



Short Communication

Isolation of ammonium bicarbonate by reactive distillation of food waste digestate liquor



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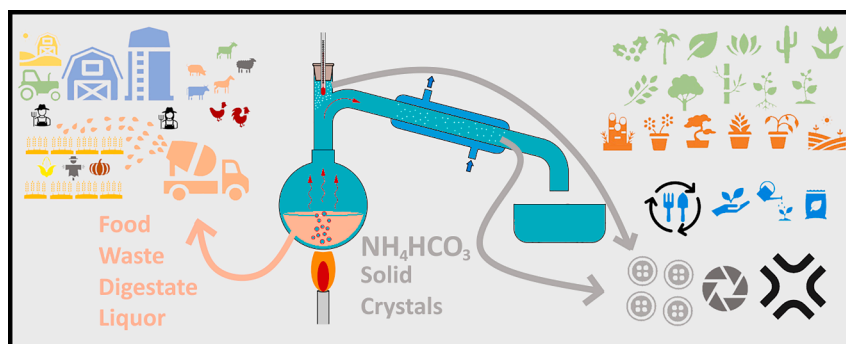
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HIGHLIGHTS

- Conventional batch distillation is a reliable method for isolating ammonium bicarbonate.
- 81 % of the ammonium bicarbonate in the food waste digestate liquor was recovered.
- Ammonium bicarbonate content in food waste digestate liquor was reduced from 50 to 10 g/L.
- Modification of the classical distillation still is required to conveniently harvest the crystals.
- Granulation and coating are required for stabilization of the solid ammonium bicarbonate.

GRAPHICAL ABSTRACT



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ABSTRACT

Distillation is among the best techniques for management of ammoniacal nitrogen in anaerobic digestate; however, the suitability of the conventional system is neglected in favor of using more advanced setups. This investigation proves the reliability of the classical batch distillation apparatus for high throughput separation of solid crystals of ammonium bicarbonate from food waste digestate (FWD) liquor. Three replicates were carried out: 80 g of FWD liquor with a content of 50 g/L NH_4HCO_3 was processed for 7.5 h under minimum heating power ($<60\text{ }^\circ\text{C}$) and 200 rpm to avoid excessive foam formation. After performing the reactive distillation, 81 % of NH_4HCO_3 was recovered as white solid crystals at the top of the distillation still. Although the distillation provided a solid material with the same structure and composition as those of the reagent-grade NH_4HCO_3 , the stability of the isolated inorganic fertilizer was poorer, and it could lead to pollution swapping.

1. Introduction

Anaerobic digestion (AD) is a well-known biodegradable organic waste treatment that produces the energy-rich stream of biogas ($\sim 65\text{ vol}\%$ CH_4 and $\sim 35\text{ vol}\%$ CO_2 ; (Budzianowski, 2012)), which is typically

fed to combined heat and power engines for the production of electricity, and a valuable soil organic amendment with high content of mineralized nutrients (Moure Abelenda et al., 2023). During anaerobic fermentation, the organic nitrogen (N) is converted to ammoniacal nitrogen ($\text{NH}_4^+\text{-N}$), due to microbial activity. Although the $\text{NH}_4^+\text{-N}$ is more

