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Recovery of Sodium Bicarbonate from Textile Dye Bath Effluent Using Carbon Dioxide Gas

V. Krishnaveni and K. Palanivelu*

Centre for Environmental Studies, Anna University, Chennai 600 025, India

ABSTRACT: Water pollution from textile industries is caused by the disposal of brackish dye bath effluent, containing a high concentration of sodium chloride. The targeted removal of Na^+ from the effluent using carbon dioxide would provide environmental benefits, both in reducing the environmental impact of disposal and in the production of valuable bicarbonate product. This paper describes a method based on the Solvay process for converting Na^+ in the saline effluent to a useful product. The production of sodium bicarbonate from the effluent using carbon dioxide has been elucidated in a batch mode. The influence of various operating conditions including concentration of ammonium hydroxide, reaction temperature, carbonation time, and the flow rate of carbon dioxide gas on the bicarbonate yield was analyzed. Moreover, the efficiency of struvite precipitation in the removal of NH_4^+ from the resulting solution of the modified Solvay process was evaluated. The highest Na^+ removal of 38% of the saline effluent and the best removal efficiency of 80% for NH_4^+ of the resulting solution were obtained. The results obtained show a feasible way to protect our environment by utilizing the brackish dye bath effluent and the industrial waste gas carbon dioxide in bicarbonate production.

1. INTRODUCTION

Carbon dioxide is the most prevalent greenhouse gas that traps heat and raises the global temperature, contributing to climate change. There are various sources of carbon dioxide emissions, which are dominated by combustion of liquid, solid, and gaseous fuels.[1] Carbon dioxide is present in the atmosphere with a volumetric concentration of 0.039%, as of July 2012. There are increasing concerns for global warming and heightened interest worldwide for reducing the emissions of greenhouse gases, particularly carbon dioxide.[2] Existing techniques to sequester carbon dioxide from power plants are forestation, ocean fertilization, mineral carbonation, underground injection, and direct ocean dump.[3] 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.[4] Proper use of carbon dioxide for chemical processing can add value to carbon dioxide gas disposal by making industrially useful carbon-based products. Carbonation is capable of binding a significant amount of carbon dioxide. New technologies and methods, which involve the use of the carbon dioxide in the production of carbonate materials, offer a new route to reduce the carbon dioxide concentration in our atmosphere.[5]

Textile dyeing industries discharge effluent ranging between 100 and 200 m^3/t of production.[6] During the reactive dyeing of cotton, salts including sodium chloride (25−80 kg/m^3)[7] are placed in a dye bath to aid the exhaustion of various dyes onto the fabric, while bases are added to raise the pH from 7 to 11 to achieve fixation. Afterward, the dye bath spent liquor is discharged with almost all the salt after the removal of color. Consequently, many raw materials are lost in the waste stream ending up in the environment as pollutants. Conventional methods for brine management are disposal via deep well injection, land disposal, evaporation ponds, and mechanical or thermal evaporation.[5] Evaporation ponds are widely used for brine disposal. Although high temperature and consequently high evaporation rates speedup water reduction, evaporation ponds still suffer from many drawbacks including the need for huge areas and the possibility of contaminant leakage into soil and groundwater.[5] An alternative approach is further processing the effluent to extract all the salts.[8,9] This has the advantages of being environmental friendly and for the production of valuable carbonate chemicals.

The present work evaluates a novel approach that utilizes a chemical reaction based on the Solvay process for converting the industrial waste gas carbon dioxide to a valuable bicarbonate product using textile dye bath effluent. In the process, carbon dioxide is passed into an ammoniated brine solution, which reacts with sodium chloride to form a precipitate of sodium bicarbonate and a soluble ammonium chloride[10] according to the following equation:

$$NaCl + NH_4OH + CO_2 \rightarrow NaHCO_3\downarrow + NH_4Cl \quad (1)$$

The focus of the study was on the recovery/conversion of Na^+ in the textile dye bath effluent to sodium bicarbonate using carbon dioxide. The process involves the absorption of carbon dioxide in an ammoniated dye bath to give a valuable product, sodium bicarbonate. The process has the dual benefit of decreasing Na^+ in the textile dye bath effluent and reducing carbon dioxide emissions to the atmosphere through the valuable bicarbonate production.[10] The potential of struvite precipitation on the removal of NH_4^+ as MAP (magnesium ammonium phosphate hexahydrate; $MgNH_4PO_4{\cdot}6H_2O$) using Mg^{2+} and PO_4^{3-} from the resulting solution of the modified Solvay process was also evaluated.

