Journal of Water Process Engineering 47 (2022) 102735

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

PLS-based soft-sensor to predict ammonium concentration evolution in hollow fibre membrane contactors for nitrogen recovery

D. Aguado [a,*], G. Noriega-Hevia [a], J. Ferrer [a], A. Seco [b], J. Serralta [a]

[a] *CALAGUA – Unidad Mixta UV-UPV, Institut Universitari d'Investigació d'Enginyeria de l'Aigua i Medi Ambient – IIAMA, Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain*

[b] *CALAGUA – Unidad Mixta UV-UPV, Departament d'Enginyeria Química, Universitat de València, Spain*

ARTICLE INFO

Keywords:
Nitrogen recovery
Hollow fibre membrane contactor
PLS
Soft-sensor

ABSTRACT

Hollow fibre membrane contactors (HFMC) have emerged as a promising technology for nitrogen-recovery that can be implemented in wastewater treatment plants (WWTPs) to promote circular economy. In this process, a hydrophobic membrane allows the transference of free-ammonia across the hollow fibres. During its operation, the ammonium concentration decreases, and real-time measurements would be of great value for process monitoring, optimization and control. Ammonium probes exist, but they are expensive and present noticeably maintenance costs. In this work, results from eight N-recovery experiments performed at different pH values using real supernatant of a full-scale anaerobic digester were analysed in terms of the time-evolution profiles of pH and total ammonium nitrogen (TAN). The pH revealed to carry relevant information related to the TAN concentration, as it decreased in the feed solution due to free ammonia stripping. The pH is an inexpensive-to-measure process variable that can be routinely acquired in any WWTP. Therefore, a data-driven soft-sensor has been developed. It uses the pH, its derivative, and the pH increments after each reagent dosing as input signals, to estimate the TAN concentration via PLS. An extended PLS-model incorporating interaction terms, quadratic and cubic forms of the three input variables improved the TAN concentration estimation. The developed soft-sensor was able to accurately reproduce the evolution of TAN concentration (in the range 0–1000 mgNH_4^+-N/L with $R^2 > 0.97$ and RMSE <40 mg/L) during the HFMC process operation, thus making it possible to monitor the process as well as enabling future development of different control and optimization strategies.

1. Introduction

The nitrogen present in wastewater has been traditionally considered a major pollutant, which can cause different impacts to the receiving aquatic ecosystem (such as toxicity, oxygen depletion and eutrophication). However, currently, with the paradigm shift towards the circular economy in the wastewater sector, nitrogen has begun to be considered a valuable resource that it is worth recovering. This nutrient is essential for many agricultural crops and, for this reason, it is a key element in many commercial fertilizers. Despite nitrogen is the most abundant gas in the atmosphere, its conversion into ammonium through the Haber-Bosch process is very energy-demanding. Moreover, this process releases a significant amount of greenhouse gases and in terms of global warming potential the production of one year of ammonium can be considered equivalent to nearly 80,000,000 people [1].

In order to recover nutrients from wastewater, several technologies have been developed in the last decades. Among them, the struvite crystallization has been widely studied at different process-scales, and even implemented in many full-scale wastewater treatment plants (WWTPs) thus, turning them into water resource recovery facilities (WRRFs). However, in this process, the nitrogen recovery efficiency is limited due to the composition of the struvite (note its equimolar stoichiometry: $MgNH_4PO_4{\cdot}6H_2O$). Robles et al. [2] have reported recovery efficiencies ranging from 80 to 90% of the PO_4^{-3} present in the reject water from anaerobic digestion but only from 20 to 30% of the NH_4^+.

Another technology with wide implementation at different process scales is air stripping. In this process, free ammonia is transferred from the waste stream (i.e., the aqueous phase) to a gas phase, which is later circulated through an air cleaner, where in the liquid phase (usually sulphuric acid) different processes (mass transfer and absorption) occur, resulting in the formation of a solution of ammonium sulphate ($[NH_4]_2SO_4$: AmS). AmS is an inorganic salt, rich in macronutrients

---

* Corresponding author.
E-mail address: daaggar@hma.upv.es (D. Aguado).

https://doi.org/10.1016/j.jwpe.2022.102735
Received 9 January 2022; Received in revised form 6 March 2022; Accepted 14 March 2022

nitrogen and sulphur (N and S), which can act as substitute of traditional fertilizers chemically-based produced from fossil resources. The operation of air stripping units leads to high energy and chemical requirements as a result of the scaling and fouling problems that frequently occur within the packing material of the towers that are used in this technology [3].