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readily available to plants than the organic N, it is also more prone to be lost by volatilization (Moure Abelenda et al., 2021b) and development of recovery (Fuchs and Drosig, 2013) or abatement mitigation technologies are necessary (Buckley et al., 2020). Distillation is among the most profitable technologies for recovering ammonia (NH₃) from aqueous solutions (e.g., anaerobic digestate, wastewater, etc.) (Kar et al., 2023; Shi et al., 2020). Interestingly, the classical distillation method is not widely regarded despite the vapor pressure of NH₃ is much higher than that of water and an easy separation could be expected. The most investigated processes are those which involve stripping NH₃ off the H₂O vapor by chemical (e.g., sulfuric acid trap (Moure Abelenda et al., 2022b, 2021b, 2021a)) or mechanical (e.g., gas permeable membrane (Lü et al., 2021; Yang et al., 2022)) methods. Since the ammonium bicarbonate (NH₄HCO₃) has an important presence in the anaerobic digestate and it rules the pH of this organic slurry (Möller and Müller, 2012), the fixation of the NH₃ volatilized by using the CO₂ as endogenous scrubbing agent (Moure Abelenda et al., 2023), rather than employing the open-loop approach with the sulfuric acid (Drapanaukaite et al., 2021), seems the most sensible and sustainable route for the isolation of this inorganic fertilizer. The opposite approach is also possible for upgrading the biogas (Bavarella et al., 2020; Moure Abelenda and Dolny, 2024), if a concentrated source of NH₃ is available, for example, by stripping the NH₃ off food waste digestate (FWD) or manure digestate (Yang et al., 2022). Instead retrieving NH₄HCO₃ from the biogas upgrading, as in the process of Burke (2010), Wang et al. (2019) promoted the decomposition of this organic compound and used the resulting stream for alkaline NH₃-treatment of the feedstock of crop residues. Regarding electrochemical methods (e.g., electro dialysis (Han et al., 2022; Jermakka et al., 2018)), Han et al. (2022) investigated a flow-electrode capacitive deionization system for retrieval of NH₄HCO₃ from swine wastewater. However, even after 30 h of functioning at the optimal operating conditions, NH₄HCO₃ could not be precipitated and a 1.61 M NH₄HCO₃ concentrated solution with 97.2 % purity was produced. Jermakka et al. (2018) was able to precipitate the NH₄HCO₃ from a simulated source-separated urine with a 3-compartment electrochemical system, by cooling the concentrate to -18 °C. Jermakka et al. (2018) observed that the maximum N recovery into solid NH₄HCO₃ was 17 %, when the current density was 100 A/m². It is important to clarify that the capture of solid NH₄HCO₃ was only feasible when competing ions are removed from the aqueous solution.

Bavarella et al. (2020) applied a modest temperature of 50 °C to the anaerobic digestate liquor of approximately 0.1 M NH₃, to attain the thermal desorption of NH₃, while minimizing the evaporation of water to produce a concentrated condensate of up to 1.7 M NH₃. Bavarella et al. (2020) subsequently modelled the rectification operation by considering a 2nd stage where a saturated solution of 6.4 M NH₃ was produced, and the crystallization of NH₄HCO₃ was initiated in a hollow fiber membrane contactor. The reactive distillation of the anaerobic digestate liquor can be performed efficiently without a membrane, although a convenient surface for crystallization of NH₄HCO₃ could assist the process (see the 1st video in the Supplementary Materials). As described by Bavarella et al. (2020) the hollow fiber membrane was evidenced to promote heterogeneous primary nucleation. Therefore, according to Bavarella et al. (2020) the synergy between thermal desorption and membrane contactor technology was able to deliver biogas upgrading, NH₃ removal from anaerobic digestate liquor, and recovery of the commercial-grade fertilizer. As a process intensification strategy, the combination of distillation operating at a low heat-up rate and pasteurization of anaerobic digestate has been already proposed with a circulating system for continuous harvesting the NH₄HCO₃ at the floating cover of the pasteurization tank (Moure Abelenda and Dolny, 2024). The synergistic approach of distillation can be also considered an abatement technology that meets the regulations (Government of Spain, 2020; UK Government, 2019) for mitigating the gaseous emissions during storage and after land application of organic manures.

The objectives of the present work were to confirm the reliability of

traditional distillation for isolation of NH₄HCO₃ solid crystals, with minimum requirements whilst achieving a high efficiency of the separation of this inorganic compound from the FWD liquor. The corresponding change in the composition of the FWD liquor, due to its lower content of NH₃ and CO₂, needs to be verified. Furthermore, the potential of the NH₄HCO₃ isolated with this method to behave as slow-release fertilizer was intended to be elucidated, based on empirical data of its stability.

