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# 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.<sup>1–3</sup> 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 CaSO<sub>4</sub> precipitate from aqueous Na<sub>2</sub>SO<sub>4</sub> system by the addition of CaO,<sup>4,5</sup> but the limitation of CaSO<sub>4</sub> 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.<sup>6</sup> 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<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>−</sup>, and SO<sub>4</sub><sup>2−</sup> by following the methods of the American Public Health Association (APHA).<sup>7</sup> The detailed preparation and characterization of the saturated ER solution were reported elsewhere.<sup>6</sup>

**Table 1. Characteristics of Saturated Solution of ER<sup>a</sup>**

parameters	values
pH	8.67
COD	5.76
chloride	215.94
sulfate	127.15
sodium	125.92
calcium	1.44
magnesium	0.51

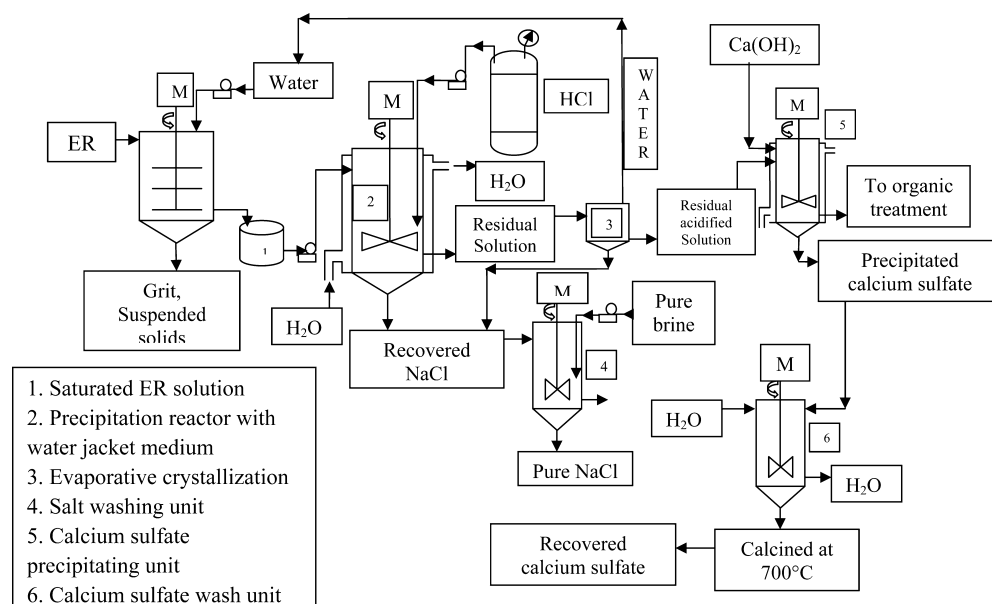
<sup>a</sup>All the values except pH are expressed in grams per liter.

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**Figure 1.** Schematic flow diagram for the separation of chloride and sulfate ions from ER generated from the leather industry.

**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 53, 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 ( $K_{sp} = 3.14 \times 10^{-5} \text{ mol}^2/\text{L}^2$ ). The solubility product of calcium sulfate and the ionic product of calcium and sulfate ions are related:

$$K_{sp, \text{CaSO}_4} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

**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  $\mu\text{m}$  gold in argon medium to capture the surface image. Scanning electron microscopy (SEM) images were observed on a scanning device attached to a JEOL JM-5600 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.

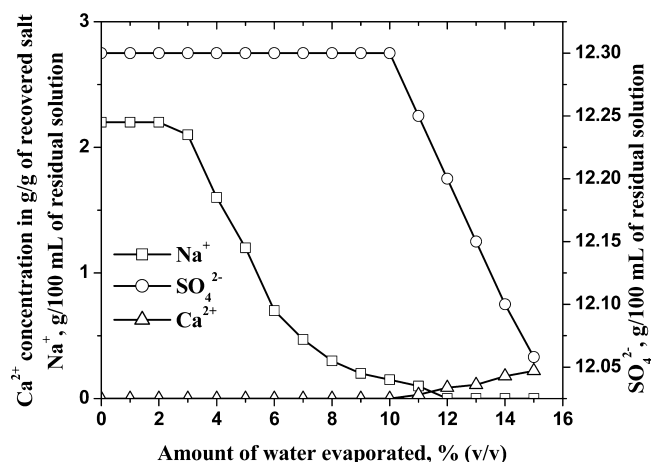
**2.4.2. Thermogravimetric Analysis (TGA) of Recovered Calcium Sulfate.** The TGA spectra were recorded for the recovered calcium sulfate before and after calcination in a pan and gravimetric analysis under reduced nitrogen atmosphere from 30 to 800 °C, using a temperature gradient of 10 °C/min, and 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.<sup>6</sup> The reactive chemical precipitation technique removed NaCl by 27g/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

