Ammonia stripping and scrubbing followed by nitrification and denitrification saves costs for manure treatment based on a calibrated model approach

Ruben Vingerhoets[a,c], Claudio Brienza[a], Ivona Sigurnjak[a], Jeroen Buysse[b], Siegfried E. Vlaeminck[c,d], Marc Spiller[c,d], Erik Meers[a]

[a] Ghent University, Department of Green Chemistry and Technology, RE-SOURCE - Laboratory for biobased resource recovery, 9000 Gent, Belgium
[b] Ghent University, Department of Agricultural Economics, 9000 Gent, Belgium
[c] University of Antwerp, Department of Bioscience Engineering, Research Group of Sustainable Energy, Air and Water Technology, 2020 Antwerpen, Belgium
[d] Centre for Advanced Process Technology for Urban Resource Recovery (CAPTURE), Frieda Saeysstraat 1, 9052 Gent, Belgium

KEYWORDS

NH_3 stripping, CO_2 stripping, techno-economic assessment, optimisation, resource recovery

ABSTRACT

Resource-efficient nitrogen management is of high environmental and economic interest, and manure represents the major nutrient flow in livestock-intensive regions. Ammonia stripping/scrubbing (SS) is an appealing nitrogen recovery route from manure, yet its real-life implementation has been limited thus far. In nutrient surplus regions like Flanders, treatment of the liquid fraction (LF) of (co-)digested manure typically consists of nitrification/denitrification (NDN) removing most N as nitrogen gas. Integrating SS before NDN in existing plants would expand treatment capacity and recover N while maintaining low N effluent values, yet cost estimations of this novel approach after process optimisation are not yet available. A programming model was developed and calibrated to minimise the treatment costs of this approach and find the balance between N recovery versus N removal. Four crucial operational parameters (CO_2 stripping time, NH_3 stripping time, temperature and NaOH addition) were optimised for 18 scenarios which were different in terms of technical set-up, influent characteristics and scrubber acid. The model shows that SS before NDN can decrease the costs by 1 to 56% under optimal conditions compared to treatment with NDN only, with 1 to 8% reduction for the LF of manure (22-29% recovered of N treated), and 11 to 56% reduction for the LF of co-digested manure (42-67% recovered of N treated), primarily dependent on resource pricing. This study shows the power of modelling for minimum-cost design and operation of manure treatment yielding savings while producing useful N recovery products with SS followed by NDN.

1 INTRODUCTION

Since the industrialisation of agriculture, nitrogen (N) inputs to sustain the current production levels have increased drastically leading to significant anthropogenic emissions of reactive N (Nr) and the exceedance of the 'planetary boundaries' [1] or safe and just Earth system boundaries [2] which stresses the importance of local tipping points associated to eutrophication, air pollution and associated health impacts in livestock-dense regions. To secure local air and water pollution standards, the Nitrates Directive (EU) 676/1991 [3] and the declaration of Nitrate Vulnerable Zones with a manure application limit of 170 kg N ha^{-1} y^{-1} are enforced limiting manure application. Hou et al. [4] reported that almost 10% of the 1.2-1.8 billion tonnes of manure produced in the EU underwent processing. However, there were significant variations among countries, with processing rates ranging from 0 to 35%. Livestock-dense regions with manure application restrictions in place and consequently an N surplus treat up to 20% of the produced manure biologically in a nitrification/denitrification (NDN) converting Nr to atmospheric dinitrogen (N_2) [5]. In a typical processing facility of (co-digested) pig manure, N is treated after solid/liquid separation with a centrifuge. The resultant liquid fraction (LF) has an estimated average treatment cost between 9-14 euro per treated tonne (t) [6] and contributes to 3% of the pig production costs [7]. On the other hand, the annual demand for Nr in the form of mineral fertilisers, produced via the energy-intensive Haber-Bosch (HB) process converting atmospheric N_2 to ammonia (NH_3), is 20 Tg N in Europe [8]. It can therefore be argued that combining NDN and HB process is an indirect manner of N recycling via the atmosphere [9]. At the global level, HB delivers 62% of the Nr input into the agri-food chain, and accounts for 1.2% of the CO_2 equivalent emissions, >1% of the energy demand, 2% of the gas use [9] [10]. This considerable energy demand and carbon footprint has been cited as incentive to develop direct N recovery technologies seeking to recover, refine and/or concentrate Nr from waste streams at lower greenhouse gas emissions than the combination of NDN and HB. This is especially relevant in livestock-dense regions with a nitrogen surplus, such as Flanders and the Netherlands [11].

Various treatment trains have been proposed including nutrient recovery steps from the (co-digested) manure LF, including processes like for instance ultrafiltration, NH_3 stripping/scrubbing (SS), chemical precipitation, etc, optionally followed by an additional effluent N polishing step with NDN. Many technologies are based on well-understood commercially available processes, yet scientific studies do not agree on their economic feasibility, where estimates depend on prices for energy and chemicals, the market value of the produced product (e.g. an ammonium sulphate solution), labour costs etc. These aspects do not only vary in terms of location, but also over time, sometimes very abruptly linked to dependence on global supply chains and geopolitical stability. N recovery has been argued to have economic potential by some authors [12] while others challenge this [13]. For the recovery of N from pig manure, De Vrieze et al. [14] found that all investigated N recovery technologies have higher net costs (Total cost – Revenue) than conventional N removal to achieve 80-90 % of influent N reduction. Brienza et al. [15] and Van Puffelen et al. [16] arrived at similar conclusions concerning the negative economic performance of N recovery technologies applied as alternative manure management. However, in contrast to LF treatment schemes including membrane filtration and precipitation, an approach of NH_3 SS for N recovery and NDN for effluent polishing has been identified as the economically most promising option for N recovery maintaining good effluent quality from concentrated streams. The reason for this is that the alternatives are associated with of high capital costs and intensive maintenance, in particular when there is a focus on membrane filtration [14] [15] [17]. Furthermore, the current global economic landscape marked by increased energy and resource costs, including mineral N, may provide favourable conditions for the economic viability of N recovery technologies in comparison to conventional N removal [18]. N recovery in the form of ammonium (NH_4^+) salts has the potential to facilitate the integration of manure-derived products into the mineral fertiliser market, as these products are likely to comply with the recently established RENURE (REcovered Nitrogen from manURE) products criteria. A novel initiative that seeks to determine which manure-derived products can be utilised as mineral fertilisers in Nitrate Vulnerable Zones under the same regulations as synthetic fertilisers [19].

A commercial NH_3 stripping solution for LF treatment usually consists of a two-step approach. In the first stage, the CO_2 stripping, the carbonate buffer is removed by transferring CO_2 from the liquid phase to the ventilation air in a packed tower with open-loop gas circulation. In the second stage, the NH_3 SS, the liquid phase is stripped in a packed tower with inert material to induce NH_3 volatilisation into the gas phase of a closed ventilation loop (Figure 1). This set-up has the advantage of lowering the buffer capacity without adding chemicals [20]. In the acid scrubber, the NH_3 in the gas phase is absorbed by contacting the NH_3-rich gas with an acidic solution recovering NH_3 in the form of NH_4^+ salts. Sulphuric acid (H_2SO_4) and nitric acid (HNO_3) are used as conventional mineral acids [21], resulting in the production of ammonium sulphate ($(NH_4)_2SO_4$, AS) ammonium nitrate (NH_4NO_3, AN) solutions respectively.

In the past, several models have been proposed to gain insights, simulate and predict the efficiency of the stripping processes. Complex chemical processing models like ASPEN are recommended for simulation purposes but are limited in the use of simple economic feasibility calculations and process optimisation as they require numerous datasets for parametrisation [22]. Liu et al. [23] and Zou et al. [24] proposed predictive models for a stripping unit removing NH_3 from the anaerobic digestate of pig manure by means of polynomial regression which were focused on parameters such as gas flow rate, dose of lime/pH, stripping time and gas-to-liquid ratio, but failed to inform on economic optimal parametrisation and underlying physio-chemical principles. On the other hand, simple calculation tools have been developed to assess the economic feasibility of the implementation of the stripping process at conventional manure treatment facilities which are directly available for the decision makers [12]. However, these calculation tools are often oversimplified and do not provide the opportunity to optimise operational parameters, nor do they consider avoided cost because of N removal in the NDN stage. Therefore, there is a need of linking biochemical, thermodynamic, and economic models to enable operational parameter optimisation and enhance the overall performance of the system. In addition to the various model proposed to optimise NH_3 stripping process, NH_3 stripping experiments have been performed to parameterise the effect of pH, temperature, air velocity and air-liquid ratio on NH_3 volatilisation efficiency in a single unit stripping process by [12] [20] [25] [16] amongst others. The interactions between the different stages in multi-stage stripping units remain largely unexplored and experimental data from full-scale NH_3 SS is limited which hinders the calibration of the dynamic mass transfer mechanisms in the proposed model.

This study aims to minimise the total cost of the two-stage stripping tower in tandem with an NDN treatment by optimising its operational system parameters and thereby addressing the knowledge gaps outlined above, namely:

- The existing literature on economic feasibility of N recovery from LF of manure/digestate has primarily focused on evaluating N recovery technologies, without considering the economic optimisation of the system’s process parameters. Therefore, this study will evaluate the economic performance of the replacement of conventional NDN treatment by N recovery scenario through NH_3 stripping together with effluent polishing by NDN after economic process optimisation for different price scenarios.

- While different NH_3 stripping models exist with varying purposes, the current modelling landscape lacks tools to inform on the optimal operational parameters for various conditions. This study will provide a dedicated modelling logic linking the biochemical, thermodynamic, and economic aspects to optimise operational parameters NH_3 stripping technology combined with NDN.
- To the knowledge of the authors, there are no studies that perform a factorial experiment on two-stage stripping with air in a full-scale unit testing temperature, pH and type of acid. This study will present NH_3 removal efficiencies for a wide range of operational parameters (temperature, pH and type of acid), while the CO_2 removal efficiencies will be assessed for a range of different temperatures. Furthermore, an assessment of the quality of the recovered NH_4^+ salt solutions will be conducted, taking into account the scrubbing agent used.