Membrane-based technologies have also been successfully used for nutrient recovery. Among them, the hollow fibre membrane contactor (HFMC) has emerged as one of the most promising membrane technologies that is being explored for the recovery of nitrogen (N). In this process, hydrophobic membranes are used to enable the transference of gaseous species (such as free ammonia) across the hollow fibres. Free ammonia is transferred from a N-rich feed solution (usually circulating by the lumen) to an acid solution (usually sulphuric acid pumped inside the hollow fibres). The difference between free ammonia concentrations at both sides of the membranes is the driving force of the stripping process. The pH in the N-rich solution should be high enough to assure that free ammonia predominates (see Fig. 1). The higher the pH, the higher the percentage of ammonium nitrogen present as free ammonia and therefore the higher the N-recovery rate. Temperature also affects the chemical equilibrium between ammonium and free ammonia. Fig. 1 shows the percentage of ammonium nitrogen which is in the form of free ammonia at different pH and temperatures.

When free ammonia passes across the membrane it is transformed into ammonium consuming protons from the acid solution. When the acid solution is exhausted, the pH suddenly increases and should be replaced. During the recovery process, the pH of the feed solution decreases due to free ammonia stripping. The pH drop will be more or less pronounced depending on the ammonium/alkalinity ratio of the feed solution (i.e. the N-rich solution). The alkalinity is due to the presence of ions (mainly carbonates and bicarbonates) that incorporate acid protons (recall that the pH is the concentration of these acid protons) into their molecules so that they are not available as a free acid that can lower the pH. Therefore, the higher alkalinity (i.e., lower ammonium/alkalinity ratio) the lower the pH variations. When the pH drops below 8.5 the recovery process rate is greatly reduced. Therefore, pH should be maintained over this value by adding chemical reagents, usually NaOH. Alkalinity of the feed solution also affects the economics of the HFMC process since it determines the amount of NaOH that is needed to raise the pH to assure a high percentage of ammonium nitrogen present as free ammonia thus enabling high N-recovery rates.

Due to the addition of NaOH required to keep high the percentage of nitrogen as free ammonia in the feed solution, HFMCs are only applied for nitrogen-rich streams such as the ones mentioned below. Diluted streams should be pre-treated by means of zeolites, exchange ion columns or electrodialysis prior to be fed to the HFMC. However, the economics of the process not only depends on the nitrogen content of feed solution but also on its alkalinity. Since alkalinity of the feed solution dampen the pH variations, the higher the alkalinity the higher operational costs of the process. In the case of the anaerobic digestion supernatant an economic and environmental study estimating costs and benefits of the HFMC technology implementation in full-scale WWTPs is presented in Noriega-Hevia et al. [4].

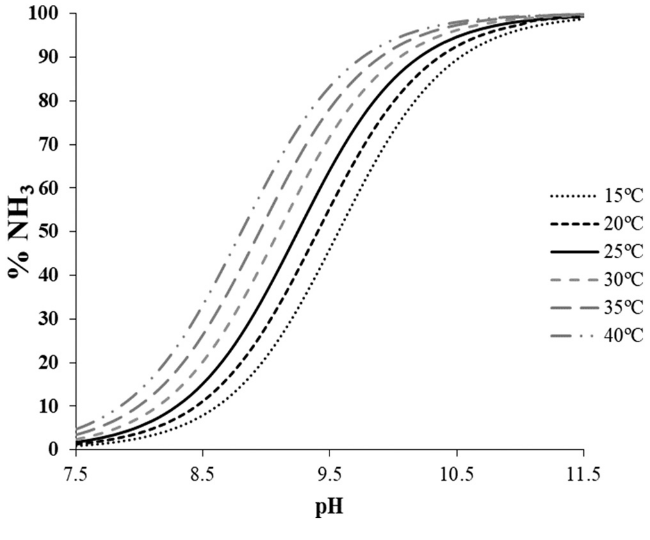


Fig. 1. Effect of pH and temperature on the free ammonia percentage.