2. Materials and methods

2.1. Sample of FWD liquor

FWD was employed in previous investigations, and it was found to contain roughly 9 g NH₄⁺-N/L (Moure Abelenda et al., 2022a, 2021c). The solid-liquid separation of the whole FWD implied obtaining a liquid phase with a greater content of NH₄⁺-N (Fuchs and Drosig, 2013) and less dirtiness problems (i.e., less clumps stuck to the walls of the glassware after the operation; see 2nd and 3rd videos of improper mixing in the Supplementary Materials). The FWD liquor was produced at a rate of 22,500 m³/y in a 1-MWh plant handling discards from big food processing factories and household food waste from 3 different councils of the United Kingdom. Two biodigesters of 2,277 m³ operated at 39 °C. To enhance the fermentation and the pasteurization stages (WRAP, 2014), the mixture of feedstock passed through a macerator that homogenized the particle size between 12 and 32 mm, as this size allowed sufficient temperature in the center of the particle and destroyed the pathogens. The liquid fraction (i.e., liquor) was obtained from the solid-liquid separation of the FWD and was stored in a closed tank of 9,744 m³ capacity. The solid fraction was disposed in landfill, due to the high content of plastic and other inert materials.

2.2. Conventional batch distillation setup

The classical batch distillation setup can be divided into reboiler, Liebig condenser, and middle point where the temperature of the vapor was measured (see the 4th video in the Supplementary Materials on last stages of distillation of agrowaste digestate (AWD) liquor with 850-ppm dose of antifoam to produce NH₄HCO₃). The red thermometer bulb at the top aims to provide the most accurate measurement of the boiling temperature, as this was located in the path of the volatilizing gases (Royal Society of Chemistry, 2016). The reboiler consisted of a heating plate (SLS Lab Basics 280c Hotplate Stirrer) with magnetic stirring function, an aluminum block, and a round-bottom (RB) flask containing a magnetic stirrer in addition to the anaerobic digestate. Continuous stirring was maintained at a low rate throughout the distillation to ensure the homogenous heating of the anaerobic digestate. The minimum stirring (200 rpm) was an alternative to anti-bumping and anti-foam agents, which would have fostered nucleation sites and the formation of small bubbles, but they would have chemically affected the composition of the anaerobic digestate and increased the operating expenses. The aluminum heating block surrounding the content of the RB flask had the same function of controlling the heat transfer. For each batch assay, approximately 80 g of FWD liquor were fed in the 250-mL RB flask, as this ensured that the level of fullness was the same as the height covered by the aluminum heating block. Therefore, there was no overheating zone while sufficient headspace was available to allow any foam formation and equilibria between the different phases. The distillation still had a small hole for operating at atmospheric pressure, and the apparatus was placed under the fume hood to properly vent any gas that would not be trapped in the distillate.

2.3. Design of experiments

For the preparation of the distillation run for isolation of the NH₄HCO₃ from the FWD liquor, the 1st step was to weigh the sample, so

