the process efficiency and reduce the formation of THMs.

The formed halogenated organic compounds could be effectively removed by adsorption using activated carbon.\textsuperscript{43} Hence, a mesoporous activated carbon packed bed column was used to remove the halogenated organic compounds after electrochemical oxidation at current densities beyond 50 mA cm\textsuperscript{2}. The results suggest that the concentration of THMs was found to be below a detectable limit for the electrochemically oxidized solution after being passed through a packed bed adsorption column. Further, the electrochemically oxidised ROC contained Cr(III) in the range of 0.1–0.2 mg L\textsuperscript{-1}. The concentration of chromium in the final solution after adsorption in a mesoporous activated carbon column was found to be below a detectable limit. Hence, the integration of electrochemical oxidation and an activated carbon packed bed column would be an effective system for the treatment of ROC.

Fluorescence spectroscopy analysis

The number, composition and structure of fluorophores in the organic matter of ROC samples are variable and essentially unknown. Researchers have devised simple techniques for summarising EEMs, to identify fluorescence peaks in effluents.\textsuperscript{44,45} The EEMs of the ROC and after electrochemical oxidation were recorded to identify the removal of organic pollutants. Fig. 7 shows peaks at λ 220–320/385–415 nm indicating the presence of humic like substances in the ROC. A blue shift is associated with the fragmentation of aromatic organic compounds into smaller compounds possibly by reducing with π-electron systems by electrolysis. A blue shift is associated with either a decrease in the number of aromatic rings, fewer conjugated bonds in a chain structure, the conversion of a linear system to a non-linear systems or elimination of particular functional groups including carbonyl, hydroxyl, and amine groups.\textsuperscript{46,47} The fluorescence intensity decreased remarkably after electrochemical oxidation as shown in Fig. 7b. This concludes that the organic content was removed significantly from the ROC by electrochemical oxidation.

Conclusions

Treatment of a reverse osmosis concentrate stream generated by the leather processing industry was investigated by electrochemical oxidation using a Cu–graphite/Cu–graphite system. The electrochemical oxidation of COD and TKN in ROC was kinetically monitored and an increase in the dilution of ROC shifted the process to being controlled by mass transport of oxidizing agents. The increase in dilution increased the COD removal efficiency, and increased the energy cost too. Further, the generation of halogenated organic compounds was controlled by decreasing the applied current density and period of electrolysis. The generated toxic halogenated organic compounds could be effectively removed by passing through an activated carbon adsorption column.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ROC</td>
<td>Reverse osmosis concentrate</td>
</tr>
<tr>
<td>DSA</td>
<td>Dimensionally stable concentrate</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed metal oxide</td>
</tr>
<tr>
<td>THM</td>
<td>Total halomethane</td>
</tr>
<tr>
<td>CETP</td>
<td>Common effluent treatment plant</td>
</tr>
<tr>
<td>APHA</td>
<td>American public health association</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>TKN</td>
<td>Total Kjeldahl nitrogen</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation and emission matrix</td>
</tr>
<tr>
<td>$k_m$</td>
<td>Mass transport coefficient (m s\textsuperscript{-1}) of COD</td>
</tr>
<tr>
<td>$E_{sp}$</td>
<td>Specific energy consumption (W h g\textsuperscript{-1} of COD)</td>
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Acknowledgements

We (Authors) thank the Council of Scientific and Industrial Research (CSIR), India for the financial assistance to carry out the work.

References


Separation of sodium chloride from the evaporated residue of the reverse osmosis reject generated in the leather industry – optimization by response surface methodology

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Reverse osmosis (RO) concentrate is being evaporated by solar/thermal evaporators to meet zero liquid discharge standards. The resulted evaporated residue (ER) is contaminated with both organic and inorganic mixture of salts. The generation of ER is exceedingly huge in the leather industry, which is being collected and stored under the shelter to avoid groundwater contamination by the leachate. In the present investigation, a novel process for the separation of sodium chloride from ER was developed, to reduce the environmental impact on RO concentrate discharge. The sodium chloride was selectively separated by the reactive precipitation method using hydrogen chloride gas. The selected process variables were optimized for maximum yield of NaCl from the ER (optimum conditions were pH, 8.0; temperature, 35°C; concentration of ER, 600 g/L and HCl purging time, 3 min). The recovered NaCl purity was verified using a cyclic voltammogram.

Keywords: reverse osmosis concentrate; NaCl recovery; precipitation of NaCl; leather industry; response surface methodology

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>UASB</td>
<td>up flow anaerobic sludge blanket</td>
</tr>
<tr>
<td>ASP</td>
<td>activated sludge process</td>
</tr>
<tr>
<td>TDS</td>
<td>total dissolved solids</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
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1. Introduction

In reverse osmosis (RO), the membrane separation could be considered as a viable and sustainable process water recovery from treated wastewater/brackish water. However, treatment/disposal of RO concentrate is regarded as the major drawback for the implementation of the RO process. Disposal of RO concentrate onto surface water bodies, coastal sites or open soil in wastewater treatment plants (WWTPs) has been under practice. The other alternatives such as modified membrane systems such as vibratory shear enhanced process and multistage RO systems could reduce the volume of reject stream. Disposal by the thermal evaporative crystalliser or solar evaporation pans is preferred for complete recovery of water. The operating cost for this evaporative crystallization method was high; still, the final ER was not reusable because of contamination with both organic and inorganic compounds.[1] The leather processing industries generate approximately 150 kg of ER from RO concentrate per ton of raw hide/skin by solar/thermal evaporation.[2] Most of the organics present in the RO concentrate are highly bio-refractory, since they have already been subjected to the extensive biological treatment in WWTP. These organics generally include: (a) natural organic matter present in the process water, (b) refractory chemicals including pesticides, pharmaceutical and personal care products, and endocrine disruptors from public discharge and (c) soluble microbial products from WWTP.[3–5]

Earlier, the ER of the RO concentrate was permitted to be dumped onto secure landfill sites. But, the inorganic salts present in the ER (the ER contains 55.2 ± 2.2% (w/w) of NaCl) are leached into the groundwater sources during the rainy season causing severe damage to the groundwater sources. Moreover, the treatment of leachate formed from the landfill sites becomes a complicated process.[6] Therefore, dumping of ER salt onto landfill sites was banned and directed by the pollution control agencies to be stored under a protective shed within the leather industry. Now, the situation becomes even worse, as there is not enough free space for dumping the ER. At this juncture, it is very much important to find an alternative method for the disposal of this residual solid waste.[7,8] There are many reports on the recovery of value-added products from RO concentrate.[9–12] However, a report on the separation of organic and inorganic salts from the ER is still limited.

There has been a constant research for alternative processes to land co-disposal technique or to recover the...
value-added products from the ER and thus to reduce the environmental impact on discharge of ER by the landfill disposal method. There are few reports on the separation of salts from the mixture of inorganic salt. However, there is no report on the separation of inorganic salt from the mixture of organic and inorganic residue generated from the leather industry.

Hence, in this present investigation an attempt has been made to separate NaCl from ER by the reactive precipitation using hydrogen chloride gas as the precipitating agent. Furthermore, a statistical model for the precipitation of NaCl was evaluated for the optimization of selected parameters by central composite design (CCD) under response surface methodology (RSM).

2. Materials and methods
2.1. Source of ER salt and characterization
The ER salt was collected from an effluent treatment Plant in a commercial export-oriented tannery, located in Ranipet, Tamil Nadu, India. The ER was transported in a polythene container and stored under moisture-free condition. The ER and saturated ER solution were characterized for the pollution parameters such as chemical oxygen demand, chloride, sulphate, sodium, calcium, magnesium, undissolved content and volatile dissolved solids by following the methodology described in American Public Health Association [21] and the values are reported in Table 1.

Table 1. Characteristics of ER and saturated ER solution.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameters</th>
<th>ER (mg/g)</th>
<th>Saturated ER solution (mg/L)</th>
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<td>1</td>
<td>pH</td>
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<td>2</td>
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<td>7</td>
<td>Magnesium</td>
<td>0.96</td>
<td>510</td>
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<tr>
<td>8</td>
<td>Undissolved content</td>
<td>51</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>Volatile organic content</td>
<td>16.5</td>
<td>–</td>
</tr>
</tbody>
</table>

*aNo unit for pH.*

2.2. Chemicals
The concentrated hydrochloric acid, sulphuric acid and sodium hydroxide used in this investigation were purchased from Merck Chemicals (India).

2.3. Experimental set-up for the precipitation of sodium chloride from the ER
A known volume of saturated ER (100 ml) solution was taken in a cylindrical jacketed glass reactor for the precipitation of NaCl. Hydrogen chloride gas was purged at a flow rate of 2.06 g/min into the saturated solution of ER through a distributor provided at the bottom of the reactor. The temperature of the solution was maintained by circulating water at a constant temperature in the jacketed medium through a thermostatic water bath. The reactor was equipped with an agitator for uniform mixing of the contents. The precipitated NaCl was washed with pure brine solution to get pure salt.

2.4. Experimental design and optimization
The CCD was used for the experimental design and the selected experimental study is presented in Table 2. The CCD with four factors of independent variables at five levels was applied using Design Export 8.0.7.1. The selected independent variables were coded at five levels between $-1$ and $+1$ which were determined by the preliminary experiments; the range of selected independent variables were: pH, 6–10; temperature, 25–45°C; concentration of ER, 500–700 g/L and HCl purging time, 1–5 min.

The total number of experiments for four factors by CCD with orthogonal blocks design was $30 = 2^K + 2K + 6$ where $K$ is the factor. Twenty-four experiments were augmented at factorial and axis points and the six design centre points were measured to evaluate the pure error as required for design by randomized run procedures. The first five columns of Table 3 show the number of run and experimental conditions of the randomized CCD design. Performance of the process was evaluated by the yield of sodium chloride.

In the optimization process, the response can be simply related to chosen factors by a linear or a quadratic model as

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j,$$

Table 2. Experimental independent variables range and levels for the precipitation of sodium chloride from ER.

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Design variables</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>A</td>
<td>–1 0.5 0 0.5 1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>B</td>
<td>25 30 35 40 45</td>
</tr>
<tr>
<td>Concentration of ER (g/L)</td>
<td>C</td>
<td>500 550 600 650 700</td>
</tr>
<tr>
<td>HCl gas Purging time (min)</td>
<td>D</td>
<td>1 2 3 4 5</td>
</tr>
</tbody>
</table>
where $Y$ is the response, $X_i$ and $X_j$ are the variables ($i = 1–4$), $\beta_0$ is the constant coefficient and $\beta_i$, $\beta_{ij}$ and $\beta_{jj}$ ($i$ and $j = 1–4$) are interaction coefficients of linear, quadratic and the second-order terms, respectively. The RSM including analysis of variance (ANOVA) was used to obtain the interaction between the process variables and the response of NaCl yield. The statistics polynomial model was expressed by the coefficient of determination $R^2$ and $R^2_{adj}$, and the statistical significance was checked by the $F$-test in the model. The desired process parameters were selected based on the maximum yield of sodium chloride precipitation.

### 2.5. Instrumental analysis

#### 2.5.1. Cyclic voltamgramm

Electrochemical work station of CH Instruments, Model 600D series with a potentiostat driven by electro analytical measuring software was connected to a computer to perform cyclic voltamgramm. Ag/AgCl (3 M KCl) and platinum wire (3 mm diameter) were used as the reference and counter electrodes. The black housed platinum wire (3 mm diameter) was used as the working electrode. The voltammetric experiments were carried out at 25°C. The solutions were degassed with nitrogen for 10 min prior to recording the voltammogram sweep analysis.

### 3. Results and discussion

#### 3.1. Precipitation of sodium chloride from saturated ER solution

The dissolution of ER in water and precipitation of sodium chloride from the saturated solution of ER is expressed in the ionic equation as given below

$$ER \text{ salt} + \text{H}_2\text{O} \rightarrow \text{Na}^+, \text{Cl}^-, \text{Ca}^{2+}, \text{SO}_4^{2-}, \text{Mg}^{2+}, \text{Org salt}, \text{H}_2\text{O}$$

The ER salt was dissolved in deionized water for the precipitation of sodium chloride, as given in Equation (2). The increase in concentration of either Na$^+$ or Cl$^-$ in this saturated ER solution will precipitate sodium chloride by the common ion effect. In the present investigation, hydrogen
chloride gas was purged to increase the concentration of Cl\(^{-}\) ions in the saturated ER solution. The increase in Cl\(^{-}\) ion concentration in the ER solution disturbed the dynamic equilibrium of ions and thereby increased the ionic product of Na\(^{+}\) and Cl\(^{-}\). The precipitation of sodium chloride was observed at a point at which the ionic product of Na\(^{+}\) and Cl\(^{-}\) exceeded the solubility product of sodium chloride (solubility product of NaCl (K\(_{sp}\)), 36 (mol/L\(^2\)) as illustrated in Equation (3).

\[
Y = -688.16 + 48.18(pH) + 6.4(Temp) \\
+ 1.4(Conc)10.15(Time) - 0.14(pH)(Temp) \\
+ 8.7 \times 10^{-4}(pH)(Conc) + 0.34(pH)(Time) \\
+ 9.25 \times 10^{-4}(Temp)(Conc) + 0.02(Temp)(Time) \\
+ 0.014(Conc)(Time) - 2.76 (pH)^2 - 0.084 \\
\times (Temp)^2 - 1.19 \times 10^{-3}(Conc)^{-2} - 3.39(Time)^2.
\]

(4)

Table 4 shows the results of ANOVA for the quadratic models. To evaluate the best model, the minimum degrees of freedom (df) should be greater than or equal to 3 for the lack of fit error and 4 for the lack of pure error. In the present model, the F-value of 6.22 implies that the precipitation of sodium chloride using hydrogen chloride gas was significant (i.e. p-value was .0006) with df 10 and 5 for the lack of fit and pure error, respectively. The signal-to-noise ratio is 7.889, which indicates that the model selected for this study fits adequately. The p-value was used to denote the significance of the coefficients and for understanding the pattern of the mutual interactions between the selected variables. The calculated F-value was less than the probability value which is less than .05; i.e. approximation of selected model should be 95% of confident level and above. This indicates that the second-order polynomial model fitted the experimental results very well. The result reveals that in this model parameters such as C, D, A\(^2\), B\(^2\), C\(^2\) and D\(^2\) are significant terms. The purpose of the statistical analysis is to determine the experimental factors that generate signals that are large in comparison to the noise. The coefficient of variation (CV) indicates the degree of precision with which the experiments are compared. The good reliability of the experiment is usually indicated by a lower value of CV. The lower value of CV (5.15) indicated a greater reliability of the experiments that were performed in this study. From Equation (4), the optimal conditions for the maximum yield of sodium chloride precipitation were obtained as follows: pH, 8.0; temperature, 35\(^{\circ}\)C; concentration of ER salt, 600 g/L and HCl gas purging time, 3 min. Under the optimized conditions, the maximum yield of NaCl was 83% (27 g per 100 ml of sample volume).

Figure 1 illustrates the response of NaCl precipitation for the selected independent process variables as coded from -1 to +1 at five equal difference levels. The increase in A and B coded values increased the maximum yield of NaCl at mid-point value of the level and decreased towards the end. But, an increase in values of C and D code level from -1 to +1 increased the yield of NaCl precipitation. The actual values are the measured response data for a particular
The solubility of NaCl is affected by temperature, and the solubility curve (i.e., solution became under-saturated). Moreover, the precipitation of sodium chloride from aqueous solution is an exothermic reaction, thus the heat of generation may redissolve the precipitated NaCl molecules back into the aqueous solution. The surface plot confirmed that the maximum yield of NaCl (83%) was achieved at the optimum pH 8.0 and a temperature of 35°C.

Figure 2(b) exemplifies the interrelation between concentration of ER salt and pH of the solution at a constant temperature of 30°C and HCl gas purging time of 3 min. The increase in concentration of ER salt from 500 to 600 g/L recorded the increase in yield of NaCl precipitation (83%) and remained constant thereafter up to 700 g/L. This illustrates that the solubility of NaCl reached saturation with 600 g of ER per litre, and beyond this, an increase in concentration did not dissolve further salt and the undissolved salt settled down at the bottom of the reactor. The concentration of ER salt below 600 g/L yielded very low recovery (62%), which may be attributed to under-saturation of the solution. Hence, the maximum yield was observed at an ER concentration of 600 g/L with 83% recovery (26.9 g per 100 ml of solution).

Figure 2(c) explores the effect of HCl gas purging time on precipitation of NaCl at a constant concentration of ER salt of 600 g/L and at a temperature of 30°C. The increase in HCl gas purging time increased the rate of precipitation and yield of NaCl. To observe the influence of HCl gas purging time, purging contact time was varied from 3 to 5 min for a batch volume of 100 ml. The maximum yield (83%) was observed for HCl purging time of 3 min. This shows that the reaction reached equilibrium at 3 min of HCl purging; hence, further increase in purging time did not increase the yield of NaCl precipitation.

Figure 2(d) shows the interaction of temperature and concentration of ER salt on NaCl precipitation. The solution temperature was varied from 25°C to 45°C for the precipitation of sodium chloride with respect to concentration of ER salt from 500 to 700 g/L. The increase in solution temperature increased the precipitation of sodium chloride up to 35°C and decreased with increase in temperature up to the temperature of 45°C. The maximum yield of sodium chloride precipitation (83%) was obtained at the mid-level point temperature of 35°C.

3.3. Analysis of response surface plot for sodium chloride precipitation

The linear and interaction effects on the selected process parameters were analysed and furnished in three-dimensional surface plots as in Figure 2. Figure 2(a) illustrates the yield of NaCl precipitation with respect to initial solution pH, 8.0; temperature, 35°C; concentration of ER salt, 600 g/L and HCl gas purging time of 3 min. The increase in yield of NaCl precipitation was achieved with an increase in pH from 6.0 to 8.0 and maximum yield was attained at this mid-level point of model coded value and decreased with increase in pH up to 10.0. The maximum yield of NaCl (83%) was observed at pH 8.0, i.e. 26.9 g of NaCl was recovered for a batch volume of 100 ml. This can be explained as initial loss of H⁺ was consumed to neutralize OH⁻ ions or to counter balance the ionic strength in the aqueous solution.[23,24] Therefore, hydrogen chloride gas was purged more than the stoichiometric balance to disturb the equilibrium condition to effect the precipitation of NaCl. The external jacketed medium with water recirculation was provided around the precipitation reactor to maintain the desired set temperature. The increase in set temperature from 25°C to 45°C showed a mixed response. The yield of NaCl was increased with temperature up to 35°C (83%) and thereafter it was decreased up to the temperature of 45°C (77.5%). This may be imputable as the change in temperature alters the solubility of NaCl by the rule of

\[ R_t = R_c (1 - e^{-K_{ct}}), \]  

(5)

The used first-order and pseudo-second-order equations.[25, 26] The used first-order and pseudo-second-order equations are expressed, respectively as
$R_t = \frac{K_2 R_e t}{1 + K_2 R_e t}$

where $R_e$ (mg/g) and $R_t$ (mg/g) are the quantities of NaCl precipitated at equilibrium and at time $t$, respectively; $k_1$ (min$^{-1}$) and $k_2$ (g/mg min) are the rate constants of pseudo-first-order and second-order equations.

The values of $R_e$, $k_1$ and $k_2$ were determined by the nonlinear regression method using solver in MS-excel and calculated values are tabulated in Table 5. The validity of the kinetic model was done based on the regression coefficient and error analysis. The values of correlation coefficients for pseudo-first order (0.99) and pseudo-second order (0.95) indicated that the experimental data are more accurately obeyed by the pseudo-first-order kinetic model (Figure 3). Furthermore, the error analysis ($\chi^2$) was carried out to validate the kinetic order of NaCl precipitation. The minimum $\chi^2$ value was observed for the pseudo-first order (0.21) compared with the pseudo-second order of reaction (0.47). This indicates that precipitation of NaCl followed pseudo-first-order reaction. This implied that mass of HCl gas purged into saturated ER solution is considered to be a rate-limiting step in the precipitation of NaCl.

### 3.5. Instrumental analysis

#### 3.5.1. Cyclic voltammogram

In order to verify the purity of the recovered sodium chloride a cyclic voltammogram using sweep techniques at a scan rate of 10 mV/s was recorded for the precipitated salt and pure sodium chloride (SD fine chemicals, India) as a reference salt. Cyclic voltammogram is used to understand the rate of electron transfer step of electro active species to the plane of electrode surface. That is, the rate of electron transfer...
Table 5. Nonlinear kinetic data for the precipitation of sodium chloride from ER.

<table>
<thead>
<tr>
<th></th>
<th>NaCl precipitate (g/100 mL) (experimental)</th>
<th>NaCl precipitate (g/100 mL) (predicted)</th>
<th>Rate constant</th>
<th>$R^2$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>26.9</td>
<td>26.1</td>
<td>1.01 min$^{-1}$</td>
<td>0.99</td>
<td>0.21</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>26.9</td>
<td>23.1</td>
<td>0.074 g/mg s</td>
<td>0.95</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Figure 3. Nonlinear kinetic model for the precipitation of sodium chloride (conditions: pH 8.0; temperature 35°C; Concentration of ER 600 g/L; volume of batch reaction 100 ml).

step is considered to be fast compared with the diffusion of molecules from the bulk solution phase to the electrode surface. The entrapped organic molecules in the precipitated NaCl were scanned through this electron-sensitive cyclic voltammogram curve. The precipitated salt (0.5 M) was dissolved and recorded at a scan rate of 100 mV/s. The same experiment was repeated with pure salt (Merck, India), as a reference salt, of the same concentration (0.5 M). By the Nernst electrochemical equation, if the peak potential difference is less than $(58/n)$ mV at all scan rates then the process is said to be quasi-reversible. Figure 4 shows the cathodic and anodic peak values for the standard NaCl (0.5 M) were 1.33 and 0.91 V, respectively. The cathodic and anodic peak values observed for the recovered NaCl and reference salt remained identical. This confirmed that the recovered NaCl was not contaminated with any impurity.