The main advantages of HFMC technology are: it is selective to free ammonia recovery; its energy consumption is lower than other technologies such as air stripping and it is appropriate for recovery of ammonium nitrogen to really low concentration [5]. High nitrogen recovery efficiencies (between 80% and 99%) have been obtained applying this technology to different streams such as chicken manure [6], reject water from anaerobic digestion [7,8], pig manure [9] or urine [10]. Although these studies were carried out at laboratory or pilot scale, recently, this technology has been implemented at the full-scale Munster WWTP [11] with recovery efficiencies close to those obtained at laboratory or pilot scale.

The acid solution (usually sulphuric acid) that circulates inside the membrane fibres reacts with free ammonia to form AmS, which is a marketable fertilizer. It should be highlighted that recovering nitrogen from the reject water in WWTPs produces several benefits such as the economic value of the produced AmS, the reduction in the energy consumption related to aeration system and the lower NOx and N_2O emissions as consequence of the lower N-load entering the biological treatment. Aeration is the most energy demanding process in a WWTP, and the nitrification process contributes to this consumption requiring over 5 kWh/kg-N.

HFMCs are usually operated in batch mode. The nitrogen rich solution is pumped from a storage tank, circulates by the lumen of the membrane module and is recycled to the storage tank. When TAN concentration of the feed solution decreases below the desired level, the process should be stopped, and the storage tank is emptied and filled again with nitrogen rich solution. Thus, for monitoring, optimization and process control purposes, it would be of great importance to know the TAN concentration in real-time in the storage tank.

Ammonium concentration is usually measured in WWTPs and WRRFs by colorimeter procedures, kits based on the Nessler or salicylate methods or ion-selective electrodes. Colorimeter procedures and kits are usually used for its determination in grab samples but there are not useful to provide continuous values of ammonium concentration. Although the ion-selective electrodes for ammonium measurements can provide on-line continuous data, they present several drawbacks. These electrodes are strongly affected by potassium and sodium ions, the range of ammonium to be spanned in HFMCs is extremely wide and cannot be covered with the same electrode and the price and their maintenance costs are high [12]. Therefore, for HFMC process monitoring, optimization and control, it would be extremely useful to be able to estimate the TAN concentration in the feed tank during the experimentation indirectly. The pH is an inexpensive easy-to-measure process variable that can be routinely acquired, which is extremely relevant for the HFMC process operation since it decreases as nitrogen is being recovered.

A soft-sensor is a computer software that maps the values from the input variables (usually secondary variables, i.e. process variables like conductivity, pH, temperature, redox, etc., that are relatively cheap and easy-to-measure) to predict the output variable/s (usually primary variables, like nutrients and organic matter in the wastewater context). Note that primary variables (mainly nutrient and organic concentration) are traditionally measured in the laboratory, thus are characterized by time-delayed responses (for example, it takes 5 days to know the value of the BOD_5 concentration of a wastewater sample, in the case of the COD concentration the required analytical procedure in laboratory makes that its value takes about 2 and a half hours to be known, …). The sensors and analysers developed to on-line measure primary variables are often associated with high capital and maintenance costs, and their availability is often limited to large WWTPs because their high capital and maintenance costs, while they are infrequently encountered in small and medium WWTPs.

In the last decade, the development of data-driven soft-sensors have become more frequent in WWTPs, although they are still far from their use and application in the process industry where the deployment of soft-sensors is fairly common. Most soft-sensors in the wastewater treatment sector have been developed for the prediction of primary variables like NH_4^+, NO_3^-, PO_4^{3-}, BOD, COD, SVI, SS [13–15] even recently to predict struvite purity [16].

The harsh conditions in WWTPs and WRRFs make reliable field measurements challenging, thus, proper instrumentation maintenance is of paramount importance for process monitoring and control of these facilities. Note that the quality of the measurements of the input sensors determines the reliability of any soft-sensor as well as its accuracy.

According to Ching et al. [13] since 2000s the main methodology that has been used by researches for soft-sensor development is based on the application of artificial neural networks (ANNs). However, as these authors state, in recent years, new approaches based on the use of machine learning algorithms have appeared exhibiting high performance and the projection statistical methods that are well suited for handling multicollinearity and noise (typical challenges in WWTP datasets) being both relevant options to be used for soft-sensor developtment.