2 MATERIAL AND METHODS

2.1 Description of SS and NDN technology

An economic optimisation model is created based on a full-scale two-stage SS unit and a series of calibration experiments (Figure 1). The SS process works as follows. The liquid fraction (LF) of digestate/manure enters the first-stage stripping tower via a heat exchanger, where the heat from the outgoing LF is partially recovered. In the first-stage stripping tower, recirculation gas strips LF to remove CO_2 and NH_3. After reducing the NH_3 concentration in the recirculation gas through the NH_3 absorber, a part of this gas is vented and replaced with fresh air from outside to lower the CO_2 concentrations. The concentration and chemical equilibria of total inorganic carbon (TIC), total ammoniacal nitrogen (TNH) and total inorganic phosphorus (TIP) affect the pH of the LF, but is mainly driven by changes in TIC concentrations. The elimination of CO_2 from LF within the first-stage SS tower induces a shift in the chemical equilibrium of the carbonate buffer toward the formation of CO_2 as described in Eq. (2) and (3). Consequently, protons (H^+) are concurrently consumed alongside the carbonate buffer, leading to an elevation in pH. However, the energy input associated with the heat loss through air venting is high. As an alternative to the CO_2 stripping, NaOH can be added before entering the second-stage stripping tower to increase the pH which facilitates, NH_3 stripping in the second-stage stripping tower by shifting Eq. (1) to the right. The second-stage stripping tower follows a similar workflow as the first-stage stripping tower, but makes use of closed air recirculation preventing further CO_2 stripping. After the stripping processes, the LF is further treated in an NDN unit that, that uses active aeration to provide O_2 an electron acceptor for nitrification and methanol dosing for the provision of carbon source in the denitrification process.

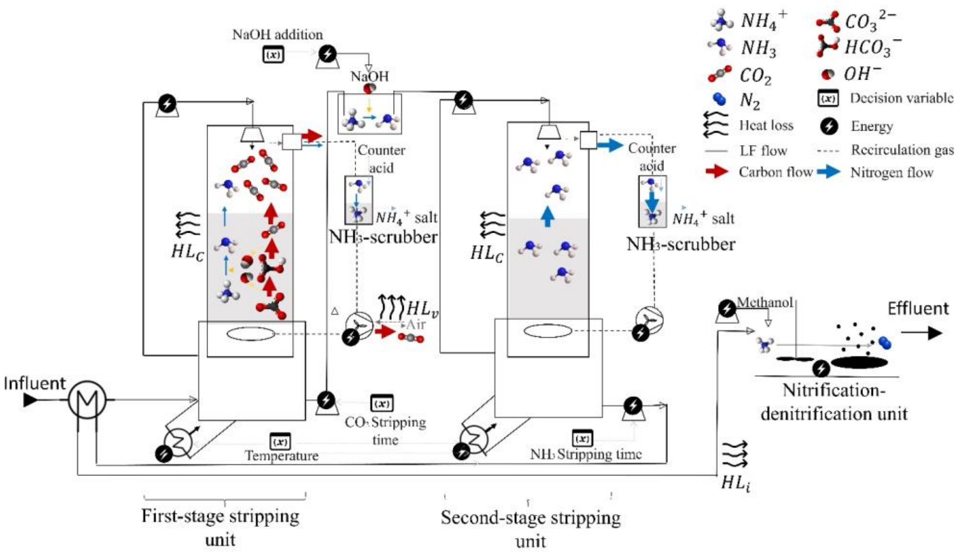

Figure 1. Schematic overview of the two-stage air-recirculation NH_3 stripping process with subsequent nitrification-denitrification treatment.

Table 1. Considered lumped components and chemical equilibrium coefficients [27].

Lumped component	Dissociation reaction	Eq	Dissociation constant	Equation based on temperature
TNH	$NH_4{}^+ \leftrightarrow H^+ + NH_3$	1	$K_{NH_4{}^+} = \frac{C_{H^+}\, C_{NH_3}}{C_{NH_4^+}}$	$e^{-\frac{6344}{T+273.2}}$
TIC	$CO_2 + H_2O \leftrightarrow H^+ + HCO_3{}^-$	2	$K_{CO_2} = \frac{C_{H^+}\, C_{HCO_3{}^-}}{CO_2}$	$10^{-356.3-0.061*(T+273.2)+\frac{21834.4}{T+273.2}+126.8*\log(T+273.2)-\frac{1684915}{(T+273.2)^2}}$
	$HCO_3{}^- \leftrightarrow H^+ + CO_3{}^{2-}$	3	$K_{HCO_3{}^-} = \frac{C_{H^+}\, C_{CO_3{}^{2-}}}{C_{HCO_3{}^-}}$	$10^{-107.9-0.033*(T+273.2)+\frac{5151.8}{T+273.2}-38.9*\log(T+273.2)-\frac{563713.9}{(T+273.2)^2}}$
TIP	$H_2PO_4{}^- \leftrightarrow H^+ + HPO_4{}^-$	4	$K_{H_2PO_4{}^-} = \frac{C_{H^+}\, C_{HPO_4^{2-}}}{C_{H_2PO_4^-}}$	$-0.020 * (T + 273.2) - \frac{1979.5}{(T + 273.2)} + 5.4$
	$H_2O \leftrightarrow H^+ + OH^-$	5	$K_{H_2O} = C_{H^+} C_{OH^-}$	$10^{-284.0-0.051*(T+273.2)+\frac{13323}{T+273.2}+102.2*\log(T+273.2)-\frac{1119669}{(T+273.2)^2}}$

2.2 Modelling approach

The economic optimisation model combines the thermodynamic, biochemical, and economic aspects. The model focuses on minimising the overall costs (OPEX and CAPEX) by changing four core operational parameters, CO_2 stripping time, NH_3 stripping time, temperature, and pH alteration by NaOH dosing. Modifying the pH through NaOH dosing and CO_2 stripping or adjusting temperature via heating will affect costs and total N removal and consequently NDN treatment costs and revenues created. Increasing the duration of NH_3 stripping has a beneficial impact on NH_3 yields; however, it concomitantly reduces pH and thus NH_3 stripping rate. Additionally, this decision incurs supplementary expenses related to heating, pumping, and CAPEX. The model will identify the CO_2 stripping time, NH_3 stripping time, temperature and NaOH addition associated to the global minimum for total costs, including energy (heating of the SS, pumps and ventilator of the SS units and aeration in NDN), capital costs (SS unit, NDN), chemicals consumption (NaOH, H_2SO_4/HNO_3 and Methanol) minus revenue generated by AS and AN production. A detailed diagram of the relationships between the parameters can be seen in Figure 2.

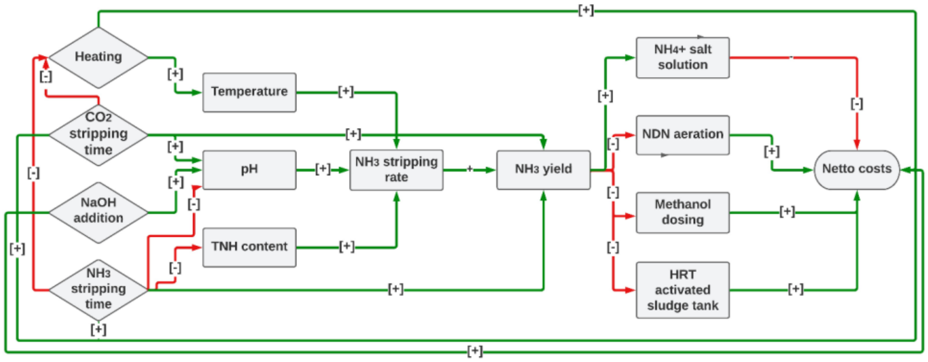

Figure 2. Relationship between stripping parameters and their effect on net costs. (Green lines define a positive relationship, while red lines define a negative relationship).

Modelling progresses in two successive steps from thermodynamic/ chemical model to an economic model (Figure 3). The thermodynamic/ chemical model creates a dataset of possible outcomes from the SS unit for the different operational parameters by running a non-linear time-step based mass transfer model with dynamic pH adjustment for a range of parameter settings. The calculated response serves as input for the actual economic optimisation through minimal cost scenario selection.

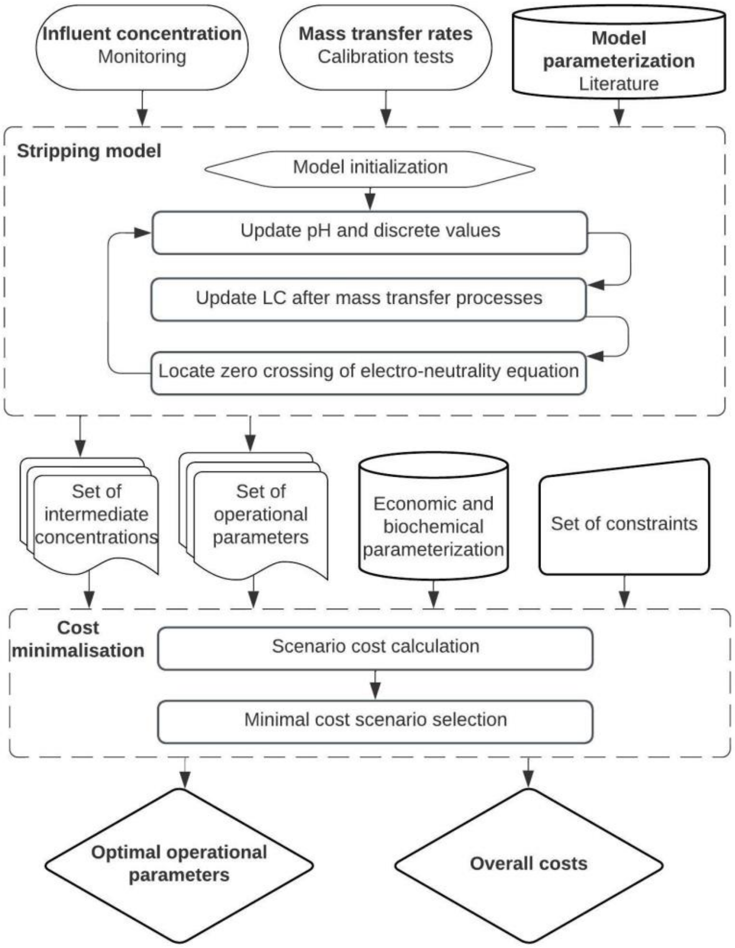

Figure 3. Overview of the followed modelling logic for the selection of economic optimal operational parameters. (LC =Lumped compounds).

2.2.1 Stripping model

For the first-stage SS unit, the model considers mass transfer processes for both NH_3 and CO_2, while only NH_3 volatilisation is considered for modelling the second-stage NH_3 SS unit (see subsequent paragraph 1). For the latter, it is assumed that CO_2 volatilisation from the LF is neglectable as the recirculated ventilation air is saturated with CO_2. As several chemical equilibria affect the pH throughout the stripping processes (Table 1), the pH alters, which affects the NH_3 volatilisation rates. Therefore, the pH changes are calculated by means of a charge balance during the dynamic simulations (see subsequent paragraph 2).