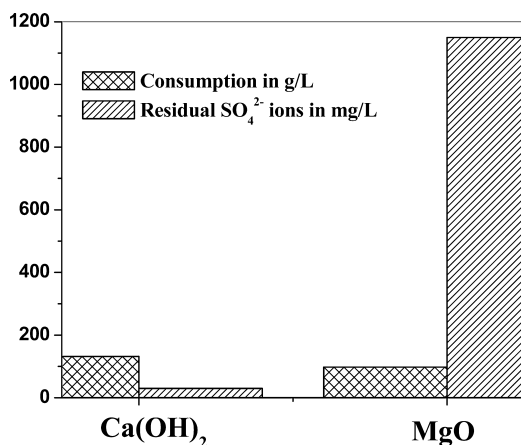


**Figure 2.** Effect of water evaporation on NaCl recovery from residual ER solution by evaporative crystallization.

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 ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) 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. Figure 2, illustrates that the removal of water from the acidified solution in the evaporative crystallization also increased the sulfate ion concentration from 12.05 to 12.3 g/100 mL solution.

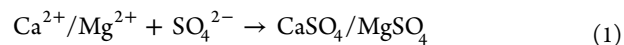
### 3.2. Separation of Sulfate Ions from the ER Solution.

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



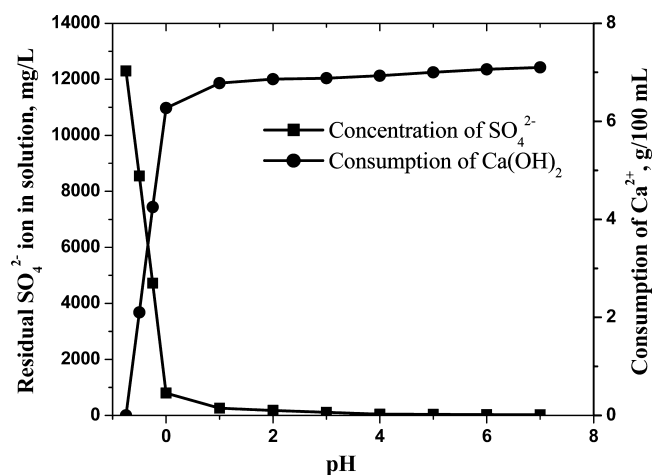
**Figure 3.** Choice of neutralizing agents on sulfate ion separation from residual acidified ER solution.

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.



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  $\text{SO}_4^{2-}$  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  $\text{Ca}(\text{OH})_2$ , rather than with MgO. Hence,  $\text{Ca}(\text{OH})_2$  was selected as the neutralizing agent for precipitation of sulfate ions from the residual acidified ER solution. Hence, the addition of  $\text{Ca}(\text{OH})_2$  separates 99.5% (w/w) of  $\text{SO}_4^{2-}$  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



**Figure 4.** Profile of solution pH and consumption of calcium hydroxide as  $\text{Ca}^{2+}$  during the precipitation of sulfate ion from residual acidified ER solution.

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  $\text{CaSO}_4$  in the solution. The precipitation of  $\text{CaSO}_4$  was observed to be very fast with the rate constant of  $0.018 \text{ s}^{-1}$  (pseudo-first order) and precipitation induction time of less than 2 s, this corroborates with the reports of Alimi et al., 2003.<sup>8</sup> The consumption of calcium hydroxide was high, until pH 0.0 was reached (consumption of  $\text{Ca}(\text{OH})_2$  as  $\text{Ca}^{2+}$ , 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

ion as calcium sulfate on exceeding its solubility product in the residual acidified solution, and thus liberation of  $\text{OH}^-$  ions raised the solution pH.

