POLITECNICO
MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Biogas production from poultry manure: inhibition reduction and possible implementations for a more sustainable future

TESI MAGISTRALE IN FOOD ENGINEERING – INGEGNERIA ALIMENTARE

AUTHOR: PAOLO FRANCESCHELLI

ADVISOR: FILIPPO ROSSI

ACADEMIC YEAR: 2021-2022

---

1. Introduction

The popularity of poultry production hides the problem of the management of manure. However, it can be used, for example, as fertilizer or to produce biogas[1] (a renewable source of energy[2]) through anaerobic digestion (AD), even if it can be inhibited by the high nitrogen content. Biogas can also lead to environmental benefits (fossil energy substitution, emission and pollution reduction, etc.). Thus, the exploitation of poultry manure for biogas production will be the main application considered.

2. Anaerobic digestion inhibition

A relevant inhibitor of AD is ammonia[3] (and, more in general, nitrogen), which can be present in equilibrium with ammonium ion[4]. To reduce the nitrogen content and the ammoniacal nitrogen (indicated as “NA”, thus free ammonia and ammonium ion) concentration (“C_{NA}” or “C_NA”), it's possible to adsorb the ammonium onto calcium alginate spheres: this process is the main object of analysis of the thesis.

2.1. Ammonia equilibrium

The equilibrium between NH_3 and NH_4^+ is influenced by pH and temperature (T)[5]: the amount of ammoniacal nitrogen present as free ammonia can be estimated through Equation (1) and plotted in Figure 1 (which highlights that, increasing the temperature and/or the pH, $\%_{NH_3}$ increases).

$$1)\ \%_{NH_3} = \frac{10^{-\left(\frac{2706}{T}+0{,}139\right)}}{10^{-\left(\frac{2706}{T}+0{,}139\right)}+10^{-pH}}$$

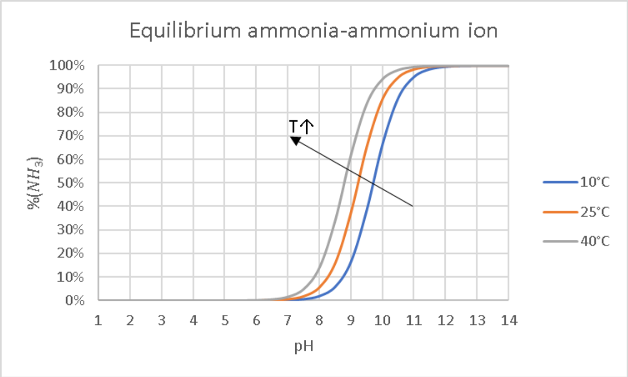

Figure 1: Fraction of ammoniacal nitrogen available as free ammonia.

2.2. Uric acid hydrolysis

Poultry manure initially contains also uric nitrogen ("NU"), which can be converted into ammonia through hydrolysis[6]. Starting from a simplified model based on a first-order kinetic and a stoichiometric ratio of 1:4, it has been derived the evolution of the NA concentration over time ("t") through Equation (2), which also allows defining a characteristic time that can reach several days. C_{NA}^0 and C_{NU}^0 indicate the initial concentrations of ammoniacal and uric nitrogen (the uric nitrogen concentration in general is C_{NU}); M_i refers to the molar mass of the chemical species "i".

$$2)\ C_{NA} = C_{NA}^0 + \frac{M_{NA}}{M_{NU}} C_{NU}^0 4\left(1 - e^{-k_H t}\right)$$

Exploiting experimental data[7], a reference value of the reaction rate constant k_H has been estimated: about 0,00577 1/h. The developed model leads to good results which are summarized in Figure 2.

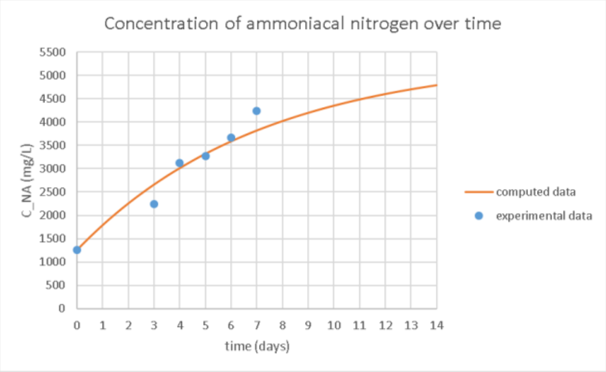

Figure 2: Ammoniacal nitrogen concentration (C_{NA}) profile during uric acid hydrolysis[7].