3.6. Cost estimation on ER management

The process used in the present investigation was able to recover NaCl by 0.203 kg per kg of ER. The cost towards the consumables such as chemicals and electrical power in the present method was 0.058 US $ per kg of ER. The selling cost of the recovered NaCl is 0.088 US $ per kg. Thus, the net expenditure on processing 1 kg of ER by the present method is 0.04 US $. The current method followed for the disposal of ER is dumping onto secure landfill the cost of which is 0.11 US $ per kg of ER (inclusive of transportation cost and handling cost at secure landfill). Hence, the proposed process on the management of ER indicates that there is a scope for the cost saving compared with dumping onto secured landfill.

4. Conclusions

In the present investigation sodium chloride was selectively precipitated from the ER of RO concentrate using hydrogen chloride gas as the precipitating agent. The process parameters were identified as follows: pH, 8.0; temperature, 35°C; concentration of ER salt, 600 g/L and HCl purging time, 3 min by CCD. The theoretical yield of NaCl through precipitation was deduced and an empirical equation was presented for the selected process key parameters. The precipitation of NaCl followed the pseudo-first-order kinetic model. The cyclic voltammogram confirmed that the recovered NaCl was relatively pure compared with the standard salt. The recovered NaCl can be reused within the leather industry or in other industry after being washed with pure brine. Thus, the recovery and reuse of NaCl may minimize the impact on disposal of ER salt; thereby, the problem of storing under the shelter can be averted completely.

Funding

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References

[1] Suman M, Khaiwal R, Dahiya RP, Chandra A. Leachate characterization and assessment of groundwater pollution near...


First Report on Separation of Sulfate Ions from Evaporated Residue of RO Reject Stream Generated from the Leather Industry

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ABSTRACT: Reverse Osmosis (RO), the membrane separation process, is widely being used on the fresh water supply to industrial and domestic sectors with the generation of reject streams containing huge concentrations of cations and anions besides organic impurities. Hence, the reject stream is advised to evaporate in solar pans/multiple effect evaporators to reduce the volume of disposal. The evaporated residue consists of a high concentration of chloride and sulfate ions along with organic impurities. In our previous study, chloride ion was separated as sodium chloride, and in the present investigation, an attempt was made to separate sulfate ions as calcium sulfate from the saturated solution of reject stream generated from the leather industry. The optimum conditions for the precipitation of calcium sulfate were observed as follows: pH 4.0 and temperature 40 °C. The separated calcium sulfate was calcined at 700 °C to destruct the occluded organic impurities. The recovered calcium sulfate was characterized for surface morphology, chemical composition, thermal behavior and crystalline modification through scanning electron microscopy (SEM), electron dispersive X-ray (EDX), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) analyses. The recovered calcium sulfate was of fine particles with increase in surface area. The recovered calcium sulfate was tested for its adsorptive property toward aqueous leather dyes.

1. INTRODUCTION

The steady growth of industry and the human population across the globe demands the need for potable water and wastewater treatment facilities. Thus, the desalination process to remove dissolved ions from the potable water and treated wastewater has been made mandatory by pollution control regulatory agencies. The conventional reverse osmosis process is an economical method to purify saline and other impaired water and wastewater. However, the major limitation of the process is the generation of a relatively large proportion (10−40%) of reject stream depending upon the dissolved solid concentration in feed stream. The reject stream, having high concentration of inorganic and organic salts and biological compounds, and thus direct disposal of the RO concentrate onto the environment, might pose an eco-toxicological threat to the organisms in receiving water bodies and in soil.

There have been many studies carried out on industrial salt recovery from RO concentrate.1−3 Generally, the increase in aqueous solution concentration increased the degree of super saturation; at this condition, there is a greater possibility for instantaneous nucleation and homogeneous crystallization of salt in the bulk solution. By rendering this concept, chloride and sulfate ions were separated from the saturated ER solution by the reactive precipitation technique. Some reports on the related research works point out that it was feasible to separate CaSO₄ precipitate from aqueous Na₂SO₄ system by the addition of CaO,4,5 but the limitation of CaSO₄ precipitation in the presence of organic compounds has not been studied much in detail. The reports on the separation or removal of sulfate ion from aqueous solutions in the presence of organic impurities are very few or perhaps nil. Hence, the focal theme of the present investigation was to separate sulfate ion from the saturated solution of evaporated residue of an RO reject stream in the presence of organic and inorganic mixture.

2. MATERIALS AND METHODS

2.1. Source of Evaporated Residue and Preparation of Saturated Solution of ER. The ER was collected from a solar evaporation pan in an Effluent Treatment Plant (ETP) of a commercial tannery in Ranipet, Tamil Nadu, India, and stored in the laboratory for further studies. The saturated solution of ER was prepared by dissolving 600 g in 1 L of distilled water under stirring.6 The undissolved sand, grit, and floating solids were separated by decantation and screening. The screened solution was passed through a sand filter to remove the suspended solids. The filtered saturated ER solution was characterized (Table 1) for pH, grit, moisture content, volatile dissolved solids at 600 °C, COD, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ by following the methods of the American Public Health Association (APHA).7 The detailed preparation and characterization of the saturated ER solution were reported elsewhere.6

Table 1. Characteristics of Saturated Solution of ER

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.67</td>
</tr>
<tr>
<td>COD</td>
<td>5.76</td>
</tr>
<tr>
<td>chloride</td>
<td>215.94</td>
</tr>
<tr>
<td>sulfate</td>
<td>127.15</td>
</tr>
<tr>
<td>sodium</td>
<td>125.92</td>
</tr>
<tr>
<td>calcium</td>
<td>1.44</td>
</tr>
<tr>
<td>magnesium</td>
<td>0.51</td>
</tr>
</tbody>
</table>

*All the values except pH are expressed in grams per liter.

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2.2. Chemicals. The concentrated hydrochloric acid, sodium hydroxide, calcium hydroxide, magnesium oxide, and calcium sulfate dihydrate used in this investigation were purchased from the Merck Chemicals (India) Pvt. Ltd. Acid black 210 and S3, acid blue 113, and tannic acid were purchased from Sigma Aldrich, India.

2.3. Experimental Setup for Chloride and Sulfate Ions Separation from ER. A known volume of saturated solution of ER (100 mL) was taken in the reactor for the selective precipitation of NaCl at the optimized conditions such as pH, 8.0; temperature, 30°C; and concentration of ER, 60% (w/v). The hydrogen chloride gas was injected at the rate of 2.06 g/min into the saturated ER solution through a distributor provided at the bottom of the reactor. The supernatant solution was transferred to the evaporative crystallization reactor to further precipitate NaCl. Then, the residual acidified ER solution was pumped to a neutralization chamber and neutralized using calcium hydroxide. The concentration of sulfate ions in the solution before and after precipitation of calcium sulfate was determined using spectrophotometer. The precipitated calcium sulfate was separated through a glass fiber filter paper and washed with deionized water. Then, it was dried at 110°C in an hot air oven and calcined at 700°C in a muffle furnace. The detailed flow sheet on the separation of chloride and sulfate ions is shown in Figure 1.

The precipitation of calcium sulfate from ER saturated solution can be explained by the common ion effect analogues to sodium chloride precipitation in our previous study. The addition of calcium hydroxide increased the calcium ion concentration in the aqueous solution, and thus, calcium sulfate is precipitated from the solution on exceeding the solubility product of calcium sulfate in the solution ($K_{sp} = 3.14 \times 10^{-5}$ mol²/L²). The solubility product of calcium sulfate and the ionic product of calcium and sulfate ions are related:

$$K_{sp, CaSO_4} = [Ca^{2+}][SO_4^{2-}]$$

2.4. Instrumental Analysis. 2.4.1. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analyses. The recovered calcium sulfate was coated with 120–130 μm gold in argon medium to capture the surface image. Scanning electron microscopy (SEM) images were observed on a scanning device attached to a JEOL JSM-6600 electron microscope at 20 kV accelerating voltage with a 5–6 nm electron beam. The energy dispersive X-ray (EDX) spectroscopy was used to record the elements present in the recovered calcium sulfate.

2.4.2. Thermogravimetric Analysis (TGA) of Recovered Calcium Sulfate. The TGA spectra were recorded for the recovered calcium sulfate before and after calcination in a pan and gravimetric analysis under reduced nitrogen atmosphere from 30 to 800°C, using a temperature gradient of 10°C/min, and scans were recorded using TGA Q50 (V20.6 Build 31).

2.4.3. X-ray Diffraction (XRD) Analysis. The XRD spectra for the recovered calcium sulfate and standard calcium sulfate were recorded with high resolution GUINER Powder X-ray diffractometer (SEIFERT, Germany).

Further, the total organic carbon was measured using a TOC-V CSH analyzer (Shimadzu) and surface area of the standard and recovered calcium sulfate was measured using a surface area analyzer (BELSORP-MAX).

3. RESULTS AND DISCUSSION

3.1. Evaporative Crystallization of Sodium Chloride from the Residual ER Solution. The separation of sodium chloride from ER was selectively removed by reactive precipitation technique using hydrogen chloride gas, as detailed in our previous work. The reactive chemical precipitation technique removed NaCl by 27 g/100 mL from ER solution. In order to increase the NaCl recovery, the residual solution was subjected to concentrate by evaporation of water molecules at 120°C. Figure 2 shows that the increase in evaporation of water increased the crystallization of NaCl. The increase in evaporation up to 10% (v/v) increased the NaCl crystallization. With evaporation of water beyond 10% (v/v), calcium and sulfate ions were also precipitated along with NaCl. Hence, the optimum evaporation of water molecules was fixed at 10% (v/v) for the secondary crystallization of pure NaCl. The maximum amount of secondary crystallization of NaCl at...
10% (v/v) water evaporation yielded 5.5 g for the working volume of 100 mL. This was due to the evaporation of water molecules from the residual ER solution, which resumed the super saturation of sodium chloride. Thus, by the solubility rule, the sodium chloride was crystallized first and settled at the bottom of the reactor. Further increase in water evaporation increased the solubility of other ions (Ca\(^{2+}\) and SO\(_4^{2-}\)) that remained in the residual solution. Thus, the cumulative yield of NaCl from reactive precipitation and evaporative crystallization was 32.5 g/100 mL ER solution; that is, the overall percentage recovery of NaCl from ER solution was 98.7%. The recovered NaCl was washed with pure saturated sodium chloride solution to get pure sodium chloride.

### 3.2. Separation of Sulfate Ions from the ER Solution.

The residual solution after evaporative crystallization still contained sulfate ions along with trace amounts of other inorganic and organic salts. The sulfate ions from the residual acidified solution were separated by reactive precipitation by the addition of neutralizing agents, calcium hydroxide, and magnesium oxide. Figure 3 shows that the effect of addition of neutralizing agents on separation of sulfate ions from the residual acidified solution. The addition of two neutralizing agents increased the ionic strength of the aqueous solution, and they were common to all the cations in the residual acidified solution. Hence, by the common ion principle, the increase in ionic strength shifts the solution equilibrium from left to right as shown in eq 1.

\[
\text{Ca}^{2+}/\text{Mg}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4/\text{MgSO}_4
\]

The consumption of neutralizers was found to be in the order, calcium hydroxide, 132 g/L, and magnesium oxide, 98 g/L residual acidified ER solution. The suitable neutralizing agent was selected based on the maximum recovery of SO\(_4^{2-}\) ions from the residual solution after evaporative crystallization. Among the two neutralizing agents, the maximum amount of sulfate ions (99.5% w/w) was precipitated with the addition of Ca(OH)\(_2\) rather than with MgO. Hence, Ca(OH)\(_2\) was selected as the neutralizing agent for precipitation of sulfate ions from the residual acidified ER solution. Hence, the addition of Ca(OH)\(_2\) separates 99.5% (w/w) of SO\(_4^{2-}\) ions along with rise in solution pH.

### 3.3. Effect of pH on Sulfate Ions Separation.

In order to study the effect of pH on sulfate ion separation, the pH of residual acidified ER solution was varied from 0.0 to 7.0 by the addition of calcium hydroxide solution. Figure 4 shows that the increase in solution pH from negative pH to 7.0 increased the separation of sulfate ions as calcium sulfate significantly. This was due to the precipitation of sulfate ions as calcium sulfate by exceeding the solubility product of CaSO\(_4\) in the solution. The precipitation of CaSO\(_4\) was observed to be very fast with the rate constant of 0.018 s\(^{-1}\) (pseudo-first order) and precipitation induction time of less than 2 s, this corroborates with the reports of Alimi et al., 2003. The consumption of calcium hydroxide was high, until pH 0.0 was reached (consumption of Ca(OH)\(_2\), as Ca\(^{2+}\), 6.27 g/100 mL), and the consumption for further increase in pH to 7.0 was 0.83 g/100 mL ER solution. This can be explained by the negative logarithmic definition of pH; the molar consumption of neutralizing agent will be logarithmic in trend with respect to a rise in the pH of the solution. Hence, the consumption of calcium hydroxide was high for the neutralization of residual acidified solution. The added calcium hydroxide initially precipitated out the sulfate ions.
3.4. Effect of Temperature on Calcium Sulfate Separation. The residual acidified solution temperature was varied from 10 to 70 °C during the addition of calcium hydroxide for the separation of sulfate ion as calcium sulfate. The solution temperature was maintained by circulating water from a constant-temperature water bath at a required set temperature through glass jacket provided to the reactor. The precipitation of calcium sulfate was spontaneous after the addition of Ca(OH)₂. As Figure 5 illustrates, the increase in solution temperature decreased the concentration of SO₄²⁻ ions in the residual solution; that is, the percentage removal of SO₄²⁻ from the residual acidified solution was increased from 99.25 to 99.93% for the increase in temperature from 10 to 70 °C. It is known that the solubility of calcium sulfate is not significantly altered with rise in solution temperature; hence, the dissolution of precipitate was negligible with increase in solution temperature during the precipitation.9 Also, the increase in temperature decreased the induction time for the precipitation of calcium sulfate in the aqueous solution, which is in close agreement with Liu et al., 1973.10,11

3.5. Separation and Purification of Calcium Sulfate. The precipitated calcium sulfate on the addition of calcium hydroxide was separated by vacuum filtration using filter cloth of mesh size 300 μm. The precipitate was washed twice with deionized water and dried in hot air oven at 110 °C for 2 h. Then, the precipitate was calcined at different temperatures 400 to 700 °C for a period of 4 h under air atmosphere for the removal of organics from the calcium sulfate particles, presumably due to surface adsorption or occlusion in the voids. The amount of organic content in the known amount of precipitate was estimated using a TOC analyzer, and sulfate ions by barium chloride precipitation method. Figure 6 shows that the organic content of calcium sulfate (rec) was decreased with the increase in calcination temperature and time of calcination. The complete removal of organic content was achieved at a temperature of 700 °C and calcination time of 1 h. This was further confirmed through the thermogravimetric analysis. There was a sharp reduction in mass up to the temperature of 695 °C, and thereafter, no loss in mass was observed. Thus, the optimized conditions were calcination temperature = 700 °C and calcination period = 1 h. The calcium sulfate (rec) after calcination can be considered as a raw material in the cement industry or as a filling material in the construction industry.

3.6. Calcium Sulfate as an Adsorbent for the Removal of Aqueous Dye. In the present investigation, reactive precipitation resulted in fine crystalline modification of calcium sulfate (rec) (confirmed through SEM) with a reasonable increase in apparent activation energy than the calcium sulfate (std). Further, the BET analysis of calcium sulfate (rec) showed an increase in surface area of 2.9 m²/g against 0.25 m²/g for calcium sulfate (std) (Merck, India). Hence, the adsorption capacity of the calcium sulfate (rec) was tested for sorption of aqueous dyes such as acid black 210, acid blue 113, and acid black 53. Table 2 shows the adsorption capacity of calcium sulfate (rec) and calcium sulfate (std) for various dyes in batch experiment. The adsorption capacity of calcium sulfate (rec) was found to be higher than the calcium sulfate (std). This could be due to the enhanced surface area of the calcium sulfate (rec) over the calcium sulfate (std). The maximum adsorption capacity of calcium sulfate (rec) was 97 mg/g, 92 mg/g, and 40 mg/g respectively for acid black 210, acid blue 113, and acid black 53; the same for calcium sulfate (std) were 50 mg/g, 42 mg/g, and 5 mg/g. The result concludes that the calcium sulfate (rec) after calcination can be used as an adsorbent for the removal of dye from industrial wastewater. The solubility of calcium sulfate (rec) was found to be 1.8 g/L. Even though the solubility of calcium sulfate (rec) liberates 1800 mg/L of SO₄²⁻ ion in aqueous solution, the SO₄²⁻ ion concentration was in limit to discharge.

3.7. Effect of Organic Impurities on the Purity of Calcium Sulfate Precipitate. To understand the influence of organic content in the residual acidified ER solution on the purity of the calcium sulfate precipitate, an experiment was carried out by spiking tannic acid at different concentrations (0.1, 0.2, and 0.3% (w/v)). Vegetable tannin is one of the major chemicals used in the leather industry for the conversion of putrescible raw skins/hides into nonputrescible leather. Hence, tannic acid was considered as a model organic pollutant in the residual acidified ER solution to study its impact on the purity of precipitated calcium sulfate. The residual acidified ER solution spiked with tannic acid was neutralized with calcium.
The recovered calcium sulfate, and standard CaSO$_4$·2H$_2$O powder were examined by X-ray powder diffraction spectrophotometer. Figure 7 shows the 2θ values at 12, 22, 29, 32, and 34° that correspond to the crystalline peaks of CaSO$_4$·2H$_2$O (std) and the same peaks were also observed in the calcium sulfate recovered in the present investigation. The results confirmed that the recovered calcium sulfate was the dihydrated salt. Additionally, the precipitated calcium sulfate diffracted at 2θ value 24° may be due to the presence of organic compounds in the precipitate. The peak corresponding to 2θ value at 24° disappeared after calcination at 700 °C for 1 h under air atmosphere, indicating that calcination at 700 °C yielded a relatively pure CaSO$_4$·2H$_2$O.

3.8. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analyses. The surface images of recovered calcium sulfate and calcined calcium sulfate were captured for the identification of structural morphology. Figure 8 shows the recovered calcium sulfate was orthorhombic in structure, resembling structural morphology of CaSO$_4$·0.2H$_2$O. The calcium sulfate (rec) appeared to be a fine white powder that looked flouiry; this was due to spontaneous precipitation from highly supersaturated solution where the crystals formed instantaneously with no induction time for the growth of crystals. The same kind of observation was recorded by Sheikholeslami (2003). Generally, a decrease in supersaturation increases the crystal size, and a longer induction period favors the crystal growth to form coarser crystals while a shorter induction period favors nucleation to form fine crystals. Elongated calcium sulfate crystal growth was seen in the CaSO$_4$·2H$_2$O (std) but agglomerated calcium sulfate crystal growth was observed in the present investigation. The presence of intentionally added additives or impurities served as nucleation to promote instantaneous crystallization leading to formation of fine crystals. The same kind of phenomena was reported by the Gominsek et al. (2005) while using the contaminated sulfuric acid for the precipitation of calcium sulfate. This was explained that the presence of impurities reshaped the crystal structure and induced the agglomeration of crystals. Further, EDX spectra indicate the presence of Ca, S, and O elements alone in the calcined precipitate, thus confirmed that recovered calcium sulfate after calcinations was in pure form.