(1) The stripping rate of the volatile compounds NH_3 and CO_2 are limited by the NH_3 and CO_2 dissociation constants and thermodynamic equilibria of the distribution of free NH_3 and CO_2 in the gas and liquid phase. To derive the logarithmic relationship of NH_3 and CO_2 removal (i.e. liquid to gas transfer) rate as function of temperature and pH (Eq. 6 and 7), the dissociation rates of NH_4^+ and HCO_3^-/CO_3^{2-} were combined into NH_3 and CO_2 with the Matter-Mueller equation for two-film theory [12].

$$-\ln\frac{C_{NH_3,t}^{T}}{C_{NH_3,0}^{T}} = \frac{C\exp\left(\frac{E}{T+273.2}\right)(T+273.2)}{1+2.528*10^{(-10+D)}\exp\left(\frac{6054}{T+273.2}\right)} \qquad \text{(Eq. 6)}$$

$$-\ln\frac{C_{C02,t}^{T}}{C_{CO_2,0}^{T}} = \frac{(10^{-pH})^2\,C\,\exp\left(\frac{E}{T+273.2}\right)\,T+273.2}{(10^{-pH})^2+10^{-pH}\,K_{CO_2}+\,K_{CO_2}K_{HCO_3^-}} \qquad \text{(Eq. 7)}$$

Where $C_{i,0}^{T}$ and $C_{i,t}^{T}$ refer to the liquid-phase concentrations of compound I (e.g. NH_3 and CO_2) at time 0 and temperature T; K_{CO_2} and $K_{HCO_3^-}$ are the dissociation constants associated to the carbon buffer. C, D and E are unknown parameters that should be derived by performing a non-linear regression analysis on the data of the calibration experiments (section 2.2.4).

(2) During the dynamic simulation of the system, the chemical dissociation processes are assumed to be in a steady state in comparison to the mass transfer processes as mass transfer processes occur at a slower rate than dissociation reactions. The prevailing pH in the SS unit is derived by solving the algebraic equation arising from the charge balance (electro-

neutrality equation, Eq. 8) which makes use of lumped components (summation of the concentration of all equilibrium forms) [27] [28].

$$\Delta = C_{H^+} - C_{OH^-} + C_{NH_4^+} - C_{HCO_3^-} - C_{CO_3{}^{2-}} - C_{H_2PO_4^-} - 2\,C_{HPO_4^{2-}} - C_{NO_3^-} + C_{Z^+} \qquad \text{(Eq 8)}$$

The used lumped components and relative dissociation constant can be found in Table 1. The concentration change due to the mass transfer processes is linked to the lumped components resulting in a mass balance for all lumped components. The dissociation reactions are excluded from the mass balance equations as they are considered a steady state. C_{Z^+} corresponds to the concentration of positive charged compounds that are not influenced by the prevailing pH equilibrium.

Substituting the equations associated with the lumped components in the electro-neutrality equation results in following equation:

$$\begin{aligned}\Delta = C_{H^+} + \frac{C_{H^+}C_{TNH}}{C_{H^+} + K_{NH_4{}^+}} - \frac{C_{H^+}\,C_{TIC}\,K_{CO_2}}{C_{H^+}{}^2 + C_{H^+}K_{CO_2} + K_{CO_2}\,K_{HCO_3{}^-}} \\ - 2\,\frac{C_{TIC}\,K_{CO_2}\,K_{HCO_3{}^-}}{C_{H^+}{}^2 + C_{H^+}K_{CO_2} + K_{CO_2}\,K_{HCO_3{}^-}} - \frac{C_{H^+}C_{TIP}}{C_{H^+} + K_{H_2PO_4{}^-}} \qquad \text{(Eq. 9)} \\ - 2\,\frac{K_{H_2PO_4{}^-}\,C_{TIP}}{C_{H^+} + K_{H_2PO_4{}^-}} - C_{NO_3{}^-} + C_{Z^+}\end{aligned}$$

The implicit equation (9) is solved for the H^+ concentration by using the iteratively Newton-Raphson method to locate the zero crossing [27].

2.2.2 Minimal cost scenario selection

The NH_3 stripping model simulations (section 2.2.1) were fed to the cost scenario model. The objective is to minimise the overall costs (TC) associated with the treatment of 1 m^3 influent (Eq. 10), which is calculated by the summation of costs associated with the SS unit (C_s) and costs incurred by NDN treatment (C_{NDN}). Eq. 11 and 17 provide the cost estimation for C_s and C_{NDN} respectively. The stripping costs are based on the total energy consumption by pumps

$(E_{a,b}^{Pumps_S})$ and heating, which include thermal energy to compensate heat loss from convection $(E_{a,b,T}^{Heatloss_{C_S}})$, air ventilation $(E_{a,T}^{Heatloss_{V_S}})$ and unrecovered heat from outgoing manure $(E_{T}^{Heatloss_{I_S}})$, consumption of NaOH (C_N^{NaOH}) to increase the pH, counter acid consumption to capture the stripped NH_3, which is calculated as a function of the NH_3 yield $(Y_{a,b,T,f}^{NH_3})$ and the depreciation costs of the capital costs associated with SS construction $C_{a,b}^{Capitalstripper}$ minus the revenue generated by the produced NH_4^+ salt. The unit price for electricity energy, heat energy, counter acid use and NH_4^+ salts are given by $P^{Electrity_E}$, P^{Heat_E}, P^{AS} and P^{CA} respectively. The cost calculation depends on the choice of operational settings: CO_2 stripping time (a), NH_3 stripping time (b), temperature (T) and addition of NaOH (f), which are used as decision variables.

$$TC = C_s + C_{NDN} \qquad \text{(Eq. 10)}$$

$$\begin{aligned} C_s = \sum_{a,b,T,f} \Big[& \big(E_{a,b}^{Pumps_S}\big)\, P^{Electrity_E} + +\big(E_{a,b,T}^{Heatloss_{C_S}} + E_{a,T}^{Heatloss_{V_S}} \\ & + E_{T}^{Heatloss_{I_S}}\big)\, P^{Heat_E} + C_f^{NaOH} - Y_{a,b,T,f}^{NH_3}\,(P^{AS} - P^{CA}) \\ & + C_{a,b,T,f}^{Capital\ stripper} \Big] \end{aligned} \qquad \text{(Eq. 11)}$$

The total thermal energy consumption of the SS unit consists of three parts (heat loss by convection, ventilation, and heat exchanger). Heat loss by convection is estimated by calculating the heat transfer coefficient over a flat plate under forced convection for the air exposed walls which is done by Eq. 12 [29].

$$E_{a,b,T}^{Heatloss_{C_S}} = \frac{(T_T - T_o)\, A^{surface}}{\frac{1}{0.036 \left(\frac{u_{\infty,i}\, L\, \rho_T}{\mu_T}\right)^{\frac{4}{5}} Pr_T^{\frac{1}{3}}\, k_T^{air}\, L} + \frac{D}{k^{\,housing}} + \frac{1}{0.036 \left(\frac{u_{\infty,o}\, L\, \rho_T}{\mu_T}\right)^{\frac{4}{5}} Pr_T^{\frac{1}{3}}\, k_T^{air}\, L}}\, Time_{a,b} \qquad \text{(Eq. 12)}$$

Where $(T_T - T_o)$ equals the difference between the operating temperature and the outside temperature. For the outside temperature, we assumed the yearly average temperature in Uccle, Belgium. $A^{surface}$ stands for the surface area of the installation that is in contact with the environment. $u_{\infty,i}$ and $u_{\infty,o}$ represent the inside and outside air speed. The characteristic length (L) along the flow equals the length of the SS unit. ρ, μ and k^{air} refer to density, viscosity and thermal conductivity of air and are dependent on the Film temperature. Also the Prandtl number (Pr) is correlated to the film temperature. The thermal conductivity and thickness of the isolated SS walls are given by $k^{housing}$ and D respectively.

In addition, a part of the heat is lost through air ventilation to lower the CO_2 concentrations in the recirculation gas during the CO_2 stripping phase and thus depends on the CO_2 stripping time and the operating temperature (Eq. 13):

$$E_{a,T}^{Heatloss_{V_S}} = V_a^{air}\, C_T^{air}\, (T_T - T_o) \qquad \text{(Eq. 13)}$$

Where V_a^{air} equals the amount of air vented, which depends on CO_2 stripping time (a), and C_T^{air} is the heat capacity of the air.

Another part of the thermal energy is lost when the LF leaves the installation. As the heat exchanger recovers a fraction of the heat energy embedded in the outgoing fraction to warm up the incoming LF with a certain efficiency $(1 - \varepsilon^{heat\ exchanger})$, only a part of the energy requirement to reach the desired operational temperature must be provided by external energy (Eq. 14).

$$E_T^{Heatloss_{I_S}} = (T_T - T_o)\, C_T^{influent}\, (1 - \varepsilon^{heat\ exchanger}) \qquad \text{(Eq. 14)}$$

Where $C_T^{influent}$ is the heat capacity of the LF of manure (depending on the prevailing temperature). The total NH_3 recovery yield ($Y_{a,b,T,f}^{NH_3}$) is assumed to be equal to the integrated amount of volatilised NH_3 during CO_2 and NH_3 stripping. This assumption is considered to be valid by the authors as the SS process is a closed process whereby only a negligible amount of NH_3 leaves the system due to the ventilation of recirculation gas. The NH_3 yields for the different operational parameters are derived from the stripping simulation model as this is the result of a strongly non-linear process with changing pH over time.

$$Y_{a,b,T,f}^{NH_3} = \int_0^{time_a} \frac{C\ \exp\left(\frac{e}{T}\right)\ T}{1 + 2.528 * 10^{(-pH_{a,T}(t)+d)}\ \exp\left(\frac{6054}{T}\right)}\, dt + \int_0^{time_b} \frac{C\ \exp\left(\frac{e}{T}\right)\ T}{1 + 2.528 * 10^{(-pH_{a,b,T,f}(t)+d)}\ \exp\left(\frac{6054}{T}\right)}\, dt \qquad \text{(Eq. 15)}$$

Both energy consumption by pumps $\left(E_{a,b}^{Pumps_S}\right)$ and the depreciation costs per cubic meter LF treated ($C_{a,b}^{Capital\ stripper}$) are a function of retention $time_{a,b}$ which depends on the selected time for CO_2 -and NH_3 stripping.

$$E_{a,b}^{Pumps_S} = U^{energy_S}\ StrippingTime_{a,b} \qquad \text{(Eq. 16)}$$

$$C_{a,b}^{capital_S} = U^{capital\_S}\ StrippingTime_{a,b}$$

Where $U^{energy\_S} and\ \ U^{capital\_S}$ are the unit cost associated to energy consumption of pumps (recirculation of LF and air) and capital costs for the SS.