Since the pH of the feed solution decreases during the N-recovery process in HFMCs due to the stripping of the free ammonia and increases when sodium hydroxide (NaOH) is added to boost the amount of nitrogen present as free ammonia, it is hypothesized that the TAN concentration in the nitrogen rich stream could be estimated by means of pH measurements. Thus, the aim of this work is to develop a soft-sensor to forecast the time-evolution of TAN concentration in the nitrogen-rich solutions fed to hollow fibre membrane contactors for nitrogen recovery using data from inexpensive and easy-to-measure sensors (pH measurements).

2. Materials and methods

2.1. Experimental set-up

Fig. 2 shows a scheme of the lab-scale set-up for N-recovery via HFMC that was used in this work. As it can be seen in this figure, the set-up consisted in two tanks, the acid tank with a volume of $1.2{\cdot}10^{-3}$ m^3 which contained sulphuric acid as acid solution and the feed tank (volume of $2.1{\cdot}10^{-3}$ m^3) where the pre-treated N-rich solution (filtered and pH adjusted) was stored, a device to keep controlled the pH in the feed tank (711 Liquino and 700 Dosino of Metrohm®) throughout each experiment dosing sodium hydroxide (NaOH 1 mol/L), two HFMCs model X50 2.5 × 8 LiquiCel ® Extraflow by 3 M manufacturer, made of polypropylene with 1.4 m^2 of membrane surface in series (and the following characteristics: 10,200 fibres, 0.16 m length, 40 μm thickness, 45% of packing density and 220 μm of internal diameter), and two peristaltic pumps to boost the fluids from the tanks. To minimize the loss of free ammonia via stripping, both tanks were closed (but not sealed).

Temperature and pH were continuously measured (one value recorded every 20 s) in each tank with electronic sensors (Two SP10T, Consort®). The signals from the sensors were collected by a multiparametric analyser (Consort C832) which sent the data to a personal computer (PC) for visualization and data storage. A control software was developed and deployed to control the pH. During the progress of each experiment whenever the pH dropped below the established set point, 2 mL of NaOH 1 mol/L were dosed by the Liquino&Dosino device. This device whenever received the order from the computer to dose NaOH, perform the action until the pH was above the set point. Since the experiments were carried out in the laboratory and their duration did not exceed 1 h, temperature variations along the experiments were negligible.

The nitrogen rich feed solution (supernatant of a full-scale anaerobic digester) was boosted through the shell side of the contactors to minimize the risk of fouling due to the larger flow cross-section available relative to the inside flow cross-section which is much smaller inside the membrane fibre [5]. The acid solution, (H_2SO_4, 0.1 mol/L) was boosted in counter-current through the lumen side. Each fluid was recycled to its respective tank (see Fig. 2). A flowrate ratio of 1:3 between the H_2SO_4 solution and the N-rich solution was maintained according to the recommendations of the membrane manufacturers to avoid membrane deformation and maintain its morphology.

2.2. Analytical methods

To chemically characterize the supernatant of the full-scale anaerobic digester several parameters were determined in the laboratory. Following the Standard Methods [17] Total Solids [method TS (2540B)], Total COD [method COD_T (5220B)], Ammonium [method NH_4^+-N (4500 NH_3-D)], Phosphate [method PO_4^{3-}P(4500P-E)]. Both nutrients phosphate and ammonium were analysed using a photometer SMARTCHEN® 450 from AMS-Alliance. The concentration of volatile fatty acids and alkalinity were determined by titration using the methodology developed by Moosbrugger et al. [18].

2.3. Feed solution

Real supernatant from the anaerobic digester of a full-scale WWTP from Valencia (Spain), with an average concentration of 800 mg NH_4^+-N/L, was used as N-rich solution in this research. This supernatant was pre-treated prior to being feed to the HFMCs. A three-stages pre-treatment was performed which included pH adjustment, followed by settling and finally filtration. Initially, NaOH (1 mol/L) was dosed to