<table>
<thead>
<tr>
<th>system</th>
<th>pH</th>
<th>conc. of dye (mg/L)</th>
<th>calcium sulfate dose (mg)</th>
<th>adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>100</td>
<td>0.1 (std)</td>
<td>50</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>3</td>
<td>100</td>
<td>0.1 (std)</td>
<td>65</td>
</tr>
<tr>
<td>acid black 53</td>
<td>4</td>
<td>100</td>
<td>0.1 (std)</td>
<td>5</td>
</tr>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>100</td>
<td>0.1 (rec)</td>
<td>97</td>
</tr>
<tr>
<td>acid black 53</td>
<td>3</td>
<td>100</td>
<td>0.1 (rec)</td>
<td>92</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>4</td>
<td>100</td>
<td>0.1 (rec)</td>
<td>40</td>
</tr>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>100</td>
<td>0.1 (rec)</td>
<td>97</td>
</tr>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>200</td>
<td>0.1 (rec)</td>
<td>86</td>
</tr>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>300</td>
<td>0.1 (rec)</td>
<td>72</td>
</tr>
<tr>
<td>acid black 210</td>
<td>3</td>
<td>200</td>
<td>0.2 (rec)</td>
<td>92</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>4</td>
<td>100</td>
<td>0.1 (rec)</td>
<td>83</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>4</td>
<td>200</td>
<td>0.1 (rec)</td>
<td>75</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>4</td>
<td>300</td>
<td>0.1 (rec)</td>
<td>64</td>
</tr>
<tr>
<td>acid blue  113</td>
<td>4</td>
<td>200</td>
<td>0.2 (rec)</td>
<td>74</td>
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<tr>
<td>acid black 53</td>
<td>3</td>
<td>100</td>
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<td>acid black 53</td>
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<tr>
<td>acid black 53</td>
<td>3</td>
<td>300</td>
<td>0.1 (rec)</td>
<td>11</td>
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<tr>
<td>acid black 53</td>
<td>3</td>
<td>200</td>
<td>0.2 (rec)</td>
<td>34</td>
</tr>
</tbody>
</table>

*Conditions: volume of solution, 100 mL; std, calcium sulfate (std); rec, calcium sulfate (rec); temperature, 30 °C; agitation speed, 100 rpm.*
3.8.3. Thermogravimetric Analysis (TGA). The thermal stability of precipitated calcium sulfate from acidified solution and after calcination at 700 °C was evaluated through thermogravimetric analysis. Figure 9 shows the loss of mass in the temperature range from 380 to 420 °C and marginal loss of mass up to 695 °C in the precipitated calcium sulfate. The standard and calcined calcium sulfate showed a similar pattern on loss of mass with rise in temperature. The weight loss in the temperature range from 80 to 140 °C was due to the evaporation loss of 1.5 H2O molecules from 2H2O molecules. The weight loss in the temperature range from 100 to 600 °C corresponds to the loss of water by 6.25% in CaSO4.0.5H2O.15,16 This reveals that all the adsorbed/occluded organic compounds were decomposed with the rise in temperature up to 700 °C. This indicates that the calcination of calcium sulfate(rec) imparted thermal stability. The average activation energies for the decomposition of standard calcium sulfate and calcium sulfate(rec) were found to be 2.81 and 15.07 KJ/mol, respectively, using the Arrhenius model.17 The 5.36 fold increase in activation energy of calcium sulfate(rec) may be correlated with its high adsorptive capacity for adsorbates, which, in turn, is a function of surface area.

3.9. Material Balance. 3.9.1. Mass Balance on Salt Separation from ER Solution. The evaporative crystallization of sodium chloride was achieved by the evaporation of residual acidified solution after the reactive precipitation of ER solution using hydrogen chloride gas. The material balance on handling 1 L of saturated ER solution after the reactive precipitation is given as the following.

3.9.2. Mass Balance on Precipitation of Sodium Chloride from ER Solution.
Calcium hydroxide as given by consideration for separation of sulfate ions as calcium sulfate using the residual acidified ER solution calcium hydroxide → precipitated sodium chloride + residual solution of ER

\[ 1.32 \text{ kg} + 0.105 \text{ kg} \rightarrow 0.268 \text{ kg} + 1.157 \text{ kg} \]  

(2)

The Na\(^+\) ion mass balance is

\[ 0.126 \text{ kg} + 0 \text{ kg} \rightarrow 0.105 \text{ kg} + 0.021 \text{ kg} \]  

(2i)

The Cl\(^-\) ion mass balance is

\[ 0.216 \text{ kg} + 0.102 \text{ kg} \rightarrow 0.162 \text{ kg} + 0.156 \text{ kg} \]  

(2ii)

The maximum precipitation of sodium chloride of 0.268 kg resulted from 1 L of saturated ER solution under the optimized conditions.\(^6\)

### 3.9.3. Mass Balance on Evaporative Crystallization of Sodium Chloride.

residual solution of ER → residual acidified ER solution + crystallized sodium chloride + condensed water

\[ 1.157 \text{ kg} \rightarrow 0.905 \text{ kg} + 0.052 \text{ kg} + 0.2 \text{ kg} \]  

(3)

The Na\(^+\) ion mass balance is

\[ 0.021 \text{ kg} \rightarrow 0.001 \text{ kg} + 0.02 \text{ kg} + 0 \text{ kg} \]  

(3i)

The Cl\(^-\) ion mass balance is

\[ 0.156 \text{ kg} \rightarrow 0.124 \text{ kg} + 0.0315 \text{ kg} + 0 \text{ kg} \]  

(3ii)

### 3.9.4. Mass Balance on Precipitation of Sulfate Ions As Calcium Sulfate.

The residual acidified ER solution was considered for separation of sulfate ions as calcium sulfate using calcium hydroxide as given by

residual acidified ER solution + calcium hydroxide → aqueous solution + calcium sulfate

\[ 0.905 \text{ kg} + 0.152 \text{ kg} \rightarrow 0.83 \text{ kg} + 0.227 \text{ kg} \]  

(4)

The Ca\(^{2+}\) ion mass balance is

\[ 0.0014 \text{ kg} + 0.0084 \text{ kg} \rightarrow 0.0326 \text{ kg} + 0.0528 \text{ kg} \]  

(4i)

The SO\(_4^{2-}\) ion mass balance is

\[ 0.1272 \text{ kg} + 0 \text{ kg} \rightarrow 0.0002 \text{ kg} + 0.127 \text{ kg} \]  

(4ii)

### 3.10. Cost Estimation on ER Management.

The cost toward the consumption of chemicals and the electrical energy was calculated for the precipitation of sodium chloride and calcium sulfate from ER solution. The same was compared with the cost toward disposal onto a secure landfill (Table 3). The overall recoveries in the present investigation were 0.32 kg of NaCl and 0.227 kg of calcium sulfate from 1 kg of ER. The commercial rates for the recovered NaCl and calcium sulfate are 0.02 and 0.0192 USD/kg ER, respectively. The cost toward the consumables used in recovery of NaCl such as chemicals and electrical energy was 0.0728 USD/kg ER. Thus, the total cost for the treatment of ER by proposed process was 0.034 USD/kg ER by selling of recovered byproducts. If the ER salt is intended to be disposed onto secure landfill, the cost toward it (including transportation cost and handling cost at a secure landfill) is 0.11 USD/kg ER. Hence, the present process on the management of evaporated residue may be regarded as remunerative compared to dumping onto secured landfill. Emission of green house gases and generation of saline leachate normally encountered in dumping onto secured landfill are eliminated in this new process.

### 4. CONCLUSIONS

The integration of evaporative crystallization along with the reactive precipitation using HCl gas significantly enhanced the percentage recovery of NaCl from 84% to 99.5%. Further, the sulfate ion in the ER 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 sulfate ions from the acidified ER solution. The optimized process parameters for the recovery of SO\(_4^{2-}\) as calcium sulfate were pH = 4.0 and temperature = 40 °C. The precipitated calcium sulfate was purified by calcination at 700 °C under air atmosphere for 1 h. The surface area of the calcium sulfate\(_{\text{rec}}\) was about 5 times greater than the surface area of calcium sulfate\(_{\text{std}}\). Thus, the calcium sulfate\(_{\text{rec}}\) could be used as an adsorbent for the adsorption of aqueous dye. The calcium sulfate\(_{\text{rec}}\) was analyzed using XRD, SEM, EDX, and TGA, and it was confirmed that the precipitated calcium sulfate after calcination was pure enough to match the standard calcium sulfate. The net profit envisaged in the proposed process was 0.076 USD/kg ER by finding a market for the recovered byproducts.

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**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

BET = Brunauer–Emmett–Teller surface area analysis  
COD = chemical oxygen demand  
EDX = energy dispersive X-ray  
ER = evaporated residue  
K\(_s\) = solubility product, (mol/L)\(^2\)

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RO = reverse osmosis
SEM = scanning electron microscopy
TGA = thermogravimetric analysis
TOC = total organic carbon
XRD = X-ray diffraction

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9246
Electrochemical treatment of evaporated residue of soak liquor generated from leather industry

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HIGHLIGHTS
- Electrochemical treatment of evaporated residue of soak liquor (ERSL) generated in Tannery.
- Copper coating on electrode surface and horizontal mounting of electrodes for ERSL treatment.
- Electrochemical oxidation of organic pollutants under high saline condition.
- The treated solution may be evaporated to dryness to get NaCl salt for hide/skin preservation.

ABSTRACT
The organic and suspended solids present in soak liquor, generated from leather industry, demands treatment. The soak liquor is being segregated and evaporated in solar evaporation pans/multiple effect evaporator due to non availability of viable technology for its treatment. The residue left behind in the pans/evaporator does not carry any reuse value and also faces disposal threat due to the presence of high concentration of sodium chloride, organic and bacterial impurities. In the present investigation, the aqueous evaporated residue of soak liquor (ERSL) was treated by electrochemical oxidation. Graphite/graphite and SS304/graphite systems were used in electrochemical oxidation of organics in ERSL. Among these, graphite/graphite system was found to be effective over SS304/graphite system. Hence, the optimised conditions for the electrochemical oxidation of organics in ERSL using graphite/graphite system was evaluated by response surface methodology (RSM). The mass transport coefficient (k∞) was calculated based on pseudo-first order rate kinetics for both the electrode systems (graphite/graphite and SS304/graphite). The thermodynamic properties illustrated the electrochemical oxidation was exothermic and non-spontaneous in nature. The calculated specific energy consumption at the optimum current density of 50 mA cm$^{-2}$ was 0.41 kWh m$^{-3}$ for the removal of COD and 2.57 kWh m$^{-3}$ for the removal of TKN.

Abbreviations: ERL, evaporated residue of soak liquor; RSM, response surface methodology; CCD, central composite design; VDS, volatile dissolved solids; APHA, American public health association; SS, stainless steel; C, concentration of ERL (w/v); j and j∞, current density and limiting current density (mA cm$^{-2}$); t, electrochemical oxidation time (min); COD, chemical oxygen demand; TKN, total Kjeldahl nitrogen; ANOVA, analysis of variance; F, Faraday constant, 96,487 (C mol$^{-1}$); k_{COD}/k_{TKN}, average mass transfer coefficient (m s$^{-1}$); A, electrode area (m$^2$); V, average cell potential (V); I, current (A); S, sample volume (L); K, equilibrium constant; R, regression coefficient; ΔG, change in Gibbs free energy (J mol$^{-1}$); ΔH, change in enthalpy (J mol$^{-1}$); ΔS, change in entropy (J mol$^{-1}$ K$^{-1}$); T, temperature (K); W, specific energy consumption (kWh kg$^{-1}$ of COD/TKN); COD$_0$ and COD$_1$, are the chemical oxygen demand at initial and at time ‘t’ min; TKN$_0$ and TKN$_1$, are the total Kjeldahl nitrogen at initial and at time ‘t’ min; [COD]$_{opt}$, concentration of COD at optimum time (120 min).

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1. Introduction

Electrochemical treatment may be considered as an alternative process to conventional treatment technologies for the elimination of pollutants in liquid wastes [1]. Generally, electrochemical processes are performed at ambient conditions and without addition of chemicals than those of other non-electrochemical treatments. Electrochemical treatment processes require compact reactors and simple equipments to control and operate the process. The process is relatively non-specific and applicable to a variety of contaminants but capable of preventing the production of unwanted side-products [2]. Hence, in recent years there has been an increasing interest in the treatment of industrial effluents by electrochemical methods as an alternative to conventional biological treatment systems [3]. There are reports on electrochemical oxidation of wastewater containing phenol [4–6], cyanides [7], nuclear wastes [8], human wastes [9], cigarette industry wastewater [10], textile wastewater [11], and tannery wastewater [12]. However, no report claims the treatment of ERSL generated from leather industry, by electrochemical oxidation.

The salt laden soak liquor is being segregated, collected and evaporated in solar evaporation pans/thermal evaporator as no viable treatment technologies exist. The current practice is to dispose ERSL onto secure landfill site, but surface and ground water contamination is a serious environmental concern due to leaching of its constituents during runoff season. Hence, it has been advised by pollution control agencies to handle/treat ERSL residue with a suitable technology to modify the current disposal mechanism. Generally, destruction of organic pollutants in the electrochemical process was achieved by direct and indirect oxidations. In direct anodic oxidation, the organic pollutants are adsorbed onto the anodic surface, and destroyed by anodic electron transfer reactions, whereas in indirect oxidation the secondary oxidants such as chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide oxidise the organic pollutants in wastewater [13]. The generation of secondary oxidants such as chlorine and hypochlorite for the removal of organics and ammonia becomes more probable and thus the electrochemical oxidation was preferred over other technologies for the management of ERSL in leather sector. The resultant electrochemical oxidised solution can be considered for recovery of sodium chloride of high purity through selective precipitation technique [14].

The central composite design (CCD) is an effective design for sequential experimentation and allows a reasonable amount of information for testing interaction of selected parameters by response surface methodology (RSM) [15–17]. In the optimisation process, the responses can be simply related to the chosen factors by linear or quadratic models. A quadratic model, which also includes the linear and interaction terms, is shown in Eq. (1).

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \epsilon_i \]  

where \( Y \) is the response, \( x_i \) and \( x_j \) are the variables (i and j = 1 to k), \( \beta_0 \) is the constant coefficient, \( \beta_i \), \( \beta_{ij} \) and \( \beta_{ij} \) are interaction coefficients of linear, quadratic (second order) and interaction terms, respectively, k is the number of independent parameters and \( \epsilon_i \) is the error. The physical significance of the second order term is to determine the real function of the selected independent variable and the interaction terms are used to evaluate the interaction between the two selected independent variables. In this study, concentration of ERSL solution (\% w/v), current density (mA cm\(^{-2}\)) and electrochemical oxidation time (min) were selected as the operational (independent) variables for the removal of organic content; COD\(_d\)/COD\(_0\) and TKN\(_d\)/TKN\(_0\) were the response (dependent) variables from the electrochemical treatment process for graphite/graphite system.

2. Materials and methods

2.1. Characterisation of evaporated residue of soak liquor (ERSL)

The ERSL was collected from a commercial export oriented tannery processing raw skins/hides into finished leather in Ranipet, Tamil Nadu, India. The industry had the provision to evaporate the soak liquor to dryness with moderate moisture. The ERSL was transported to the laboratory and stored in the dry atmosphere until for further use. The ERSL was characterised for moisture content, Chemical Oxygen Demand (COD), Volatile Dissolved Solids (VDS), Oils & fats, NH\(_4^+\)–N and sodium chloride by following the methods of APHA, 1999 [18] (Table 1).

2.2. Experimental set-up and electro chemical oxidation of ERSL

A glass jacketed electrochemical cell (length, 15; width, 3.5 and height, 15 cm) with a working volume of 500 mL was fabricated using poly acrylate material and used for the electrochemical oxidation ERSL solution by batch experiments. Three numbers of graphite electrodes (length, 15 cm and diameter, 2.5 cm) were positioned parallel to each other with an equidistance of 1 cm between the successive electrodes in the electrochemical cell. The electrodes were mounted onto the reactor walls horizontally and extended outside the reactor for the electrical connection as shown in Fig. 1. In order to reduce the electrical contact resistance and to ensure better connectivity, the graphite electrodes across their length were coated with metallic copper for a distance of 2 cm in one end to act as terminal for electrical connection. Similarly, another electrochemical cell with the same dimensions was fabricated with SS304 as anode and graphite as cathode materials. The AC to DC rectifier (0–60 V and 0–5 A) was used to supply predetermined current density and voltage for the experiments. The required bulk solution temperature of the electrochemical cell was maintained through water circulation in external jacket provided to the reactor/electrochemical cell using cryostat (Labnet, India). The oxygen required for the oxidation of organics in ERSL solution was supplied in the form of air using compressor at pressure 2 kg cm\(^{-2}\). The air was distributed at the bottom of the electrochemical cell through fine bubble spargers.

The solution of ERSL was prepared by dissolving a known quantity of the dried ERSL in one litre of deionised water. The concentration of 60% (w/v) of ERSL means, 60 g of dried ERSL dissolved in 100 mL of distilled water. The suspended solids were filtered using glass fibre filter paper. Then, the ERSL solution (500 mL) was used in the electrochemical cell to optimise the process parameters. Aliquots of samples of volume 10 mL were withdrawn from the electrochemical cell at regular time intervals for the characterisation of pH, COD and TKN.

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture content (% w/v)</td>
<td>12.3 ± 1.5</td>
</tr>
<tr>
<td>2</td>
<td>Chemical oxygen demand (mg g(^{-1}))</td>
<td>5.57 ± 0.04</td>
</tr>
<tr>
<td>3</td>
<td>Volatile dissolved solids (mg g(^{-1}))</td>
<td>18.8 ± 2.5</td>
</tr>
<tr>
<td>4</td>
<td>Oil and fats (mg g(^{-1}))</td>
<td>0.06 ± 0.02</td>
</tr>
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<td>5</td>
<td>Ammonium-nitrogen (mg g(^{-1}))</td>
<td>0.25 ± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>Total Kjeldahl nitrogen (mg g(^{-1}))</td>
<td>0.68 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>Soluble salt (% w/v)</td>
<td>59.2 ± 2.0</td>
</tr>
<tr>
<td>8</td>
<td>Sodium chloride (mg g(^{-1}))</td>
<td>540 ± 12.8</td>
</tr>
</tbody>
</table>
The organic content of the oxidised ERSL was evaluated after purifying it through column (C18) chromatography. The adsorbed organics was eluted in n-hexane and in ethanol (most of the aliphatic and aromatic halides are soluble in ethanol). The eluted compounds were concentrated under vacuum (Roto evaporator, Medica Instruments Mg Co, India) and evaluated through Thin layer Chromatography and FT-IR spectroscopy.

The influence of various process parameters on the destruction of organics in ERSL solution was evaluated for the graphite/graphite electrode system by varying the concentration of ERSL, C (30, 45 and 60% [w/v]); current density, \( j \) (25, 50 and 75 mA cm\(^{-2}\)), and electrochemical oxidation time, \( t_{\text{eco}} \) (60, 120 and 180 min). Further, the solution temperature was varied from 10 to 50 °C to determine the thermodynamic parameters for electrochemical oxidation of ERSL solution using graphite/graphite electrode system.

### 2.3. Parameters of investigation

During the electro chemical oxidation of ERSL the aliquots of samples (10 mL) were withdrawn from the electrochemical reactor for characterisation at predetermined time intervals. The COD was determined by following the methodology (specific to high salt containing liquid waste) as described by Vyrides [19]. In accordance with the procedure, the digestion mixture was prepared by adding \( K_2Cr_2O_7 \), 3 g (which was previously dried at 103 °C for 2 h), to conc. \( H_2SO_4 \), 167 mL and \( HgSO_4 \), 33 g and made up to 500 mL with distilled water. The mixture was cooled to room temperature before it was diluted to 1000 mL. The sulphuric acid reagent (2.5%, w/v) was prepared by dissolving \( Ag_2SO_4 \) in \( H_2SO_4 \). The sampling of wastewater and digestion of the sample was carried out in accordance with methodology described under the analysis of water and wastewater [18]. Total free chlorine by DPD (N,N-diphenyl-p-phenylenediamine) using spectrophotometer at \( \lambda_{\text{max}} \) 515 nm and hydrogen peroxide concentration were estimated according to the standard methods [18]. The electrochemical analyser (Model CHI 660D, Sinsil India Ltd.) was used for the spectral run of linear sweep voltammetry (reference electrode, Ag/AgCl; counter electrode, Pt wire) to determine the working potential of the electrodes.

### 2.4. Experimental design and optimisation

The CCD with three factors at three levels was applied to optimise the process parameters using Design-Expert\textsuperscript{®} 8.0.7.1. In this study, concentration of organic load, current density, and electro chemical oxidation time were selected as independent variables for the electrochemical treatment of ERSL solution using graphite/graphite system. Each independent variable was coded at three levels between \(-1\) and \(+1\) with an alpha value of 1 by face centred design as shown in Table 2. The type of electrode system can also be considered as a dependent variable, however, graphite/graphite system was found to be effective over SS304/graphite system (from the results and discussion of Section 3.1). Hence, the optimised conditions were evaluated by response surface methodology (RSM) for graphite/graphite system alone.

The total number of experiments with three factors was obtained as 20 (=2\(^k\) +2\(k\)+6), where \( k \) is the number of selected factors (=3). Fourteen experiments were augmented with six replicates at the design centre points to evaluate the pure error and were carried out in randomised order as required in many design procedures. Performance of the process was evaluated with respect to removal of COD and TKN from the initial ERSL solution using graphite/graphite system.

The quality of the fit of polynomial model was expressed by the coefficient of variance determination, \( R^2 \) and \( R_{\text{adj}}^2 \). And the statistical significance was checked by the F-test in the programme during the statistical analysis. For optimisation, a module in Design-Expert software searched for a combination of factor levels that simultaneously satisfy the requirement placed on each of the responses and factors. The desired goals were selected based on maximum reduction in COD and TKN. In Design-Expert programme, goal settings were designated with plus (+) symbols and corresponding importance of goals were selected (+++++) for the highest in the programme for all the dependent & independent variables. These individual goals were combined into an overall desirability function by Design-Expert software for maximisation to find the best operating conditions for the treatment of ERSL solution by electrochemical oxidation using graphite/graphite electrode system [20].

### Table 2

Selection of range and levels for the independent variables.