The NDN cost is calculated based on the energy requirement for aeration $E_{a,b,T,f}^{Aeration}$, depreciation costs associated with construction $C_{a,b,T,f}^{capital_{NDN}}$ and costs associated with the consumption of methanol $C_{a,b,T,f}^{Methanol}$ to facilitate the denitrification.

$$C_{NDN} = E_{a,b,T,f}^{Aeration} \quad P^{Electricity_E} + \; C_{a,b,T,f}^{capital_{NDN}} \; + C_{a,b,T,f}^{Methanol} \qquad \text{(Eq. 17)}$$

To calculate the aeration requirement of the NDN processing, the biological phases model was used which considers the biological processes occurring in the anoxic and aerobic phases of a typical NDN system, following the reasoning of Fabbricino and Pirozzi [30]. The algorithm makes use of the mass balance equations between input and output flows for the considered substrates and microorganisms (Supplementary materials (SM) A). The actual aeration energy is calculated based on the oxygen consumption of autotrophic and heterotrophic biomasses, yielded after parametrisation of the model, assigning influent concentrations modelled by the previous model step for the operational stripping strategies and limiting the allowed effluent concentration, divided by the aeration efficiency (Eq. 18).

$$E_{a,b,T,f}^{Aeration} = \frac{(\% \; \frac{1-Y_H}{Y_H} * u_H * X^{B,H} \; \mathrm{V}_{a,b,T,f} + \% \frac{4{,}57-Y_A}{Y_A} * u_A * X_{a,b,T,f}^{B,A}}{Aeration\ efficiency} \qquad \text{(Eq. 18)}$$

Equation system S1-S5, derived from activated sludge model (ASM), expresses constraints associated with the consumption and break-down of organic matter (Eq S1), nitrification and biomass assimilation/respiration of NH_3 (Eq S2), denitrification of NO_3^- (Eq S3), and heterotrophic (Eq S4) and autotrophic (Eq S5) microorganisms growth.
An additional constrain was defined to comply with the desired effluent quality characteristics for NDN processing of (co-digested) LF pig manure, namely $C_{NH,e}$ and $C_{NO,e}$ should both be equal to the values found by effluent monitoring samples characterisation.

The capital costs associated with the use of the NDN tank were calculated by multiplying the required tank volume fraction $\frac{\mathrm{V}_{a,b,T,f}}{V_{reference}}$ with the reference unit cost price $U_{Reference}^{capital\_NDN}$, while the methanol consumption was derived from the assumption that the biodegradable COD in the influent ($C_{a,b,T,f}^{CODb,i}$) plus COD provided by the methanol addition ($A_{a,b,T,f}^{Methanol}$) should be at least 5 times the denitrified N content $\left(C_{a,b,T,f}^{TN,i} - C_{a,b,T,f}^{TN,e}\right)$.

$$C_{a,b,T,f}^{capital_{NDN}} = U_{Reference}^{capital\_NDN} \frac{V_{a,b,T,f}}{V_{reference}} \quad \text{(Eq. 19)}$$

$$5 * \left(C_{a,b,T,f}^{TN,i} - C_{a,b,T,f}^{TN,e}\right) \leq C_{a,b,T,f}^{CODb,i} + A_{a,b,T,f}^{Methanol} \cap C_{a,b,T,f}^{Methanol} = P^{Methanol} A_{a,b,T,f}^{Methanol} \quad \text{(Eq. 20)}$$

The full economic and biochemical parameterizing can be found in SM B. After the scenario cost calculation, the minimal cost scenario was selected by means of minimum selection Matlab script.

2.2.3 Model scenarios

In this study, we have optimised the operational settings for 18 scenarios including two inputs (i.e. LF of manure and LF of co-digested manure), three treatment trajectories (i.e. NDN, stripping (AS) + NDN, stripping (AN) +NDN) and three market situations (low, medium and high resource prices) (Table 2). The pricing scenarios used in this study were derived from the cost prices of resource commodities during three different time periods. The first period, which represented pre-inflation conditions before the onset of significant price increases in the global economy in 2021, corresponded with the low-price scenario. The second period, which captured the price peaks observed between March and May 2022, corresponded with the high price scenario. Finally, the third period, which reflected stabilised prices at a high plateau during the end of 2022 and beginning of 2023, corresponded with the medium price scenario. The pricing scenarios were developed based on the factors contributing to price fluctuations, including ongoing complications from the COVID-19 pandemic, supply chain disruptions and geopolitical tension.

NDN_0-Scenarios are the default scenario where the conventional treatment practices are modelled for (co-digested) LF of manure, i.e., inserting the feedstock in NDN unit without any pre-treatment. Other scenarios simulate the optimal setting for a SS placed before an NDN tank working with different scrubbing acids H_2SO_4 (NDN_{SS_AS}) and HNO_3 (NDN_{SS_AN}) to treat (co-digested) LF of manure. As it is assumed that co-digestion occurs on-site, the SS unit can make use of the excess heat originating from the combined heat and power unit associated with co-digestion which is cheaper than heating the LF by electrical heating as occurs in the scenarios involving undigested manure treatment. We assumed that there was no difference in stripping efficiency between the scenarios using a different counter acid as indicated by the results yielded in the calibration experiments (section 2.2.4). The scenario set up and the resource price assumptions for each scenario are summarised in Table 2. SM C provides an overview on the CAPEX calculation.

Table 2. Overview of the main assumption of each scenario.

Scenario tree			
Input material	Price level	Treatment	Scenario
LF manure	Low	NDN	Scenario M-L$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario M-L$_{€}$-NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario M-L$_{€}$-NDN$_{SS\_AN}$
	Medium	NDN	Scenario M-M$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario M-M$_{€}$-NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario M-M$_{€}$-NDN$_{SS\_AN}$
	High	NDN	Scenario M-H$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario M-H$_{€}$-NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario M-H$_{€}$-NDN$_{SS\_AN}$
LF co-digested manure	Low	NDN	Scenario D-L$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario D-L$_{€}$-NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario D-L$_{€}$-NDN$_{SS\_AN}$
	Medium	NDN	Scenario D-M$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario D-M$_{€}$-NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario D-M$_{€}$-NDN$_{SS\_AN}$
	High	NDN	Scenario D-H$_{€}$-NDN$_{0}$
		Stripping-scrubbing (H_2SO_4) + NDN	Scenario D-H$_{€}$- NDN$_{SS\_AS}$
		Stripping-scrubbing (HNO_3) + NDN	Scenario D-H$_{€}$- NDN$_{SS\_AN}$

Material	Unit	Price level		
		Low	Medium	High
Electrical energy[a]	€ kWh^{-1}	0.15	0.3	0.6
Heat energy[b]	€ kWh^{-1}	0.07	0.07	0.07
NaOH-pellets[c]	€ t^{-1}	600	700	800
H_2SO_4 (98%)[c]	€ t^{-1}	120	210	260
HNO_3 (60%)[c]	€ t^{-1}	200	300	400
AS (7.2 %N)[d]	€ t^{-1}	79	151	216
AN (19.1 %N)[d]	€ t^{-1}	210	401	573
Methanol[c]	€ t^{-1}	411	667	852

Sources: [a] [31]. [b] [32]. [c] Price quote of retailer [d] [33].

2.2.4 Experimental set-up of calibration experiments

To calibrate the proposed model, batch experiments were conducted in a full-scale air stripping tower at the Bio Sterco manure processing plant in Hooglede, Belgium. The SS unit, developed by Detricon bvba (Belgium) with a capacity to process 2 m^3 h^{-1}, consists of two vertical acrylate stripping columns (2.5m x 3m x 2m) with scrubbing column (2.5m x 3m x 2.5m). Each stripping tower contains 9 spraying nozzles and is filled with pall rings as packing material. Both stripping columns receive a ventilation flow of 1,440 m^3 h^{-1} with an air speed of 0.2 - 0.8 m s^{-1}. The NH_3-rich air circulates over a scrubber column where NH_3 is absorbed by a diluted counter acid solution (H_2SO_4 or HNO_3) which generates an AS or AN solution, respectively.

The performance of the first-stage stripping tower (Figure 1) and its effect on the chemical composition of the LF was evaluated by performing batch experiments at different operational temperatures (20, 35 and 50 °C) with an open ventilation loop. Samples were taken periodically (15 minutes) from liquid storage tank at the bottom of the stripping column to determine Electrical Conductivity (EC), TIC and NH_4^+-N content. Each experiment was conducted with a batch of 2 m^3 and a constant airflow rate for 2 hours without any pH adjustments. The second-stage SS unit was evaluated by performing factorial batch experiments under different operational conditions including pH (8, 8.6, 9 and 10), temperature (20, 30, 35 and 50 °C) and counter-acid (HNO_3 and H_2SO_4) with a closed ventilation loop. The stripping column was loaded with 2 m^3 of LF and was brought to the designated temperatures. Before the LF was stripped, the loaded LF was adjusted to the desired pH values by adding 60% NaOH solution. The experiments were conducted for 2-3 hours, and samples were taken every 15 minutes from a liquid storage tank at the bottom of the stripping column to analyse EC and NH_4^+ content.

2.2.5 Input and product characterisation

A monitoring campaign for the LF of (co-digested) manure, and NDN effluent was carried out to parameterise the influent and effluent concentrations fed to the different model scenarios. The produced AN and AS were characterised to determine their compliance with RENURE and Fertilising Products Regulation (FPR) criteria and thus potential market price. All monitoring samples were collected at the Bio Sterco manure processing plant, except the LF of digestate which was sampled at the IVACO manure processing plant in Gistel. This plant is equipped with an anaerobic digester processing circa 12,500 t of manure and co-substrates. The analysed parameters included pH, EC, Dry Matter (DM), total Chemical Oxygen Demand (COD_T), soluble Chemical Oxygen Demand (COD_S), Biological Oxygen Demand (BOD), Total N (TN), NH_4-N, NO_3-N, Sulphur (S), Total Organic Carbon (TOC), Copper (Cu) and Zink (Zn). The corresponding analysis methods are described in SM D.

3 RESULTS

3.1 Input and product characterisation

The average composition of the LF of manure, LF of co-digested manure, effluent of NDN and produced AN and AS found in this study are summarised in Table 3. The results of the LFs and effluent characterisations are used to feed the economic optimisation model, while the results of the produced AN and AS give an indication about the product quality and pricing.

Table 3. Characterisation (mean ± standard deviation) on fresh weight (FW) of LF of manure, LF of co-digested manure, effluent of NDN, ammonium nitrate (AN) solution and ammonium sulphate (AS) solution.