the loss of weight during the run can be determined. Since the aim of this investigation was to confirm the reliability of traditional distillation for isolation of NH_4HCO_3 solid crystals, the design of experiments consisted in running 3 replicates of processing ~ 80 g FWD liquor at very low heating rate and temperature (i.e., always below 60°C) for up to 8 h. The Liebig condenser was connected in countercurrent to ensure the most efficient cooling and condensation of the volatilizing gases; hence zero mass losses could be considered, assuming complete deposition of NH_3 and CO_2 gases as solid NH_4HCO_3 . The system was left cooling overnight, before harvesting the NH_4HCO_3 crystals at the top of the still (i.e., around the bulb of the thermometer; see 5th video in the [Supplementary Materials](#) on NH_4HCO_3 crystallization below 60°C during distillation AWD liquor) the following morning, to calculate the mass balance and the yield of inorganic fertilizer as accurately as possible. In addition to weigh the FWD liquor in the RB flask before and after the distillation, the titration of this material diluted 5 times (i.e., 1 mL FWD liquor mixed with 4 mL filtered water) was carried out by adding volumes of 0.5 mL of an acid solution (0.6 mol HCl/L) and an alkali solution (0.13 mol NaOH/L) to overcome M, P and OH alkalinities and reach the titration endpoints (pHs below 2 and above 12). Descriptive statistics were used to assess the significant differences of the titration curves of the replicates of the FWD liquor before and after the distillation, and to confirm the extraction of the NH_4HCO_3 . Furthermore, to investigate the stability of the NH_4HCO_3 crystals, the solid samples were analyzed with the Cary 630 Fourier-Transform Infrared (FTIR) Spectrometer of Agilent Technologies, with Attenuated Total Reflectance (ATR) sampling module. Descriptive statistics were used to assess the height of the ATR-FTIR profiles of the samples, which gave an indication of the vibrational energy of the atomic bonds in the samples of the inorganic material. The analysis of the samples with the ATR-FTIR machine was performed with the NH_4HCO_3 solid crystals as retrieved from the distillation setup and after vacuum-drying leading to destabilization of clumps and formation of ultrafine powder. The ATR-FTIR spectroscopy analysis of a reagent-grade NH_4HCO_3 , which was procured from the chemical supplier Thermo Fisher Scientific Inc., was used to confirm the structure and composition, and to aid the determination of the stability of the inorganic fertilizer recovered via distillation of the FWD liquor. In addition to report the average yield of NH_4HCO_3 and standard deviations for the 3 reactive distillations, the titration curves of the FWD liquor before and after the distillation, and the ATR-FTIR profiles for the solid samples of NH_4HCO_3 as retrieved from the top of the apparatus and after being vacuum-dried, the 5-min video recordings of the 3 experiments are available in the [Supplementary Materials](#) (6th, 7th, and 8th video recordings).

3. Results and discussion

3.1. Progress of the reactive distillations of FWD liquors for each of the 3 replicates

Since it was difficult to maintain exactly the same operating conditions due to the complexity of the heterogenous aqueous solutions and the foam formation, each of the 3 replicates was recorded separately (see supplementary 5-min video recordings in the [Supplementary Materials](#)), and the difficulties of controllability were reported in [Tables S1–S3](#). [Table S1](#) summarizes the 7.5 h of reactive distillation and the subsequent 15 h of cooling down overnight of the 1st replicate. [Table S2](#) summarizes the 7 h of reactive distillation and the subsequent 16 h of cooling down overnight of the 2nd replicate. [Table S3](#) summarizes the 8 h of reactive distillation and the subsequent 12 h of cooling down overnight of the 3rd replicate.

3.2. Yield of NH_4HCO_3 solid crystals and depletion of FWD liquor

The amount of NH_4HCO_3 recovered was 3.33 ± 0.37 g ($n = 3$) because the weight of the FWD liquor decreased from 81.44 ± 1.02 g ($n = 3$), before starting the distillation, to 78.12 ± 1.25 ($n = 3$) after completing the 7.5 ± 0.5 h ($n = 3$) of reactive distillation and 14.3 ± 2.1 h ($n = 3$) of overnight cooling down. [Fig. 1](#) shows the titration curves of the FWD whole (both with solid and liquid fractions) ($n = 1$), FWD liquors (sampled on different dates from the AD plant) before the distillation ($n = 2$), and depleted FWD liquors after the distillation ($n = 4$).

The reactive distillation increased the slope of the titration curve and decreased buffer capacity (and therefore, the NH_4HCO_3 content) of the FWD liquor samples, because lower doses of titrants were necessary to change the pH. It should be noted that the dose of basic titrant is expressed as a negative dose of acid. The OH, P, and M alkalinities were found at pHs 12.5, 9.5, and 5.5 in the FWD before and after the reactive distillation. The pHs of the FWD before and after the reactive distillation were 8.59 ± 0.11 and 10.10 ± 0.05 ([Fig. 1](#)). Therefore, the increase in the pH also implied that it was necessary to add acidic titrant rather than basic titrant to the depleted FWD liquors to overcome the P alkalinity, because the same chemical species derived from the dissociation of NH_4HCO_3 were responsible of regulating the pH. Based on the calibration performed in previous investigations ([Moure Abelenda and Dolny, 2024](#)) to correlate the titration curves with the content of NH_4HCO_3 in the aqueous solutions, the content of this inorganic compound decreased from 50 g/L to 10 g/L in the FWD liquors, due to the reactive distillation. The calculation of the amount of NH_4HCO_3 isolated, as difference between the contents of this inorganic compound in the fresh and depleted FWD liquors was 3.29 g (calculation: $50 \times 0.08144 - 10 \times 0.07812$ g), which did not deviate significantly from the amount derived from the difference of the weight of the FWD liquor before and after 3.33 ± 0.37 g (calculation: $81.44 - 78.12$ g). This represented an 80.82 % recovery of NH_4HCO_3 from the FWD liquors. Given the sufficient headspace in the 250-mL RB flask used as reboiler, any foam formed was sufficiently confined (see 6th, 7th, and 8th videos in the [Supplementary Materials](#)) and no significant losses were found as result of the performance assessment. The 2 replicates of the titration of the depleted FWD liquor from the 2nd distillation were specified in [Fig. 1](#) because they differ significantly from each other, and one looks more like the titration curve of the depleted FWD liquor from the 1st distillation and the other looks more like the titration curve of the depleted FWD liquor from the 3rd distillation.