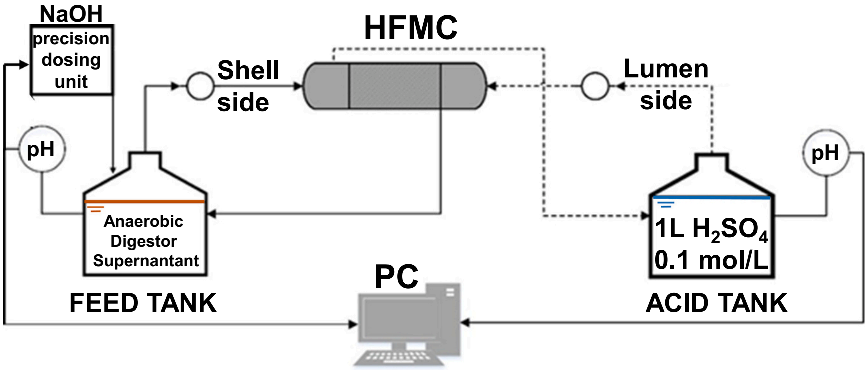


Fig. 2. Scheme of the laboratory-scale set-up for nitrogen recovery via HFMC.

increase the pH up to the desired value (between 9 and 11). At this high pH value, precipitates formed like calcium carbonate and calcium phosphate which could clog the membranes. In order to minimize the possible clogging of the membranes, the digester supernatant was settled for 8 min and the supernatant from the settling was filtered through a 0.45 μm filter pore size prior to being feed to the HFMC. The characterization of the real supernatant as obtained from the full-scale anaerobic digester (i.e., prior to the pre-treatment applied in this research work), and after the pre-treatment (feed solution) is shown in Table 1.

2.4. Experiments

Eight experiments were performed in laboratory at 25 °C, at a feed flow rate of 2.5×10^{-5} m^3/s varying the pH between 9 and 11.

2.5. Statistical analysis

The main objective of this work is to develop a data-driven soft-sensor solution based on PLS to extract primary information on the ammonium concentration evolution in the HFMC, which would be especially useful for process monitoring, optimization and control of this process.

The PLS will extract relevant information from the pH data which is an easy-to-measure process variable that can be routinely acquired and it is available in almost every WWTP.

PLS is a multivariate statistical technique that connects two data matrices: X (which contain the predictors) and Y (which contain the responses or variables to be predicted), capturing simultaneously the correlation structure among all the variables. Latent variables are extracted through linear combination of the original variables, trying to capture the underlying phenomenon that drives the process that is being studied. PLS aims at finding latent variables that explain as much variance in X as possible, but focusing on that part of the variance in X that allows better forecasting of the variables in matrix Y.

Fitting and prediction with the PLS technique were performed using the software SIMCA-P 10.0 (Umetrics, Sweden).

3. Results and discussion

3.1. Feature engineering

Temperature and pH were the only two variables continuously recorded (one value each 20 s) in both tanks of the experimental set-up: the tank that contained the feed solution and the tank that contained the acid solution. Since the experimental set-up was in the laboratory, and the experiments were short, the temperature along the different experiments relatively constant (at 25 °C) with minimal variation, thus, no other information than that to check that the process was operated at the pre-set temperature, could be obtained. However, the pH value in the tank that stored the feed solution varied significantly during each experiment. Fig. 3 shows the time-evolution of the pH as well as the TAN concentration in a previous experiment carried out without pH control. As can be seen in this figure, the pH drops from 9 to 8.1 along the duration of the experiment (30 min) while the TAN concentration decreased from 350 to 223 mg NH_4^+-N/l. Nitrogen recovery rate significantly decreased during the experiment due to the pH decrease. Almost 50% of the nitrogen recovered was achieved in the first 5 min ($pH > 8.8$) and 90% of the nitrogen recovered was achieved in the first half of the experiment ($pH > 8.5$). When the pH dropped below 8.5 the nitrogen recovery rate was almost negligible. As commented in the introduction section, the higher the pH in the feed solution tank, the higher the rate of nitrogen recovery due to the higher the percentage of ammonium nitrogen is in the form of free ammonia. Thus, a pH control system was implemented to keep the pH in the N-rich solution tank (i.e., feed tank) close to the desired level.