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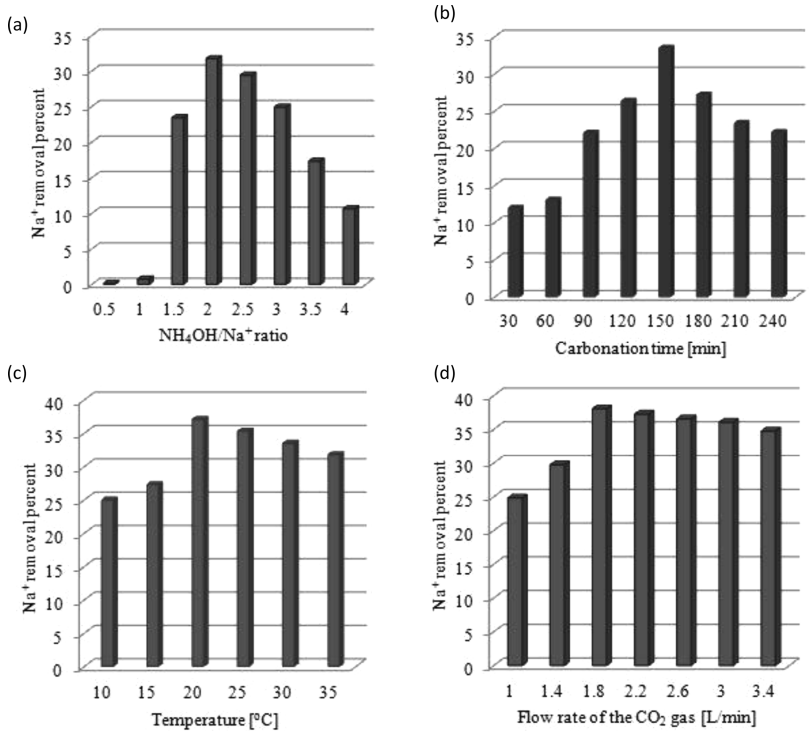

Figure 1. Effect of (a) NH_4OH/Na^+ molar ratio (experimental conditions: reaction time, 120 min; reaction temperature, 30 °C; CO_2 gas flow rate, 2 L/min), (b) carbonation time (experimental conditions: NH_4OH/Na^+ ratio, 2; reaction temperature, 30 °C; CO_2 gas flow rate, 2 L/min), (c) reaction temperature (experimental conditions: NH_4OH/Na^+ ratio, 2; carbonation time, 150 min; CO_2 gas flow rate, 2 L/min), and (d) flow rate of CO_2 gas (experimental conditions: NH_4OH/Na^+ ratio, 2; carbonation time, 150 min; reaction temperature, 20 °C) on Na^+ removal efficiency.

2. MATERIALS AND METHODS

2.1. Materials. All chemicals used were of analytical grade. The textile dye bath effluent was collected from the textile dyeing industry situated in Erode, Tamil Nadu, India. Ammonia solution with 25% w/v NH_3, purchased from Merck, India, was employed to ammoniate the effluent. Research grade carbon dioxide gas, 99.9%, was purchased from Supreme Engineering Services; India, and used as a source of carbon dioxide. Magnesium chloride hexahydrate and dipotassium hydrogen phosphate were used as received from Merck, India, and fed as a source of Mg^{2+} and PO_4^{3-}, respectively. Sodium hydroxide purchased from Merck, India, was used to control the pH of the solution. All experimental solutions were prepared using demineralized water.

2.2. 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 the study, where 500 mL of ammoniated dye bath effluent was 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 endure intense mixing. The tube was extended to the bottom of the reactor tank. The reactor was equipped with several ports for gas and liquid feeds. A peristaltic pump was used to recycle the ammoniated effluent as well as to enhance mixing.

In the struvite precipitation process, 50 mL of the supernatant of the modified Solvay process in a 250 mL of conical flask was mixed with the measured salts of magnesium chloride hexahydrate and dipotassium hydrogen phosphate, and the solution pH was adjusted to 9 by adding sodium hydroxide solution. Mixing was accomplished through a Shaker run at 130 rpm for 3 h, and the supernatant was decanted into a bottle and then analyzed for NH_4^+ of the supernatant. The sodium bicarbonate and the struvite precipitates were dried at 105 °C for an hour and preserved for further characterization. All the experiments were carried out in duplicate.