**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  $\text{Ca}(\text{OH})_2$ . As Figure 5 illustrates, the increase in

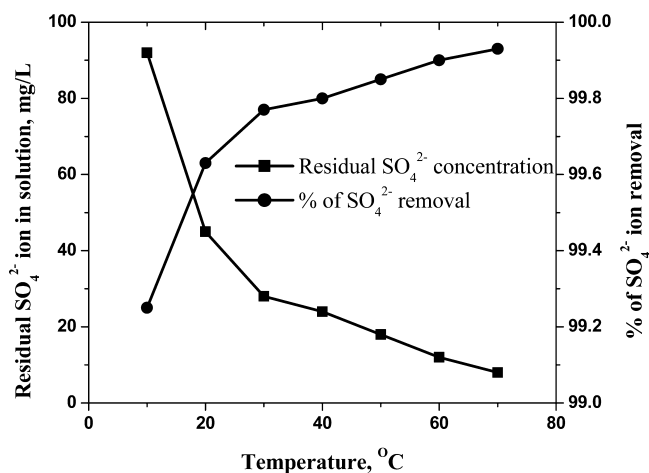


Figure 5. Effect of temperature on sulfate separation from residual acidified ER solution.

solution temperature decreased the concentration of  $\text{SO}_4^{2-}$  ions in the residual solution; that is, the percentage removal of  $\text{SO}_4^{2-}$  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.<sup>9</sup> 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.<sup>10,11</sup>

**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  $\mu\text{m}$ . 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<sub>(rec)</sub> 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

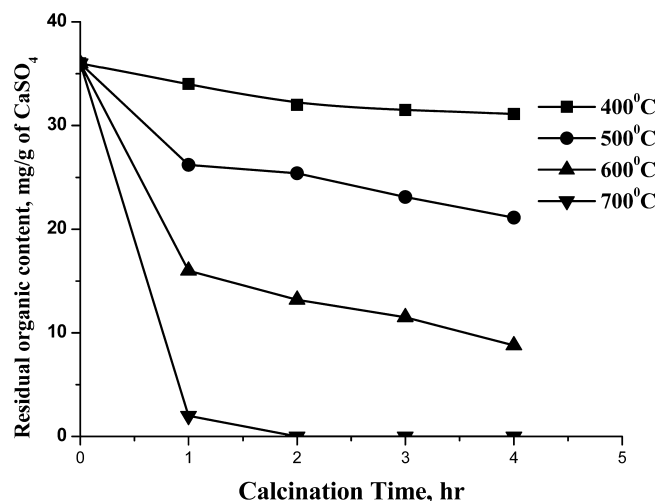


Figure 6. Effect of calcination temperature on the removal of occluded organic impurities from the precipitated calcium sulfate.

observed. Thus, the optimized conditions were calcination temperature = 700 °C and calcination period = 1 h. The calcium sulfate<sub>(rec)</sub> 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<sub>(rec)</sub> (confirmed through SEM) with a reasonable increase in apparent activation energy than the calcium sulfate<sub>(std)</sub>. Further, the BET analysis of calcium sulfate<sub>(rec)</sub> showed an increase in surface area of 2.9  $\text{m}^2/\text{g}$ , against 0.25  $\text{m}^2/\text{g}$  for calcium sulfate<sub>(std)</sub> (Merck, India). Hence, the adsorption capacity of the calcium sulfate<sub>(rec)</sub> 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<sub>(std)</sub> and calcium sulfate<sub>(rec)</sub> for various dyes in batch experiment. The adsorption capacity of calcium sulfate<sub>(rec)</sub> was found to be higher than the calcium sulfate<sub>(std)</sub>. This could be due to the enhanced surface area of the calcium sulfate<sub>(rec)</sub> over the calcium sulfate<sub>(std)</sub>. The maximum adsorption capacity of calcium sulfate<sub>(rec)</sub> 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<sub>(std)</sub> were 50 mg/g, 42 mg/g, and 5 mg/g. The result concludes that the calcium sulfate<sub>(rec)</sub> after calcination can be used as an adsorbent for the removal of dye from industrial wastewater. The solubility of calcium sulfate<sub>(rec)</sub> was found to be 1.8 g/L. Even though the solubility of calcium sulfate<sub>(rec)</sub> liberates 1800 mg/L of  $\text{SO}_4^{2-}$  ion in aqueous solution, the  $\text{SO}_4^{2-}$  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