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Notation</th>
<th>Design variables</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(-1) 0 (+1)</td>
</tr>
<tr>
<td>Concentration of ERSL ([% (w/v)]</td>
<td>C</td>
<td>A</td>
<td>30 45 60</td>
</tr>
<tr>
<td>Current density (mA cm(^{-2}))</td>
<td>( j )</td>
<td>B</td>
<td>25 50 75</td>
</tr>
<tr>
<td>Electro chemical oxidation</td>
<td>( t_{\text{eco}} )</td>
<td>C</td>
<td>60 120 180</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Selection of anode material for the destruction of organic compounds in ERSL solution

The efficiency of electrochemical oxidation of organic pollutants in wastewater is strongly dependent on the nature of anodic material [21,22]. Graphite/graphite and SS304/graphite systems were employed in the present investigation for the evaluation of dimensionally stable electrodes in electrochemical oxidation of ERSL solution. The experiment was conducted at a constant current density of 50 mA cm$^{-2}$.

The residual pH, COD and TKN of the ERSL solution at different $t_{	ext{eco}}$ are presented in Fig. 2 for graphite/graphite and SS304/graphite electrode systems at temperature, 25 °C; COD$_{0}$, 2870 mg L$^{-1}$ and TKN$_{0}$, 310 mg L$^{-1}$. The COD and TKN were removed by 93% & 87% and 76% & 70% respectively for graphite/graphite and SS304/graphite system for an electrochemical oxidation time of 4 h. In SS304/graphite system, the SS304 electrode was rapidly corroded and large amount of iron precipitate was observed, while there was no appreciable amount of material loss during the electrochemical oxidation of ERSL solution using graphite as anodic material. The percentage loss in mass of SS304 and graphite was found to be 1.98 and 0.008% (w/w) respectively for the electro-oxidation period of 4 h. This may be attributed to the evolution of excess oxygen at the SS electrode surface. The solution pH was decreased from 7.85 to 3.45; this may be due to the generation of H$^+$ ions during the oxygen evolution at the anodic surface. However, graphite/graphite electrode system retained their dimensional stability at this acidic pH and also at all the tested conditions. Hence, the graphite electrode was considered as an ideal electrode material over SS304 for the electrochemical oxidation of ERSL solution.

The efficiency of indirect oxidation depends on the rate of generation of oxidants, diffusion of oxidants into the bulk solution, solution temperature and solution pH [13]. The indirect oxidation of organic compounds in ERSL solution may be due to the generation of hydrogen peroxide under acidic conditions and hypochlorous acid from the chlorides of ERSL solution. The hydrogen peroxide was electrochemically produced by reducing oxygen at cathode surface in the presence of hydrogen ion [23]. The concentration of H$_2$O$_2$ in the analyte was found to be 134 mg L$^{-1}$ and 34 mg L$^{-1}$ respectively for the graphite/graphite and SS304/graphite systems. The higher concentration of hydrogen peroxide observed in graphite/graphite system may be attributed to the presence of high active surface area (owing to the porous structure) than with SS304/graphite system. Further, the generation of hypochlorous acid was responsible for the elimination of TKN content, probably by converting it into chloramine and then into nitrogen [24]. Thus, there was a substantial reduction in COD and TKN of ERSL solution during electrochemical oxidation using graphite/graphite electrode system.

![Graph showing pH, COD, and TKN variation over time](image-url)

Fig. 2. The profile of variation in (a) pH, (b) COD and (c) TKN with time during electrochemical oxidation of ERSL solution with graphite/graphite and SS304/graphite system (conditions: current density (j), 50 mA cm$^{-2}$; COD$_{0}$, 2480 mg L$^{-1}$; TKN$_{0}$, 310 mg L$^{-1}$; temperature, 25 °C).
Table 3
Analysis of variance for electrochemical oxidation of ERSL solution using graphite/graphite electrode system.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Means square</th>
<th>F-value</th>
<th>P &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>0.36</td>
<td>9</td>
<td>0.04</td>
<td>4.87</td>
<td>&lt;0.0001 (significant)</td>
</tr>
<tr>
<td>Residual</td>
<td>0.081</td>
<td>10</td>
<td>8.12 × 10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.08</td>
<td>5</td>
<td>0.016</td>
<td>63.53</td>
<td>0.002 (significant)</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.00126</td>
<td>5</td>
<td>0.00025</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TKN removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>0.26</td>
<td>9</td>
<td>0.029</td>
<td>12.39</td>
<td>&lt;0.0003 (significant)</td>
</tr>
<tr>
<td>Residual</td>
<td>0.024</td>
<td>10</td>
<td>2.39 × 10⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.024</td>
<td>5</td>
<td>4.73 × 10⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.0001</td>
<td>5</td>
<td>0.0001</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2. Evaluation of experimental results with Design-Expert

The requirement of model transformation was based on the response maximum to minimum ratio. Design-Expert® advised that the transformation is required only when the maximum to minimum ratio of response is greater than 10. The response of COD and TKN removal were found to be ranged from 165 to 1175; and from 45 to 142 respectively yielding the maximum to minimum ratio of 7.12 and 3.15 respectively. These values suggest that no transformation is required for the present investigation. The evaluated ANOVA results for the responses of COD/0/0 and TKN/0/0 are presented in Table 3. The F-value of the selected model was 15.12 and 16.75 for the COD and TKN removal, which implied that the model is highly significant for COD and TKN removal by electrochemical oxidation of organic content in ERSL solution. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable. In this investigation the ratio for COD/0/0 and TKN/0/0 was 15.42 and 16.92 respectively, which indicates that the adequate signals for the selected model could be used to navigate the design space. The values of Prob > F less than 0.05 showed that the selected model terms are significant, whereas values greater than 0.10 pointed out that the model terms are not significant. For the COD/0/0 and TKN/0/0 Prob > F was less than 0.0002 indicating that terms are significant in the model. The coefficient of variance for COD/0/0 and TKN/0/0 was found to be 23.51% and 11.99% respectively. The transformation probability for the selected model was (R² = 0.93 and 0.87) and adjusted R-square (R²adj) = 0.94 and 0.88 for COD/0/0 and TKN/0/0 removal indicated a good fit for the selected independent variables.

3.3. Optimisation of operational parameters

The experimental results were evaluated by Design Expert software using approximating functions of dependent variables for the response to COD and TKN removal. The approximating response function of COD/0/0 and TKN/0/0 is given in Eqs. (2) and (3). In this study, most effective operating variables were preferred in the range of concentration of ERSL(C), 30–60% (w/v); current density (j), 25–75 mA cm⁻² and electrochemical oxidation time (t_{eco}), 0–180 min to effectively handle the ERSL solution.

\[
\frac{\text{COD}}{\text{COD}_0} \times (Y_1) = 0.996 - 0.023(C) + 0.01055(j) - 7.98 \times 10^{-3}(t_{eco})
\]

\[
-2.89 \times 10^{-6}(C)(j) - 2.62 \times 10^{-5}(C)(t_{eco})
\]

\[
+ 8.02 \times 10^{-6}(j)(t_{eco}) + 4.22 \times 10^{-4}(C)^2
\]

\[
+ 2.39 \times 10^{-5}(j)^2 + 3.38 \times 10^{-5}(t_{eco})^2
\]

(2)

\[
\frac{\text{TKN}}{\text{TKN}_0} \times (Y_2) = 0.987 - 2.46 \times 10^{-3}(C) - 1.65 \times 10^{-3}(j) - 0.011(t_{eco})
\]

\[
- 4.39 \times 10^{-5}(C)(j) + 3.59 \times 10^{-5}(C)(t_{eco})
\]

\[
- 2.59 \times 10^{-5}(j)(t_{eco}) + 1.55 \times 10^{-5}(C)^2
\]

\[
+ 5.76 \times 10^{-5}(j)^2 + 3.77 \times 10^{-5}(t_{eco})^2
\]

(3)

Fig. 3a and b depicts the interaction of concentration of ERSL (C) and electrochemical oxidation time (t_{eco}) on organic removal at a constant current density of 50 mA cm⁻². The increase in t_{eco} increased the elimination of COD and TKN from ERSL solution, and they attained the peak values, 93% and 87% respectively at t_{eco} of 120 min and ERSL concentration of 45% (w/v). The response showed that the initial rate of electrochemical oxidation (decrease in COD/min) was high and reached the equilibrium condition within 120 min. The presence of inorganic salt, NaCl, increased the electrical conductance significantly at constant current density; thereby the required residence time was also decreased for the electrochemical oxidation [25]. The increase in t_{eco} stimulated the generation of secondary oxidants such as chlorine gas and hypochlorite which are responsible for indirect oxidation. Moreover, the increase in t_{eco} enhanced the diffusion of oxidants from the electrode surface to bulk solution to oxidise the organic pollutants [8,26].

Fig. 3c and d shows the response surface plot on the effect of current density (j) and t_{eco} on COD/0/0 and TKN/0/0 removal indicated a good fit for the selected independent variables.

Fig. 3e and f shows the interaction effect of concentration of ERSL (C) and current density (j) for an electrochemical oxidation period (t_{eco}) of 120 min. Fig. 3e and f illustrates the increase in concentration of ERSL solution up to 45% (w/v) increased the removal efficiency of COD and TKN (93% and 87% respectively) and thereafter the removal efficiency was decreased with increase in concentration of ERSL solution. The increase in concentration of ERSL solution decreased the initial organic content [expressed...
in terms of high initial COD and TKN value]. Hence, the concentration of ERSL solution was maintained at 45% (w/v) in the rest of the study. Addition of NaCl has been under practice to remove colour through the generation of hypochlorous acid and to increase the current flow efficiency in electrochemical oxidation of industrial dye effluents [28,29]. The ERSL solution itself contained high amount of NaCl (243 g L$^{-1}$ in aqueous ERSL, 45% (w/v)) and thus high electrical conductance and easy flow of current were observed as benefits. Hence, no external addition of NaCl was envisaged in the present investigation. The increase in solution conductivity resulted in the reduction of cell voltage and thus substantial decrease in specific electrical energy consumption was recorded [30].

3.4. Formation of hydroxyl radical and free chlorine gas

The electro generation of free chlorine gas during the electrolysis was estimated for the evaluation of efficiency and their removal of excess product. The chlorine gas generated at the anodic surface is converted into hypochlorous acid (HOCl) and hypochlorite ion as indicated in Eqs. (5) and (6). The sum of dissolved chlorine gas, hypochlorous acid and hypochlorite is termed as free chlorine. Hypochlorite ion is the major component of the free chlorine in the normal pH range of water (≥7.5).

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad (4)$$

$$\text{Cl}_2 \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (5)$$

$$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^- \quad (6)$$

Fig. 4a shows the maximum evolution of free chlorine concentration was found to be 7, 12.5 and 14 mg L$^{-1}$ at current densities 25, 50 and 75 mA cm$^{-2}$ respectively for the electrolysis time 120 min. As expected, the increase in current density and electrolysis time increased the concentration of free chlorine in the bulk solution. The observed working potential for the selected current density (25–75 mA cm$^{-2}$) was found to be varied from 2.5 to 4.2 V. This was found to be lower than the reported values for other non-active electrodes [31]. Generally, smaller the working potential for the same current density, lesser the generation of free chlorine gas.
The free chlorine gas generated was responsible for the indirect oxidation of organic compounds present in the ERSL solution by the mechanism as in Eqs. (5) and (6) [32].

There are many reports on the probability of formation of chloro and bromo organic compounds with free chlorine gas [33,34]. However, the formation of chloro and bromo organic compounds was not observed in the present study. This was confirmed from the selective elution of the electro oxidised ERSL solution (dialysed) after adsorption onto C18 column using n-hexane and ethanol. The solvent extracted compounds (before and after electro oxidation) showed the same \( r_f \) values in Thin Layer Chromatography. The solvent eluted compounds were analysed with FT-IR spectroscopy. The spectral analysis revealed that (Fig. 4b), there was no peak corresponding to C-Cl and C-Br stretchings at around 750–850 cm\(^{-1}\) and 650–485 cm\(^{-1}\) in electro oxidised ERSL solution [35,36]. However, the formation of trace quantities of chloro and bromo organic compounds cannot be ruled out. This can be effectively removed by adsorption using activated carbon.

3.5. Specific energy consumption (\( W \))

The specific energy consumption for the electro oxidation of ERSL solution on COD and TKN removal was evaluated using Eqs. (7) and (8).

\[
W (\text{kWh m}^{-3}) = \frac{(tV)/S_v/(1 \times 10^4)}{\Delta \text{COD}/(1 \times 10^6)}
\]  

\[
W (\text{kWh m}^{-3}) = \frac{(tV)/S_v/(1 \times 10^3)}{\Delta \text{TKN}/(1 \times 10^6)}
\]

where ‘\( t \)’ is the time of electrolysis in hours, \( V \) is the average cell potential, \( I \) is current (\( \Lambda \)), \( S_v \) is the sample volume in litres and; \( \Delta \text{COD} \) and \( \Delta \text{TKN} \) are the difference in COD and TKN in time “\( t \)” in mg L\(^{-1}\).

Fig. 5 shows the cumulative specific energy consumption for the removal of COD and TKN for all the current density (\( j \)). The increase in applied current density increased the specific energy consumption for the removal of both COD and TKN in ERSL solution. The calculated specific energy consumption for the removal of COD at 25, 50 and 75 mA cm\(^{-2}\) was 0.17, 0.41 and 0.71 kWh m\(^{-3}\) respectively. The specific energy consumption for the removal of TKN was 1.03, 2.57 and 4.31 kWh m\(^{-3}\) at current densities 25, 50 and 75 mA cm\(^{-2}\) respectively.

3.6. Kinetic model study

Kinetic study on the removal of COD and TKN from ERSL solution was analysed based on the limiting current density during the electrolysis for the graphite/graphite and SS304/graphite system. The limiting current density could be related to [COD]o by the mathematical expression

\[ j_l = nFk_m(COD)_0 \]  

(9)

where \( j_l \) is the limiting current density (mAM\(^{-2}\)) at the instant \( t \), \( n \) is the number of electrons transferred, \( F \) is the Faraday constant (96,487 C mol\(^{-1}\)), \( k_m(COD) \), the average mass transport coefficient (m s\(^{-1}\)) based on COD removal. Then, the COD removal rate (\( r \)) can be expressed as [30],

\[ r = \frac{j_l}{nF} = k_m(COD)[COD] \]  

(10)

From the mass balance of the whole system operating under batch mode, we get,

\[
\frac{d[COD]}{dt} = -\frac{A}{V}r
\]  

(11)

![Fig. 4. (a) Formation of free chlorine on electro oxidation of ERSL solution using graphite/graphite electrode system and (b) FT-IR spectral analysis for electro chemical oxidised ERSL solution (inner graph for the scale of 900–400 cm\(^{-1}\)).](image-url)

![Fig. 5. Variation of specific energy consumption for the electrochemical oxidation of ERSL solution using graphite/graphite electrode system.](image-url)
where \( A \) is the electrode area (m\(^2\)) and \( v \) is the total volume of the solution (m\(^3\)) being processed. Integration and simplification yield,

\[
\ln \left( \frac{[\text{COD}]_t}{[\text{COD}]_0} \right) = -\frac{A k_m [\text{COD}]}{v} t \tag{12}
\]

Similarly for the removal of TKN in ERSL solution is,

\[
\ln \left( \frac{[\text{TKN}]_t}{[\text{TKN}]_0} \right) = -\frac{A k_m [\text{TKN}]}{v} t \tag{13}
\]

The values of \( k_m \) at different current densities were calculated from the plot (Fig. 6) and presented in Table 4 for graphite/graphite and SS304/graphite systems. The linear plot of Eqs. (12) and (13) showed that the removal of COD and TKN followed pseudo first order model. Hence, the mass transport may be regarded as the rate controlling step for the electrolysis of ERSL. The calculated mass transfer coefficient \( (k_m) \) for COD was found to vary in the range from \( 0.15 \times 10^{-5} \) to \( 0.37 \times 10^{-5} \) m s\(^{-1}\) for graphite/graphite system and \( 0.12 \times 10^{-5} \) to \( 0.26 \times 10^{-5} \) m s\(^{-1}\) for the SS304/graphite systems. In the case of TKN removal, the \( k_m \) was varied from \( 0.22 \times 10^{-5} \) to \( 0.28 \times 10^{-5} \) m s\(^{-1}\) for graphite/graphite system and for \( 0.12 \times 10^{-5} \) to \( 0.18 \times 10^{-5} \) m s\(^{-1}\) for SS304/graphite system (Table 4). The results illustrate that mass transfer coefficient for graphite/graphite system was higher than SS304/graphite system because COD and TKN removal rate was higher for graphite/graphite system than for SS304/graphite. This is further expected that the increase in working potential of the electrode increased the driving force of electro-oxidation. In this study, working potential of the copper coated graphite/graphite system (1.817 V) was higher than the SS304/graphite system (0.107 V). Further, the removal of ammonia is favoured when indirect oxidation is dominant by rule of competition, whereas the removal of COD takes place under the dominance of direct and indirect oxidations [37]. Ammonia oxidation takes place due to an indirect oxidation with electro-generated hypochlorous acid, according to a mechanism analogous to the breakpoint chlorination reactions [38–40].

**Table 4**

<table>
<thead>
<tr>
<th>( J ) (mA cm(^{-2}))</th>
<th>( k_m ) ( (\times 10^{-5} ) m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphite/graphite</strong></td>
<td><strong>Based on COD removal</strong></td>
</tr>
<tr>
<td>25</td>
<td>0.156</td>
</tr>
<tr>
<td>50</td>
<td>0.251</td>
</tr>
<tr>
<td>75</td>
<td>0.376</td>
</tr>
</tbody>
</table>
Table 5

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Equilibrium constant ($K_e$)</th>
<th>$\Delta G$ (J mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.841</td>
<td>407.43</td>
<td>-5.32</td>
<td>-1.89</td>
</tr>
<tr>
<td>293</td>
<td>0.877</td>
<td>319.72</td>
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<td></td>
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<tr>
<td>303</td>
<td>0.904</td>
<td>254.24</td>
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<tr>
<td>313</td>
<td>0.916</td>
<td>228.32</td>
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<td></td>
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<tr>
<td>323</td>
<td>0.932</td>
<td>189.11</td>
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<td></td>
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</table>

4. Conclusion

Evaporated residue of soak liquor (ERSL) was characterised and treated through electrochemical oxidation using graphite/graphite and SS304/graphite electrode systems. Amongst the two electrode systems, the graphite/graphite system has established a significant removal in COD and TKN than SS304/graphite system. The optimised process parameters by RSM for the treatment of ERSL solution using graphite/graphite system were found to be: concentration of ERSL, 45% (w/v); current density, 50 mA cm$^{-2}$ and electrochemical oxidation time, 120 min. The calculated mass transport coefficient was higher for the graphite/graphite electrode system than SS304/graphite system. The thermodynamic parameters revealed that, the secondary oxidants were the priority agents for the oxidation of organic pollutants in the ERSL solution. The electro oxidation of organics in ERSL solution was exothermic and non-spontaneous in nature. The calculated specific energy consumption at the optimum current density of 50 mA cm$^{-2}$ was 0.41 kWh m$^{-3}$ for the removal of COD and 2.57 kWh m$^{-3}$ for the removal of TKN.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.05.027.

References

A First Report on the Selective Precipitation of Sodium Chloride from the Evaporated Residue of Reverse Osmosis Reject Salt Generated from the Leather Industry

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ABSTRACT: The reverse osmosis process has been actively implemented in the leather sector for the recovery of water from secondary biologically treated wastewater. The membrane reject stream is evaporated in solar evaporation pan/multiple effect evaporator. The evaporated residue (ER) of the reject stream from reverse osmosis lacks reusable characteristics, owing to a high contamination of inorganic and organic salts. In this investigation, an attempt was made to separate sodium chloride from the saturated solution of ER by the common ion effect in the presence of other inorganic and organic contaminants, using hydrogen chloride gas. The optimized process parameters for the selective precipitation of sodium chloride were as follows: time, 3 min; pH, 8.0; temperature, 40 °C; and concentration of ER, 60% (w/v). The ER and the recovered salts were characterized, using SEM-EDX and XRD. This is probably the first report on the precipitation of sodium chloride from the ER. The cost toward the disposal of this ER was also analyzed.

1. INTRODUCTION

The leather industry uses a wide spectrum of chemicals that are classified under natural and synthetic organic chemicals, alkali salts, alkaline earth salts, and heavy metal salts for the conversion of putrescible collagen fiber aggregate into non-putrescible leather matrix. One ton of raw hide produces 250 kg of finished leather besides the generation of wastewater (48 m³), sodium chloride (200 kg), and organic salts (2–4 kg).¹ Traditional leather processing in the leather industry employs chemicals which are higher by 40–75% over the stoichiometric requirement.² The unspent chemicals contribute toward the pollution load, and most of them have poor biodegradable index. The untreated tannery wastewater was characterized by a biological oxygen demand (BOD₅) of 2099 ± 1185 mg/L, chemical oxygen demand (COD) of 4767 ± 2422 mg/L, and total dissolved solids (TDS) of 7677 ± 4084 mg/L³ (Table 1). The conventional treatment options are primary clarification, secondary biological anaerobic/aerobic treatment, and tertiary treatment processes for the removal of the pollution load.⁴–⁹

The treated wastewater was characterized by a BOD₅ of 104 ± 91 mg/L, COD of 430 ± 292 mg/L, and TDS of 5584 ± 1804 mg/L. The data presented in Table 1 shows that the tannery wastewater after the biological treatment contains a high amount of inorganic TDS, besides the dissolved organics found as BOD₅ and COD.³ Hence, the reverse osmosis process has been made mandatory for the recovery of water from secondary biological treated tannery wastewater, leaving refractory organic and inorganic salts in the reject stream. Membrane separation has become increasingly attractive for the treatment and recycling of wastewater.¹⁰,¹¹ However, the recovery of water by this process is limited only up to 70%, and the remainder 30% of feed stream is discharged as reject stream. The membrane reject stream was characterized by a BOD₅ of 408 ± 325 mg/L, COD of 1533 ± 857 mg/L, and TDS of 20003 ± 6140 mg/L³ and is presented in Table 1. The reject stream is evaporated in solar evaporation pans to reduce its volume (for small volume of discharge and making use of solar energy to reduce the cost of evaporation) or in a multiple effect evaporator (MEE) (for large volume of discharge) leaving behind a solid residue known as evaporated residue (ER). However, the ER lacks a reusable option as it contains high concentrations of organic compounds (COD, 38 mg/g)¹² and other inorganic impurities along with sodium chloride as shown in Table 2.