2.3. Analytical Techniques. At the end of each experiment, the reactor contents were drained from the reactor and filtered. The solids were kept in an oven at 105 °C for a period of 1 h and then used for SEM, XRD, and FTIR analyses. The filtrate was analyzed for Na^+ in the saline effluent using a flame spectrophotometer (Systronics FPM 128), while the solid was analyzed for the estimation of sodium carbonate and sodium bicarbonate by the alkalinity titration method.[11] The NH_4^+ was measured by the phenate method[12] using a spectrophotometer (Systronics Visiscan 167). X-ray diffraction patterns were collected using a Philips X'pert MPD system with Cu $K\alpha_1$ radiation (λ = 1.54060 Å) in a 2θ range of 5−84° at ambient temperature. The SEM images were taken by SEM-JSM 6360 with ion sputter coated with gold target technique. Fourier transform infrared analysis of the precipitate was carried out in a PerkinElmer GX spectrophotometer. The spectra were recorded in the range of 400−4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellets.

3. RESULTS AND DISCUSSION

The present study consisted of several batch experiments to determine the efficiency of the modified Solvay process for the removal of Na^+ from the effluent in the form of sodium bicarbonate using carbon dioxide.

3.1. Recovery of Na^+ from Textile Effluent. *3.1.1. Characterization of Untreated Textile Effluent.* The effluent collected during the study had the following composition

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(mg/L): COD, 1588; TDS, 86701; Na^+, 27070; Cl^-, 41635. The pH and EC of the effluent were 10.6 and 102 mS/cm, respectively. Characteristics of the effluent show a higher concentration of Na^+ and greater values for TDS, salinity, and COD against allowable limits for the effluent disposal.

3.1.2. Effect of Concentration of Ammonium Hydroxide on Na^+ Removal Efficiency. The role of ammonium hydroxide in the carbonation reaction is important because the ammonium hydroxide buffers the solution at the basic pH.[5] Lack of ammonium hydroxide will obstruct the precipitation of sodium bicarbonate due to the acidic nature of the reactor content.[5] Experiments were conducted with different concentrations of ammonium hydroxide from 1.2 to 9.6 M in the dye bath solution at a reaction temperature of 30 °C and carbon dioxide gas flow rate of 2 L/min for a period of 120 min. The results depicted in Figure 1a indicate that the Na^+ removal efficiency increased with increasing NH_4OH/Na^+ molar ratio and attained a maximum Na^+ removal of 31.7% at a NH_4OH/Na^+ ratio of 2. The removal efficiency of Na^+ was observed to decrease with further increase in the NH_4OH/Na^+ ratio because the excess of ammonium hydroxide reacted with sodium bicarbonate to form an ammonium carbonate. The solubility of sodium chloride was reduced at a higher concentrations of ammonium hydroxide according to a study conducted by Jibril and Ibrahim.[13]

3.1.3. Effect of Carbonation Time on Na^+ Removal Efficiency. Subsequent studies were performed to evaluate the effect of carbonation time on the conversion of Na^+ in the textile effluent. The carbonation time was varied from 30 to 240 min under identical conditions, that is, reaction temperature of 30 °C, NH_4OH/Na^+ ratio of 2, and the gas flow rate of 2 L/min. The results illustrated in Figure 1b indicate that there was a negligible conversion in the first 30 min and Na^+ conversion slowly reached the maximum of 33.4% in 150 min. In the early carbonation period, the Na^+ removal percentage increased due to a higher driving force, resulting from the absorption enhanced reaction between carbon dioxide gas and ammonium hydroxide.[13] However, with further increase in the carbonation time, the Na^+ conversion efficiency decreased, since the equilibrium of ammonium carbonate approached in the reactions (eqs 2 and 3). Jibril and Ibrahim[13] reported that at the beginning of the conversion, the concentration of ammonium carbonate was predominant, while further carbonation leads to the formation of ammonium bicarbonate followed by sodium bicarbonate, according to the following reactions:

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

$$NH_2COO^- + H_2O \rightarrow NH_3 + HCO_3^- \quad (3)$$

$$NH_4^+ + HCO_3^- \rightarrow NH_4HCO_3 \quad (4)$$

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl \quad (5)$$

3.1.4. Effect of Temperature and Flow Rate of Carbon Dioxide Gas on Na^+ Removal Efficiency. The carbonation has been investigated at different reaction temperatures from 10 to 35 °C with NH_4OH/Na^+ ratio of 2 and the carbon dioxide gas flow rate of 2 L/min for a period of 150 min. From the results summarized in Figure 1c, it can be seen that the minimum Na^+ in the filtrate (37% of Na^+ removal) was observed at the reaction temperature of 20 °C. The increase in carbon dioxide absorption capacity in the ammoniated brine solution is attributed to the precipitation of sodium bicarbonate. At a higher reaction temperature, the conversion of Na^+ to sodium bicarbonate was less because the absorption of carbon dioxide gas decreased with the increase in temperature. It was reported that the reaction is exothermic with a negative heat of reaction, up to a temperature of 41 °C.[5] Beyond this temperature, the reaction becomes endothermic.

