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# Recovery of baking soda from reverse osmosis reject of desalination plant using carbon dioxide gas

A Aishwaryalakshmi[1]& K Palanivelu*[,1,2]

[1]Centre for Environmental Studies, College of Engineering Guindy, Anna University, Chennai, Tamil Nadu, India;
[2]Centre for climate change and disaster management, College of Engineering Guindy, Anna University, Chennai, Tamil Nadu, India.

E-mail: kpvelu@annauniv.edu

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The extraction of baking soda from the reverse osmosis (RO) reject of desalination plant using $CO_2$ gas has been studied. The novel idea of using amino acid additives to improvise the conventional Solvay process and thereby increasing the $Na^+$ recovery efficiency has been explored. Three amino acid additives namely Glycine, L-Arginine and L-Alanine are studied for their effect on increasing $Na^+$ recovery and the best suitable additive is selected. Necessary parameters governing the recovery such as concentration of amino acid, reaction temperature, flowrate of $CO_2$ and carbonation time have been optimized with a view to get a maximum recovery efficiency by the modified Solvay process. Under the optimized conditions maximum sodium recovery of 70% is obtained. The modified Solvay process has yielded a higher recovery efficiency compared to the conventional Solvay process (33%). Amino acid additive (alanine) has increased the conversion efficiency and has also helped in reducing the ammonia requirement of the process. The results obtained show a feasible way to protect our environment by utilizing the reject of the desalination plant and the industrial waste gas carbon dioxide in bicarbonate production.

**Keywords:** Alanine, Baking soda recovery, Carbon dioxide utilization, Modified Solvay process, RO reject brine

Carbon dioxide is the most widespread greenhouse gas that traps infrared radiation and converts it to heat, thereby raising the global temperature and contributing to climate change. At present, more than 80 per cent of the world's energy requirement is being met by the burning of fossil fuels[1].This has contributed to increased emission of greenhouse gases comprising mainly of carbon dioxide. Concentration of carbon dioxide in air has risen from 270 ppm during the pre- industrialization era, to the current level of about 415 ppm, resulting in 0.7 per cent rise in the global temperature over the last 140 years. The $CO_2$ concentration is steadily increasing at the rate of about 1.5 ppm per year[2].Existing techniques to sequester carbon dioxide are forestation, ocean fertilization, mineral carbonation, underground injection and deep ocean dump. There are ecological concerns, regarding the consequences of storing carbon dioxide in the ocean and in the geological formations as well as the extensive energy required to implement the existing carbon dioxide sequestration techniques[3]. Hence the usage of carbon dioxide in the production of valuable chemicals, can be a better solution to reduce the carbon dioxide concentration in our atmosphere[4].

Desalination has become the need of the hour to meet the high demand for portable water, owing to a rapid growth in population as well as climate change due to varied rainfall. The main issue concerned withthe desalination plant is the reject brine (which is highly concentrated) and is often discharged into the sea[5]. This has rising environmental concerns because the untreated brine when discharged may lead to the destabilization of sea water and many ecological disturbances[6].Conventional methods like disposal through deep well injection, land disposal and evaporation ponds are accompanied by many drawbacks[7]. Thus the processing of brine with carbon dioxide to extract the salts can be a good alternative solution for this problem[4]. This has a dual benefit of reducing the $CO_2$ concentration in the atmosphere and the production of useful carbonate product. The chemical reaction of reject brine with carbon dioxide is believed to be effective, economic and eco-friendly[8].

Solvay process was primarily developed for the manufacture of sodium bicarbonate, where a concentrated brine solution on reaction with ammonia and carbon dioxide formed ammonium bicarbonate, which on reaction with sodium chloride yielded an insoluble precipitate of sodium bicarbonate and soluble ammonium chloride according to the following equations[1].

$$NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl \quad \ldots(1)$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O \quad \ldots(2)$$

Solubility of sodium bicarbonate plays a prime role in the success of the process. Hence it is mandatory to optimize the parameters which influence the solubility and to maintain it as low as possible to achieve a maximum conversion[9].