**Table 2.** Adsorption of Aqueous Dyes Using Calcium Sulfate<sup>a</sup>

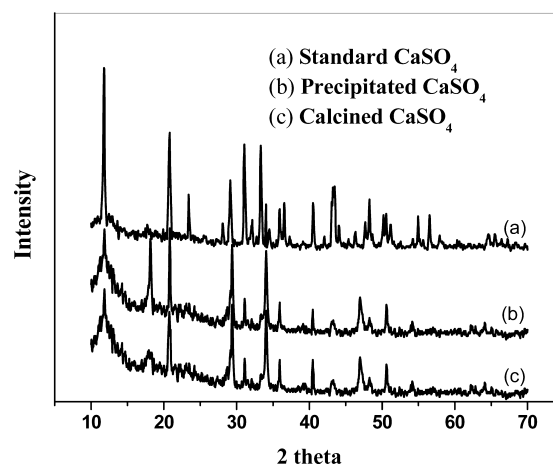
system	pH	concn. of dye (mg/L)	calcium sulfate dose (mg)	adsorption capacity (mg/g)
acid black 210	3	100	0.1 (std)	50
acid blue 113	3	100	0.1 (std)	65
acid black 53	4	100	0.1 (std)	5
acid black 210	3	100	0.1 (rec)	97
acid black 53	3	100	0.1 (rec)	92
acid blue 113	4	100	0.1 (rec)	40
acid black 210	3	100	0.1 (rec)	97
acid black 210	3	200	0.1 (rec)	86
acid black 210	3	300	0.1 (rec)	72
acid black 210	3	200	0.2 (rec)	92
acid blue 113	4	100	0.1 (rec)	83
acid blue 113	4	200	0.1 (rec)	75
acid blue 113	4	300	0.1 (rec)	64
acid blue 113	4	200	0.2 (rec)	74
acid black 53	3	100	0.1 (rec)	40
acid black 53	3	200	0.1 (rec)	22
acid black 53	3	300	0.1 (rec)	11
acid black 53	3	200	0.2 (rec)	34

<sup>a</sup>Conditions: volume of solution, 100 mL; std, calcium sulfate<sub>(std)</sub>; rec, calcium sulfate<sub>(rec)</sub>; temperature, 30 °C; agitation speed, 100 rpm.

hydroxide to precipitate out calcium sulfate. The settling velocity of the precipitate was evaluated using a batch settler. The settling velocities of the calcium precipitate were 2.25, 1.33, and 1.07 mm/h for tannic acid concentrations of 0.1, 0.2, and 0.3% (w/v). The decrease in settling velocity of calcium sulfate precipitate with increase in tannic acid concentration may be correlated with surface adsorption of tannic acid onto the calcium sulfate particles, which retards the further growth of precipitate particles. The size of the particles decreased, and thus, settling velocities were also decreased drastically with increase in concentration of tannic acid. This corroborates with the observation recorded by Hung et al. (2007) in crystal growth of hydroxyapatite with aspartic acid as an impurity.<sup>12</sup> The influence of organic impurities on precipitation was verified by evaluating the amount of organic content in the precipitated calcium sulfate at varied concentrations of tannic acid. The masses of organic content occluded in the calcium sulfate precipitate were found to be 88, 111, and 129 mg/g at tannic acid concentrations of 0.1, 0.2, and 0.3% (w/v) respectively. Hence, the organic pollutants in the aqueous solution may be considered as growth inhibitors, and they yielded a smaller size of calcium sulfate precipitate.

**3.8. Instrumental Analysis.** **3.8.1. X-ray Diffraction of Recovered Calcium Sulfate.** The recovered calcium sulfate,

calcined calcium sulfate, and standard CaSO<sub>4</sub>·2H<sub>2</sub>O powder were examined by X-ray powder diffraction spectrophotometer. Figure 7 shows the 2θ values at 12, 22, 29, 32, and 34° that



**Figure 7.** X-ray diffraction spectra of (a) calcium sulfate<sub>(std)</sub>, (b) precipitated calcium sulfate, and (c) calcium sulfate<sub>(rec)</sub> after calcination at 700 °C.

correspond to the crystalline peaks of CaSO<sub>4</sub>·2H<sub>2</sub>O<sub>(std)</sub>, and the same peaks were also observed in the calcium sulfate recovered in the present investigation.<sup>13,14</sup> 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<sub>4</sub>·2H<sub>2</sub>O.