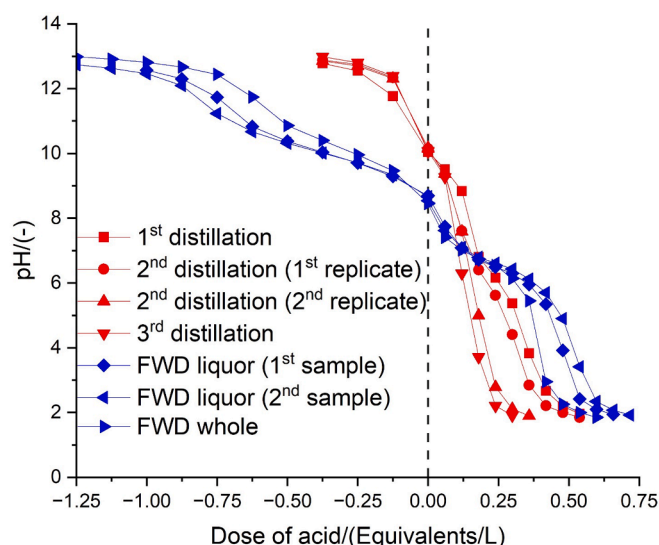


Fig. 1. Titration curves of the FWD whole (both with solid and liquid fractions) ($n = 1$), FWD liquors (sampled on different dates at the AD plant) before the distillation ($n = 2$), and depleted FWD liquors after the distillation ($n = 4$). Two replicates of FWD liquor depleted in the 2nd distillation are reported because they differ significantly from each other.

3.3. Stability of NH_4HCO_3 solid crystals

Fig. 2 confirms that the solid NH_4HCO_3 crystals isolated by reactive distillation of FWD liquors had similar molecular structure and composition to those of the commercial-grade NH_4HCO_3 . Fig. 2 shows that the same peaks of absorbance were found in all samples, and these corresponded to the composition of NH_4HCO_3 . A similar analysis was previously carried out by Han et al. (2022), who used X-Ray Diffraction (XRD) and Raman spectroscopies to verify the NH_4HCO_3 enrichment of synthetic swine wastewater with the flow-electrode capacitive deionization system. Similarly, Bavarella et al. (2020) used XRD spectroscopy to prove the formation of NH_4HCO_3 , since there was concerns about cation competition (e.g., Ca^{2+}) from the anaerobic digestate liquor. It should be noted that in the reactive distillation process, ions were not expected to be volatilized but still was necessary to demonstrate that thermal desorption guaranteed the formation of the preferred crystalline reaction product. Fig. 2 also informs about the lower stability and greater availability of the valorized inorganic fertilizer to crops, based on the enhanced FTIR spectra (i.e., higher peaks) compared to that of the purchased chemical. The difference in the height of the peaks should be related to more stretching and bending vibrations at higher energy, due to greater instability and availability of NH_4^+ -N for crops, rather than to a more concentrated sample (Moure Abelenda and Dolny, 2024). While the highest absorbance in the commercial-grade NH_4HCO_3 was 0.20, peaks of up to 0.49, 0.47, 0.71, 0.40, 0.87, and 0.39 were found for the solid crystals retrieved from the 1st replicate, 1st replicate vacuum-dried, 2nd replicate, 2nd replicate vacuum-dried, 3rd replicate, and 3rd replicate vacuum-dried, respectively (Fig. 2).