The conventional Solvay process has a very low efficiency of (33 to 38%). The main reason for this shortfall can be the high concentration of ammonia required[2]. Exposure to high concentration of ammonia instigates several environmental and health effects like burning of skin, nose, throat and respiratory tract, alveolar and bronchiolar edema and respiratory failure[10]. The prime role played by ammonia is to buffer the reaction to a basic pH, or else the reaction would take over an acidic phase and hinder the precipitation of sodium bicarbonate[11]. Recovery of ammonia is an energy intensive step and this further adds to the cost of the process[12]. The aim of the present study, therefore, is to modify the Solvay process to improve the efficiency in terms of sodium recovery and to reduce the drawbacks associated with the requirement of high concentration of ammonia with the use of suitable additives.

A solvent to be selected for $CO_2$ absorption must possess the following characteristics- high absorption, fast reaction kinetics, low degradation rate, low regeneration energy and the ability to handle large amounts of exhaust streams[13]. Amines can be used as additives to improve the efficiency of the conventional Solvay process, but their usage is associated with problems like limited cyclic $CO_2$ loading capacity, high equipment corrosion rate, high energy consumption for regeneration, solvent losses by evaporation and degradation in an oxygen rich atmosphere[14]. Hence, amino acid is proposed in this study. The properties of amino acid which make them competent over amines are their higher stability towards oxidative degradation, high chemical reactivity with carbon dioxide, low vapor pressure, and their ability to form solid precipitate when absorbing $CO_2$[15]. Thus the present work was mainly to improve the efficiency of the conventional Solvay process in terms of sodium recovery by the use of suitable amino acid additives and to reduce the ammonia requirement. When this process is carried out using $CO_2$, it will have dual benefit of reduction in the $CO_2$ concentration as well as the production of useful bicarbonate.

## Experimental Section

### Materials

All the chemicals used were of analytical grade. The RO reject was collected from the desalination plant situated in Chennai, Tamil Nadu, India and the sea water from Chennai coast. Ammonia solution with 30% w/v $NH_3$, purchased from Merck, India, was employed to ammoniate the effluent. Analytical grade carbon dioxide gas, 99%, was purchased from Supreme Engineering Services; India, and used as a source of carbon dioxide. Amino acids L-Alanine, L-Arginine and Glycine were used as purchased from Merck, India. All experimental solutions were prepared using demineralized water.

### Apparatus and procedure

A carbon dioxide gas absorption reactor made of Plexiglas with an inner diameter of 90 mm and an overall height of 170 mm was used in this study as depicted in Fig 1. RO reject (300 mL) of the desalination plant was ammoniated and amino acid additive was added to it. This mixture was then exposed to a continuous flow of carbon dioxide gas at a certain flow rate and a fixed time. Carbon dioxide gas was passed through a special feeding tube with a diffuser at the end to generate fine bubbles and ensure intense mixing. The tube was extended to the bottom of the reactor tank. Temperature of the reaction was maintained by using a water jacket facility in which low temperature was maintained by circulating cold

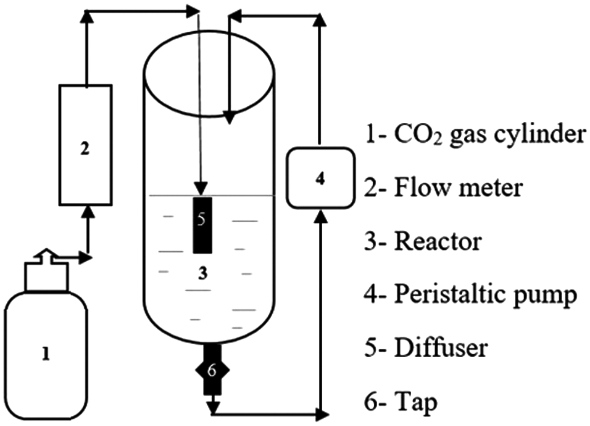

Fig. 1 — Carbon dioxide capture apparatus

water at the temperature of 15°C around the reactor. Similarly high temperature was maintained by circulating hot water at the temperature of 40°C around the reactor. A peristaltic pump was used to recycle the contents as well as to enhance mixing. A tap provided at the bottom was used to collect the solid contents after the reaction.

### Analytical techniques

At the end of each experiment, the reactor contents were drained from the reactor and filtered. The precipitate recovered was dried in an oven at 105°C for a period of 1 h and then used for SEM analyses. The SEM images were taken by SEM-JSM 6360 with an ion sputter coated with gold target technique. The filtrate and the precipitate were analyzed for sodium using a flame spectrophotometer (Systronics FPM 128). The precipitate was analyzed for the estimation of sodium carbonate and sodium bicarbonate by the alkalinity titration method[16]. The $NH_4^+$ was measured by the phenate method using a spectrophotometer at 640 nm (SystronicsVisiscan 167) [17].