**3.8.2. 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<sub>4</sub>·0.2H<sub>2</sub>O. The calcium sulfate<sub>(rec)</sub> appeared to be a fine white powder that looked floury; 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).<sup>15</sup> 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.<sup>14</sup> Elongated calcium sulfate crystal growth was seen in the CaSO<sub>4</sub>·2H<sub>2</sub>O<sub>(std)</sub>, 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)<sup>13</sup> 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.<sup>14</sup> 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.

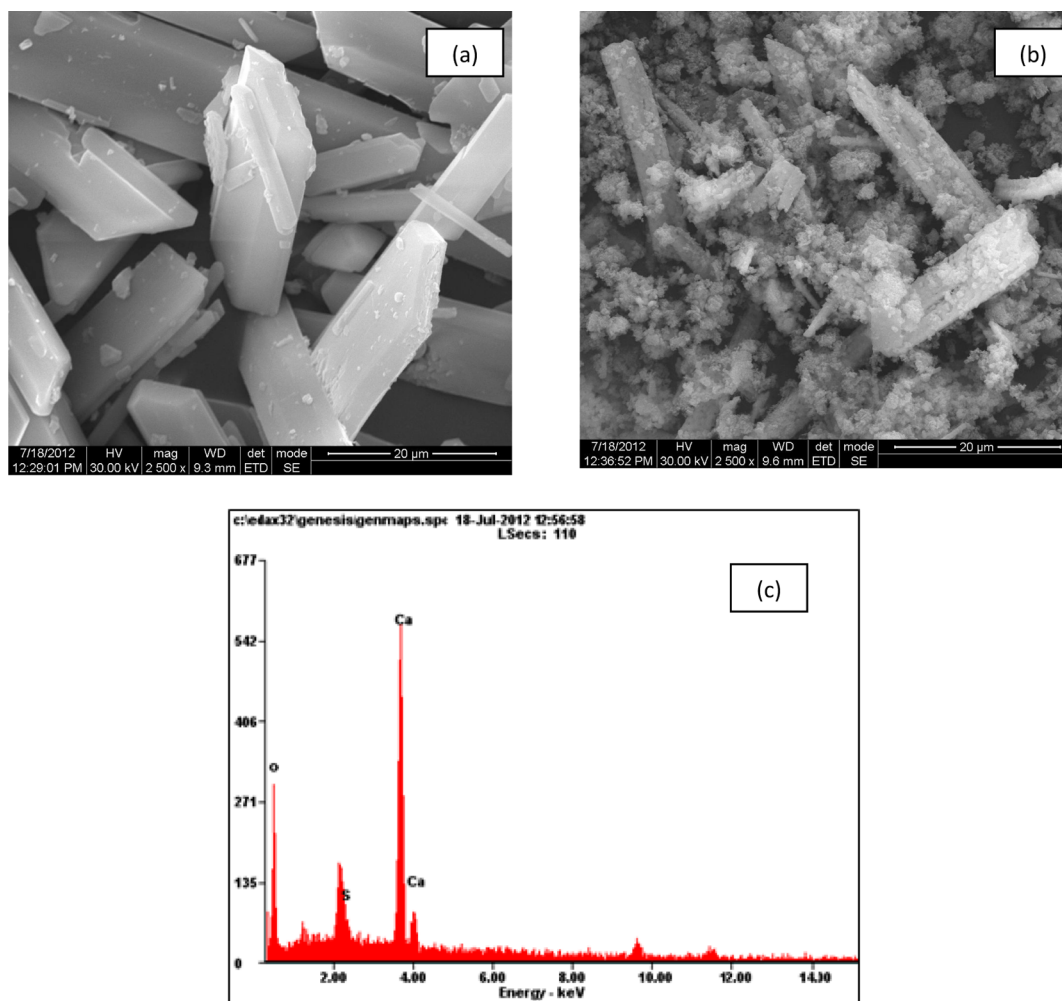


Figure 8. Scanning electron microscopy images of (a) calcium sulfate<sub>(std)</sub> and (b) calcium sulfate<sub>(rec)</sub>. (c) EDX spectrum of calcium sulfate<sub>(rec)</sub>.