The plots presented in this summary, when possible, have been based on reasonable data about poultry manure[7]. Moreover, it should be mentioned that, in this part of the thesis, hydrolysis and adsorption have been investigated separately, while later in the text they will be studied simultaneously (in a possible plant).

3. Adsorption and desorption

The fundamental part of the thesis concerns the analysis of the process to reduce the inhibition through the contact of the poultry manure with calcium alginate (which can adsorb the ammonium ion). This process has been mathematically modelled through an adsorption isotherm approximated by a "Langmuir-type" equation[8], as indicated in Equation (3):

$$3)\ q_{NA}^{eq} = \frac{q_{NA}^{\infty} b C_{NA}}{1 + b C_{NA}}$$

q_{NA} (which is often called "load", and sometimes indicates as "q_NA") indicates the adsorbed ammoniacal nitrogen per unit of mass of alginate (q_{NA}^{eq} and q_{NA}^{∞} refer to the equilibrium and saturation conditions, respectively), and b is the adsorption constant. If q_{NA} is lower than the equilibrium load (q_{NA}^{eq}), the adsorption process occurs, otherwise, the desorption of ammonium can happen, according to Equation (4). k_c is the mass transfer coefficient: it can be used also to estimate the characteristic time of adsorption, leading to lower values than the one concerning hydrolysis, indicating thus a process that is generally faster.

$$4)\ \frac{dq_{NA}}{dt} = k_c a_p \left(q_{NA}^{eq} - q_{NA}\right)$$

Through mathematical steps, the developed model can be used to describe the evolution of C_{NA} (fundamental information to evaluate if the risk of inhibition has been reduced), as indicated in Equation (5), which has been numerically integrated leading to satisfactory results, as reported in the example in Figure 3 (the blue curve). In particular, m_{alg} and V_L are the alginate mass and the solution volume respectively; a_p is the ratio "surface area/volume" for the alginate particles; q_{NA}^0 indicates the initial load.

$$5)\ \frac{dC_{NA}}{dt} = -m_{alg} k_c a_p \left(\frac{q_{NA}^{\infty} b C_{NA}}{1 + b C_{NA}} - q_{NA}^0 - \frac{V_L}{m_{alg}}\left(C_{NA}^0 - C_{NA}\right)\right)$$

Moreover, assuming high values of b (or, better, of the parameter $\boldsymbol{bC_{NA}}$), the analytical solution reported in Equation (6) can be obtained:

$$6)\ C_{NA} = C_{NA}^0 - \frac{m_{alg}}{V_L}\left(q_{NA}^{\infty} - q_{NA}^0\right)\left(1 - e^{-k_c a_p t}\right)$$

This equation corresponds to the solution of a simplified model. The results of this simplified approach and of the numerical integration are extremely similar if the parameter bC_{NA} is high, as confirmed by the example provided in Figure 3 (in which a high bC_{NA} has been used). In case of lower values of the parameter bC_{NA}, instead, only the numerical integration of Equation (5) should be utilized.

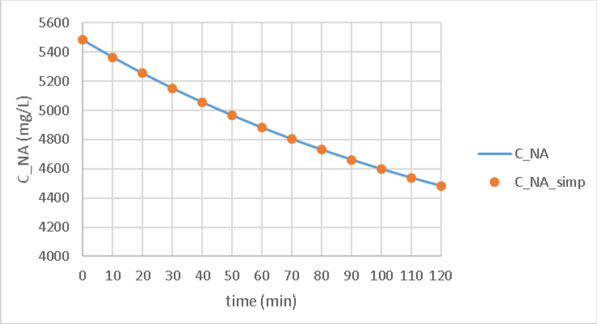

Figure 3: C_{NA} profile during adsorption, comparison between the numerical integration and the simplified ("simp") approach.

The mentioned equations describe well the experimental data[7], as reported in Figure 4, in which the results coming from the developed model follow the experimental pattern satisfactorily.