The disposal of ER onto secured landfill sites is banned because the constituent ions are leached into aqueous solution, and the treatability of leachate becomes more difficult for its high salinity.¹³–¹⁵ Hence, the salt laden evaporated residue is being heaped up in the leather industry. Thus, there has been a constant research for the management of ER. Although the volume is reduced by various disposal techniques, the concentrations of both inorganic and organic salts in ER are higher. The ER bearing such a high concentration of inorganic and organic salts confronts the disposal problems, since many regulations are based on the concentration and volume of discharge. The recovery of salt and other minerals from ER is the most obvious solution to the disposal problem. Reports are available on the recovery of salts from various sources such as from salt lakes,¹⁶–¹⁸ seawater,¹⁹–²² textile effluent,²³ sugar decolourization plant,²⁴ industrial effluents,²⁵–²⁷ and multi-stage flash distillation.²₈,²⁹ However, no single report is available on the recovery of sodium chloride from the evaporated residue of the RO reject stream containing high concentrations of inorganic and organic salts from leather industry. This reject stream contains a high concentration of refractory organics, besides inorganic compounds. Thus, the separation of sodium chloride gas. The optimized process parameters for the selective precipitation of sodium chloride were as follows: time, 3 min; pH, 8.0; temperature, 40 °C; and concentration of ER, 60% (w/v). The ER and the recovered salts were characterized, using SEM-EDX and XRD. This is probably the first report on the precipitation of sodium chloride from the ER. The cost toward the disposal of this ER was also analyzed.

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Published: March 19, 2012
chloride from the reject stream consisting of a high concentration of organic salts is of special significance, as the leather industry in India is advised to dump the evaporated residue onto a secure landfill.

Hence, the focal theme of the present investigation was on the development of a process for the precipitation of high-quality sodium chloride from ER. This work forms the first report on the recovery of sodium chloride from the evaporated residue of a RO reject stream from the leather industry.

2. EXPERIMENTS

2.1. Source of Evaporated Residue. The ER was collected from a solar evaporation pan in an ETP of a commercial tannery in Ranipet, Tamil Nadu, India, and transported to the laboratory for this study.

2.2. Preparation of Saturated Solution of ER. The saturated solution of ER was prepared by dissolving 600 g in 1 L of distilled water under agitation. The undissolved sand, grit, and floating solids were separated by decantation and screening. The screened solution was passed through a sand filter to remove the suspended solids. The filtered, saturated ER solution was characterized for pH, grit, moisture content, volatile dissolved solids at 600 °C, COD, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ by following the methods of APHA.30

2.3. Chemicals. The concentrated hydrochloric acid and sodium hydroxide used in this investigation were purchased from Merck Chemicals, India.

2.4. Principle on Precipitation of Sodium Chloride from ER. The sodium chloride is highly soluble in water, and it reaches saturation at 35% (w/v) and supersaturation at 36% (w/v).31 The mathematical expression for the equilibrium constant for the NaCl in water is given by

$$K_s = \frac{[Na^+][Cl^-]}{[NaCl]_{(s)}}$$

where, $K_s$ is the solubility product of sodium chloride, 36.0 (mol/L)². The magnitude of solubility product ($K_s$) measures the highest concentration of dissolved ionic species in aqueous solution. Thus, in a saturated solution, the solubility product is equal to the product of all the ions, that is, $K_s = [Na^+][Cl^-]$. This dynamic equilibrium can be disturbed by changing either

<table>
<thead>
<tr>
<th>parameter</th>
<th>value, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical oxygen demand</td>
<td>38</td>
</tr>
<tr>
<td>chloride</td>
<td>360</td>
</tr>
<tr>
<td>sulfate</td>
<td>205</td>
</tr>
<tr>
<td>sodium</td>
<td>270</td>
</tr>
<tr>
<td>calcium</td>
<td>75</td>
</tr>
<tr>
<td>magnesium</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of Untreated, Treated, RO Permeate, and RO Reject Stream in Leather Industry (K. Ranganathan et. al., 2011)

<table>
<thead>
<tr>
<th>parameters</th>
<th>untreated wastewater</th>
<th>after biological treated/RO feed</th>
<th>RO permeate</th>
<th>RO reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH&quot;</td>
<td>4.12–4.68 (4.53)</td>
<td>7.03–8.21 (7.65)</td>
<td>6.87–7.25 (7.22)</td>
<td>6.85–7.55 (7.5)</td>
</tr>
<tr>
<td>total dissolved solids</td>
<td>7.67 ± 4.08</td>
<td>5.58 ± 1.80</td>
<td>0.25 ± 0.13</td>
<td>20.0 ± 6.14</td>
</tr>
<tr>
<td>biological oxygen demand</td>
<td>2.09 ± 1185</td>
<td>0.10 ± 0.091</td>
<td>0.40 ± 0.32</td>
<td>1.53 ± 0.85</td>
</tr>
<tr>
<td>chemical oxygen demand</td>
<td>4.76 ± 2.42</td>
<td>0.43 ± 0.29</td>
<td>0.005 ± 0.007</td>
<td>3.96 ± 1.67</td>
</tr>
<tr>
<td>sodium</td>
<td>1.60 ± 1.44</td>
<td>1.65 ± 0.53</td>
<td>0.05 ± 0.02</td>
<td>4.99 ± 2.20</td>
</tr>
<tr>
<td>chloride</td>
<td>1.30 ± 0.42</td>
<td>1.30 ± 0.40</td>
<td>0.07 ± 0.02</td>
<td>5.55 ± 1.95</td>
</tr>
<tr>
<td>sulfate</td>
<td>2.67 ± 1.58</td>
<td>2.31 ± 1.25</td>
<td>0.01 ± 0.02</td>
<td>20.0 ± 6.14</td>
</tr>
</tbody>
</table>

"All the values are expressed in g/L, except pH.

Table 2. Characteristics of Evaporated Residue (ER)

<table>
<thead>
<tr>
<th>parameter</th>
<th>value, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical oxygen demand</td>
<td>38</td>
</tr>
<tr>
<td>chloride</td>
<td>360</td>
</tr>
<tr>
<td>sulfate</td>
<td>205</td>
</tr>
<tr>
<td>sodium</td>
<td>270</td>
</tr>
<tr>
<td>calcium</td>
<td>75</td>
</tr>
<tr>
<td>magnesium</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Figure 1. Schematic flow diagram for the selective precipitation of sodium chloride from ER.
[Na+] or [Cl−]. According to Le chatelier’s principle the sodium chloride is precipitated out from the aqueous solution when the ionic product of [Na+] and [Cl−] is greater than $K_{sp}$ of NaCl.

A known volume of saturated solution of ER (100 mL) was taken in a reactor for the selective precipitation of NaCl. The hydrogen chloride gas was injected at 2.06 g/min into the solution through a distributor provided at the bottom of the reactor. The temperature of the reactor was thermostatically controlled using external water circulation system. The reactor was equipped with an agitator for uniform mixing. The reactor was washed with pure brine solution to get a high purity salt. The inorganic ions such as Na+, Ca2+, Mg2+, Cl−, and COD (contributed by refractory organic compounds), the values of which were estimated by adopting the method reported in APHA.30

3.2. Precipitation of Sodium Chloride from the Saturated Solution of ER. The ions movement during the preparation and precipitation are expressed in the form of equation as given below:

$$\text{ER} + \text{H}_2\text{O} \rightarrow \text{Na}^+\text{Cl}^-, \text{Ca}^{2+}, \text{SO}_4^{2-}, \text{Mg}^{2+}, \text{org salt}, \text{H}_2\text{O}$$  \hspace{1cm} (1)

3.2. Instrumental Analysis. 2.5.1. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analyses. The ER and recovered NaCl were coated with 120–130 μm gold in argon medium. Scanning electron microscopy (SEM) observations were performed on a scanning device attached to a JEOI JM-5600 electron microscope at 20 kV accelerating voltage with a 5–6 nm electron beam. Energy dispersive X-ray (EDX) analysis was carried out for the identification of heavy metals present in the ER and recovered sodium chloride.

2.5.2. X-ray Diffraction (XRD) Analysis. The XRD spectra of the ER and recovered NaCl were recorded with high resolution GUINER powder X-ray diffractometer (SEIFERT, Germany).

3. RESULTS AND DISCUSSION

3.1. Characterization of a Saturated Solution of ER. The characteristics of a saturated ER solution are shown in Table 3. The results illustrate that the ER consists of a high amount of inorganic ions such as Na+, Ca2+, Mg2+, Cl−, SO42−, and COD (contributed by refractory organic compounds), the values of which were estimated by adopting the method reported in APHA.30

Table 3. Characteristics of Saturated Solution of ER

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.67</td>
</tr>
<tr>
<td>chemical oxygen demand</td>
<td>5.76</td>
</tr>
<tr>
<td>chloride</td>
<td>215.94</td>
</tr>
<tr>
<td>sulfate</td>
<td>35.17</td>
</tr>
<tr>
<td>sodium</td>
<td>125.92</td>
</tr>
<tr>
<td>calcium</td>
<td>1.44</td>
</tr>
<tr>
<td>magnesium</td>
<td>0.51</td>
</tr>
</tbody>
</table>

“All the values are expressed in g/L, except pH.

The in situ precipitation of sodium chloride (solubility product of NaCl, $(K_{sp})$ is 36 (mol/L)2) and thus the precipitation of sodium chloride was achieved from the saturated solution of ER as illustrated in eq 2.

3.2.1. Effect of Contact Time on Sodium Chloride Precipitation. The influence of contact time on the precipitation of sodium chloride from the ER solution was carried out by varying the time of the hydrogen chloride gas injection from 0.5 to 3 min at a pH and temperature of 8.0 and 40 °C, respectively. The precipitation of NaCl could be achieved by the optimum contact time for the maximum salt precipitation at the selected flow rate of HCl gas. Figure 2a shows that the mass of precipitated NaCl was increased with increase in HCl gas injection time up to 3 min and leveled off with 81% salt recovery. The plateau region resulted may be due to the condition that the rate of precipitation of NaCl becomes equal to the rate of dissolution of sodium chloride. The dissolution may be due to the decrease in ionic strength of the solution as the time progressed. Hence, the optimum time required for the precipitation of NaCl from the ER solution was fixed at 3 min. The mass of precipitated NaCl at this optimum time was 26.7 g with 81% of recovery with respect to the dissolved salt concentration (solubility of NaCl is 35 g in 100 mL of water).

3.2.1.1. Nonlinear Kinetic Model Study. To investigate the order of reaction and the rate-controlling step for the precipitation of NaCl, the following kinetic rate equations were used to validate the experimental data. The kinetic data obtained under batch studies were evaluated using first-order, second-order reaction kinetics, pseudo-first- and pseudo-second-order equations.32,33 The pseudo-first-order and pseudo-second-order rate equations are expressed, respectively, as

$$R_{t} = R_{e}(1 - e^{-kt})$$  \hspace{1cm} (3)

$$R_{t} = \frac{k_{r}R_{e}^{2}t}{1 + k_{r}R_{e}t}$$  \hspace{1cm} (4)

Where $R_{e}$ (g) and $R_{t}$ (g) are the quantities of salt precipitated at equilibrium and at time $t$, respectively, and $k_{1}$ (min$^{-1}$) and $k_{2}$ (g min$^{-1}$)$^{-1}$ are the rate constants of pseudo-first-order and second-order reactions. The values of $R_{e}$, $k_{1}$, and $k_{2}$ were determined by nonlinear regression models using solver in MS-excel as shown in Table 4. The validity of the kinetic model was verified based on two criteria, regression coefficient ($R^{2}$) and chi-square error ($\chi^{2}$) analysis. The correlation coefficients of first order (0.97), second order (0.92), pseudo-first-order (0.99) and pseudo-second-order (0.95) rate kinetics indicated that the exper-
imental data were more accurately obeyed by the pseudo-first-order kinetic model (Figure 3). Furthermore, the minimum $\chi^2$ value was observed in the pseudo-first-order (0.21) kinetic model than the other kinetic models (first order, 3.4; second order, 0.72; and pseudo-second-order, 0.47). This indicates that the precipitation of NaCl followed the pseudo-first-order rate kinetics. This implies that the precipitation of NaCl was controlled by the concentration of NaCl rather than HCl gas even when HCl gas was supplied at surplus quantity (mass of HCl gas was selected such that excess HCl gas was allowed to dissolve in the solution).

### 3.2.2. Effect of pH on Sodium Chloride Precipitation

The effect of initial pH (Figure 2b) on the precipitation of NaCl from the ER solution was studied by varying the pH from 1.0 to 9.0 for a fixed contact time of 3 min and temperature of 40 °C at constant flow rate of HCl gas (2.06 g/min). The magnitude of NaCl precipitation was observed to be less in the acidic pH ranged from 1 to 6 and the mass of precipitation increased with rise in pH and it continued up to pH 8.0. The maximum amount of NaCl precipitation (26.9 g) was observed at pH 8.0 (native pH of the ER solution). There was no growth of crystal in the range of pH between 7 and 8.Mohameed and Ulrich explained the effect of pH on the salting out of crystalline substances in solution based on hydration theory. Most cations and anions are hydrated in aqueous solution. The $H^+$ ion being

### Table 4. Nonlinear Kinetic Model for the Precipitation of Sodium Chloride

<table>
<thead>
<tr>
<th>parameters</th>
<th>first-order reaction</th>
<th>second-order reaction</th>
<th>pseudo-first-order reaction</th>
<th>pseudo-second-order reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate constant, $k$</td>
<td>$0.517 \text{ min}^{-1}$</td>
<td>$0.04 \text{ g min}^{-1}$</td>
<td>$1.01 \text{ min}^{-1}$</td>
<td>$0.074 \text{ g min}^{-1}$</td>
</tr>
<tr>
<td>regression coefficient ($R^2$)</td>
<td>0.97</td>
<td>0.96</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>chi-square ($\chi^2$)</td>
<td>3.40</td>
<td>0.722</td>
<td>0.21</td>
<td>0.47</td>
</tr>
</tbody>
</table>

*Conditions: time, 3 min; pH, 8.0; temperature, 40°C; concentration of ER 60% (w/v).*

![Figure 2. Precipitation of sodium chloride: (a) effect of time (conditions: pH, 8.0; temperature, 40 °C; mass of ER, 60% (w/v)); (b) effect of initial pH (conditions: time, 3 min; temperature, 40 °C; concentration of ER, 60% (w/v)); (c) effect of temperature (conditions: time, 3 min; pH, 8.0; concentration of ER, 60% (w/v)); (d) effect of concentration of ER (conditions: time, 3 min; pH, 8.0; temperature, 40 °C).](image)

![Figure 3. Kinetic models for precipitation of sodium chloride (conditions: time, 3 min; pH, 8.0; temperature, 40 °C; concentration of ER, 60% (w/v)).](image)
the smaller in size is characterized by the highest enthalpy of hydration and thus has a stronger tendency of interaction with
water molecules in the presence of other cations so that a competition among ions to acquire water molecules takes place. The Na+ ions have low probability to acquire the critical hydration number and therefore they tend to drift toward the
crystalline solid surface rather than to remain in the solution. On the another hand, in alkaline solution the OH− ions have
low tendency to hydrate themselves, so that Na+ ions have more probability to acquire the critical hydration number leading to drive into the solution. At high OH− concentration, the tendency of hydration of the OH− ions prevails and the Na+ ions are pushed into the solution again.30 It is known that NaCl in
water establishes ionic equilibrium with sodium ion, hydroxide ion, chloride ion, and hydronium ion (formed from water). Hence, the presence of a high concentration of hydrogen ion at low pH favors the rate of dissolution of NaCl. Moreover, at this acidic pH range the consumption of hydrogen chloride gas was also increased and the solution was undersaturated. Hence, the precipitation of NaCl was retarded with respect to the dissolved ion concentration. The residual supernatant solution after precipitation was highly acidic (pH = −0.72) in nature. The hydrogen ion concentration of the residual solution was determined by volumetric analysis and the pH was calculated using the Debye–Hückel ionic equation. The drop in pH was due to the replacement of Na+ ions by H+ ion in the solution, which is due to the supply of HCl gas. The authors of this technical paper have developed a patented process for the management of the acidic stream resulting after the precipitation of NaCl (Indian Patent No: DEL1898, 2010).

3.2.3. Effect of Temperature on the Precipitation of Sodium Chloride. The temperature of the saturated salt solution of ER was varied from 10 to 80 °C for the precipitation of NaCl. The pH of the initial solution was maintained at the optimum pH (8.0), and the time of precipitation was 3 min. Figure 2c shows that the mass of precipitated NaCl increased with an increase in temperature up to 40 °C. The mass of precipitation increased with an increase in the initial temperature range of 10–40 °C. The maximum amount of NaCl precipitation (27 g with 82% recovery) was achieved at 40 °C. Beyond this temperature and up to 80 °C, NaCl precipitation decreased with an increase in temperature drastically. Hence, the increase in temperature beyond the optimum temperature of 40 °C favored the reverse reaction, that is, dissolution of the precipitated NaCl back into the bulk solution.

3.2.4. Effect of Concentration of ER on Precipitation of Sodium Chloride. The concentration of the ER [40–65% (w/v)] was varied to determine the effect on precipitation of NaCl. The initial solution pH, temperature, and time were fixed as 8.0, 40 °C, and 3 min, respectively. The results are presented in Figure 2d, which shows that the percentage of salt recovery increased with the increase in concentration of ER. In general, precipitation depends on the concentration of dissolved ions in solution. As the initial concentration of ER was increased, the dissolved ions concentration was also increased in the solution and reached the saturation limit at a concentration of 60% (w/v). The maximum amount of NaCl precipitation (27 g with 82% recovery) was achieved with a saturated ER solution (60% (w/v)). Hence, the optimum concentration of ER for the precipitation of NaCl was fixed at 60% (w/v) (60 g of ER in 100 mL of distilled water).

3.2.5. Analysis of Thermodynamic Parameters. The thermodynamic parameters such as Gibbs–free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS) were calculated for the precipitation of NaCl from a saturated solution of ER using the classical Van’t Hoff equation, and the values are presented in Table 5. The ΔH and ΔS values were obtained from the slope and intercept of the plot between ln Kc versus 1/T.

Table 5. Thermodynamic Parameters of Sodium Chloride Precipitation from a Saturated Solution of ER

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>pseudo-first-order rate constant, k (min−1)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (kJ/K.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>1.12</td>
<td>+1097.23</td>
<td>+74.27</td>
<td>+0.336</td>
</tr>
<tr>
<td>293</td>
<td>1.16</td>
<td>+943.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>1.18</td>
<td>+524.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.19</td>
<td>+522.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>1.11</td>
<td>+1064.44</td>
<td>−173.9</td>
<td>−2.57</td>
</tr>
<tr>
<td>333</td>
<td>1.06</td>
<td>+1386.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>0.96</td>
<td>+1681.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>0.93</td>
<td>+2217.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The thermodynamic parameters presented in table 5 are consistent with the results obtained from Figure 2c. The ΔG value decreased from +1097 kJ/mol, and it attained the minimum value (+522.11 kJ/mol) at 313 K and again increased to +2217.66 kJ/mol at 353 K. This indicates that the process of precipitation of NaCl was nonspontaneous and the non-spontaneity was decreased at 313 K. The positive value of enthalpy suggests that the NaCl precipitation process was endothermic in nature in the lower temperature range (283–313 K) and was exothermic in the higher temperature range (323–353 K).

3.3. Removal of Impurities from Precipitated Sodium Chloride Salt. The precipitated sodium chloride was washed with pure brine solution to increase the purity of salt. The washed recovered salt was dried in hot air oven at 110 °C for reuse purpose. The recovered salt was sodium chloride. This was further evidenced through the EDX spectroscopy and determination of melting point of the recovered salt. The melting point of the recovered sodium chloride coincided with the melting point of the analar grade sodium chloride (SD fine chemicals Ltd., India).

3.4. Material Balance. The material balance on the preparation of saturated ER solution of volume 1 L and precipitation of sodium chloride was calculated as follows.