Subsequent experiments were conducted to test the influence of the gas flow rate on the removal of Na^+ from the effluent. The flow rate of the carbon dioxide gas was varied between 1 and 3.5 L/min. A plot of Na^+ removal percentage as a function of the gas flow rate is shown in Figure 1d. The carbon dioxide gas flow rate of 1.8 L/min was found to be the optimum for the maximum Na^+ removal of 38%. The conversion efficiency of Na^+ to sodium bicarbonate was increased by increasing the flow rate of carbon dioxide gas, but at a higher flow rate of the gas, the removal of Na^+ decreased because the diffusivity of the gas decreased with an increase in the flow rate of the gas.[14]

3.1.5. Characterization of the Carbonate Precipitate. Precipitation of sodium bicarbonate was carried out under the optimized reaction conditions (NH_4OH/Na^+ ratio of 2, reaction temperature of 20 °C, flow rate of the CO_2 gas of 1.8 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. The 97% sodium bicarbonate and only 3% sodium carbonate were found in the precipitate at the optimized conditions. It is clear that the precipitate formed mainly consists of sodium bicarbonate.

3.1.5.1. FTIR Analysis. Much understanding of the molecular structure of a material can be readily obtained through its vibration spectra. The FT-IR spectrum of the solid presented in Figure 2a, matched well with the spectrum found in the literature.[15] The prominent peaks at 1318 cm^{-1} for sodium

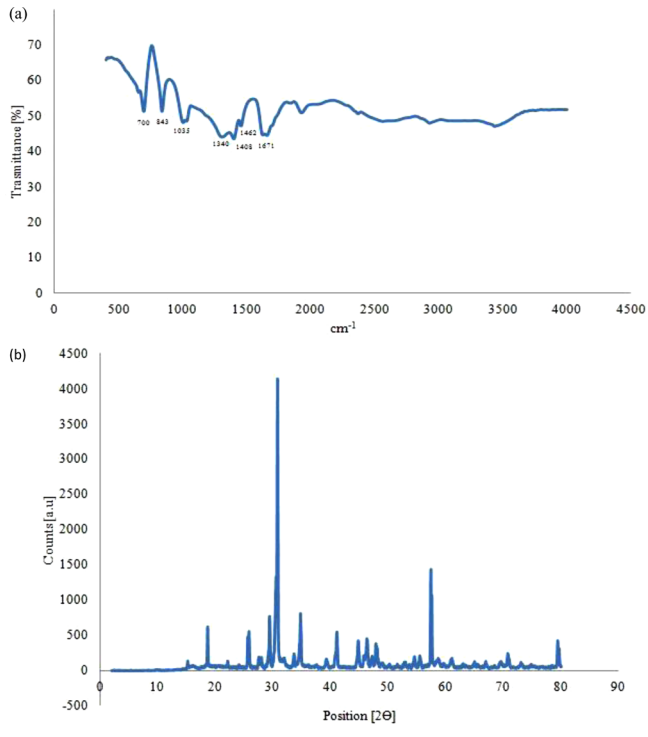

Figure 2. (a) FTIR and (b) XRD spectra of the sodium bicarbonate precipitate.

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bicarbonate and at 1405 cm^{-1} for sodium carbonate were due to the carbonate asymmetric stretching. The partial decomposition of the sodium bicarbonate resulted in the formation of sodium carbonate. The FTIR peaks indicate the formation of sodium bicarbonate with negligible amount of sodium carbonate. The band at 1032 cm^{-1} was assigned to the symmetric stretching mode of the carbonate unit.[16] The IR bands observed at 1461 and 1659 cm^{-1} were assigned to this vibration mode. The occurrence of the peaks at 842, 1032, 1318, and 1659 cm^{-1} suggest the presence of sodium bicarbonate.[17] The combination of peaks at 1032, 1318, and 1659 cm^{-1} have been previously assigned to the sodium bicarbonate.[18]

3.1.5.2. XRD and SEM Analysis. Sodium bicarbonate was represented by the diffraction lines at 15.16, 18.66, 22.06, 25.80, 27.64, 29.38, 30.80, 33.60, 34.78, and 39.20 (degree 2θ).[17] The XRD pattern (Figure 2b) of the precipitate obtained resembled that of the published result[19] for the sodium bicarbonate. Besides the scanning electron micrograph of the solid (Figure 3) shows a needle type structure similar to the structure of a pure sodium bicarbonate.[5]