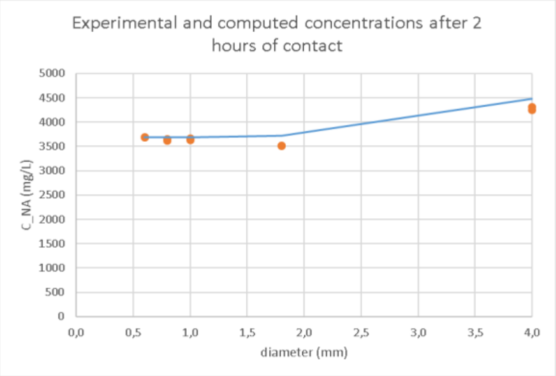

Figure 4: Experimental (dots) and simulated (line) C_{NA}, after 2 hours of contact with calcium alginate, depending on the diameter of the particles[7].

Concerning the desorption process, which can be used to obtain reusable particles (optimizing, thus, the whole plant), it could be approximately considered a linear relation between q_{NA}^{eq} and C_{NA}. However, a more precise approach is based on the integration of Equation (5) during desorption, obtaining the results summarized in Figure 5.

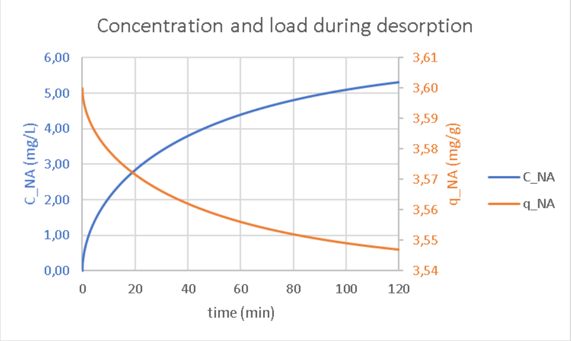

Figure 5: Ammoniacal nitrogen concentration in solution and load, over time, during desorption.

To improve the desorption, continuously "new" pure water can be used. If this is the case, the results can be estimated through Equation (7), considering $q_{NA}^{eq} \approx 0$ mg/g.

$$7)\ q_{NA} = q_{NA}^{eq} + (q_{NA}^{0} - q_{NA}^{eq})\, e^{-k_c a_p t}$$

4. Process and plant analysis

Assuming mainly CSTR configurations, a possible real plant[7], characterized by the main components summarized in Figure 6, has been analyzed both theoretically and numerically (the numerical simulation is reported in the *main text of the thesis*). It is based on an initial phase of hydrolysis and adsorption, followed by the desorption step. In the next equations, the number in the subscript indicates the corresponding flow; F and G are the slurry and alginate flowrates respectively; τ_R is the residence time; ρ_p is the alginate density; $\mathring{q}_{NA}$ identifies $q_{NA,3}$. The flowrate R has been set equal to 0 L/s for the sake of simplicity. Obviously, the process is effective if reduces the nitrogen content of the poultry manure.

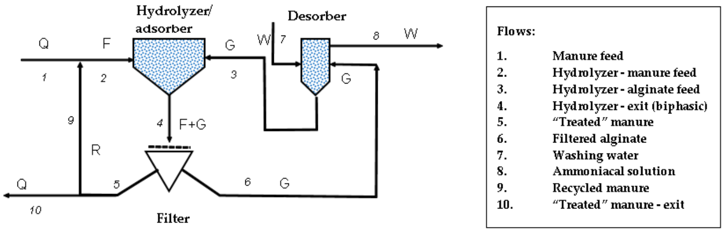

Figure 6: Scheme of the plant[7].