<table>
<thead>
<tr>
<th>mass of ER + deionized water → sat. ER solution + grit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 kg + 1 kg → 1.32 kg + 0.28 kg</td>
</tr>
</tbody>
</table>

3.4.1. Mass Balance on Preparation of Saturated ER Solution. The mass of saturated solution of ER was 1.32 kg, obtained by dissolving 0.6 kg of ER in 1 L of deionized water. The undissolved grit (0.28 kg) mainly consists of sand, lime, and clay being nonhazardous in nature, that can be disposed of onto a secure landfill.

sat. ER sol. + HCl gas → precipitated NaCl + residual sol. |
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.32 kg + 0.105 kg → 0.268 kg + 1.157 kg</td>
</tr>
</tbody>
</table>

3.4.2. Mass Balance on Precipitation of Sodium Chloride. The maximum precipitation of sodium chloride of 0.268 kg was resulted from 1 L of saturated ER solution under the optimized conditions.
3.5. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analyses of ER and Recovered NaCl.

The surface morphology of the ER and recovered NaCl was captured and analyzed. Figure 4a suggests that the ER was aggregated in nature, due to the presence of inorganic and organic salts. Figure 4b shows the cubic morphology of the recovered salt crystal and this corroborates with the observation recorded by F. Armellini et al., (1993).37

Figure 5c shows the EDX spectrum of the ER. The spectrum has evidence for the presence of Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Pb elements along with Na and Cl. Figure 5d shows the EDX spectrum of recovered sodium chloride, indicating that Na and Cl were alone present in the recovered salt; hence the precipitated constituent was confirmed to be NaCl. The spectral results proved that the recovered sodium chloride was of high purity. This was further confirmed with XRD analysis.

3.6. XRD Analysis of ER and Recovered NaCl.

XRD spectra of ER and precipitated NaCl salt are shown in Figure 5. Figure 5a shows that the peak at 2θ of 26° indicates the presence of calcium and sulfate ions and 28° may be attributed to the presence of silica in the ER. These ions may be sourced from leather processing chemicals or from process water.

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Figure 4. Scanning electron microscopy images of (a) ER, (b) recovered sodium chloride, (c) energy dispersive X-ray spectra of ER, (d) recovered sodium chloride.

Figure 5. X-ray diffraction (XRD) spectra of ER (a) and recovered sodium chloride salt (b).
other 2θ values of 27°, 29°, 31°, and 45° peaks may correspond to many diffracting planes of the sodium chloride crystal in ER. Figure 5b shows the crystalline peaks corresponding to the 2θ value at 27°, 31°, 45°, 56°, 66°, and 75°, indicating the sodium chloride salt alone. The XRD spectra obtained for recovered sodium chloride and analar grade NaCl remained the same, which confirms the recovered sodium chloride was of high purity.38

3.7. Cost Estimation on ER Management. The cost toward the consumption of chemicals and the electrical energy was calculated for the precipitation of sodium chloride from the ER and compared with the cost toward disposal onto a secure landfill (Table 6). The proposed process recovered 0.203 kg of NaCl from 1 kg of ER. The cost of the recovered NaCl was 0.088 US $ per kg and cost toward the consumables used in recovery of NaCl such as chemicals and electrical energy was 0.058 US $ per kg of ER. Thus, net expenditure on processing one kilogram of ER was 0.04 US $. The cost toward disposal onto a secure landfill (inclusive of transportation cost and handling cost at the secure landfill) is 0.11 US $ per kg of ER. Hence, the proposed process on the management of evaporated residue indicates that there is a scope for the cost saving compared to dumping onto a secured landfill. Moreover, the dumping onto a secure landfill can be considered as a short-term measure. Elimination of green house gas emission and generation of saline leachate normally encountered in dumping onto a secured landfill are eliminated in this new process, and they may be considered as indirect benefits.

4. CONCLUSION

The separation of sodium chloride from the evaporated residue of a RO reject stream was achieved by selective precipitation under batch mode. The optimum conditions were found to be the following: time, 3 min; pH, 8.0; temperature, 40 °C, and the initial concentration of the ER, 60% (w/v). The surface morphology and elemental analysis of ER and the recovered NaCl salt were processed through SEM and EDX analyzer. The EDX analysis and X-ray diffraction confirmed the purity of the recovered NaCl salt. The proposed process for the management of ER was relatively lower in cost than the other disposal methods, and also the process has the scope to recover the sodium chloride.

APPENDIX 1

Nonlinear Kinetic Model Study

The pseudo-first-order rate constant for the precipitation of NaCl was determined at different temperatures (Table 5), and the rate constant was used to calculate the activation energy of reaction. The activation energies for the precipitation of sodium chloride in the temperature range of 10–40 °C and 50–80 °C were found to be 21.37 and 85.5 kJ/mol, respectively (the standard activation energy of NaCl crystal growth is 60 kJ/mol). The activation energy observed in the present investigation was much lower at the lower temperature range. The higher activation energy at the higher temperature range suggests that precipitation of NaCl from ER solution required higher energy than the reported value of sodium chloride crystallization at the standard conditions. This indicates that the formation of NaCl crystal from the constituent ions in this present condition was more favored at the lower temperature range.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

RO = reverse osmosis
MEE = multiple effect evaporator
ER = evaporated residue
APHA = American Public Health Association
NaCl = sodium chloride
HCl = hydrogen chloride
TDS = total dissolved solids
BOD₅ = biological oxygen demand
COD = chemical oxygen demand

Notes


(31) Handbook of Chemistry and Physics, 27th ed.; Chemical-Rubber Publishing Co.: Cleveland, Ohio, 1943.


Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: kinetic, isotherm, and thermodynamic studies

Ramasamy Boopathy · Sekar Karthikeyan · Asit Baran Mandal · Ganesan Sekaran

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Abstract Ammonium ions are one of the most encountered nitrogen species in polluted water bodies. High level of ammonium ion in aqueous solution imparts unpleasant taste and odor problems, which can interfere with the life of aquatics and human population when discharged. Many chemical methods are developed and being used for removal of ammonium ion from aqueous solution. Among various techniques, adsorption was found to be the most feasible and environmentally friendly with the use of natural-activated adsorbents. Hence, in this study, coconut shell-activated carbon (CSAC) was prepared and used for the removal of ammonium ion by adsorption techniques. Ammonium chloride (analytical grade) was purchased from Merck Chemicals for adsorption studies. The CSAC was used to adsorb ammonium ions under stirring at 100 rpm, using orbital shaker in batch experiments. The concentration of ammonium ion was estimated by ammonia distillate, using a Buchi distillation unit. The influence of process parameters such as pH, temperature, and contact time was studied for adsorption of ammonium ion, and kinetic, isotherm models were validated to understand the mechanism of adsorption of ammonium ion by CSAC. Thermodynamic properties such as ΔG, ΔH, and ΔS were determined for the ammonium adsorption, using van't Hoff equation. Further, the adsorption of ammonium ion was confirmed through instrumental analyses such as SEM, XRD, and FTIR. The optimum conditions for the effective adsorption of ammonium ion onto CSAC were found to be pH 9.0, temperature 283 K, and contact time 120 min. The experimental data was best followed by pseudosecond order equation, and the adsorption isotherm model obeyed the Freundlich isotherm. This explains the ammonium ion adsorption onto CSAC which was a multilayer adsorption with intraparticle diffusion. Negative enthalpy confirmed that this adsorption process was exothermic. The instrumental analyses confirmed the adsorption of ammonium ion onto CSAC.

Keywords Coconut shell activated carbon (CSAC) · Adsorption · Ammonium ion removal · Kinetic and isotherms of adsorption · Thermodynamic analysis

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CSAC</td>
<td>Coconut shell-activated carbon</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>APHA</td>
<td>American Public Health Association</td>
</tr>
<tr>
<td>qe, qt</td>
<td>Amount of ammonium ion adsorbed (mg/g) at equilibrium and at time t</td>
</tr>
<tr>
<td>C0, Ct</td>
<td>Initial ammonium concentration and ammonium concentration at time t (mg/L)</td>
</tr>
<tr>
<td>V</td>
<td>Volume of solution (L)</td>
</tr>
<tr>
<td>m</td>
<td>Mass of adsorbent (g)</td>
</tr>
<tr>
<td>k1, k2</td>
<td>Pseudofirst order and pseudosecond order rate constants (1/min and g/mg min)</td>
</tr>
<tr>
<td>kp</td>
<td>Intraparticle diffusion model constant (mg/g min0.5)</td>
</tr>
<tr>
<td>t</td>
<td>Time (min)</td>
</tr>
<tr>
<td>KL</td>
<td>Langmuir adsorption constant (L/mg)</td>
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<tr>
<td>RF</td>
<td>Freundlich constant</td>
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<tr>
<td>KC</td>
<td>Equilibrium constant</td>
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<tr>
<td>CA, CS</td>
<td>Amount of ammonium ion adsorbed onto the adsorbent from the solution and at equilibrium</td>
</tr>
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</table>

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Background, aim, and scope

Extent of surface and ground water contaminations have risen due to large quantities of industrial and domestic waste discharges to the environment. Rise in urban population increases nitrogen concentration in domestic waste water which is significant among other pollutants. High concentration of organics and ammonia nitrogen were observed in many industrial waste waters such as tannery, textile, landfill leachate, fertilizer, etc. Ammonium ions, in particular, are toxic to some fish even at concentrations as low as 3 ppm (Benefield and Judkins 1982). Ammonium ion is a potential source of nitrate and nitrite in drinking water for household uses and is implicated in human diseases like methemoglobinemia. Effluents from urea, ammonia, and fertilizer plants; mine and mill effluents; and even some municipal waste waters often contain high concentrations of ammonia (Melcer and Nuff 1988; Neytizzell-Dewilde 1977; Booker et al. 1996). Currently, regulatory agencies in many jurisdictions postulated the removal of ammonia from waste water before they are discharged to water systems.

Biological processes for nitrogen removal are very important for waste water treatment because discharge of nitrogen containing pollutants into surface water results in oxygen depletion, which is responsible for algal bloom. Effectiveness of bacteria in biological denitrification and nitrification processes are based on favorable environmental conditions. However, the biological processes are not effective with waste water at high ammonium ion concentration.

In order to enhance the nitrogen removal from the ammonium ion-rich waste water, several studies on retreatment such as air stripping, wet air oxidation, membrane process and chemical precipitation of magnesium ammonium phosphate have been conducted. These processes, however, required complicated configuration and had difficulties in maintenance due to the scale formation during precipitation and stripping processes (Benefield and Judkins 1982; Melcer and Nuff 1988; Neytizzell-Dewilde 1977; Hung et al. 2003; Bodalo et al. 2005). There are many technologies available for the removal of ammonium ion, but most of them have one or more significant drawbacks. For example, technologies like air stripping simply results in the transfer of phase (liquid to gas) of the pollutant rather than in its chemical destruction.

The drive to develop environmentally friendly chemical processes has motivated a significant increase in research activities that encompass understanding and design of adsorption process (Ali and Gupta 2007; Gupta et al. 2006, 2007a, b).

Adsorption process has been demonstrated to be competitive with other methods of pollutant removal both in terms of performance to cost (Melcer and Nuff 1988; Gupta and Ali 2008; Gupta et al. 2003, 2004, 2008a, 2009a, b, 2011a, b) and selection of biosorbent (Gupta et al. 2007a, b, c, 2010a, b; Gupta and Rastogi 2009; Gupta and Rastogi 2008a, b, c) and other residues as adsorbents (Gupta et al. 1997, 1998, 2000).

Various adsorbents such as zeolite (Bernal and Lopez-Real 1993; Booker et al. 1996; Englert and Rubio 2005; Wang et al. 2006; Bergero et al. 1994), activated alumina (Saha and Deng 2010), limestone (Hussain 2006), rice husk, and composite of BaCl2/vermiculite (Veselovskaya et al. 2012) are being used for the adsorption of ammonium ion from various industrial effluents. Among these adsorbents, activated carbons have a tendency to adsorb a wide variety of pollutants from aqueous medium.

In this study, coconut shell was activated and used to adsorb ammonium ions from the synthetically prepared solution for understanding the adsorption mechanism. The finding can be extended to treat ammonium ion-contaminated waste water in domestic and industrial applications.

Material and methods

Preparation of support and characterization

Activated carbons were prepared in two steps. The first step was precarbonization and the second step was chemical activation. In the precarbonization process, the coconut shell was heated to 400°C at the rate of 10°C/min for about 4 h under N2 atmosphere and then cooled down to room temperature at the same rate. This is labeled as precarbonized carbon. The precarbonized carbon was then subjected to chemical activation. In the chemical activation process, 50 g of the precarbonized material was agitated with 250 g of aqueous solution containing 85 % H3PO4 by weight. The ratio of chemical-activating agent/precarbonized carbon was fixed at 4:2. The chemical activant and precarbonized carbon were homogeneously mixed at 85°C for 4 h in a mixer. After mixing, the precarbonized carbon slurry was dried under vacuum at 110°C for 24 h. The resulting samples were then activated in a vertical cylindrical furnace at 800°C under N2 atmosphere at a flow rate of 100 mL/min. After cooling, the activated carbon was washed successively several times with hot water until the pH became neutral and finally with cold water to remove the excess phosphorous compounds. The washed samples were dried at 110°C to get the final product. The sample heated at 800°C was labeled as coconut shell-activated carbon (CSAC). The chemical characteristics of the CSAC were carbon, 50.34 %; hydrogen, 0.91 %; nitrogen, 0.13 %; bulk density, 0.76 g/cc; and surface area, 198 m2/g. Samples were sieved to sizes of 300 and 600 μm for the adsorption of ammonium ion from aqueous solution.
Synthetic aqueous ammonium ion solution preparation

Analytical grade ammonium chloride salt (NH₄Cl) was purchased from Merck Chemicals Pvt. Ltd., India, and distilled water was used for the preparation of a stock NH₄⁺ solution of 2,000 mg/L. Ammonium solution of different concentrations were prepared by diluting the NH₄Cl stock solution with distilled water.

The ammonium ion concentrations were determined using the colorimetric method based on nitrogen distillation (APHA 1998) using boric acid. Nitrogen distillation was carried out using a Buchi distillation unit (Model: K-350).

Adsorption experiments

The adsorption experiments were conducted by taking 2 g of CSAC with 50 mL of synthetic ammonium ion solution at the desired concentration and pH. The flasks were capped and agitated in an orbital shaker (REMI, India) at 100 rpm for 120 min to ensure equilibrium between ammonium ion and CSAC. Samples were drawn at frequent intervals for the analysis of residual ammonium ion and the determination of kinetics for ammonium ion adsorption till equilibrium value was reached.

At a given time (t), the amount of ammonium ion adsorbed onto CSAC, \( q_t \) (milligram per gram) was obtained as follows,

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \( C_0 \) and \( C_t \) (milligram per liter) are the initial aqueous ammonium ion concentration and aqueous ammonium concentration at time \( t \), respectively; \( V \) is the volume of the aqueous solution (liter); and \( m \) is the mass of adsorbent used (gram).

Effect of pH and temperature on ammonium adsorption onto CSAC

The effect of pH on the removal of ammonium ions was studied by conducting equilibrium sorption tests at different solution pH (5.0, 6.0, 7.0, 8.0, 9.0, and 10.0). The pH of solution was adjusted by using NaOH and HCl solutions to get the desired pH. To determine the effect of temperature, isothermal experiments were carried out at five different temperatures (283, 293, 303, 313, and 323 K) for 120 min. In addition, to study the effect of particle size, two different mesh-sized particles (600 and 300 μm) were chosen for ammonium ion adsorption.

Equilibrium isotherms

An adsorption isotherm study was performed for four different initial concentrations of ammonium ion (500, 1,000, 1,500, and 2,000 mg/L) solution by dilution from the stock solution. Fifty milliliters of ammonium ion solution was taken, solution pH adjusted to pH 9.0 in four different Erlenmeyer conical flasks and then 2 g of CSAC was added in each flask and kept in the thermal orbital shaker at 100 rpm and 10°C as surrounding temperature. The residual ammonium ion concentration was analyzed after reaching the equilibrium as given in adsorption experiments.

Instrumental analysis

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses

The morphology of the CSAC and the CSAC after ammonium ion adsorption was done by SEM. The observations were performed on a scanning device attached to a JEOL JM 5600 electron microscope at 20 kV accelerating voltage with a 5–6-nm electron beam. EDX analysis was carried out for the determination of elements which were present in the CSAC and CSAC after adsorption.

Fourier transform infrared spectroscopy (FTIR)

The functional groups of CSAC and the CSAC after ammonium ion adsorption were identified through Perkin Elmer Fourier transform infrared spectroscopy. The samples with KBr (spectroscopic grade) pellets were prepared in the size range of about 10–13 mm in diameter and 1 mm in thickness. The samples were scanned in the spectral range of 4,000–400 cm⁻¹.

X-ray diffraction (XRD) analysis

The XRD pattern of the CSAC and CSAC after ammonium ion adsorption was recorded with high-resolution Guiner Powder X-ray diffractometer (Seifert, Germany).

Results and discussion

The percentage adsorption of ammonium ion was found to vary from 58 % to 93 %, based on the initial ammonium ion concentration using CSAC as adsorbent.

Effect of pH

The removal of different compounds from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The effect of pH on adsorption of ammonium ion by CSAC adsorbent for particle sizes of 300 and 600 μm were investigated and results are given in Fig. 1a.
Ammonium nitrogen may be present in ionized ($\text{NH}_4^+$) and nonionized ($\text{NH}_3$) forms, depending on pH and temperature of the aqueous medium, according to the following equation:

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-.$$

It was observed that for pH values below 7, ammonium ion exists mainly as $\text{NH}_4^+$, irrespective of temperature. For pH values higher than 7, the $\text{NH}_4^+$ concentration diminishes significantly with increasing temperature, equilibrium being displaced towards the formation of ammonia gas ($\text{NH}_3$). This study revealed that increased adsorption was observed when increasing pH from 5.0 to 9.0, accomplished the maximum adsorption capacity at pH 9.0 (2.48 mg/g and 2.28 mg/g for 300 µm and 600 µm, respectively) and then decreased towards the pH at 10.0. The minimum equilibrium adsorption capacity was observed at pH 5.0 (0.98 mg/g and 0.83 mg/g for 300 µm and 600 µm, respectively). A similar trend was observed for the adsorption of ammonium ion by zeolites synthesized from fly ash (Wu et al. 2006) and by composite of g-alumina/KAS gel (Okada et al. 2007). This may be explained that the lower ammonium adsorption is due to competition of $\text{H}^+$ and $\text{NH}_4^+$ ions for the exchange of sites on the adsorbent surfaces. This translated that the adsorption of ammonium ion onto CSAC decreased with decrease in solution pH. This ionic competitiveness may disappear when the aqueous solution pH increases (Yian et al. 2012). At alkaline pH, the active sites of the adsorbent becomes negatively charged, which enhanced the binding of the ammonium ion onto CSAC.

In addition, it was seen that the decrease in particle size increased the adsorption rate. This may be explained by the increase in active adsorption sites with decrease in particle size. Hence, higher ammonium adsorption was observed for 300 µm CSAC.

**Effect of temperature**

The adsorption capacity of ammonium ion onto CSAC varied with temperature from 283 K to 323 K as shown in Fig. 1b. The adsorption of ammonium ion decreased with increase of temperature from 283 K to 323 K. The adsorption capacity was observed to be maximum (2.48 mg/g) at temperature of 283 K for the initial ammonium concentration of 500 mg/L at pH 9.0. This suggested that ammonium ion exchange capacity was more favorable at lower temperatures (Sabah et al. 2002). Adsorption rate is slow in the process of chemical adsorption, and the increase in temperature may favor improvement of the adsorption rate. However, too high temperature is unfavorable to exothermic reaction once it reaches the equilibrium. Therefore, there is a tendency for the ammonium ion to desorb from the solid.

![Graph](image-url)
adsorbent to the bulk solution phase with an increase in the temperature (Karadag et al. 2006). In addition, an increase in temperature increases the rate of solute movement in the bulk solution and decreases the retarding forces acting on the adsorbate ions.

Effect of contact time and adsorption rate kinetics mechanism

The study of adsorption kinetics describes the solute uptake and the time required for the adsorbate uptake at the solid–solution interface including the diffusion process. The experiment was run to measure the effect of contact time in the batch adsorption with the initial conditions, ammonium ion concentration 500 mg/L, temperature 303 K and solution pH 9.0 as shown in Fig. 1c. It is obvious that the increase in contact time from 10 to 150 min enhanced the removal of ammonium ions significantly. A rapid initial adsorption followed by slow approach at the end of the adsorption process was observed. The concentration of ammonium ion in aqueous solution decreased to 180 mg/L and remained constant even after increase in contact time up to 150 min. Hence, the optimum contact time for the adsorption of ammonium ion onto CSAC was fixed as 120 min. This can be explained by the nature of adsorbent and its available active site which are responsible for the time needed to reach the equilibrium.