	Unit	LF of manure	LF of co-digested manure	Effluent of NDN	AN solution	AS solution
pH		8.1 ± 0.25	8.4 ± 0.38	7.8 ± 0.21	6.5 ± 0.38	6.2 ± 0.47
EC	mS cm^{-1}	29 ± 3	31 ± 4	27 ± 4	343 ± 21.9	286 ± 9.1
DM	g kg^{-1}	35.6 ± 6.3	30.7 ± 5.8	13.6 ± 2.1	178 ± 13.1	298 ± 26.7
TIC	g kg^{-1}	30.5 ± 2.3	18.3 ± 4.1	n.d.	n.d.	n.d.
TOC	g kg^{-1}	n.d.	n.d.	n.d.	<1	<1
COD_S	g kg^{-1}	13.1 ± 3.6	6.1 ± 1.3	n.d.	n.d.	n.d.
COD_T	g kg^{-1}	33.7 ± 4.8	22.3 ± 3.1	12.4 ± 4.5	n.d.	n.d.
BOD_5	g kg^{-1}	11.7 ± 2.1	3.4 ± 0.6	0.9 ± 0.4	n.d.	n.d.
TN	g kg^{-1}	5.3 ± 0.42	4.2 ± 0.71	0.6 ± 0.2	191 ± 27.9	72.4 ± 11.3
NH_4^+-N	g kg^{-1}	3.7 ± 0.30	2.9 ± 0.38	0.3 ± 0.1	91 ± 18.1	72.3 ± 14.2
NO_3^--N	g kg^{-1}	0.02 ± 0.01	0.06 ± 0.02	0.26 ± 0.12	96 ± 15.0	0.005 ± 0.002
S	g kg^{-1}	n.d.	n.d.	n.d.	0.37 ± 0.061	83.2 ± 21.8
Cu	mg kg^{-1}	28.7 ± 13.9	24.9 ± 6.3	23.5 ± 9.9	12.6 ± 7.3	22.1 ± 8.6
Zn	mg kg^{-1}	52.9 ± 11.2	48.2 ± 9.1	36.4 ± 8.6	34.3 ± 12.8	55.6 ± 24.1

3.2 Calibration tests

3.2.1 NH_3 stripping rate

Figure 4 shows the NH_3 removal efficiency obtained by the block experiment for NH_3 stripping. The block experiment examined the effect of pH (8, 8.6, 9 and 10), temperature (20, 30, 35 and 50°C) and scrubber acid (HNO_3 and H_2SO_4) on the NH_3 stripping rate. For a constant temperature (30 °C) and air flow rate (1,440 m^3 h^{-1}), the removal efficiencies significantly improved from 27% to 40% for a pH elevation from 8 to 10. However, from the pH value of 9, a reduced efficiency increase is observed, and a stagnant phase of maximal efficiency is reached from a pH of 9.2

onwards. For higher temperature values, this trend already started to occur at lower pH values. As temperature influences both the free NH_3 fraction (δ_{NH3}) and $K_{L,NH3}$, it strongly affects the NH_3 removal rate. A temperature alteration from 20°C to 30°C enhanced the stripping rate from 20% to 52% for a pH of 8, while the same temperature alteration enhanced the stripping rate from 29% to 69% at a pH of 9. It can be observed that the interplay between temperature and pH is crucial to derive the stripping rate in an accurate manner. However, there was no difference in removal rates observed between the different counter acid.

A nonlinear multivariate regression was conducted on equation 6 with unknown parameters C, D and E to reveal the relation between the slopes of linear regressions and both pH and temperature. C, D and E were estimated to 638, -4116 and -0.8 respectively. The nonlinear multivariate regression analysis showed a high correlation coefficient (R= 0.99). The regressed NH_3 stripping rate in function of pH and temperature based on the calibrated equation 6 is shown in Figure 4C. The results of the CO_2 stripping calibration tests can be found in SM E.

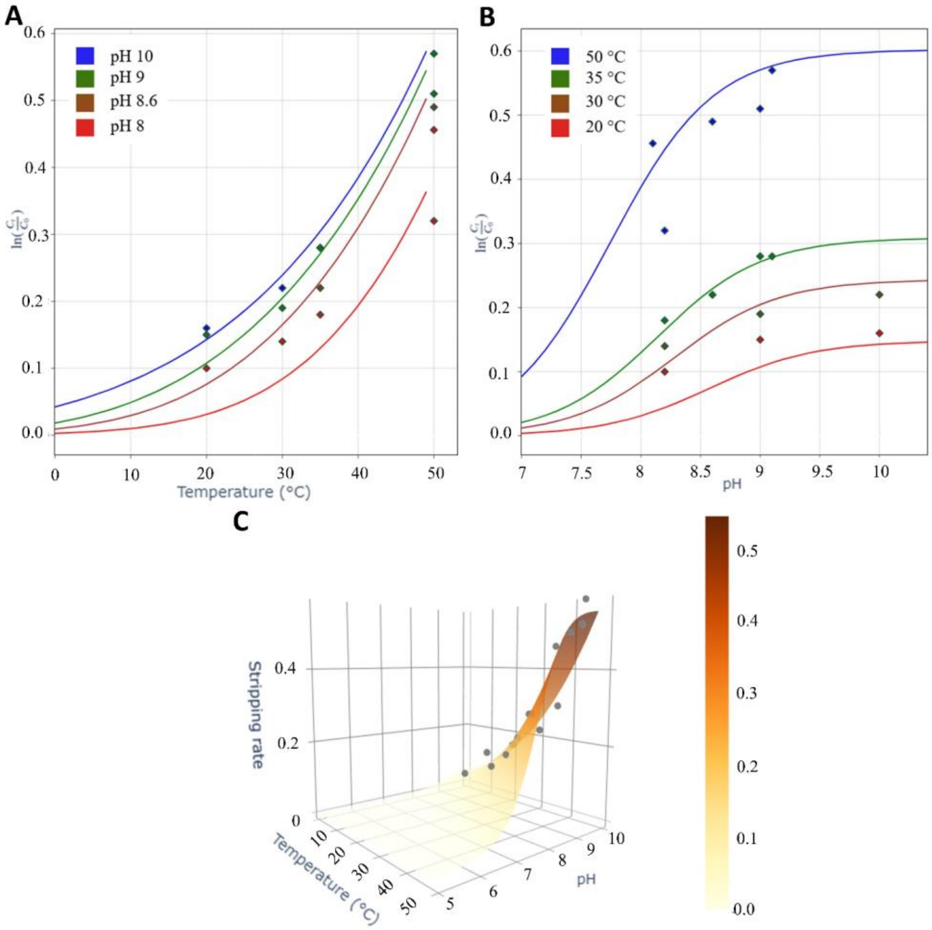

Figure 4. Regressed NH_3 removal efficiency based on two film model for different pH and temperatures. The experimental results are represented by the plotted dots. A) NH_3 removal efficiency in function of temperature B) NH_3 removal efficiency in function of pH C) NH_3 removal efficiency in function of temperature and pH.

3.3 Optimisation modelling

3.3.1 Technical results of the scenarios

Figure 5 presents, per scenario, the optimal operational parameters to reach the minimal costs, the amount of N recovered, amount of energy used per compartment, methanol and counter acid consumption. Results show that, when a SS unit is included, a higher fraction of N was recovered when processing the LF of co-digested manure (1.57-2.40 kg N t^{-1}) as compared to the LF of manure (1.03-1.34 kg N t^{-1}). This is due to the higher stripping temperatures applied for LF of co-digested manure (50°C vs 40-50 °C), as in the co-digestion scenarios energy prices are decoupled from the market price and the model therefore operates the SS at high temperatures and uses a longer retention time in the CO_2 stripping (85-185m vs 25-30m). Furthermore, NDN processing of LF originating from co-digested manure requires a larger input of methanol to sustain the denitrification process (Eq. 15) as compared to LF of manure, resulting in additional avoided cost when stripping a large fraction of N. When increasing the revenue from NH_4^+ salt ($Y_{c,n,T,N}^{NH_3}$ $(P^{AS} - P^{CA})$) production incrementally from 1.1 to 3 € kg^{-1} N because of higher resource pricing, the amount of recovered N gradually increased from 1.57 to 2.40 kg N t^{-1} for co-digested manure. This was realised by prolonging the CO_2 stripping time (85m to 185m) and NH_3 stripping time (40 to 70m) as elevated electrical energy prices did not strongly affect this economic balance of these scenarios.

For the treatment of the LF of manure, removing a large quantity of the carbonate buffer to increase the pH is solely economically favourable compared to NaOH-addition when energy prices are low due to significant heat losses associated with CO_2 stripping. Therefore, the model adds NaOH in the medium (2.6 kg t^{-1}) and high (3.4-3.8 kg t^{-1}) pricing scenarios to achieve the desired pH increment. Additionally, lower operational temperatures were recorded for the higher pricing scenarios (40-46°C) as compared to low pricing scenarios (50°C) due to elevated costs associated with heat losses during SS processes. However, at lower operational temperatures, similar N recovery can still be achieved between scenarios, by increasing the operational pH through the addition of NaOH, which compensates for the reduced NH_3 volatilisation at lower temperatures. Between 0.01 and 0.26 kg more N is recovered when using HNO_3 as compared to H_2SO_4 as a counter acid in the medium and high pricing scenario, due to higher profit margins on the produced NH_4^+ salt. For the low pricing scenario, H_2SO_4 seemed to be the more profitable counter acid.