## Results and Discussion

The present study consisted of several batch experiments for the selection of suitable amino acid additive which could improve the efficiency of the modified Solvay process for the recovery of $Na^+$ from the reject brine in the form of bicarbonate using carbon dioxide.

### Characterisation of RO reject

The sea water and the reject collected from the desalination plant for the present study had the characteristics as furnished in Table 1

Table 1 — Characteristics of sea water and RO reject

| Parameter | Sea Water (mg/L) | RO Reject (mg/L) |
|---|---|---|
| Sodium | 13400 | 25750 |
| Chloride | 16400 | 32967 |
| Calcium | 420 | 760 |
| Magnesium | 1385 | 2089 |
| Carbonate | 89 | 190 |
| Bicarbonate | 142 | 320 |
| Total solids | 40500 | 74020 |
| Total dissolved solids | 33400 | 70140 |
| Total suspended solids | 7100 | 3880 |
| Electrical conductivity(mS/cm) | 50.10 | 70.50 |
| Salinity | $37230\times10^3$ | $54309\times10^3$ |
| *p*H | 8.0 | 8.5 |

[a] All values except *p*H and Electrical conductivity are in mg/L.

Characterization reveals that the sea water and the reject are slightly alkaline and the RO reject contain high sodium content and the sodium content of the reject is approximately twice that of sea water

### Identification of suitable amino acid additive

In this study, amino acids namely Glycine, L-Arginine and L-Alanine were investigated for $CO_2$ capture and sodium bicarbonate recovery from the RO reject. The experimental conditions under which the reactions were conducted:Volume of RO Reject – 300 mL; $Na^+$ in the RO Reject –25,750 mg/L; $CO_2$ Gas Flow Rate – 2 L/min; carbonation time- 180 min; Temperature – 27°C. The sodium recovery for the three amino acids when the ammonia concentration was varied from 2 M to 3 M is presented in Fig. 2.

The sodium recovery and the quantity of precipitate recovered were comparatively high when alanine (amino acid) was used as the additive. The sodium recovery was nearly 56% when 2.3 moles of ammonia and 0.01 moles of alanine were used. Further characterization of the precipitate showed that the sodium and carbonate content of the precipitate was comparatively higher. The recovery was higher when 2.3 moles of $NH_3$ was used for all the three amino acids considered. This shows that the use of amino acid additive alanine has reduced the requirement of ammonia by 1 mole, from (3.3 moles [1] to 2.3 moles) further it has increased the efficiency of the Solvay process with respect to sodium recovery. From these data obtained, it can be concluded that alanine is the appropriate amino acid additive for Solvay process. Hence detailed optimization was carried out using alanine as the additive.

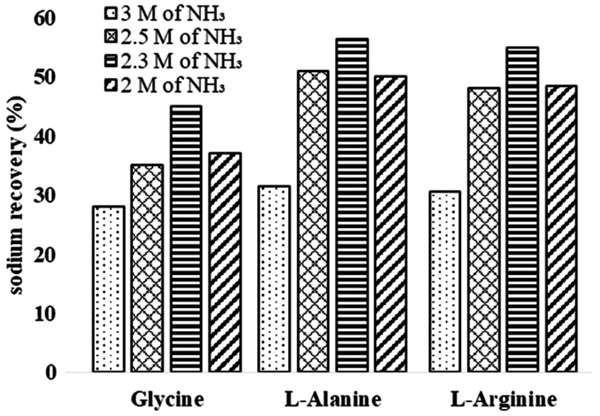

Fig. 2 — Comparative analysis of sodium recovery at different $NH_3$ concentrations

## Optimisation of process parameters

### Effect of carbon dioxide gas flow rate

The reactor contents were kept in the mole ratio of [$Na^+$: $NH_3$: Amino acid] -1:2.3:0.01 and the flow rate of $CO_2$ gas was varied from 1.2 L/m to 2 L/m for a period of 180 min at room temperature (27°C). A plot of $Na^+$ removal percentage as a function of the gas flow rate is shown in Fig. 3(a). As the $CO_2$ gas flow rate increased, the $Na^+$ recovery also increased and the maximum recovery was obtained at a flow rate of 1.6 L/m. On further increase of flow rate the $Na^+$ recovery and the precipitate yield got reduced. This clearly shows that at higher flow rates the diffusion of $CO_2$ gas in the solution reduced and resulted in reduced conversion efficiency[18]. Thus 1.6 L/m was taken as the optimum flow rate for $CO_2$ gas with a $Na^+$ recovery of nearly 62%.