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as the mass transfer process. In order to investigate the mechanism of adsorption, the pseudofirst-order, pseudosecond-order kinetic models, and the intraparticle diffusion model (Ji et al. 2007; Gurses et al. 2004; Ozcan et al. 2006) were used to test dynamical experimental data obtained for particle sizes of 300 and 600 μm.

\[
q_t = q_e \left(1 - e^{-k_1 t}\right)
\]

(2)

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]

(3)

\[
q_t = k_p t^{1/2}
\]

(4)

where \(q_e\) (mg/g) and \(q_t\) (mg/g) are the amounts of ammonium ion adsorbed at equilibrium and at time \(t\), respectively; \(k_1\) (per minute), \(k_2\) (gram per milligram per minute) and \(k_p\) (milligram per gram per minute) are the rate constants of pseudofirst-order reaction, pseudosecond-order reaction, and intraparticle diffusion rate, respectively. The correlation coefficients and other parameters were calculated from the models given in Table 1. From these mechanisms, it was observed that for both sizes of particles, the first-order kinetic model did not adequately fit the experimental values (\(R^2 < 0.97\)). In contrast, the pseudosecond order rate equation for adsorption of ammonium ion onto CSAC agreed well with the experimental data for particle sizes of 300 and 600 μm (Fig. 2). As seen from Table 1, the

<table>
<thead>
<tr>
<th>Size</th>
<th>CSAC—300 μm</th>
<th>Rate constant</th>
<th>(R^2)</th>
<th>CSAC—600 μm</th>
<th>Rate constant</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_e,exp) (mg/g)</td>
<td>(q_e,pre) (mg/g)</td>
<td></td>
<td></td>
<td>(q_e,exp) (mg/g)</td>
<td>(q_e,pre) (mg/g)</td>
</tr>
<tr>
<td>Pseudofirst order</td>
<td>2.3</td>
<td>2.19</td>
<td>0.099 l/min</td>
<td>0.97</td>
<td>2.06</td>
<td>1.95</td>
</tr>
<tr>
<td>Pseudosecond order</td>
<td>2.3</td>
<td>2.31</td>
<td>0.186 g/mg min</td>
<td>0.99</td>
<td>2.06</td>
<td>2.05</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>2.3</td>
<td>2.32</td>
<td>0.03 mg/g min(^{0.5})</td>
<td>0.97</td>
<td>2.06</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Table 1 Nonlinear kinetic data for the adsorption of ammonium onto CSAC for particle sizes 300 μm and 600 μm.

Fig. 2 Nonlinear kinetic model for adsorption of ammonium by CSAC for particle sizes a 300 μm and b 600 μm (Conditions: pH 9.0, temperature 283 K, concentration of ammonium ion 500 mg/L).
calculated equilibrium adsorption capacity, $q_{\text{ecal}}$, for the second-order model were 2.31 mg/g and 2.02 mg/g; for the $q_{\text{exp}}$ value, 2.32 mg/g and 1.96 mg/g for the particle sizes 300 and 600 $\mu$m, respectively, with a high $R^2$ value (0.999). These results suggest that the adsorption of ammonium ion by CSAC follows the pseudosecond-order model. Therefore, it can be said that more than one step may be involved in the adsorption process.

Further, Huang et al. (2010) pointed out that the sole rate-limiting step of adsorption process was verified through plotting intraparticle diffusion model. The intraparticle diffusion plot for ammonium adsorption is given in Fig. 2. As seen from Fig. 2, the adsorption mechanism can be described by two steps. In the first step, a sharp increase in adsorption was attributed to the diffusion of adsorbate from the bulk solution to the external surface of the adsorbent or the boundary layer diffusion of ammonium ions. The second step describes internal diffusion of ammonium ions from a macroporous site to a microporous site. This was evidenced through the residual ammonium ion concentration in the bulk solution and the SEM image of CSAC after ammonium ion adsorption. The correlation coefficients for the intraparticle diffusion model ($R^2$) for the CSAC particle sizes of 300 and 600 $\mu$m were 0.99 and 0.98, respectively. These values indicate that the adsorption of ammonium ion onto CSAC may be followed by intraparticle diffusion at the beginning of the adsorption process.

Adsorption isotherms

Adsorption properties and equilibrium data describe how pollutants interact with adsorbents and so they are critical to optimize the use of adsorbents. The adsorption equilibrium data are conveniently represented by adsorption isotherms which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent, $q_e$, and the solute concentration in the solution at equilibrium, $C_e$. The equilibrium data for ammonium ion adsorption onto CSAC were fitted to describe experimental data of adsorption isotherms. The most famous isotherms are Langmuir and Freundlich isotherms (Armagan et al. 2003; Freundlich 1906; Krishna and Arunima 2005). The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has successful application for monolayer adsorption process:

$$q_e = \frac{K_L C_e}{1 + b C_e}$$  \hspace{0.5cm} (5)

where $q_e$ is the equilibrium ammonium ion concentration on the adsorbent (milligram per gram), $C_e$ is the equilibrium ammonium concentration in the solution (milligram per liter), $b$ is the Langmuir constant (liter per milligram), and $K_L$ is the Langmuir adsorption constant (liter per gram) and is related to the free energy of adsorption. The essential features of the Langmuir adsorption isotherm can be expressed as a dimensionless separation factor, $R_L$, which is derived as follows:

$$R_L = \frac{1}{1 + b C_0}$$  \hspace{0.5cm} (6)

where $C_0$ is the initial concentration of ammonium ion (milligram per liter). The $R_L$ value is used to indicate the shape of the isotherm, whether the adsorption process is

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (L/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>300 $\mu$m</td>
<td>2.261</td>
<td>0.0026</td>
</tr>
<tr>
<td>600 $\mu$m</td>
<td>2.04</td>
<td>0.00205</td>
</tr>
</tbody>
</table>

Fig. 3 Adsorption isotherms for ammonium onto CSAC for particle sizes a 300 $\mu$m and b 600 $\mu$m (Conditions: pH 9.0, temperature 283 K, contact time 120 min)
favorable (0<R_L<1) or unfavorable (R_L>1). According to Mckay, R_L values between 0 and 1 indicate favorable adsorption. The calculated R_L values for ammonium ion adsorption were observed to be 0.75 and 0.86 for the particle sizes 300 μm and 600 μm, respectively. The data obtained represent a favorable adsorption for the selected adsorbent of CSAC.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems:

\[ q_e = K_F C_e^{1/n} \]  

where, \( K_F \) (liter per gram) and \( n \) are Freundlich adsorption isotherm constants, representing the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorbent, respectively.

The amount of adsorbent required to reduce any initial concentration to a predetermined final concentration can be calculated. The values for the Langmuir and Freundlich constants and the correlation coefficients (\( R^2 \)) for the different sizes of CSAC particles are given in Table 2. The adsorption capacity, \( K_F \), was observed to be high for the CSAC particles of size 300 μm (44.98). The value of \( n \), which reflects the intensity of adsorption, also presented the same trend. Figure 3 and the correlation coefficient (\( R^2 \)) confirmed that the present adsorption process was best obeyed for the Freundlich isotherm. Therefore, the adsorption process concluded that the adsorption of ammonium ion onto CSAC was multilayer.

Thermodynamic study

The thermodynamic parameters, including change in Gibbs free energy (\( \Delta G \)), enthalpy (\( \Delta H \)), and entropy (\( \Delta S \)), were determined by using following equations and represented as:

\[ K_C = \frac{C_A}{C_S} \]  

\[ \Delta G = -RT \ln K_C \]  

\[ \ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  

where \( K_C \) is the equilibrium constant, \( C_A \) is the amount of ammonium adsorbed on the adsorbent from the solution at equilibrium (milligram per liter), and \( C_S \) is the equilibrium concentration of ammonium ion in aqueous solution (milligram per liter). \( \Delta H \) and \( \Delta S \) were calculated from the slope and intercept of van't Hoff plots of \( \ln K_C \) against 1/T (Fig. 4). The results are given in Table 3. The Gibbs free energy indicates the degree of spontaneity of the adsorption process where more negative values reflect a greater energetically favorable adsorption process. Generally, the change in free energy for physisorption is between ~20 and 0 kJ/mol, but chemisorption is in the range of ~80 to ~400 kJ/mol (Ugurlu et al. 2008; Ugurlu and Karaoglu 2011). In this investigation, \( \Delta G \) for adsorption of ammonium ion by CSAC was observed as ~2.137 kJ/mol at 283 K and ~1.5 kJ/mol at 313 K (Table 4). In addition, \( \Delta H \) that was calculated for CSAC was found to be ~0.108 kJ/mol. The negative value of \( \Delta H \) showed that the ammonium ion adsorption onto CSAC was exothermic. The lower \( \Delta H \) values reflects the weak interactions between the ammonium ions and the negatively charged sites on the surface of the CSAC. These results were in well agreement with an earlier report (Saltali et al. 2007). The negative value of change in entropy (\( \Delta S \)) for ammonium adsorption onto CSAC (~0.271 J/kmol K) concluded that the adsorption process was spontaneous in the low temperature range.

Instrumental analysis

**Scanning electron microscopy (SEM)**

Surface morphology of CSAC and the CSAC after ammonium ion adsorption are shown in Fig. 5. Figure 5a, the microscopic image of CSAC, shows the presence of a highly porous structure of the carbon surface and subsurface.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Equilibrium constant ( (K_C) )</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/kmol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>2.48</td>
<td>-2.137</td>
<td>-0.108</td>
<td>-0.271</td>
</tr>
<tr>
<td>293</td>
<td>2.34</td>
<td>-2.070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>2.25</td>
<td>-2.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.78</td>
<td>-1.500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The pore sizes of the particles were in the range of 5 and 20 μm. The porous nature was due to the chemical activation by phosphoric acid. Figure 5b shows the CSAC after ammonium ion adsorption, and the image explores that the pores were masked by white mass. This clearly confirms the ammonium ion adsorption onto the CSAC.

XRD analysis

X-ray diffraction patterns of the CSAC and CSAC after ammonium ion adsorption are shown in Fig. 6. The XRD pattern of CSAC shows Fig. 6a amorphous structure, and Fig. 6b shows the sharp crystalline peaks after ammonium ion adsorbed onto CSAC. The 2θ values of 22, 27, 29, 38, and 56 peaks confirmed that the ammonium ions were adsorbed onto the CSAC. The same kind of response from the XRD pattern for the ammonium ion adsorption was reported by Narten (1970).

Fourier transform infrared spectroscopy (FTIR)

Figure 6c and 6d show the spectra of CSAC before and after ammonium ion adsorption. CSAC has a wide band at about 2,850–3,000 cm⁻¹ due to the O–H stretching and adsorbed water molecule. The peak at 2,950 cm⁻¹ may be due to the aliphatic C–H stretching. A broad shoulder peak at about 1,180 cm⁻¹ indicates the presence of phosphorus. This can be explained by the use of phosphoric acid to activate the CSAC (Kennedy et al. 2007). A small peak at 800 and 470 cm⁻¹ indicate the presence of silica in CSAC.
Figure 6d illustrates an increased C–H stretching peak at 1,080–3,500 cm⁻¹ that was due to adsorption of ammonium ion onto CSAC. The strong masng between 2,600 cm⁻¹ and 3,600 cm⁻¹ may be due to the adsorption of inorganic ammonium ion (Lingyu et al. 2005).

Conclusions

In this investigation, CSAC was prepared for the removal of ammonium ion from the aqueous solution by batch adsorption study. The influence of process parameters, such as effect of pH, effect of temperature, and contact time, was evaluated. The optimized conditions for the effective ammonium adsorption were pH 9.0, temperature 283 K, and contact time 120 min. The second order rate kinetic model was followed as the best model, and the adsorption isotherm model was obeyed by the Freundlich equilibrium model. The thermodynamic properties of ammonium ion adsorption concluded that the process was spontaneous and favorable by the adsorption of CSAC. The adsorption of ammonium ion was confirmed through SEM, XRD, and FTIR analyses. This material can be used to remove ammonium ion from domestic and industrial waste water.

Acknowledgments  The authors thank the Council of Scientific and Industrial Research, India for its financial support to carry out the present investigation.

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Characterisation and recovery of sodium chloride from salt-laden solid waste generated from leather industry

R. Boopathy · S. Karthikeyan · A. B. Mandal · G. Sekaran

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Abstract In this present investigation, physical and chemical characteristics of salt-laden solid waste (SLSW) generated from leather industry during soaking process of raw skins/hides and reverse osmosis reject stream were determined. The disposal of SLSW onto landfill was banned due to the possibility of ground water contamination by leachate, and its treatment process becomes tedious and cost intensive. The detailed characterisation of SLSW was evaluated for the development of effective methods for the treatment and/or disposal of SLSW. In the present study, sodium chloride was recovered to reduce the impact of the disposal of SLSW. The recovery of sodium chloride was achieved by selective precipitation using hydrogen chloride gas as a precipitating agent. The optimum conditions for the precipitation of sodium chloride were concentration of SLSW, 60 % (w/w); HCl gas purging, time 3 min (for a batch volume of 100 mL); pH, 8.0; and temperature, 30–40 °C. The scanning electron microscopy images of SLSW and the recovered sodium chloride were captured to observe the surface morphology. The recovered salt showed purity equivalent to that of standard reference salt. The recovered salt can be reused within leather sector or to the other process industries that meet their specification.

Keywords Leather industry · Salt-laden solid waste (SLSW) · Soak liquor · RO reject · NaCl precipitation

Abbreviations
SLSW Salt-laden solid waste
RO Reverse osmosis
SEM Scanning electron microscopy
TDS Total dissolved solids
CETP Common effluent treatment plant
COD Chemical oxygen demand
VDS Volatile dissolved salt
HCl Hydrogen chloride
NaCl Sodium chloride
TKN Total Kjeldahl nitrogen

Introduction
The leather industry, which plays a significant role in today’s global economy, is to transform animal hides/skins into a physically and chemically stable material by subjecting them to chemical and mechanical sequential processes. The leather industry is the fourth largest of India’s export industries and stakes 10 % of global production. The production of goat and buffalo-based leathers are major strength of India, and it turns out best possible quality leathers from relatively low-quality hides. Out of 3,000 tanneries in India, Tamil Nadu accounts for 50 % of leather production (Money 2005).

The characteristics of solid wastes generated from the leather industry are well documented; but reports on characteristics of inorganic salt-laden solid waste (SLSW) are rare (Ozgunay et al. 2007). According to the data received from the studies of several researchers, approximately 200 kg of leather is manufactured from 1 ton of wet-salted skin/hide (Veeger 1993). More than 600 kg of solid waste is generated during the transformation of
1,000-kg raw skin/hide into leather, which constitutes 30–40 % of inorganic salts in the SLSW. The inorganic salts are removed before proceeding to leather process by two or three stage of soaking process for good quality leather production. However, the soaking process involves dissolution of soluble proteins such as albumin and globulin by dung and blood in suspension besides NaCl which was applied for preservation of hides/skins. The SLSW is dried in solar evaporation pans, but this dried salt finds no use indeed; because of high organic and bacterial loading. The second and third soaked bath wastewater were mixed along with other process wastewater streams, which influence on the increase in total dissolved solids (TDSs) in the tannery effluent.

Table 1 shows the characteristics of various streams of leather industry wastewater. The secondary biological treated wastewater is subjected to membrane-separation process for the recovery of water or the removal of TDS content. Membrane-separation process has become increasingly attractive for the treatment and recycling of wastewater. However, the efficiency of the process is limited only up to 70 % and rest 30 % of feed stream is considered as reject stream. The reject stream is evaporated in solar evaporation pans (for small volume of discharge) or in multiple effect evaporator (for large volume of discharge) leaving behind the SLSW. The SLSW lacks the reusable option as it contains high concentration of organic, biological and microbiological impurities. Hence, the soak liquor and reverse osmosis (RO) reject stream after solar evaporation pans were dumped onto land lined with impervious polymeric membranes. The risk factor of the land fill sites is leachability of salts leading to the ground water contamination. The pollution control agencies have banned the land filling of SLSW for not meeting the disposal standard of the leachate wastewater. Moreover, investment and maintenance cost of leachate from secure landfill are very expensive. At present, the SLSW is being packed and stored in the storage yard in all ETPs and common effluent treatment plants (CETPs) of leather sector. The conditions become worsen that the new land space is required for storing the fresh generation of SLSW in proportion to the production capacity. There has been constant research on the disposal of this SLSW in an environment sound manner. Even though, the researchers are focusing on the alternative preservative systems for leather processing such as mobile freezer for transporting raw hides/skins from the slaughter houses to leather process industries. Still, the generated SLSW needs to be disposed off by an environmentally safe method.

The burden on disposal of SLSW is due to contamination of inorganic salts with organic salts. The disposal techniques for the organic solid waste mixed with high level of inorganic salt are rare. The separation of inorganic salts from the mixture becomes mandatory for the disposal onto secure landfill sites. The recovered salt can be reused within the leather industry or may be used in the industries such as textile, dye and dye intermediates and paper and pulp industries. Thus, an attempt was made in the present investigation to separate sodium chloride from the SLSW by chemical precipitation process. In order to do so, first a detailed characterisation of SLSW was also done as the part of the investigation.

### Materials and methods

#### Source of SLSW

The SLSW sample was collected from the solar evaporation pan used in a commercial tannery for soak liquor and RO reject stream. In order to get wide range of characteristics, SLSW were collected from various industries that process goat skin and buffalo hide as raw materials. The samples were labelled as $S_1$ and $S_2$ for SLSW generated from soak liquor of goat skin and buffalo hide, dried in solar evaporation pan respectively. $R_1$ and $R_2$ for SLSW generated from RO reject stream of goat skin and buffalo hide, dried in solar evaporation pan respectively.

---

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Parameters</th>
<th>Untreated wastewater</th>
<th>Biological treated water/RO feed</th>
<th>RO permeate</th>
<th>RO reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>4.12–4.68 (4.53)</td>
<td>7.03–8.21 (7.65)</td>
<td>6.87–7.25 (7.22)</td>
<td>6.85–7.55 (7.5)</td>
</tr>
<tr>
<td>2</td>
<td>TDSs</td>
<td>7677 ± 4084</td>
<td>5584 ± 1804</td>
<td>259 ± 138</td>
<td>20003 ± 6140</td>
</tr>
<tr>
<td>3</td>
<td>Biological oxygen demand$_5$</td>
<td>2099 ± 1185</td>
<td>104 ± 91</td>
<td>-</td>
<td>408 ± 325</td>
</tr>
<tr>
<td>4</td>
<td>COD</td>
<td>4767 ± 2422</td>
<td>430 ± 292</td>
<td>5.6 ± 7</td>
<td>1533 ± 857</td>
</tr>
<tr>
<td>5</td>
<td>Sodium</td>
<td>1608 ± 1443</td>
<td>1656 ± 532</td>
<td>55 ± 25</td>
<td>3960 ± 1675</td>
</tr>
<tr>
<td>6</td>
<td>Chloride</td>
<td>1302 ± 420</td>
<td>1303 ± 408</td>
<td>74 ± 23</td>
<td>4993 ± 2203</td>
</tr>
<tr>
<td>7</td>
<td>Sulphate</td>
<td>2671 ± 1582</td>
<td>2310 ± 1250</td>
<td>16 ± 21</td>
<td>5559 ± 1955</td>
</tr>
</tbody>
</table>

* All the values are expressed in mg/L, except pH (range and median value)
Methods of analysis

The SLSW samples were randomly selected among the leather industries processing goat skin and buffalo hide. Inorganic SLSW were homogenised and dried at 60–65 °C and stored for further experiments.

The various process parameters such as moisture content, pH, soluble organic substances in dichloromethane, Total Kjeldahl nitrogen (TKN) and sodium chloride were carried out using the methods in accordance with APHA (1998). In order to determine Cr, Fe, Na and Ca in SLSW samples, they were first pretreated with an acid digestion process. Then, the samples were made up to 100 mL with distilled water. Cr, Fe, Na and Ca contents of digested samples were determined using Atomic Absorption spectrophotometer (Perkin-Elmer 3110). Cr was measured at $\lambda = 357.9$ nm with 0.7 slit intervals by using air–acetylene mixture, Fe was measured at $\lambda = 248.3$ nm with 0.2 slit intervals by using air–acetylene mixture, Na was measured at $\lambda = 589.6$ nm with 0.2 slit intervals by using air–acetylene mixture, and Ca was measured at $\lambda = 422.7$ nm with 0.7 slit intervals by using air–acetylene mixture.

Precipitation of sodium chloride from the SLSW

The mathematical expression for equilibrium constant for the dissolution of sodium chloride in water is given by;

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl_{sp}]}$$

$$K_{sp} = [Na^+][Cl^-], \quad K_c = K_c[NaCl_{sp}]$$

The value of solubility product ($K_{sp}$) measures the highest concentration of dissolved ionic species in aqueous solution. Thus, in a saturated solution, the solubility product is equal to the product of all the ions, i.e. $K_{sp} = [Na^+][Cl^-]$. This dynamic equilibrium can be disturbed by changing the concentration of either [Na$^+$] or [Cl$^-$]. According to Le Chatelier’s principle, the sodium chloride is precipitated out from the aqueous solution when the ionic product of [Na$^+$] and [Cl$^-$] is greater than $K_{sp}$ of NaCl.

In order to study the precipitation of NaCl from SLSW, R$_1$ was selected as model SLSW sample. Six hundred grams of R$_1$ was dissolved in 1 L of deionised water to get saturated solution of SLSW. The undissolved sand, grit and floating solids were separated by decantation and screening as pretreated step. The screened solution was passed through a sand filter to remove the suspended solids. The undissolved content was found to be 270 g and dissolved salt was 330 g/L of SLSW solution. Then the known volume of pretreated saturated SLSW solution (100 mL) was taken in a glass reactor for the precipitation of NaCl. The grit and other floating matters are disposed of safely by landfill sites. The hydrogen chloride gas was purged at a flow rate of 2.06 g/min into the solution through a distributor provided at the bottom of the reactor. The temperature of the reactor was thermostatically controlled using external water circulation system. The reactor was equipped with agitators for the uniform mixing. The precipitated NaCl was filtered through a polypropylene filter cloth and washed with pure brine solution to get a pure salt.