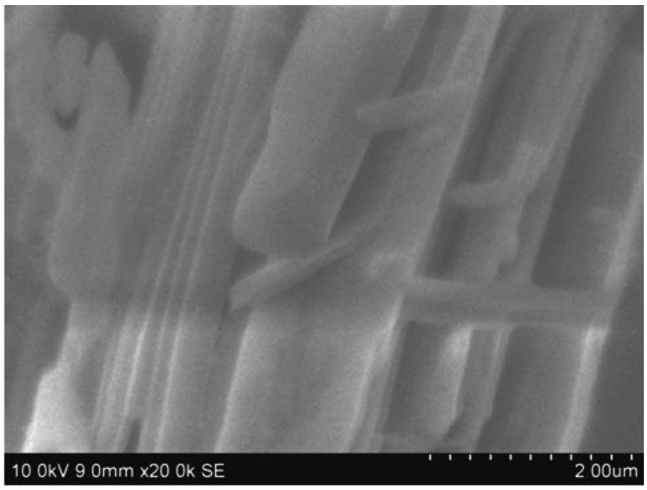

Figure 3. SEM of the sodium bicarbonate precipitate.

3.1.6. Mass Balance for the Removal of Na^+. Under the optimized conditions, the maximum conversion of sodium chloride from 1 L of dye bath to sodium bicarbonate was 37.61 g (Figure 4). Following the precipitation of sodium bicarbonate, the resulting solution was taken for NH_4^+ estimation. This was found to be 35 g/L in the resulting solution.

3.2. Recovery of NH_4^+ from the Supernatant of Modified Solvay Process. The regeneration of NH_4^+ from the resulting solution of the Solvay process using activated carbon has been studied.[4] Since this method has a very low NH_4^+ removal efficiency, an attempt was made to remove NH_4^+ from the resulting solution of the modified Solvay process as struvite, which is a valuable fertilizer.[20] Subsequent experiments have been undertaken to evaluate the importance of pH and the concentration of Mg^{2+} and PO_4^{3-} on the removal of NH_4^+ through MAP precipitation:

$$Mg^{2+} + HPO_4^{2-} + NH_4^+ + 6H_2O \leftrightarrow MgNH_4PO_4{\cdot}6H_2O\downarrow + H^+ \quad (6)$$

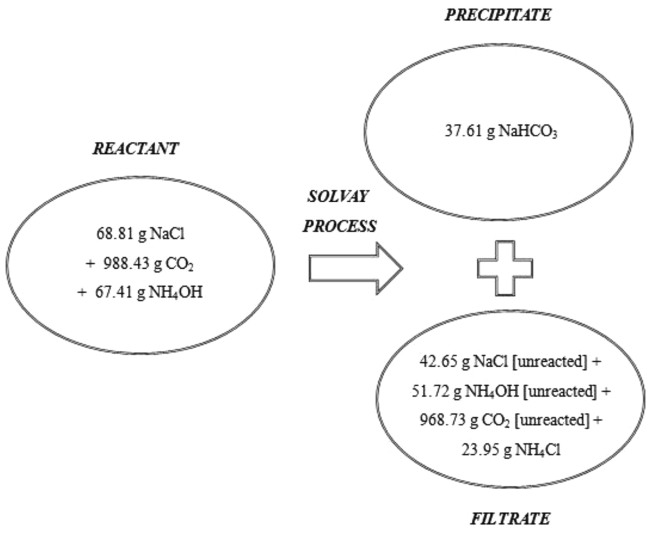

Figure 4. Flowchart of mass balance for the removal of Na^+ from the dye bath effluent.

3.2.1. Effect of Concentration of Mg^{2+} on NH_4^+ Removal Efficiency. Studies were performed to evaluate the effect of Mg^{2+} concentration on the removal of NH_4^+ through MAP precipitation. The concentration of Mg^{2+} was varied between 0.3 and 2.7 M, keeping the other conditions (reaction temperature of 30 °C, PO_4^{3-} of 1.7 M, stirring speed of 130 rpm, and the solution pH of 9) constant. Figure 5a illustrates that there was an insignificant NH_4^+ removal of 2.5% at 0.3 M and the highest removal of 80% for NH_4^+ was obtained at 1 M of Mg^{2+}. A further increase in the concentration of Mg^{2+} between 1.4 and 2.7 M caused a slow decrease in the removal efficiency of NH_4^+. The removal efficiency of NH_4^+ decreased in a higher concentration of Mg^{2+} because of the coprecipitation of newberyite and cattiite in the struvite precipitation.[21] Mijangos et al.[22] have found that at a higher Mg^{2+} concentration, the number of magnesium species coprecipitated including magnesium phosphate, reduced the driving force for the precipitation of struvite. The increase of Mg^{2+} concentration in the resulting solution accompanied by an increase of the chloride concentration (counterion), resulted in a higher ionic strength and a lower supersaturation ratio with respect to struvite in the solution.[21] They further noted that an increase in the Mg^{2+} concentration in the solution not only affected the struvite precipitation but also had a significant effect on the crystal size of the crystalline precipitate.[23] In the latter experiments, 1 M Mg^{2+} and reaction time of 3 h were adopted to obtain high removal efficiency of the NH_4^+.