Through an approximated version of the material balances at the hydrolyzer, the "outgoing" C_{NA} (mainly depending on the parameters previously mentioned) can be estimated through Equation (8).

$$8)\ C_{NA,4} = C_{NA,2} + \frac{M_{NA}}{M_{NU}} 4\tau_R \frac{k_H C_{NU,2}}{1+k_H\tau_R} + \frac{G}{F}\rho_p\left(\mathring{q}_{NA} - q_{NA}^{\infty}\right)$$

A more precise version is, instead, provided in Equation (9), based on the general NA material balance at the hydrolyzer.

$$9)\ \left(F_2 C_{NA,2} - F_4 C_{NA,4}\right) + \frac{M_{NA}}{M_{NU}} 4V_L k_H C_{NU,4} +$$
$$G\rho_p\left(q_{NA,3} - \frac{q_{NA}^{\infty} b C_{NA,4}}{1+bC_{NA,4}}\right) = 0$$

The alginate has been assumed to leave the hydrolyzer in equilibrium conditions (considered, only in the simplified solution, corresponding to

q_{NA}^{∞}). Eventually, to optimize the plant, the particles leaving the hydrolyzer can undergo a desorption process using pure water (with a flow rate "W"): a mass balance at the desorber can be written as reported in Equation (10).

$$10)\ C_{NA,8} = \frac{G}{W}\rho_p\left(q_{NA,4} - q_{NA,3}\right)$$

5. Potential of biogas

The poultry manure, after the pretreatment, can be exploited for biogas generation. Obtaining biogas from manure represents a "sustainable bioenergy system"[9] and the whole planet can be in some way involved in the production and consumption of biogas and/or biomethane (the "upgraded" version of biogas, very similar to the "normal" natural gas). These gases start from a low level but are among the fastest-growing forms of bioenergy, in addition, the availability of sustainable feedstocks for these applications is expected to grow over the next decades[10]. Biogas and biomethane can also enable higher flexibility which, indirectly, can contribute to the development of systems based on wind or solar energy too[11]; moreover, these gases can act as clean cooking fuels and as alternatives to more polluting solutions[12]. Eventually, in the biogas sector, innovation in business models and financing access can be very relevant, requiring collaboration among the different "actors" [10].

6. Possible implementations

The possible <u>implementation of systems for ammonia removal from poultry manure</u> (like the ones described), coupled with biodigesters for biogas production (and, potentially, also with upgrading systems), has been investigated in the EU and in countries with low access to clean cooking, to identify examples of possible countries which could be further investigated in case of real projects.

6.1. EU – first analyzed case

In the EU, the scenario analyzed considers the energy crisis induced by the Russian invasion of Ukraine and by the following events, which determined a general "lack" of natural gas, mainly in countries that used to import significant "fractions" of gas from Russia (such as Germany and Italy). Biogas and biomethane could, at least partially, alleviate this situation[13]. In particular, they can be used to obtain also heat and power.

6.2. Access to clean cooking – second analyzed case

In several regions (Africa, Asia, etc.), millions of people lack access to clean cooking fuels, relying instead on polluting energy sources which can lead to severe health and environmental damages[10][14]. Technologies based on biogas can reduce this issue: it has been proven that they can lower air pollution and personal exposure to pollutants, "reduce" the negative health impact (for example related to breathing), etc.[15] Moreover, <u>using biogas obtained from manure *for cooking* would bring benefits to the food sector</u>.
In order to investigate the evolution of PM2.5 (a pollutant) concentration ($C_{PM2.5}$) in a kitchen, it can be presented a simple model[16] based on an ideal situation in which the air in the room is perfectly mixed, leading to Equation (11) [16]. C^0 is the concentration at the beginning of the observation period (considered equal to the outdoor one); Q is the air flow rate; V is the kitchen (air) volume; C_{inf} is the "stationary" (steady-state) concentration and depends also on the emission rate (in fact, the stoves can emit particulate matter).

$$11)\ C_{PM2.5} = C_{inf} - \left(C_{inf} - C^0\right)\exp\left(-\frac{Q}{V}t\right)$$

Considering several cooking events, and cycles of emission (during cooking) and "removal" (after cooking) of the PM2.5, the comparison between biogas stoves (blue) and traditional biomass stoves (orange) is provided in Figure 7, which confirms the "better performances" (at least in health and pollution terms) experienced in the biogas case.