### Effect of carbonation time

Subsequent studies were performed to evaluate the effect of carbonation time on the recovery of $Na^+$ from the reject brine. The carbonation time of the reaction was varied from 80 to 180 minutes, under identical conditions, that is, mole ratio of [$Na^+$: $NH_3$: Amino acid] -1:2.3:0.01, flow rate of $CO_2$ gas as 1.6 L/m at room temperature. The $Na^+$ recovery was found for each case and the results are provided in Fig. 3(b). Initially as the carbonation time increased the recovery % also increased and reached a maximum of nearly 67% at 150 min. However, with further increase in the carbonation time, the $Na^+$ ion conversion efficiency decreased, since the equilibrium of ammonium carbonate approached in the equations (3 and 4)[19,20]. At the beginning of the conversion, the concentration of ammonium carbonate was predominant, while further carbonation has lead to the formation of ammonium bicarbonate followed by sodium bicarbonate[9]. Hence the optimum carbonation time was taken as 150 min.

$$CO_2 + 2NH_3 \rightarrow NH_2COO^- + NH_4^+ \quad \ldots(3)$$

$$NH_2COO^- + H_2O \rightarrow NH_3 + HCO_3^- \quad \ldots(4)$$

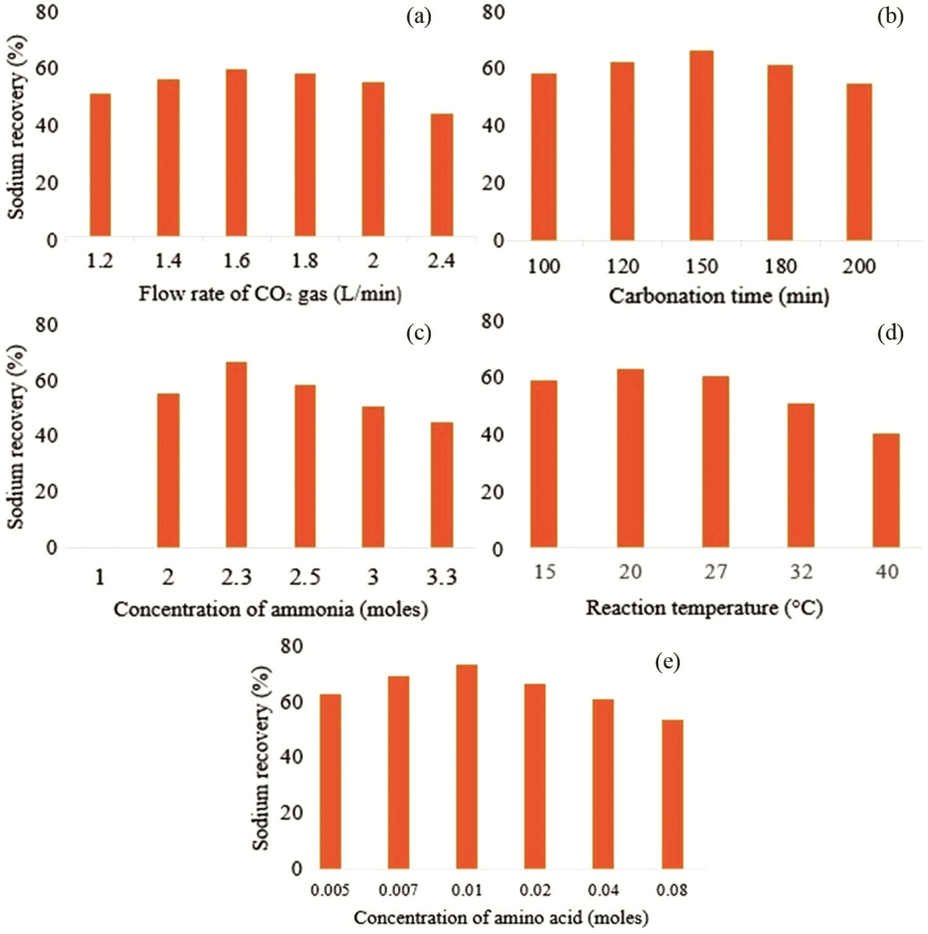

Fig. 3(a) — $Na^+$ recovery percentage as a function of $CO_2$ gas flow rate, (b) Effect of carbonation time, (c) Effect of ammonia concentration, (d) Effect of reaction temperature, (e) Effect of amino acid (alanine) concentration