3.2.2. Effect of Concentration of PO_4^{3-} on NH_4^+ Removal Efficiency. Experiments were carried out varying the concentration of PO_4^{3-}, ranging between 0.3 and 2.7 M, at 1 M Mg^{2+} and solution pH of 9. The results depicted in Figure 5b point out that the NH_4^+ removal percentage increased with increasing the concentration of PO_4^{3-} from 0.3 to 1 M and reached the maximum removal of 80.2% at 1.4 M of the PO_4^{3-}. The conversion efficiency of NH_4^+ decreased with increasing the PO_4^{3-} concentration of 1.7 to 2.7 M, due to the formation of other complexes including magnesium phosphate. The change of PO_4^{3-} concentration in the solution was in accordance with the change in pH. Stratful et al.[24] demonstrated that at a higher PO_4^{3-} concentration, more hydrogen was released into the solution when struvite is formed, resulting in a decrease in the

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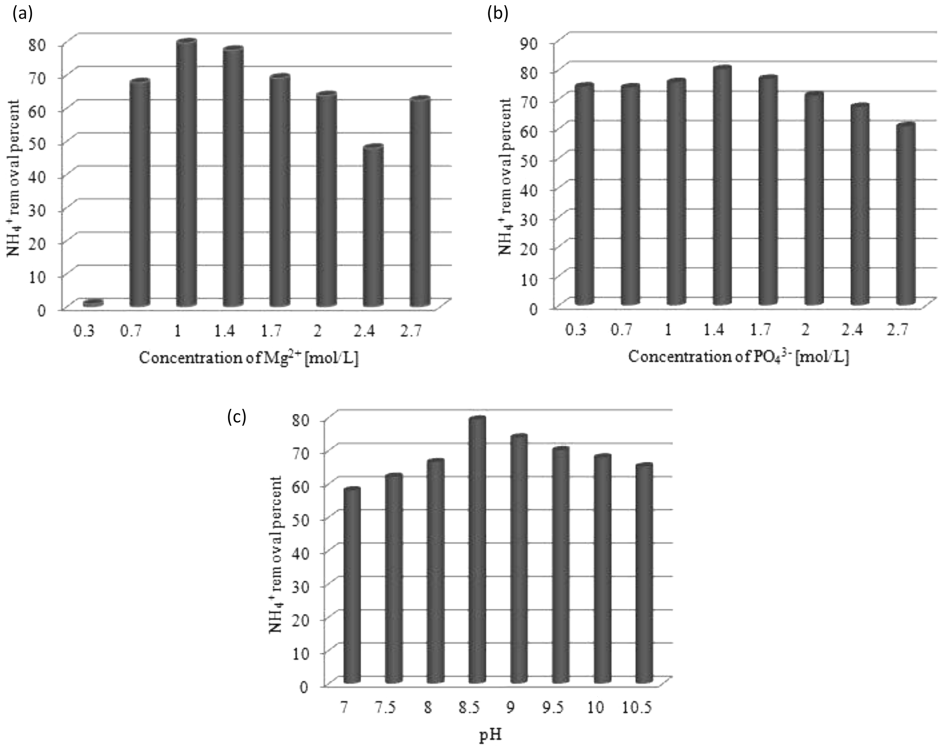

Figure 5. Effect of (a) concentration of Mg^{2+} (experimental conditions: reaction temperature, 30 °C; concentration of PO_4^{3-}, 1.7 M; stirring speed, 130 rpm; pH 9), (b) concentration of PO_4^{3-} (experimental conditions: reaction temperature, 30 °C; concentration of Mg^{2+}, 1 M; stirring speed, 130 rpm; pH 9), and (c) pH (experimental conditions: reaction temperature, 30 °C; concentration of Mg^{2+}, 1 M; stirring speed, 130 rpm; concentration of PO_4^{3-}, 1.4 M) on the removal of NH_4^+.

pH of the solution. It was therefore speculated that at low pH, further crystallization and precipitation of struvite was inhibited by the dissolution of struvite. This also caused an increase in the residual concentration of PO_4^{3-}. Moreover, at a higher concentration of PO_4^{3-}, the main product was magnesium dihydrogen phosphate, which leads to an undesired consumption of ions involved in the struvite precipitation.[24]