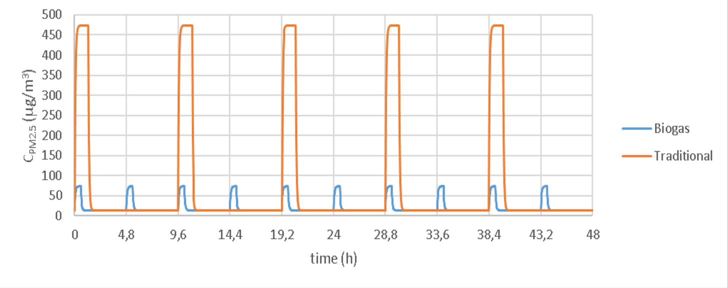

Figure 7: Comparison ($C_{PM2.5}$) between the 2 solutions (the traditional solution and the one based on biogas), during 48 hours[15].

6.3. The "priority" coefficient

For the 2 analyzed cases (6.1 and 6.2), a priority coefficient has been defined as the average "poultry" population density in a specific country, multiplied by an "urgency coefficient" which, in turn, was determined considering: for the EU, the reliance on Russian natural gas (analyzing 2020 data), assuming that the countries want to reduce it[17]; for Africa and some countries in "developing Asia", the proportion of the population with access to clean cooking[18]. Eventually, the countries selected (excluding those with a particularly low poultry population) have been ordered according to the priority coefficient which considers both the "potential" of the country and the urgency (thus, the "need") to act there. This is an approximated analysis that analyze only some factors, in a real situation this could be the starting point for a wider study. However, this coefficient can be used to select countries in which the mentioned systems may be implemented, and to define the corresponding priority.

6.4. The results

In this section, the results obtained through the priority coefficient will be presented: among the potential choices in the EU, there are also the Netherlands, Poland, Germany, and Italy, which have a "high" poultry population density and used to rely on Russian gas. Instead, considering the problems related to access to clean cooking facilities, "high" priority values are presented mainly by some countries of West Africa (like Senegal, Ghana, Nigeria, etc.); while in developing Asia, Bangladesh, Pakistan, and Indonesia can be mentioned as examples. However, the situation is worrying also in countries such as China and India in which, even if the proportion of people with access to clean cooking is not too low, the amount of people without access is still impressive[18].

7. Overview of the poultry sector

Poultry production and population have been investigated to highlight the relevance of this sector for the food industry and to show its growth. Moreover, its prosperity could be a driving force for the implementation of the systems proposed at the beginning of this thesis. It can also be assumed that high poultry production and population may be correlated to a high manure generation, leading also to a great potential for biogas production. Eventually, analyzing the countries in which the poultry sector is successful can provide further information about regions in which it could be possible to implement the systems analyzed.

The analysis shows that, since 1961, global poultry production has significantly grown[19]. In particular, mathematical considerations showed that the rate of growth seems to be generally increased over time. Poultry production has already overcome the production in other animal sectors. The main producers are U.S.A. and China, while in the EU the protagonists are Poland, France, Spain, Germany, and Italy (which has experienced faster growth than the average of the Union)[19]. However, global egg production increased significantly over time too; and the main egg producers worldwide and in the EU are, even in this case, the ones indicated in the previous sentence (with a different ranking)[20]. Eventually, it should be mentioned that what is more related to the amount of manure produced is the *number of poultry birds*. The global data have been analyzed, and they show that the poultry population significantly grew, in a way that, generally, has been more than linear in the last 6 decades[20]. In particular, the growth in the number of "birds" has been generally faster in comparison to other animal sectors, with a "change" of +119% in the number of poultry birds in the period 2000-2020 (while the changes in the number of "cattle and buffaloes", "sheep and goats" and "pigs" have all been smaller than +40%) and of +705% in the period 1961-2020 [20]. This information makes what is presented in the previous parts even more promising, under the assumption of a sort of proportionality between the number of poultry birds and the amount of manure generated and, thus, between the poultry population growth and the one of the poultry manure.