The optimum conditions for the effective precipitation of sodium chloride from the SLSW solution were determined by varying the following parameters: mass of untreated SLSW, 40–65 % (w/w); HCl gas purging time, 0–3 min; pH, 1–9; and temperature, 10–60 °C.

Scanning electron microscopy (SEM)

Surface morphology of S$_1$, S$_2$, R$_1$, R$_2$ and recovered sodium chloride were captured and recorded using JEOL JM—5600 electron microscope. The samples were coated with gold using a gold sputtering device for 7 min for the better visibility of the surface morphology.

Results and discussion

Moisture content and pH of SLSW

Table 2 shows that the maximum moisture content of the SLSW for the goat skin and buffalo hide of soak liquor and RO reject streams from the industry processing were found to be 14.3 and 15.3 %, respectively. The moisture content of SLSW differs to a greater extent with the mode of collection, storage conditions and climate. The percentage

<table>
<thead>
<tr>
<th>Type of SLSW</th>
<th>Moisture content (%)</th>
<th>pH$^a$</th>
<th>COD (mg/g)</th>
<th>VDS (mg/g)</th>
<th>Fats and oil (%)</th>
<th>Nitrogen (mg/g)</th>
<th>Salt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_1$</td>
<td>12.3 ± 1.5</td>
<td>7.4–8.6 (7.8)</td>
<td>67.1 ± 0.8</td>
<td>18.8 ± 2.5</td>
<td>0.06 ± 0.02</td>
<td>0.25 ± 0.1</td>
<td>59.2 ± 2.0</td>
</tr>
<tr>
<td>R$_1$</td>
<td>12.8 ± 2.3</td>
<td>6.8–8.8 (7.6)</td>
<td>48.0 ± 0.5</td>
<td>15.3 ± 2.0</td>
<td>0.01 ± 0.01</td>
<td>0.05 ± 0.02</td>
<td>55.2 ± 2.2</td>
</tr>
<tr>
<td>S$_2$</td>
<td>12.8 ± 1.5</td>
<td>7.5–8.3 (8.0)</td>
<td>64.3 ± 0.6</td>
<td>20.2 ± 2.5</td>
<td>0.04 ± 0.05</td>
<td>0.23 ± 0.1</td>
<td>58.5 ± 2.2</td>
</tr>
<tr>
<td>R$_2$</td>
<td>13.0 ± 2.3</td>
<td>7.0–8.4 (7.7)</td>
<td>42.4 ± 0.4</td>
<td>15.1 ± 2.0</td>
<td>0.01 ± 0.01</td>
<td>0.04 ± 0.02</td>
<td>53.4 ± 2.2</td>
</tr>
</tbody>
</table>

$^a$ pH value is expressed as range and median value
of moisture content of SLSW is of great significance at the
time of storage and use. Owing to the high amount of water
in leather wastes, or natural environment conditions like
rain or snow, infusion of the soluble salts in leather waste
into soil and surface/ground waters cause the deterioration
of the natural and structures of these receiver environ-
ments. The damage is very high in the case of solid wastes
containing soluble inorganic salts. Researchers have
reported the infusion of inorganic salts into plants and
ground waters and into soil. The disposal of SLSW onto
soil surface turns it soil as an infertile land.

The moisture-free SLSW \((S_1, S_2, R_1\) and \(R_2\)) of weight
1 g was dissolved in 100 mL of deionised water, the pH of
the \(S_1\) and \(S_2\) solutions were observed to be in the neutral
range, from 7.5 to 8.6. Generally, pH of the RO feed is
maintained in the range of 6.8–7.5 to avoid precipitation of
inorganic salt onto the active surface of the membrane. The
pH of the SLSW (\(R_1\) and \(R_2\)) generated from RO reject
stream was increased to the range 7.8–8.5 which may be
due to the increase in concentration of divalent and mul-
tivalent ions in the RO reject.

Chemical oxygen demand (COD) and volatile dissolved
solids (VDSs)

The raw hide/skin contains high percentage of fats and
proteins. During the soaking of the raw skin/hide in the
soaking chamber for a long period of time, the animal fats,
tissues, stained blood, albumin and globulin are dissolved
in water. This constitutes to the organic content of the soak
wastewater. The examined results showed (Table 2), the
maximum amount of organic content was obtained to be
67.9 and 48.5 mg/g for soak liquor SLSW (\(S_1\) and \(S_2\)) and
RO reject stream SLSW (\(R_1\) and \(R_2\)), respectively. The excessive organic content of the evaporated residue of soak
liquor and RO reject stream may also due to the algae
growth and atmospheric contamination during the evapo-
ration in solar evaporation pans.

The VDS was determined in both the SLSW (soak
liquor and RO reject) using muffle furnace. First moisture
content of the known weight of SLSW was determined
using hot air oven for 90 min at 110 °C followed by
heating in the muffle furnace for 60 min at 550 °C. The
results revealed that the VDS were varied from 10 to
20 mg/g of SLSW (\(S_1, S_2, R_1\) and \(R_2\)).

The soluble substances in dichloromethane
(fats and other soluble)

The fat in raw hide/skin affects leather processes by pro-
hibiting the penetration of chemicals into the hide/skin and
may also cause a strong smell due to increase in microbial
activity and defects like spew on leathers. For this reason,
vast amounts of fat in hides/skins are removed before
tanning by degreasing process. Bienkiewicz (1983) noted
that fat content varied between 0.5 and 4 % in cattle and
horse hides, 3 and 30 % in sheep skin, and 3 and 10 % in
goat skin over dry weights. Another source for oils and fat
in solid wastes is the natural or synthetic fats used in the fat
liquoring process to provide the leather with features like
softness, elasticity and resistance, and to allow the leather
fibres to slide easily over one another according to the
leather type and purpose of use. The dissolved fat in
wastewater was removed as much as possible in the pri-
mary treatment step and the rest escaped were treated in the
biological treatment process. The membrane-separation
processes retain the fatty substances either in the free form
or in combined forms with divalent/multivalent salts and
they are contained in the RO reject stream. Then, the
evaporated residue of soak liquor and RO reject stream
contains a considerable concentration of fatty substances.
The percentage of fat content was within the range of 0.06
and 0.01 % (Table 2) in the soak liquor SLSW (\(S_1\) and \(S_2\))
and RO reject stream SLSW (\(R_1\) and \(R_2\)), respectively. It is
concluded that the amount of soluble fats in the dichloro-
methane is very less compared to other solid waste gen-
erated from leather industry. The presence of fat and other
soluble organics are due to the particulates of fleshing that
were removed from the raw skin/hide along with sodium
chloride salt in the vigorous agitation process. However, in
the case of RO reject salt, the soluble fat content was very
less, because of the elimination of most of the organic
matter including fats in wastewater pretreatment steps.

Nitrogen content of SLSW

Determination of nitrogen in SLSW gives an idea about the
amount of proteinaceous content in the SLSW. The results
obtained from TKN determination for SLSW from soak
liquor and RO reject stream are presented in Table 2.
Table 2 shows that the nitrogen content of SLSW for soak
liquor SLSW (\(S_1\) and \(S_2\)) and RO reject stream (\(R_1\) and \(R_2\))
were lie in the range of 0.23–0.25 and 0.04–0.05 mg/g,
respectively. The nitrogen content was very less in the
SLSW of \(R_1\) and \(R_2\) than in SLSW of \(S_1\) and \(S_2\). The
soluble protein dissolved during the soaking of skins/hides
is responsible for the increase in ammoniacal nitrogen in
SLSW. A very less TKN content in \(R_1\) and \(R_2\) may be
attributed to maximum elimination of TKN during primary
and secondary biological treatments of wastewater. The
secondary treated wastewater on chlorination to eliminate
ammoniacal nitrogen as ammonium chloride along with the
destruction of microorganism. In general, the fleshing
wastes are the ones generated by the removal of a hypo-
dermis layer, which is rich in fat and poor in protein (Gish
2000; Taylor and Diefendore 1997).
Sodium chloride content of SLSW

The salt contents in terms of sodium chloride were examined; it was found that salt proportion in both the sources of samples varied between 50 and 60 % (w/w). The sodium chloride used in preservation was desalted and removed by soaking process before it was taken for leather processing; otherwise, it affects the quality of the leather and increased the chemical consumption in the leather processing. The complete removal of sodium chloride is achieved in two to three soaking of hide/skin. The soak wastewater is evaporated in solar evaporation pan before it is stored in the storage yard. The R₁ and R₂ generated from the thermal evaporation followed by solar evaporation. These salts find no use indeed because of the impure nature. They have been dumped onto the secured land fills provided with impervious polymeric protective lining along with in situ monitoring devices for leachate detection. However, during the spring season dissolution of salt in leachate causes groundwater contamination and thus severely affects the surrounding ecological systems. In addition, high salinity or TDSs in surface water causes high osmotic pressure, which results in reduced water availability to plants and retarded plant growth in salt intolerant crops (Money 2005). The disposal of this SLSW becomes troublesome; otherwise it ends up with some other cost intensive environmental problems. Instead of considering the disposal of SLSW techniques for SLSW, recovery of specific major constituent from SLSW may be an ideal approach. Thus, to reduce the impact of SLSW, the recovered salt can be reused. This approach may certainly minimise the cost towards the application of feed stock. The pollution control board is also enforcing the leather industry to adopt eco-friendly disposal technique or the better alternative process such as recovery of valuables from the SLSW.

Determination of Na, Cr, Fe, Zn, Ca, Mg ions in SLSW

The various ions were detected in SLSW, generated from the leather industry and they are presented in the Table 3. Sodium content in the SLSW can be originated from sodium chloride, sodium sulphate, sodium carbonate, sodium formate or sodium sulphide used in leather processing. The amount of salts used may vary widely based on the production of various types of leather and various processes. For example, tanning processes carried out at low pH values or strong acidic conditions require pickling and more buffer salts. Similarly, in neutralisation and basification processes various Na-based buffering salts and alkali salts are also used, they are responsible for the Na content in waste stream. High concentrations of sodium ions in irrigation water adversely affect the soil structure by causing dispersion of clay. Deterioration in soil permeability can occur depending on sodium, calcium and magnesium ion concentrations in the soil. The chrome content was detected to be less in all SLSW (S₁, S₂, R₁ and R₂). The absence of chromium in SLSW is due to the fact that salts were not added during the soaking process and the RO pretreatment processes reduced or eliminated the chromium ions in the feed water. However, about 90 % of hides/skins in the world are still tanned with basic chromium sulphate as tanning agent, because other tanning materials fail to give the leather a high hydrothermal stability and other valued properties that chrome provides. National and as well as international scenario present that the chrome content was completely recovered and reused within the industry. Iron content of SLSW was generally not very high, and varied according to the iron content of the water used in processing, and the process after which the waste is generated. A trace amount of zinc was observed in SLSW (S₁, S₂, R₁ and R₂). The presence of calcium and magnesium ions in the SLSW (S₁ and S₂) was due to the usage of natural potable water in the soaking process. The liming and de-liming processes are responsible for the presence of calcium ion in the tannery wastewater. The secondary treated wastewater still contains some amount of calcium ion. Thus, the calcium ion was concentrated and accumulated in the RO reject stream from RO process.

Precipitation of sodium chloride from SLSW

Effect of concentration of SLSW

The concentration of SLSW (R₁) was varied from 40 to 65 % (w/w) to evaluate the efficiency of NaCl precipitation. The other process parameters such as temperature, 30 °C; native pH, 8.0 and HCl purging time, 3 min were

<table>
<thead>
<tr>
<th>Type of SLSW</th>
<th>Na (mg/g)</th>
<th>Cr (mg/g)</th>
<th>Fe (mg/g)</th>
<th>Zn (mg/g)</th>
<th>Ca (mg/g)</th>
<th>Mg (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>264</td>
<td>0.01</td>
<td>20</td>
<td>0.018</td>
<td>86</td>
<td>50</td>
</tr>
<tr>
<td>R₁</td>
<td>234</td>
<td>0.03</td>
<td>7</td>
<td>0.01</td>
<td>128</td>
<td>70</td>
</tr>
<tr>
<td>S₂</td>
<td>252</td>
<td>0.03</td>
<td>10</td>
<td>0.013</td>
<td>94</td>
<td>63</td>
</tr>
<tr>
<td>R₂</td>
<td>246</td>
<td>0.01</td>
<td>4</td>
<td>0.017</td>
<td>118</td>
<td>72</td>
</tr>
</tbody>
</table>
kept constant. The results (Table 4a) show that the mass of NaCl increased with increase in concentration of SLSW up to 60 % (w/w) and remained constant even after increase in SLSW concentration. This reveals that at the concentration of 60 % (w/w) the ions in the solution equals the solubility of the NaCl, below this concentration the solution became under saturated; hence, mass of NaCl precipitated was very less. The concentration of SLSW above 60 % (w/w) does not alter the ionic strength of the solution. Hence, the same mass of NaCl was precipitated even at a concentration of 65 % (w/w). Hence, the optimum SLSW concentration was fixed at 60 % (w/w).

**Effect of hydrogen chloride gas purging time**

The HCl gas purging time required for the precipitation of sodium chloride was varied from 30 s to 3 min for the 100 mL volume of SLSW-saturated solution at temperature 30 °C, pH 8.0 and concentration of SLSW 60 % (w/w) (dissolved salt 33 % (w/w)). Table 4b shows that as the purging time was increased, the mass of NaCl salt precipitated was also increased up to 3 min and thereafter no precipitation was observed. This shows that the reaction equilibrium may be attained by balancing the product of ionic salts with the salting out of sodium chloride. The maximum percentage recovery of sodium chloride was 82 % (27 g/100 mL volume). Hence, the optimum time required for the precipitation of pretreated SLSW saturated solution was fixed at 3 min.

**Effect of pH**

The effect of pH on sodium chloride precipitation in the SLSW-saturated solution was studied by varying the pH from 1.0 to 9.0 at temperature 30 °C and concentration of SLSW was 60 % (w/w) for 3 min of HCl purging time.

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**Table 4** Precipitation of sodium chloride from the SLSW of RO reject stream (R1); (a) effect of concentration of SLSW (conditions: pH 8.0, temperature 30 °C, HCl gas purging flow rate 2.06 g/min, contact time 3 min), (b) effect of HCl purging time (conditions: pH 8.0, temperature 30 °C, concentration of SLSW 60 % (w/w)), (c) effect of solution pH (conditions: temperature 30 °C, concentration of SLSW 60 % (w/w), contact time 3 min), (d) effect of temperature (conditions: pH 8.0, concentration of SLSW 60 % (w/w), contact time 3 min)

(a)

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Concentration of SLSW % (w/w)</th>
<th>Dissolved solid (g/100 mL)</th>
<th>Mass of sodium chloride recovered (g/100 mL)</th>
<th>% Recovery with reference to dissolved solid</th>
<th>Time (min)</th>
<th>Mass of sodium chloride salt recovered (g/100 mL)</th>
<th>% Recovery with reference to dissolved solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>22</td>
<td>9.85</td>
<td>44.8</td>
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<td>45</td>
<td>24.75</td>
<td>12.3</td>
<td>49.7</td>
<td>0.5</td>
<td>12.4</td>
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<td>3</td>
<td>50</td>
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<td>16.5</td>
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<tr>
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<td>20.5</td>
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<tr>
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<td>33</td>
<td>26.9</td>
<td>81.2</td>
<td>2</td>
<td>23.2</td>
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<td>33</td>
<td>27</td>
<td>81.8</td>
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<td>4</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>5</td>
<td>27</td>
<td>81.8</td>
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</table>

(b)

<table>
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<tr>
<th>Sl. no.</th>
<th>Initial pH of SLSW-saturated solution</th>
<th>Mass of sodium chloride recovered (g/100 mL)</th>
<th>% Recovery with reference to dissolved solid</th>
<th>Temperature (°C)</th>
<th>Mass of sodium chloride salt recovered (g/100 mL)</th>
<th>% Recovery with reference to dissolved solid</th>
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<tr>
<td>1</td>
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<tr>
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<td>46.9</td>
<td>80</td>
<td>15.5</td>
<td>46.9</td>
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</table>
Table 4c shows the precipitation of NaCl was not favoured in the acidic pH range from 1 to 6. The mass of precipitated NaCl was increased from pH 6.0 and continued up to pH 8.0 and then decreased at pH 9.0. The maximum amount of NaCl precipitation (26.9 g) was observed at pH 8.0 (native pH of SLSW solution). Sodium chloride in water established ionic equilibrium with sodium ion, hydroxide ion, chloride ion and hydronium ion (formed from water). The presence of hydrogen ion lowered the solubility of sodium chloride; hence, the mass of precipitate was less in the acidic pH range i.e. the solution becomes under saturated and thus increased the HCl gas purging time. The results confirmed that the native pH (8.0) was regarded as the optimised pH value for the precipitation of NaCl.

The excess HCl (required for the separation of NaCl from SLSW) in the solution was neutralised with calcium hydroxide to separate out sulphate ions as calcium sulphate in the second step of SLSW management. Calcium sulphate is an insoluble product; hence, it was separated out by simple settling process. This was followed by destruction of organic compounds and crystallisations of organic free calcium chloride are described under patent filed by the authors of the present publication (Vide No: DEL1898, 2010).

**Effect of temperature**

The influence of temperature on the precipitation of sodium chloride from saturated solution of SLSW was carried out by varying the temperature from 10 to 80 °C at constant native pH (8.0); HCl purging time, 3 min and concentration of SLSW, 60 % (w/w). Table 4d shows that the mass of precipitated NaCl increased with increase in temperature up to 40 °C. This may be due to the difference in solubility of NaCl with respect to the temperature. At low temperature the solubility of NaCl was retarded; hence, mass of NaCl precipitation was decreased. The maximum amount of NaCl precipitation (27 g/100 mL of volume with 82 % recovery) was achieved in the temperature range 30–40 °C. The increase in temperature above 40 °C favoured the reverse reaction, i.e. dissolution of the precipitated NaCl molecules back into the bulk solution. Hence, the maximum mass of NaCl precipitation was achieved at 30–40 °C and it was considered as the optimum temperature for the precipitation of sodium chloride from the saturated solution of SLSW.

**Scanning electron microscopy (SEM)**

The surface morphology of the S1, S2, R1 and R2 and recovered NaCl are shown in Fig. 1. The SLSW from soak liquor (S1 and S2) (Fig. 1a, b) seems to be crystalline structure because sodium chloride salt was used in both buffalo and goat hide/skin preservation. The salt applied over the skin surface is removed by immersing the raw material in water for over night. The irregular rod shapes of the image showed salt contamination with other inorganic and organic salts of Ca, Mg, fats, protein and blood tissues, etc. Figure 1c and d show the surface morphology of the SLSW from RO reject stream (R1 and R2) with irregular masked image. Thus, it confirms the RO reject salts are contaminated with the residual chemicals along with sodium and chloride ions. Figure 1e shows the cubic structure of recovered sodium chloride from the SLSW of RO reject stream as crystals. Further, the recovered salt purity was compared with reference sodium chloride (SD fine chemical limited). The same concentration (0.5 N) of both the reference and the recovered NaCl were dissolved and recorded their solution conductivity; the observed solution conductivity (0.32 mS/cm) remained the same for the reference and the recovered salt. This confirmed that the recovered salt was NaCl and the purity was relatively equivalent to that of selected reference salt.

**Cost analysis for SLSW disposal**

The cost towards disposal of SLSW onto secure landfill site in India (inclusive of transportation cost and handling cost) is 0.11 US $ per kg of SLSW. The cost towards the reuse of the recovered NaCl was 0.088 US $ per kg and cost towards the consumables such as chemicals and electrical energy was 0.058 US $ per kg of SLSW. Thus, net expenditure on processing 1 kg of SLSW was 0.04 US $. Hence, the proposed process on the management of evaporated residue indicates that there is a scope for the cost saving compared to dumping onto secured landfill. Moreover, the dumping onto secure landfill can be considered as a short term measure besides problem of saline leachate normally encountered in secured landfill sites are eliminated in this new process, and they may be considered as indirect benefits.

**Conclusions**

The quality of leather goods produced from the raw skins/hides depends on the desirability of preservation and chemicals used for the leather processing. The saline wastewater generated in the processes of soaking and RO reject stream are evaporated in solar evaporation pans. The evaporated residue is required to be managed in an environmentally sound manner. The evaporated residue of soak liquor and RO reject stream were characterised. The characteristics clearly revealed that SLSW generated in leather sector indeed finds no use. It has been attempted to recover the NaCl from the SLSW for reuse purposes. A
new methodology to recover NaCl (82%) by chemical precipitation has been investigated. The optimum conditions for the recovery of NaCl were concentration of SLSW, 60% (w/w); HCl purging time, 3 min; pH, 8.0; and temperature, 30–40°C for the batch volume of 100 mL. The recovered NaCl was relatively pure comparable with reference salt and its reuse may certainly reduce the impact on the cost of disposal.

References


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Veeger L (1993) Ecological procedure to solve the tannery waste problems. JALCA 88(9):326