$$NH_4^+ + HCO_3^- \rightarrow NH_4HCO_3 \quad \ldots(5)$$

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl \quad \ldots(6)$$

### Effect of ammonia concentration

The ammonia concentration for the reaction was varied from 1 to 3 moles, keeping all other parameters constant, the $Na^+$ ion recovery was found for each case and the results are depicted in Fig. 3(c). On reducing the ammonia concentration the recovery of sodium increased and it has reached a maximum of nearly 67% for 2.3 mole of ammonia. On further reduction, the yield got reduced, because lack of ammonium hydroxide has obstructed the precipitation of sodium bicarbonate due to the acidic nature of the reactor content[21]. Thus the optimized concentration of ammonia was taken as 2.3 moles. The addition of amino acid additive alanine has helped to reduce the quantity of ammonia required for the Solvay process from 3.3 moles(conventional Solvay process, without the addition of amino acids)[2] to 2.3 moles (using alanine) and has also increased the sodium recovery% to two times. Thus, this study proves that the use of amino acid additive alanine has reduced the ammonia requirement with increased sodium recovery from 33 to 67%.

### Effect of alanine concentration

The alanine concentration for the reaction was varied from 0.005 to 0.080 moles, under identical conditions, that is, Mole Ratio [$Na^+$: $NH_3$] -1:2.3, flow rate of $CO_2$ gas as 1.6 L/m at room temperature for a reaction time of 150 min. A plot of $Na^+$ removal percentage as a function of alanine concentration is presented in Fig. 3(d). The highest recovery% was obtained when 0.01 moles of Alanine was used. Amino acids dissolved in water are in a zwitterion form, which means that the amino group is protonated and hence less reactive towards $CO_2$ at low *p*H[22]. In order to activate the amino group, certain amount of ammonia was added into the aqueous solution to create the alkaline medium[23]. On further increase of alanine content, the yield and the sodium recovery% reduced due the low *p*H (less than 7) conditions that prevailed. This shows that the amino acid additive is required only in lesser concentration (0.01 mole) to give a higher yield as observed by other researchers[24].

### Effect of reaction temperature

The carbonation has been investigated at different reaction temperatures from 15 to 35°C with the mole Ratio of [$Na^+$: $NH_3$: Amino acid] -1:2.3:0.01, and the carbon dioxide gas flow rate of 1.6 L/min for a period of 150 min. The temperature of the reaction was maintained using a water jacket facility. A plot of $Na^+$ removal percentage as a function of alanine concentration is presented in Fig. 3(e).The $CO_2$ capture increased with decreasing the temperature since the solubility of $CO_2$ gas increases with decreasing the temperature. The optimum temperature observed in this study is 20°C. According to (Zhu.*et al*. 2013) the temperature recommended is 19.3°C. Lower the reaction temperature is, the less stripping of ammonia and more stable is the reaction inside the reactor[19]. On further increase of temperature, the sodium recovery efficiency got reduced as reported above.

### Characterization of the recovered precipitate

Precipitation of sodium bicarbonate was carried out under the optimized reaction conditions (mole Ratio of [$Na^+$: $NH_3$: Amino acid] -1:2.3:0.01, reaction temperature of 20°C, flow rate of the $CO_2$ gas of 1.6 L/min, and the carbonation time of 150 min). The precipitate was dried at 105°C for an hour and then taken for carbonate and bicarbonate analyses by alkalinity titration method. Nearly 40% of bicarbonate and 60% carbonate were found in the precipitate at the optimized conditions. It is clear that the precipitate formed contains a mixture of sodium carbonate and sodium bicarbonate. On further prolongation of the carbonation time to 190 min the bicarbonate content of the precipitate got increased to nearly 90%. The bicarbonate and carbonate content of the precipitate for different carbonation time and the variation of *p*H with respect to the carbonation time obtained from the reaction is shown in Fig. 4. From the Fig. 4, it is clear that as the carbonation time increased from 120 to 190 min, the *p*H of the solution has decreased from 10.2 to 8.5. Initially at 120 min the carbonate content of the precipitate was high nearly 80%, but slowly on prolongation of the time from 120 to 190 min the bicarbonate content of the precipitate has increased.