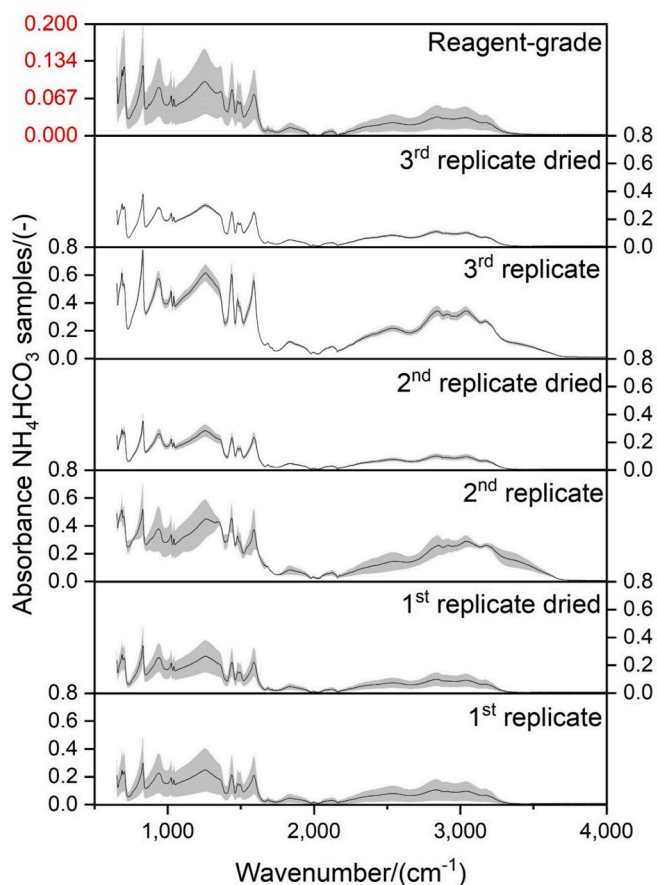


Fig. 2. Comparison of the ATR-FTIR spectrum of the commercial-grade NH_4HCO_3 to those of the crystals obtained directly from the reactive distillations of FWD liquors and after vacuum-drying. In all cases, the number of measurements was 5 ($n = 5$).

4. Discussion

The optimization of the conditions of the reactive distillation of FWD liquor for isolation of solid NH_4HCO_3 was challenging because of the inertia of the system and the foam formation. The greatest deposition of NH_3 and CO_2 as NH_4HCO_3 was seen during the ramping up or cooling down of the system, although these transient conditions could also promote the decomposition of the existing crystals, as can be seen at the 2 min and 50 s of the recording of the 3rd replicate (see 8th video in the Supplementary Materials). It is necessary to design equipment with less inertia (i.e., closer monitoring of the boiling temperature of the FWD liquors) and which offers better controllability of the distillation conditions for treating anaerobic digestates. Although thermal insulation of the distillation would help to improve the heat and mass transfer, and the homogeneous boiling of the FWD liquor, using double bubble reflective aluminum foil negatively affected the vision and monitoring of foam formation. The use of antifoam would contaminate the anaerobic digestate and the operation at a higher heating power would lead to the production of a saturated NH_4HCO_3 aqueous solution condensate/distillate. The reactive distillation at low heating power was found to be a reliable and reproducible technology, which avoided the need for cooling below room temperature and the use of antisolvent to promote the supersaturation of the aqueous solution of condensate or distillate, for precipitation of the NH_4HCO_3 crystals. A more advanced apparatus needs to be developed to have closer control of all the independent variables, including the heating up rate, the condensation temperature, and the location of the condensation. It is important to clarify that, according to the Royal Society of Chemistry (Royal Society of Chemistry, 2016), the bulb of the thermometer should be in the path of the vapor and if this is too low or too high, an inaccurate value for the boiling point would be determined. This was the way in which the classical batch distillation setup has been designed, but harvesting the NH_4HCO_3 solid material was not convenient because disassembling of the equipment was necessary. In this way, including a surface for aiding nucleation and crystal growth in a more accessible location could assist the process (see the 1st video in the supplementary material on periodically harvesting NH_4HCO_3 crystals).