3.2.3. Effect of pH on NH_4^+ Removal Efficiency. The pH is the most important and determining variable in the struvite precipitation. In order to remove struvite from the supernatant by precipitation, the pH value of the solution should be in the pH range of 8.0−9.0, where struvite solubility is minimal. In this study, to determine the optimum pH for the maximum NH_4^+ removal, experiments were performed with varying pH between 7 and 10.5 with an optimized concentration of 1 and 1.4 M Mg^{2+} and PO_4^{3-}, respectively. The experimental results are shown in Figure 5c. The NH_4^+ removal efficiency increased rapidly with the increase in the pH and reached 80% at a pH of 8.5. In the struvite precipitation, the pH of the supernatant decreased at the beginning, which might correspond to the formation of struvite followed by the liberation of H^+ ions in the supernatant caused by the addition of K_2HPO_4 in the pH range of 7−9. The addition of NaOH neutralized the H^+ ions in the supernatant to control the pH in the range of 8−9 to minimize the struvite solubility and loss of ammonia. The struvite precipitation rate increased with a rise in pH because an increased pH would increase the rate constant by improving the nucleation rate. The improved nucleation would have given more surface area on which crystal growth could take place. When the pH was beyond the optimum range, magnesium phosphate was formed instead of struvite in the process, leading to a decrease in the removal efficiency of NH_4^+. Finally, this resulted in a decrease in the NH_4^+ removal efficiency.[25] Moreover, if the pH value becomes too high, the NH_4^+ is converted to ammonia,[26] which would also lower the yield of struvite. The liberation of NH_3 occurred at a high pH around 10−12 because of the reaction between NaOH and NH_4^+. NH_4^+ removal at above pH 9 might be due to the conversion of NH_4^+ to NH_3 at these pH ranges rather than struvite formation.

$$NaOH + NH_4^+ \rightarrow NH_3\uparrow + H_2O + Na^+ \qquad pK_a = 9.26 \tag{7}$$

If the pH value were slightly alkaline, then the struvite would be the major product. However, with further increase in pH, the product would include magnesium phosphate and magnesium hydroxide and the solubility of struvite would be increased. When the solution pH rises above 10, the following reactions take place easily:

$$3Mg^{2+} + 2PO_4^{3-} \rightarrow Mg_3(PO_4)_2 \tag{8}$$

$$Mg^{2+} + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2H^+ \tag{9}$$

So, the pH not only controls the struvite solubility but also the major removal pathway of NH_4^+.

3.2.4. Struvite Characterization. 3.2.4.1. XRD and SEM Analysis. The XRD analysis was used to characterize the purity of the struvite deposits collected from the resulting solution. The X-ray diffractogram exhibited several peaks, indicating the presence of struvite, as illustrated in Figure 6a. The XRD pattern generated from the precipitated matter matched well with the database model for struvite, that is, position and intensity of the peaks.[27] To determine the morphology, the precipitated matter was also examined by SEM and the SEM

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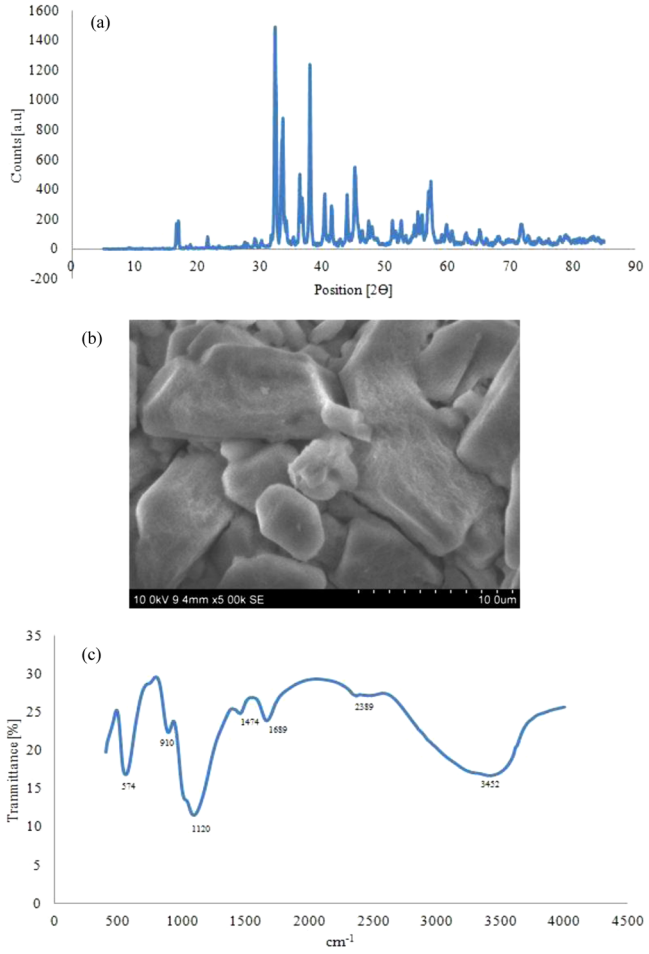