8. Conclusions

This thesis provides tools to model, analyze, and describe the opportunity to better exploit poultry manure for biogas production, through inhibition reduction (due to ammoniacal nitrogen removal through adsorption). Mathematical models for the different steps have been developed and simulated, "creating" a solid basis for the implementation of real systems. Specifically, mathematical considerations have been provided concerning the equilibrium ammonia-ammonium ion, the uric acid hydrolysis (a slow process that generates ammonia), adsorption (characterized by a lower characteristic time in comparison with hydrolysis), and desorption. In particular, adsorbent materials like calcium alginate can capture ammonia (and a model to evaluate the variation of concentration over time has been developed, in order to understand if the risk of inhibition has been sufficiently alleviated), and the used particles can then be "recovered" through desorption. Considering also the growing relevance of the poultry sector, optimizing the exploitation of these wastes can be essential to improve the production of sustainable energy sources like biogas and biomethane in the next years. In particular, problems such as the "difficult" relationship of the UE with Russia and the low access to clean cooking facilities in several African and Asian countries (and not only) could further boost the utilization and production of systems like the ones described. Concerning this last point, in particular, it has also been shown that the emissions of PM2.5 coming from biogas stoves are significantly smaller than those coming from the use of "traditional solutions".

9. Bibliography

The *main* sources used are:

References

[1] E. M. Ribeiro *et al.*, "Feasibility of biogas and energy generation from poultry manure in Brazil" *Waste Manag. Res.*, vol. 36, no. 3, pp. 221–235, 2018, doi: 10.1177/0734242X17751846.

[2] P. G. Kougias and I. Angelidaki, "Biogas and its opportunities—A review" *Front. Environ. Sci. Eng.*, vol. 12, no. 3, 2018, doi: 10.1007/s11783-018-1037-8.

[3] O. Yenigün and B. Demirel, "Ammonia inhibition in anaerobic digestion: A review" *Process Biochem.*, vol. 48, no. 5–6, pp. 901–911, 2013, doi: 10.1016/j.procbio.2013.04.012.

[4] C. Fabbri and S. Piccinini, "Pollina per biogas , buone rese ma attenzione ai dosaggi" 2013.

[5] H. Hartley, "The dissociation of the ammonium ion and the basic strength of ammonia in water" pp. 190–204, 1938.

[6] H. E. Schefferle, "The Decomposition of Uric Acid in Built Up Poultry Litter" *J. Appl. Bacteriol.*, vol. 28, no. 3, pp. 412–420, 1965, doi: 10.1111/j.1365-2672.1965.tb02171.x.

[7] "Poultry manure technical report" 2017.

[8] "Langmuir Adsorption - an overview." https://www.sciencedirect.com/topics/engineering/langmuir-adsorption (accessed Oct. 29, 2022).

[9] "Potential and utilization of manure to generate biogas in seven countries." https://www.ieabioenergy.com/blog/publications/potential-and-utilization-of-manure-to-generate-biogas-in-seven-countries/ (accessed Sep. 15, 2022).

[10] International Energy Agency, "Outlook for biogas and biomethane. Prospects for organic growth." *IEA Publ.*, pp. 1–93, 2020.

[11] "How biogas can support intermittent renewable electricity." https://www.iea.org/articles/how-biogas-can-support-intermittent-renewable-electricity (accessed Oct. 07, 2022).

[12] I. Bisaga and K. Campbell, "Clean and modern energy for cooking" 2022.

[13] International Energy Agency, "A 10-Point Plan to Reduce the European Union's Reliance on Russian Natural Gas" 2022, Accessed: Oct. 01, 2022. [Online].

[14] "Household air pollution and health." https://www.who.int/news-room/fact-sheets/detail/household-air-pollution-and-health (accessed Oct. 08, 2022).

[15] Berkeley Air Monitoring Group, "Quantifying the health impacts of ACE-1 biomass and biogas stoves in Cambodia Final Report" no. December, pp. 1–52, 2015.

[16] M. Derudi, "Ventilazione Generale degli ambienti di lavoro" pp. 1–20.

[17] "Energy trade visualisation tool." https://ec.europa.eu/eurostat/cache/infographs/energy_trade/entrade.html?lang=en&lang=en&lang=en (accessed Oct. 01, 2022).

[18] International Energy Agency, "SDG7 Database - Data product - IEA." https://www.iea.org/data-and-statistics/data-product/sdg7-database#access-to-clean-cooking (accessed Oct. 01, 2022).

[19] "Poultry production, 1961 to 2020." https://ourworldindata.org/grapher/poultry-production-tonnes?tab=chart (accessed Sep. 30, 2022).

[20] "FAOSTAT." https://www.fao.org/faostat/en/#data/QCL (accessed Sep. 15, 2022).