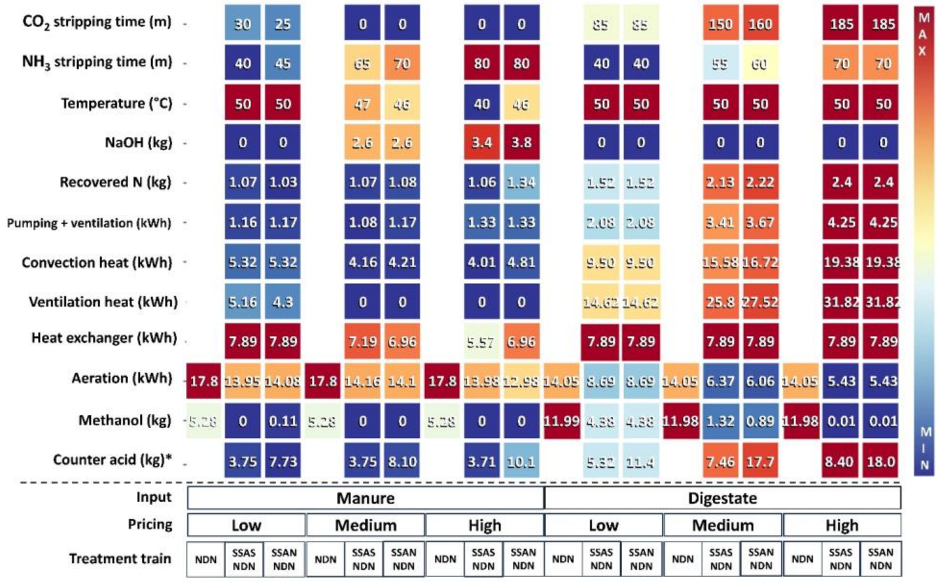

Figure 5. Technological results for the different sub-scenarios, calculated for the treatment of 1 t LF of manure/co-digestate. The colour scale represents the normalise results per parameter. Colours indicates weighted result per technological characteristic. *98% H_2SO_4 for SS_{AS} and 60% HNO_3 for SS_{AN}

When comparing the difference in energy consumption between scenarios, the on-site energy consumption of scenarios including SS is clearly higher (24.9-68.7 kWh t^{-1}) than non-stripping scenarios (14.1-17.8 kWh t^{-1}) as adding the energetically intensive SS process leads to an increased overall energy consumption (Figure 5). The energy required to process LF of co-digested manure using the treatment line of SS followed by NDN (42.8-68.7 kWh t^{-1}) is greater than the energy needed for processing the LF of manure through SS followed by NDN (24.9-33.5 kWh t^{-1}). This can be attributed to lower-priced heat energy that makes higher N recovery through prolonged stripping times and elevated operational temperatures the preferred option. Scenarios with an elevated N recovery in the form of NH_4^+ salt were associated higher energy consumption. This improved N removal also reduced the amount of N reaching the NDN unit, but this alone could not fully offset elevated energy consumption in the stripping unit. Furthermore, it's worth considering that producing 1 kg of mineral N through the HB process consumes 9.5 kWh [34], which can be saved when N is recovered by SS.

3.3.2 Economic results of the scenario

Figure 6 shows the economic results of the different modelled scenarios. Optimal use of the SS unit decreased the overall processing costs compared to the conventional scenario by 1% to 56 % depending on the scenario considered.

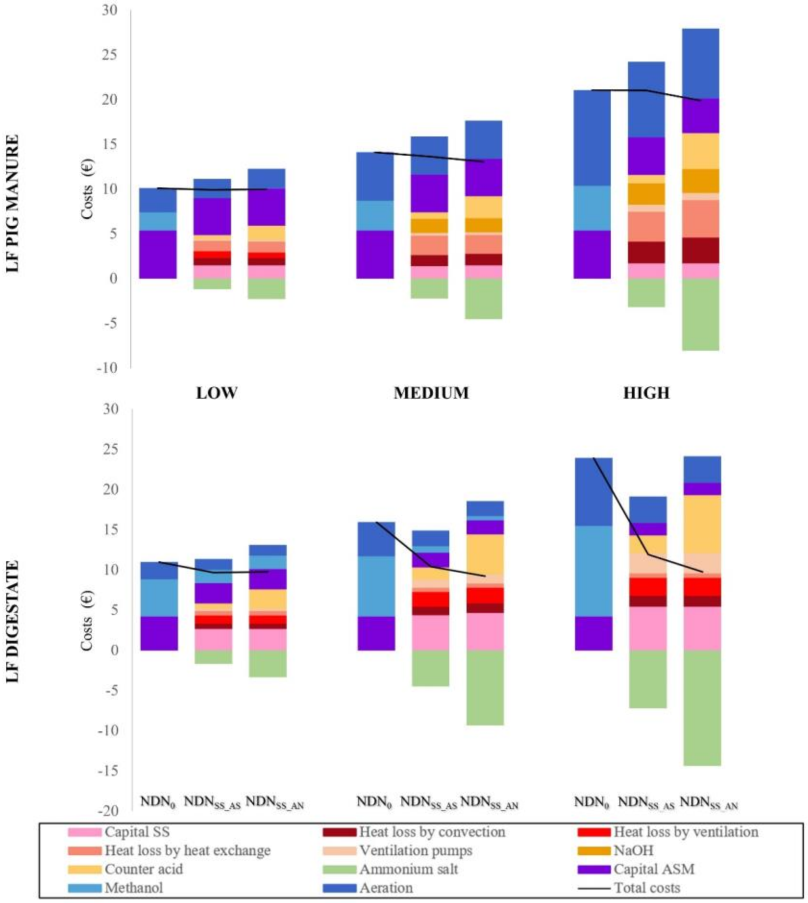

Figure 6. Economic results for the different sub-scenarios, calculated for the treatment of 1 t LF of (co-digested) manure. Each triplet includes the three treatment scenarios: NDN$_0$ (left), NDN$_{SS\_AS}$ (middle), NDN$_{SS\_AN}$ (right). From left to right the triplets are shown according to a pricing scenarios (low, medium and high). The upper row contains scenarios involving the treatment of LF of pig manure, while the bottom row shows the scenarios involving co-digested LF of pig manure.

When using the conventional treatment scenario, the processing costs of one t of LF of manure ranges from 10.1 to 21.1 € t^{-1} treated depending on the pricing of the resources, which includes capital cost of the NDN plant (5.4 € t^{-1}), costs associated with the purchase of methanol (2.0 – 5.0 € t^{-1}) and aeration costs (2.8 – 10.7 € t^{-1}). The model does not consider the cost associated with sludge and effluent disposal, as the authors presumed that the cost variation between scenarios is insignificant due to the relatively minor difference in sludge production related to N removal (ranging between 1.0 – 2.2 kg volatile suspended solids t^{-1}). The change in overall costs is thus solely due to a change in capital costs of the installation, consumption of energy and consumables and NH_4^+ salt yield. Scenarios involving manure treatment via SS with SA followed by NDN are characterised by additional costs associated with the installation (1.4 – 1.7 € t^{-1}) and operation (3.4 – 9.9 € t^{-1}) of an SS unit. However, when considering the avoided costs associated with further treatment in an NDN tank (-3.9 – -8.5 € t^{-1}) and income of mineral N fertiliser purchase (-1.2 – -3.2 € t^{-1}), the output indicates that the stripping scenario is slightly more economical than no N recovery (1 – 4%). Especially, the margin between NH_4^+ salt revenue and counter acid costs makes the SS unit a cost-reducing investment when recovering a large fraction of mineral N compared to the baseline scenario. As the profit margin between AN and its counter acid is even higher than AS and its counter acid (for the medium and high pricing scenario), the overall costs for scenarios M-M$_{€}$-NDN$_{SS\_AN}$ and M-H$_{€}$-NDN$_{SS\_AN}$ are even further reduced (5 – 8%).

The overall costs of co-digested manure LF processing through conventional NDN (12.0 – 23.9 € t^{-1}) are similar to the overall processing costs of manure LF (10.1 - 21.1 € t^{-1}) in the different pricing scenarios, while the magnitude of elements contributing to the overall costs strongly differs. Costs associated with LF of co-digested manure processing mainly originate from the consumption of methanol (4.6 – 11.3 € t^{-1}) due to the low COD:N ratio after digestion. Therefore, there is a high economic potential for N recovery from the LF of co-digested manure which in combination with lower heat energy prices resulted in higher N recovery through elevated temperatures and longer NH_3 and CO_2 stripping times. Therefore, costs associated with the infrastructure of the SS unit in scenario D-X-NDN$_{SS\_AS}$ were elevated (2.5 – 5.4 € t^{-1}) as compared to scenarios M-X-NDN$_{SS\_AS}$, while operational costs remained quasi the same (3.1 – 8.9 € t^{-1}). However, the effect on avoided costs was more distinct: NDN tank (-5.5 – -19.1 € t^{-1}) and income of mineral N fertiliser purchase (-1.7 – -7.2 € t^{-1}), which resulted in an overall reduction of 12 to 50% when implementing a SS unit with H_2SO_4 as counter acid. When using HNO_3 as counter acid the overall costs could be even lower (11 – 56%), because the higher profit margin between AN and its counter acid for the medium and high pricing scenarios allows to recover additional N units at higher marginal costs. The costs analysis per kg-N^{-1} processed can be found in SM F.

4 DISCUSSION

4.1 Calibration experiments

Over the last decades, experiments to access the removal rates of NH_3 stripping technology have been performed on laboratory, pilot and full-scale. The removal rates found during our experiment were similar to the removal rates found by other studies; Brienza et al. [15] found a NH_3 stripping efficiency of 22% while evaluating a pilot installation processing LF of digestate at low temperature (25°C) and low pH (8.0) with an average retention time of 2 hours, Baldi et al. [35] reached a removal efficiency of 62% when performing a stripping trial on digestate for 2 hours at a temperature of 48°C and an increased pH 9.5 by adding NaOH, Pintucci et al. [36] performed NH_3 stripping at low pH (7.8) and high temperature (55-65°C) and achieved a NH_3-removal between 28 and 46% depending on the temperature. Liu et al. [12] obtained a set of hourly NH_3-removal rates (8%; 15%, 30%, 53% and 57%) for different air flow rates (60, 120, 240, 600 and 840 m^3 h^{-1} m^3) when stripping urine at a temperature of 50°C and a pH of 10. These removal rates are at high air flow rates slightly higher than the NH_3-removal efficiency found in this study. This could be due to the higher COD content in manure than urine which jeopardised the NH_3 volatilisation rate by binding NH_4^+ to OM [15]. As Liu et al. [12] showed that further increasing the airflow rate above 600 m^3 h^{-1} m^{-3} could hardly enhance NH_3-removal rates. Therefore, we can assume that the airflow was not limiting the stripping efficiency in our study. The similarity of our results to those of other studies suggests that our calibration set is both reliable and applicable to a wider range of scenarios.

4.2 Economic performance

The economic viability of N recovery via a pathway including a NH_3 stripping technology is often questioned as conventional reactive N removal by NDN in waste streams as N_2 and refixed via HB seems to be the economic superior option for the treatment of LF of (co-digested) manure. De Vrieze et al. [14] found that the costs associated to NDN equal 10.95 € t^{-1} manure or 2.32 € kg-N^{-1} processed, while the treatment scenario containing SS followed by NDN had an elevated treatment cost of 16.51 or 3.51 € kg-N^{-1} processed. Brienza et al. [15] found that a combined system of NH_4^+ recovery through NH_3 stripping and an aerated constructed wetland (17.1 € t^{-1} LF of digestate, 3.71 € kg-N^{-1} processed) to achieve 90% N removal was economically undesirable compared to N removal from digestate by NDN (16.0 € t^{-1} processed, 3.40 € kg-N^{-1} processed). Menkveld and Broeders [37] achieved a total N removal of 85% on an SS digestate at a cost of 2.47 € kg-N^{-1} processed. Bolzonella et al. [17] provided a techno-economic assessment of a stripping system recovering less than 40% of the influent digestate N indicating a processing cost of 3.77 € kg-N^{-1} processed. The existing literature has so far focused on evaluating and monitoring new nutrient recovery technologies and concepts, without considering the economic optimisation of the system's process parameters. As a result, the economic performance of nutrient recovery may have been underestimated, leaving potential for further improvement. In our study, we demonstrate that an economically optimised two-step process involving N recovery followed by NDN to remove 90% of N embedded in LF of manure (9.92 € t^{-1} processed, 2.02 € kg-N^{-1} processed) or LF of co-digested manure (9.66 € t^{-1} processed, 2.54 € kg-N^{-1} processed) can result in superior economic performance compared to the conventional treatment of LF of manure (10.09 € t^{-1} processed, 2.06 € kg-N^{-1} processed) and LF of co-digested manure (11.98 € t^{-1} processed, 3.23 € kg-N^{-1} processed), even under low pricing scenarios. The net cost reduction achieved under a low resource price market is only 1-12% and under the high price scenario 4-56%. This is because under circumstances of higher resource prices N recovery through SS becomes even more economically advantageous as the increased operational expenditures are more than offset by the corresponding increase in revenues from sales of AS and AN. This is especially the case when processing LF of co-digested manure, because the energy costs are decoupled from higher market values for chemicals.