**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

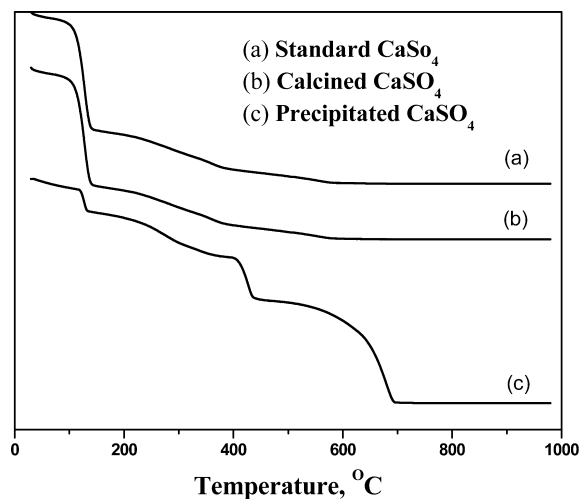


Figure 9. Thermogravimetry spectra of (a) calcium sulfate<sub>(std)</sub>, (b) calcined calcium sulfate<sub>(rec)</sub>, and (c) precipitated calcium sulfate.

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 H<sub>2</sub>O molecules from 2H<sub>2</sub>O molecules. The weight loss in the temperature range from 100 to 600 °C corresponds to the loss of water by 6.25% in CaSO<sub>4</sub> · 0.5 H<sub>2</sub>O.<sup>15,16</sup> 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<sub>(rec)</sub> imparted thermal stability. The average activation energies for the decomposition of standard calcium sulfate and calcium sulfate<sub>(rec)</sub> were found to be 2.81 and 15.07 KJ/mol, respectively, using the Arrhenius model.<sup>17</sup> The 5.36 fold increase in activation energy of calcium sulfate<sub>(rec)</sub> 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.**

Table 3. Comparison of Costs (in USD/kg ER) of the Present Process with Disposal onto Secure Landfill

mode of disposal	nature of consumables	cost on consumables (USD)	cost on recovery of NaCl and calcium sulfate (USD)	total cost on treatment (USD)
disposal onto secure landfill	landfill maintenance cost	0.11		0.11
present process	hydrogen chloride gas	0.049 <sup>a</sup>	0.02 <sup>d</sup>	0.034 [(a + b + c) – (d + e)]
	electrical energy	0.023 <sup>b</sup>		
	lime	0.0008 <sup>c</sup>	0.0192 <sup>e</sup>	

saturated ER solution + HCl gas  
→ precipitated sodium chloride  
+ residual solution of ER

$$1.32 \text{ kg} + 0.105 \text{ kg} \rightarrow 0.268 \text{ kg} + 1.157 \text{ kg} \quad (2)$$

The Na<sup>+</sup> ion mass balance is

$$0.126 \text{ kg} + 0 \text{ kg} \rightarrow 0.105 \text{ kg} + 0.021 \text{ kg} \quad (2i)$$

The Cl<sup>−</sup> ion mass balance is

$$0.216 \text{ kg} + 0.102 \text{ kg} \rightarrow 0.162 \text{ kg} + 0.156 \text{ kg} \quad (2ii)$$

The maximum precipitation of sodium chloride of 0.268 kg resulted from 1 L of saturated ER solution under the optimized conditions.<sup>6</sup>

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

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

$$1.157 \text{ kg} \rightarrow 0.905 \text{ kg} + 0.052 \text{ kg} + 0.2 \text{ kg} \quad (3)$$

The Na<sup>+</sup> ion mass balance is

$$0.021 \text{ kg} \rightarrow 0.001 \text{ kg} + 0.02 \text{ kg} + 0 \text{ kg} \quad (3i)$$

The Cl<sup>−</sup> ion mass balance is

$$0.156 \text{ kg} \rightarrow 0.124 \text{ kg} + 0.0315 \text{ kg} + 0 \text{ kg} \quad (3ii)$$

**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

$$0.905 \text{ kg} + 0.152 \text{ kg} \rightarrow 0.83 \text{ kg} + 0.227 \text{ kg} \quad (4)$$

The Ca<sup>2+</sup> ion mass balance is

$$0.0014 \text{ kg} + 0.0084 \text{ kg} \rightarrow 0.0326 \text{ kg} + 0.0528 \text{ kg} \quad (4i)$$