The reactive distillation of anaerobic digestates could be regarded as a mitigation technology that prevents pollution swapping, depending on whether the rate of release of NH_4^+ -N, upon land application of the inorganic fertilizer, would be sufficiently slow to be absorbed by plants through their roots while preventing gaseous emissions. In addition to the solid crystals of NH_4HCO_3 , the distillation process provided a more stabilized anaerobic digestate, which was less prone to release gases during storage and land application. It is necessary to study the rheology of the homogenized mixture, to consider the fluid-mechanical behavior of the treated matrix, and to confirm the easier land application of the depleted soil organic amendment. It would be necessary to assess the stability of the NH_4HCO_3 solid crystals with the closed chamber method (Moure Abelenda et al., 2022b, 2021b, 2021a; Wester-Larsen et al., 2022), with sulfuric acid and sodium hydroxide solutions in the headspace, or a brine of NaCl or CaCl_2 (Moure Abelenda and Roberts, 2024), to account the release of NH_3 and CO_2 during incubation under the desired conditions of storage or land application. Granulation and coating of the isolated NH_4HCO_3 solid crystals should be investigated as a measurement to manage the instability and the availability of NH_4^+ -N from the inorganic fertilizer (Brondi et al., 2023).

5. Conclusions

This study encourages the scientific community to revise the traditional distillation as a method for separating the NH_4HCO_3 from waste aqueous solutions, before testing more advanced modifications of this technique. The isolation of NH_4HCO_3 via reactive distillation of FWD liquor, at low heating power and reaching temperatures below 60 °C, was a reliable and reproducible process with high throughput (80.82 %

recoverability in 7.5-h operation) but it was necessary to improve the controllability due to the excessive foam formation. This technology was suitable for improving the management of $\text{NH}_4^+\text{-N}$ contained in the FWD liquor because, in addition to the production of a commercial-grade inorganic fertilizer, the organic manure was stabilized for subsequent storage and land application (i.e., minimizing losses of NH_3 via volatilization). The system to harvest NH_4HCO_3 conveniently from the distillation apparatus and solid surfaces, which would foster crystallization, needs more development to avoid routinely disassembling. The solid NH_4HCO_3 crystals retrieved from the FWD liquor need further stabilization to improve the behavior as slow-release fertilizer, and granulation and coating methods should be investigated.

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CRediT authorship contribution statement

Alejandro Moure Abelenda: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2024.130592>. Tables S1–S3 summarize the reactive distillation of the FWD liquor and the subsequent overnight cooling down of the 3 replicates. 1st video recording of harvesting NH_4HCO_3 crystals during the distillation of anaerobic digestates: <https://youtu.be/C2PffTHEdVf0>. 2nd video recording on foam formation due to high heating rate and improper mixing of antifoam 2,500 ppm during distillation: <https://www.youtube.com/watch?v=VgAddxXvXoA>. 3rd video recording on excess of antifoam stuck to the walls of the round-bottom flask during distillation of digestate liquor: <https://www.youtube.com/watch?v=XbPAaeBloc0>. 4th video recording on the last stages of distillation of AWD liquor with 850-ppm dose of antifoam to produce NH_4HCO_3 : <https://www.youtube.com/watch?v=kYp2UtX5W9A>. 5th video recording on NH_4HCO_3 crystallization below 60 °C during distillation AWD liquor: <https://www.youtube.com/watch?v=7u8M5-pyDec>. 6th, 7th, and 8th video recordings (5-min long) of the isolation of NH_4HCO_3 by reactive distillation of FWD liquor: <https://youtu.be/7jXu9qjeiFk> (1st replicate); https://youtu.be/s7_qD_dQV1E (2nd replicate); https://youtu.be/rGuA7k_A4Z4 (3rd replicate).

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