To calculate the net costs of the proposed N recovery pathway, it was assumed that the produced AS and AN solution could be sold according to the current N fertilisation prices. This can be assumed as the produced NH_4^+ solutions comply with the quality criteria for manure-derived RENURE products and liquid inorganic macronutrient fertiliser set by European FPR [19]. The concentration of TOC stays well below the prescribed 1%, while being in line with the minimum required TN content (Table 4). In addition, the AS and AN solutions are both in line with the maximal TOC:TN and the mineral N:TN ratio. The concentrations of the hazardous elements Cu and Zn in the NH_4^+ solutions are also far below the RENURE and FPR requirements. Hence, it can be inferred that the AS and AN solutions produced during the SS process can be considered as equivalents of mineral N, thereby confirming this pricing assumption [38].

Table 4. Composition requirements for the different fertilisers products defined by the Fertilising Product Regulation (EU) 1009/2019 and Joint Research Centre (JRC) RENURE products [19].

Fertiliser type	TN ($g\ kg^{-1}$ FW)	TOC ($g\ kg^{-1}$ FW)	TOC:TN	mineral-N_l:TN (%)	Cu ($mg\ kg^{-1}$ DW)	Zn ($mg\ kg^{-1}$ DW)
PFC 1(C)(I)(b)(i) (Fertilising Product Regulation)	≥ 50	≤ 10			≤ 600	≤ 1500
RENURE product (JRC)			≤ 3*	≥ 90*	≤ 300	≤ 800
AS solution	72	<1	<0.1	100	22.1	55.6
AN solution	191	<1	<0.1	100	12.6	34.3

*RENURE products should either comply with TOC:TN ratio or NH_4-N:TN ratio threshold.

4.3 Process optimisation model

Based on the results simulated with the proposed model, useful insights could be gained in optimal SS operations. When interpreting the results, one should be careful as our study and model is based on several assumptions and has some limitations. Firstly, the model was calibrated by performing stripping experiments on a commercial SS plant focussing on some specific aspects (CO_2 stripping time, NH_3 stripping time, temperature, and NaOH-addition) of the operations. The plant processing optimisation can be improved by including a wider set of parameters. Dimensioning and operational parameters related to gas mass transfer (e.g. gas/liquid speed and ratio) influence the transfer of volatile elements, thus are key for further improvement [39]. In addition, reactors can also differ in heat exchange properties through altered isolation material, wall thickness, air contact surface area and capital costs because of a different construction philosophy [40]. This means that the found optimal CO_2 stripping time, NH_3 stripping time, temperature and NaOH dosing are specific for the installation under study. However, our modelling logic can serve as example for the optimisation of other configurations by adapting the parameters accordingly. Furthermore, we used simplified assumptions to model the scrubbing unit by presuming that all stripped NH_3 is captured from the recirculation gas, implying that the scrubbing unit is working optimally and no accumulation of NH_3 occurs in the returning gas to the stripping unit which would negatively affect the stripping rate. As we found that the NH_3 concentration in the recirculation gas did not exceed 2 ppm, the authors concluded that the drawn assumption was valid for the tested situation. However, when the scrubbing process makes use of weak acid such as citric acid or a biological acidification process, a higher scrubber pH is expected which limits the scrubber efficiency and leads to a non-optimal NH_3-removal [41]. This would cause NH_3 accumulation in the recirculation gas, compromising the NH_3 volatilization rate in the stripping unit [42]. Therefore, a more advanced scrubbing process simulation should be added when other than strong counter acids are used.

To estimate the costs associated with NDN treatment a steady state ASM model was used, therefore the model excludes dynamic microbiological interactions from modelling but rather focuses on simple approach to estimate aeration and SRT requirement to achieve the desired effluent concentration [43]. Therefore, the model does not consider seasonality which can have a strong influence on the ASM parameterisation. We opted to model the optimal operational parameters for the average temperature found for Flanders. However, different results can be expected for summer and winter conditions. The pricing by the ASM model only considered the conventional NDN processes, whereas processes such as nitritation/denitritation and partial nitritation/anammox were excluded. Both nitritation/denitritation and nitritation/anammox could benefit from the elevated temperatures of the LF fraction after stripping. As these processes are characterised with reduced aeration requirements (0.8-2 kWh kg-N^{-1} vs 4 kwh kg-N^{-1}), the implementation of this alternative treatment route could be considered in the future [44].

5 CONCLUSIONS

This paper presents a model to minimise the costs associated with LF treatment via two-stage stripping in tandem with NDN by optimising four operational system parameters, including CO_2 stripping time, NH_3 stripping time, temperature, and NaOH-addition, for 12 new scenarios which were compared to 6 default scenarios. Lower treatment costs were realised compared to the conventional scenarios for all cases including an optimised SS unit. For the SS scenarios processing the LF of manure, the net costs decreased from 1 to 8% compared to the conventional N removal scenario mainly depending on resource pricing, while for LF of co-digested manure processing a reduction between 11 and 56 % was found. The results of the technical analysis indicated that optimal operational parameters strongly vary according to the prevailing economic scenery, influent and mineral acid. High energy prices push the system to low temperatures and CO_2 stripping times to reduce heat losses, while large quantities of NaOH are added to maintain N recovery efficiency. When lower-priced heat energy is available, the model opts to further strip NH_3 at high temperature (50°C) and maintain long CO_2 and NH_3 stripping times. This research enhanced understanding of the performance of a two-stage SS unit followed by NDN treatment and illustrates the importance of operating with an optimal operational management of the SS unit to increase economic viability.

ACKNOWLEDGEMENTS

This work was supported by the European Union's Horizon 2020 Research and Innovation programme under project "Innovative nutrient recovery from secondary sources – Production of high-added value fertilisers from animal manure" [FERTIMANURE, Grant Agreement number 862849]. We also thank Marie-Chantal Herteleer for her support during laboratory activity. For support with stripping experiments, we thank Wouter Naessens.

SOURCES

[1] B.M. Campbell, D.J. Beare, E.M. Bennett, J.M. Hall-Spencer, J.S. I. Ingram, F. Jaramillo, R. Ortiz, N. Ramankutty, J.A. Sayer, D. Shindell, Agriculture production as a major driver of the Earth system exceeding planetary boundaries, Ecol. Soc. 22 (4) (2017) 8-. https://doi.org/10.5751/ES-09595-220408.

[2] J. Rockström, J. Gupta, D. Qin, S.J. Lade, J.F. Abrams, L.S. Andersen, D.I. Armstrong McKay, X. Bai, G. Bala, S.E. Bunn, D. Ciobanu, F. DeClerck, K. Ebi, L. Gifford, C. Gordon, S. Hasan, N. Kanie, T.M. Lenton, S. Loriani,.., D. Obura, Safe and just Earth system boundaries, Nat. 619 (7968) (2023) 102–111. https://doi.org/10.1038/s41586-023-06083-8

[3] Commission regulations (EU) No 142/2011 of 25 February 2011 implementing Regulation (EC) No 1069/2009 of the European Parliament and of the Council laying down health rules as regards animal by-products and derived products not intended for human consumption and implementing Council Directive 97/78/EC as regards certain samples and items exempt from veterinary checks at the border under that Directive.

[4] Y. Hou, G. L. Velthof, J. P. Lesschen, I. G. Staritsky, O. Oenema, Nutrient Recovery and Emissions of Ammonia, Nitrous Oxide, and Methane from Animal Manure in Europe: Effects of Manure Treatment Technologies, Environ. Sci. Technol. 51 (2017) 375–383. https://doi.org/10.1021/acs.est.6b04524

[5] R. Vingerhoets, M. Spiller, J. De Backer, A. Adriaens, S. E. Vlaeminck, E. Meers, Detailed nitrogen and phosphorus flow analysis, nutrient use efficiency and circularity in the agri-food system of a livestock-intensive region, J. Clean. Prod. 410 (2023) 137278–. https://doi.org/10.1016/j.jclepro.2023.137278

[6] A. Derden, R. Dijkmans, Addendum Bij de Studie “Beste Beschikbare Technieken (BBT) Voor Mestverwerking-Derde Uitgave” Mestverwerkingstrajecten: BBT En “Technieken in Opkomst” Met Focus Op Nutriëntrecuperatie Eindrapport. https://emis.vito.be/sites/emis/files/study/Eindrapport_addendum_bij_BBT_mestverwerking_versie_sept_2020.pdf/, 2020 (accessed 15 March 2023).

[7] Departement Landbouw & visserij, Landbouwmonitoringsnetwerk: Landbouwcijfers & sectoroverzicht. https://lv.vlaanderen.be/, 2023 (accessed 03 June 2023).

[8] A. Leip, C. Caldeira, S. Corrado, N. J. Hutchings, J. P. Lesschen, M. Schaap, W. de Vries, H. Westhoek, H. J. van Grinsven, Halving nitrogen waste in the European Union food systems requires both dietary shifts and farm level actions, Glob. Food Sec. 35 (2022) 100648-. https://doi.org/10.1016/j.gfs.2022.100648.