The SO<sub>4</sub><sup>2−</sup> ion mass balance is

$$0.1272 \text{ kg} + 0 \text{ kg} \rightarrow 0.0002 \text{ kg} + 0.127 \text{ kg} \quad (4ii)$$

**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)<sub>2</sub> and MgO, the Ca(OH)<sub>2</sub> was effective on the separation of sulfate ions from the acidified ER solution. The optimized process parameters for the recovery of SO<sub>4</sub><sup>2−</sup> 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<sub>(rec)</sub> was about 5 times greater than the surface area of calcium sulfate<sub>(std)</sub>. Thus, the calcium sulfate<sub>(rec)</sub> could be used as an adsorbent for the adsorption of aqueous dye. The calcium sulfate<sub>(rec)</sub> 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

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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<sub>sp</sub> = solubility product, (mol/L)<sup>2</sup>



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

## ■ REFERENCES

- (1) Kilic, O.; Kilic, A. M. Recovery of salt co-products during the salt production from brine. *Desalination* **2005**, *186* (1–3), 11–19.
- (2) Estefan, S. F.; Awadalla, F. T.; Yousef, A. A. Process technology for recovery of magnesia from brines. *Powder Technol.* **1980**, *27* (2), 233–240.
- (3) Drioli, E.; Curcio, E.; Criscuoli, A.; Profio, G. D. Integrated system for recovery of  $\text{CaCO}_3$ ,  $\text{NaCl}$ , and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  from nanofiltration retentate. *J. Membr. Sci.* **2004**, *239* (1), 27–38.
- (4) Cheng-ming, L.; Zhong-ming, H. U.  $\text{SO}_4^{2-}$  disposal process by calcium method. *China Chlor-Alkali* **2004**, *5*, 18–20.
- (5) Xiao-chun, S. Experiment of sulfate disposal by calcium chloride. *China Chlor-Alkali* **2000**, *5*, 10–11.
- (6) Boopathy, R.; Gnanamani, A.; Mandal, A. B.; Sekaran, G. A First Report on the Selective Precipitation of Sodium Chloride from the Evaporated Residue of Reverse Osmosis Reject Salt Generated from the Leather Industry. *Ind. Eng. Chem. Res.* **2012**, *51* (15), 5527–5534.
- (7) *Standards Methods for the Examination of Water and Waste Water*, 19th ed.; American Public Health Association: Washington, DC, 1998.
- (8) Alimi, F.; Elfil, H.; Gadri, A. Kinetics of the precipitation of calcium sulfate dihydrate in a desalination unit. *Desalination* **2003**, *157* (8), 9–16.
- (9) ASME *Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; American Society of Mechanical Engineers: New York, 1989.
- (10) Liu, S. T.; Nancollas, G. H. Linear crystallization and induction period studies of the growth of calcium sulfate dihydrate crystals. *Talanta* **1973**, *20*, 211–216.
- (11) Luo, K.; Li, C.; Xiang, L.; Li, H.; Ning, P. Influence of temperature and solution composition on the formation of calcium sulfates. *Particuology* **2010**, *8* (3), 240–244.
- (12) Hung, S. P.; Zhou, K. C.; Li, Z. Y. Inhibition mechanism of aspartic acid on crystal growth of hydroxyapatite. *Trans. Nonferrous Metal Soc. China* **2007**, *17* (3), 612–616.
- (13) Gominsek, T.; Lubej, A.; Pohar, C. Continuous precipitation of calcium sulfate dihydrate from waste sulfuric acid and lime. *J. Chem. Technol. Biotechnol.* **2005**, *80* (8), 939–947.
- (14) Yang, J. C.; Wuc, H. D.; Teng, N. C.; Ji, D. Y.; Lee, S. Y. Novel attempts for the synthesis of calcium sulfate hydrates in calcium chloride solutions under atmospheric conditions. *Ceram. Int.* **2012**, *38*, 381–387.
- (15) Sheikholeslami, R.; Ong, H. W. K. Kinetics and thermodynamics of calcium carbonate and calcium sulfate at salinities up to 1.5 m. *Desalination* **2003**, *157* (1–3), 217–234.
- (16) Sheikholeslami, R.; Lau, G. T. Effect of bacteria and salinity on calcium sulfate precipitation. *Desalination* **2012**, *287*, 301–309.
- (17) Kok, M. K. Use of thermal equipment to evaluate crude oils. *Thermochim. Acta* **1993**, *214* (2), 315–324.