Figure 6. (a) XRD, (b) SEM, and (c) FTIR of the struvite precipitate.

micrograph is illustrated in Figure 6b. Since the crystalline struvite powder decomposed to an amorphous residue upon heating from 90 to 200 °C,[28] there are some noisy patterns with a reduction in the peak size and the definition in the XRD diffractogram of the solid. Hence the shape of the crystal recovered was different from the familiar needle-like structure of struvite. However, the solid recovered had the same surface characteristics of a pure struvite crystal. Both of them had a flake-like structure and triangular cavity on the surface, revealing the same lattice arrangement.[29]

3.2.4.2. FTIR Analysis. A broad band was observed at 3452 cm^{-1} in the FTIR spectrum of struvite precipitate, belonging to the H−O−H stretching vibration of water. The band at 2389 cm^{-1} was assigned to H−O−H stretching vibration of a cluster of water molecules. The symmetric bending vibration of N−H in NH_4 was at 1689 cm^{-1}. The band seen at 1474 cm^{-1} was the asymmetric bending vibration of N−H of NH_4. The symmetric and asymmetric stretching vibrations of PO_4 units were observed at 910 and 1120 cm^{-1}, respectively. The band at 574 cm^{-1} was due to the metal−oxygen bond. The FTIR spectra (Figure 6c) of the struvite precipitate exhibited the characteristic PO_4^{3-} band at 1120 cm^{-1}, the characteristic NH_4^+ band at 1474 cm^{-1}, and the band of metal−oxygen at 574 cm^{-1}, respectively. A similar spectrum for struvite has been reported in the literature.[30]

3.3. Cost Evaluation on Modified Solvay Process and Struvite Precipitation. The economic evaluation for the removal of Na^+ as $NaHCO_3$ from 1 L of the textile dye bath effluent using modified Solvay process and the removal of NH_4^+ as struvite from 1 L of the supernatant of the process was carried out. In this assessment, only the cost toward the consumption of chemicals and the electrical energy were taken into account. The market prices of the chemicals used and energy consumed for the removal of Na^+ and the precipitation of struvite are given in Table 1. It could be calculated that the total operating cost of the struvite precipitation was $1.105/L and for the recovery of $NaHCO_3$, it was $0.098/L. The recovered $NaHCO_3$ and struvite were 0.038 and 0.378 kg, respectively. About 25% of the net operating cost for the modified Solvay process and the struvite precipitation could be reduced by marketing the recovered sodium bicarbonate and the struvite at a favorable price of $0.023 and $0.227, respectively.

Table 1. Cost Evaluation of Modified Solvay process and Struvite Precipitation

process	nature of consumable	consumption per liter	price ($)	total operating cost ($)
modified Solvay process	ammonia solution	0.144 L	0.086	0.098
	electrical energy	0.15 kWh	0.012	
struvite precipitation	$MgCl_2·6H_2O$	0.207 kg	0.180	1.105
	K_2HPO_4	0.237 kg	0.567	
	NaOH	0.010 kg	0.020	
	electrical energy	4.14 kWh	0.338	

4. CONCLUSION

This paper was focused on how the briny textile dye bath effluent could be used as a raw material for the valuable bicarbonate chemical production using carbon dioxide gas. From the experimental results, it can be concluded that the highest Na^+ removal of 38% could be obtained and the optimized reaction conditions were as follows: NH_4OH/Na^+ ratio of 2, reaction temperature of 20 °C, flow rate of the CO_2 of 1.8 L/min, and carbonation time of 150 min. Among various reaction conditions, 1 M of Mg^{2+}, 1.4 M of PO_4^{3-}, and solution pH of about 8.5, rendered the best removal efficiency of 80% for NH_4^+ from the resulting solution of the modified Solvay process. The collected precipitate was positively identified as struvite by XRD, FTIR, and SEM analyses. The results indicate that the new approach can be designed to reduce carbon dioxide gas emissions, as well as to decrease the Na^+ in textile effluent by recovering it as sodium bicarbonate.

AUTHOR INFORMATION

Corresponding Author

*Tel: + 914422359014. Fax: + 914422354717. E-mail: kpvelu@annauniv.edu (K. Palanivelu).

Notes

The authors declare no competing financial interest.

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