[9] M. Spiller, M. Moretti, J. de Paepe, S. E. Vlaeminck, Environmental and economic sustainability of the nitrogen recovery paradigm: Evidence from a structured literature review, Resourc. Conserv. Recycl. 184 (2022) 106406-. https://doi.org/10.1016/j.resconrec.2022.106406

[10] C. Scheer, K. Fuchs, D. E. Pelster, K. Butterbach-Bahl, Estimating global terrestrial denitrification from measured $N2O:(N2O + N2)$ product ratios, Curr. Opin. Environ. Sustain. 47 (2020), 72–80. https://doi.org/10.1016/j.cosust.2020.07.005

[11] R. Vingerhoets, J, de Backer, A. Adriaens, S. Verbesselt, M. de Corte. S. Vlaeminck, M. Spiller, E. Meers, Begroting van stikstof-, fosfor- en eiwitstromen in het agrovoedingssysteem in Vlaanderen: Indicatoren voor efficiëntie en circulariteit. https://omgeving.vlaanderen.be/nl/begroting-van-stikstof-fosfor-en-eiwitstromen-in-het-agrovoedingssysteem-in-vlaanderen-indicatoren/, 2021 (Accessed 20 May 2023).

[12] B. Liu, A. Giannis, J. Zhang, V. W.-C. Chang, J.-Y. Wang, Air stripping process for ammonia recovery from source-separated urine: modeling and optimization, J. Chem. Technol. Biotechnol. 90 (2015) 2208–2217. https://doi.org/10.1002/jctb.4535

[13] C. Vaneeckhaute, V. Lebuf, E. Michels, E. Belia, P. A. Vanrolleghem, F. M. G. Tack, E. Meers, Nutrient Recovery from Digestate: Systematic Technology Review and Product

Field Code Changed

Field Code Changed

Formatted: Dutch (Belgium)

Formatted: Dutch (Belgium)

Classification, Waste Biomass Valori. 8 (1) (2017), 21–40. https://doi.org/10.1007/s12649-016-9642-x

[14] J. De Vrieze, G. Colica, C. Pintucci, J. Sarli, C. Pedizzi, G. Willeghems, A. Bral, S. Varga, D. Prat, L. Peng, M. Spiller, J. Buysse, J. Colsen, O. Benito, M. Carballa, S. E. Vlaeminck, Resource recovery from pig manure via an integrated approach: A technical and economic assessment for full-scale applications, Bioresour. Technol. 272 (2019) 582–593. https://doi.org/10.1016/j.biortech.2018.10.024

[15] C. Brienza, N. Donoso, H. Luo, R. Vingerhoets, D. de Wilde, D. van Oirschot, I. Sigurnjak, J. K. Biswas, E. Michels, E. Meers, Evaluation of a new approach for swine wastewater valorisation and treatment: A combined system of ammonium recovery and aerated constructed wetland, Ecol. Eng. 189 (2023) 106919–. https://doi.org/10.1016/j.ecoleng.2023.106919

[16] J. L. van Puffelen, C. Brienza, I. C. Regelink, I. Sigurnjak, F. Adani, E. Meers, O. F. Schoumans, Performance of a full-scale processing cascade that separates agricultural digestate and its nutrients for agronomic reuse, Sep. Purif. Technol. 297 (2022) 121501-. https://doi.org/10.1016/j.seppur.2022.121501

[17] D. Bolzonella, F. Fatone, M. Gottardo, N. Frison, Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full scale applications, J. Environ. Manage. 216 (2018) 111–119. https://doi.org/10.1016/j.jenvman.2017.08.026

[18] Acatech, The Impacts of the War in Ukraine on Energy Prices and Security of Supply in Europe, Academies' Project "Energy Systems of the Future (ESYS). https://en.acatech.de/publication/energy-prices-and-security-of-supply/, 2022 (accessed 20 May 2023).

[19] D. Huygens, G. Orveillon, E. Lugato, S. Tavazzi, S. Comero, A. Jones, B. Gawlik, H. Saveyn,, 2020. Technical proposals for the safe use of processed manure above the threshold established for Nitrate Vulnerable Zones by the Nitrates Directive (91/676/EEC). EUR 30363 EN, Publications Office of the European Union. https://dx.doi.org/10.2760/373351

[20] J. Junjie, Z. Hongguang, J. Jin, 2018. Study on two-stage air-recirculation ammonia stripping process for membrane concentrate in livestock and poultry breeding. E3S Web of Conferences, 194. https://doi.org/10.1051/e3sconf/202019402015

[21] C. Brienza, I. Sigurnjak, T. Meier, E. Michels, F. Adani, O. Schoumans, C. Vaneeckhaute, E. Meers, Techno-economic assessment at full scale of a biogas refinery plant receiving nitrogen rich feedstock and producing renewable energy and biobased fertilisers, J. Clean. Prod. 308 (2021) 127408–127408. https://doi.org/10.1016/j.jclepro.2021.127408

[22] Aspen Technology, inc. (2013). ASPEN PLUS.

[23] L. Liu, C. Pang, S. Wu, R. Dong, Optimization and evaluation of an air-recirculated stripping for ammonia removal from the anaerobic digestate of pig manure, Process Saf. Environ. Prot. 94 (2015) 350–357. https://doi.org/10.1016/j.psep.2014.08.006

[24] M. Zou, H. Dong, Z. Zhu, Y. Zhan, Optimization of Ammonia Stripping of Piggery Biogas Slurry by Response Surface Methodology, Int. J. Environ. Res. 16 (20) (2019) 3819–. https://doi.org/10.3390/ijerph16203819

[25] J. Arogo, R H Zhang, G. L. Riskowski, L. L. Christianson, D. L. Day, Mass Transfer Coefficient of Ammonia in Liquid Swine Manure and Aqueous Solutions, J. Agric. Eng. Res. 73 (1999) 77-86. https://doi.org/10.1006/jaer.1998.0390

[26] S. Guštin, R. Marinšek-Logar, Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. Process Saf. Environ. Prot. 89 (1) (2011) 61–66. https://doi.org/10.1016/j.psep.2010.11.001

[27] E. Volcke, S. van Hulle, T. Deksissa, U. Zaher, P. Vanrolleghem, 2005. Calculation of pH and concentration of equilibrium components during dynamic simulation by means of a charge balance. https://modeleau.fsg.ulaval.ca/fileadmin/modeleau/documents/Publications/pvr570.pdf/, 2005 (accessed 12 March 2023).

[28] G. Baquerizo, A. Magrí, J. Illa, W. C. Bonilla-Blancas, A. Gonzalez-Sanchez, S. Revah, Efficient dynamic simulation of pH in processes associated to biofiltration of volatile inorganic pollutants. https://upcommons.upc.edu/bitstream/handle/2117/100118/2010%20Washington%20Baquerizo.pdf/, 2010. (accessed 20 March 2023).

[29] A.K. Datta, Biological and bioenvironmental heat and mass transfer, Marcel Dekker Inc, New York, 2002.

[30] M. Fabbricino, F. Pirozzi, Designing and upgrading model of pre-denitrification systems. Clean Technol. Environ. Policy. 6 (3) (2004) 213–213. https://doi.org/10.1007/s10098-003-0233-8

[31] VREG, Energiemarkt in cijfers. https://www.vreg.be/nl/energiemarkt-cijfers/, 2023 (Accessed 22 March 2023).

[32] Warmtenetwerk Vlaanderen, https://warmtenet.ode.be/, 2023 (Accessed 22 March 2023).

[33] WUR, Database - Agrarische prijzen. https://agrimatie.nl/Prijzen.aspx?ID=15125/ (Accessed 22 March 2023).

[34] C. Smith, A. K. Hill, L. Torrente-Murciano, Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape, Energy Environ. Sci. 13 (2) (2020) 331–344. https://doi.org/10.1039/c9ee02873k

[35] M. Baldi, M. Collivignarelli, A. Abbà, I. Benigna, The Valorization of Ammonia in Manure Digestate by Means of Alternative Stripping Reactors, Sustainability. 10 (9) (2018) 3073–. https://doi.org/10.3390/su10093073

[36] C. Pintucci, M. Carballa, S. Varga, J. Sarli, L. Peng, J. Bousek, C. Pedizzi, M. Ruscalleda, E. Tarragó, D. Prat, G. Colica, M. Picavet, J. Colsen, O. Benito, M. Balaguer, S. Puig, J. M.

Formatted: English (United States)

Formatted: English (United States)

Formatted: English (United States)

Lema, J. Colprim, W. Fuchs, S. E. Vlaeminck, The ManureEcoMine pilot installation: advanced integration of technologies for the management of organics and nutrients in livestock waste, Water Sci.Technol. 75 (5-6) (2017) 1281–1293. https://doi.org/10.2166/wst.2016.559

[37] H. W. H. Menkveld, E. Broeders, Recovery of ammonia from digestate as fertilizer, Water Pract. Technol. 13 (2) (2018) 382–387. https://doi.org/10.2166/wpt.2018.049

[38] I. Sigurnjak, C. Brienza, E. Snauwaert, A. De Dobbelaere, J. De Mey, C. Vaneeckhaute, E. Michels, O. Schoumans, F. Adani, E. Meers, Production and performance of bio-based mineral fertilizers from agricultural waste using ammonia (stripping-) scrubbing technology, Waste Manage. 89 (2019) 265–274. https://doi.org/10.1016/j.wasman.2019.03.043

[39] C. Matter-Müller, W. Gujer, W. Giger, Transfer of volatile substances from water to the atmosphere, Water Res. 15 (11) (1981) 1271-1279. https://doi.org/10.1016/0043-1354(81)90104-4

[40] T. Zhang, A. Li, Q. Hari, X. Li, Y. Rao, H. Tan, S. Du, Q. Zhao, Economic thickness and life cycle cost analysis of insulating layer for the urban district steam heating pipe, Case Stud. Therm. Eng. 34 (2022) 102058–. https://doi.org/10.1016/j.csite.2022.102058

[41] C. Van der Heyden, E. Brusselman, E. I. P. Volcke, P. Demeyer, Continuous measurements of ammonia, nitrous oxide and methane from air scrubbers at pig housing facilities, J. Environ. Manage.181 (2016) 163–171. https://doi.org/10.1016/j.jenvman.2016.06.006

[42] F. Di Capua, F. Adani, F. Pirozzi, G. Esposito, A. Giordano, Air side-stream ammonia stripping in a thin film evaporator coupled to high-solid anaerobic digestion of sewage sludge: Process performance and interactions, J. Environ. Manage. 295 (2021) 113075–113075. https://doi.org/10.1016/j.jenvman.2021.113075

[43] M. Peces, G. Dottorini, M. Nierychlo, K. S. Andersen, M. K. D. Dueholm, P. H. Nielsen, Microbial communities across activated sludge plants show recurring species-level seasonal patterns, ISME Commun. 2 (1) (2022) 18-. https://doi.org/10.1038/s43705-022-00098-4

[44] S. Lackner, E. M. Gilbert, S. E. Vlaeminck, A. Joss, H. Horn, M. C. M. van Loosdrecht, Full-scale partial nitritation/anammox experiences – An application survey, Wat. Res. 55 (2014) 292–303. https://doi.org/10.1016/j.watres.2014.02.032