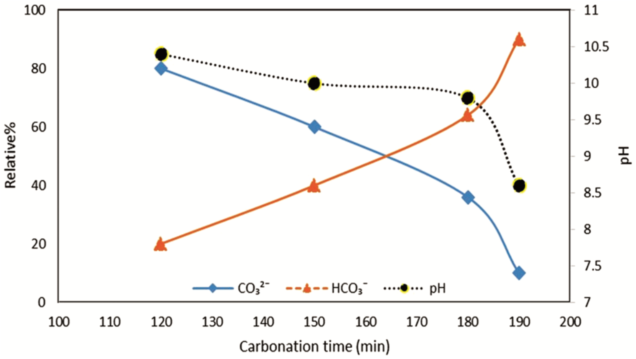

Fig. 4 — Speciation of carbonates and bicarbonates

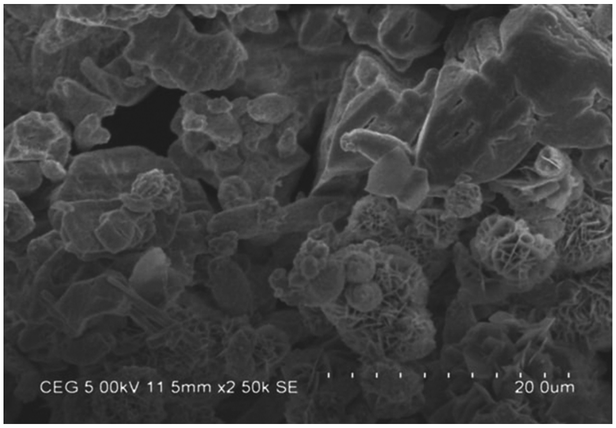

Fig. 5 — Enlarged SEM images of sodium bicarbonate and sodium carbonate of the recovered precipitate of modified Solvay process

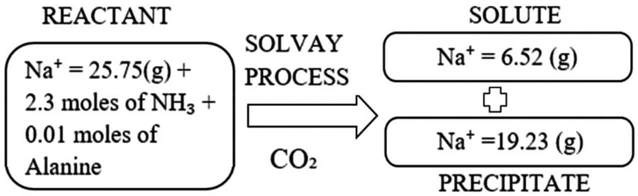

Fig. 6 — Mass balance of modified Solvay process for the RO reject

A maximum sodium bicarbonate of 90% was obtained at 190 min in the isolated precipitate.

#### SEM analysis

The scanning electron microscopic image of the recovered precipitate in Fig. 5, revels needle like structures which confirms the presence of sodium bicarbonate and sodium carbonate.[25, 26]

#### Mass balance for the removal of $Na^+$

Under the optimized conditions, the maximum recovery of sodium from 1litre of the RO reject of desalination plant was 19.23 g as depicted in Fig. 6. The precipitate contains nearly 70% of sodium. Under the carbonation time of 190 min the bicarbonate recovery was found to be 90%. This proves that the recovered precipitate is mainly of sodium bicarbonate. The isolated precipitate can be easily converted to sodium carbonate by simple heating as per Equation (2), if needed.

## Conclusion

In this study amino acid additives were used to improve the efficiency of the conventional Solvay process to recover baking soda from the RO reject of desalination plant. Amino acid additives Glycine, L-Alanine, L-Arginine, were screened and the appropriate amino acid alanine was selected. Under the optimized conditions of flow rate of 1.6 (L/min) and carbonation time of 150 min using 2.3 moles of ammonia and 0.01 moles of alanine at the temperature of 20 (°C) the efficiency of the modified Solvay process for sodium recovery was ≈ 70%. Thus, this study proves that the use of amino acid additive alanine has reduced the ammonia requirement by nearly 1 mole and also has increased the sodium recovery% twice, compared to the conventional Solvay process. The alanine concentration required for this process is also very less (0.01 moles). From this study, it is clear that amino acids can be used as additives to improve the efficiency of Solvay process and to reduce the ammonia required for Solvay process. This process developed has a dual environmental benefit of reducing the $CO_2$ gas in the atmosphere and safe disposal of RO reject.

## Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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