Fig. 4 shows the pH evolution pattern observed along an experiment carried out with pH control, together with the TAN concentration at relevant time instants. As can be seen in this figure, the pH decreased linearly along the whole experiment but when the pH dropped until a value of 10, it was raised by NaOH dosing. It should be highlighted that with the same amount of NaOH dosed, the increment achieved in the pH of the feed solution was higher as the TAN concentration was lower. Another interesting fact that could be observed in the pH profile along the experiment, was that its derivative (i.e., its slope), in absolute value, between every two dosages was smoother/lower as the TAN concentration was lower. The pH slope depends on nitrogen recovery rate which in turns depends on free ammonia concentration in the feed solution.

Therefore, taking into account the underlying scientific principles and the technical knowledge of the process, it became evident that in addition to the variable pH itself, other variables such as the pH derivative and the pH increment after each NaOH dosing could carry relevant information for prediction of TAN concentration. Thus, they were included as inputs to develop the soft-sensor based on projection to latent structures model. The fully specified architecture of the proposed soft-sensor is shown in Fig. 5.

Fig. 6 shows the time evolution of the pH and the TAN concentration along five experiments, throughout which the TAN concentration in the feed solution was reduced from more than 950 mg NH_4^+-N/L to less than 100 mg NH_4^+-N/L. These data will be used to fit the PLS-based soft-sensor.

To develop the ammonium soft-sensor 75% of the data (i.e. 6 experiments) were used for model fitting and the remaining 25% (i.e. 2

Table 1
Chemical characterization of the anaerobic digestion supernatant before (as obtained from the full-scale digester) and after the pre-treatment (feed solution).

Parameter (units)	Anaerobic digester supernatant (prior to the pre-treatment)	After the pre-treatment (feed solution)
NH_4^+-N (mg/L)	820 ± 180	713 ± 168
PO_4^{3-}-P (mg/L)	30.5 ± 1.5	2.3 ± 0.8
COD (mg/L)	1320 ± 15	620 ± 22
TSS (mg/L)	5606 ± 50	<L.D.
Ca^{2+} (mg/L)	60.8 ± 10	[a]
Mg^{2+} (mg/L)	12.9 ± 3.5	[a]
K^+ (mg/L)	345.8 ± 15	[a]
Fe^{2+} (mg/L)	50.6 ± 10	[a]
pH	8.1 ± 0.1	9–11
Alkalinity (mg $CaCO_3$/L)	2733.9 ± 31.1	[a]

<L.D. means a concentration of the analyte that is lower than the Limit of Detection.

[a] It was different depending on the pH achieved in the pre-treatment.

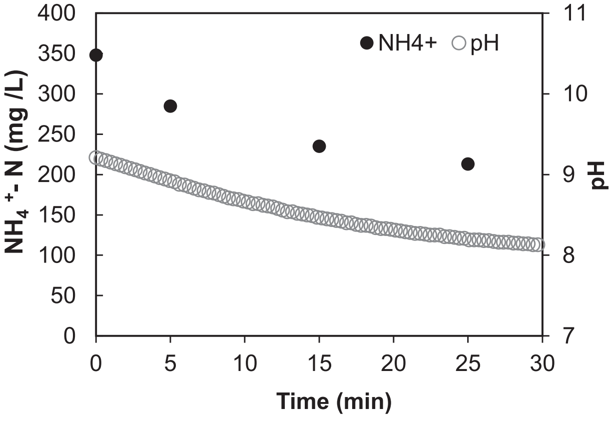


Fig. 3. Time-evolution of the pH and the TAN concentration along an experiment performed without pH control.

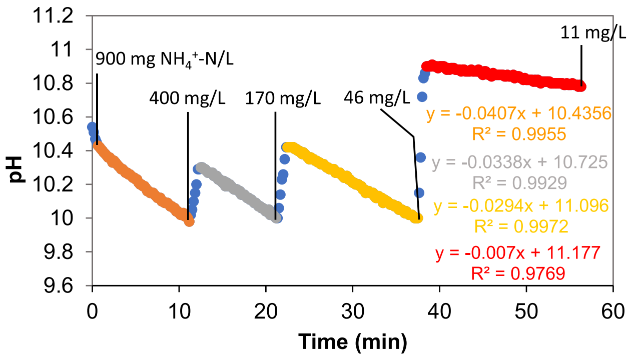


Fig. 4. pH evolution along one experiment. The TAN concentration (mg NH_4^+-N/L) at each relevant time instant and the value of the descending slope (i.e., derivative) of the pH is indicated.

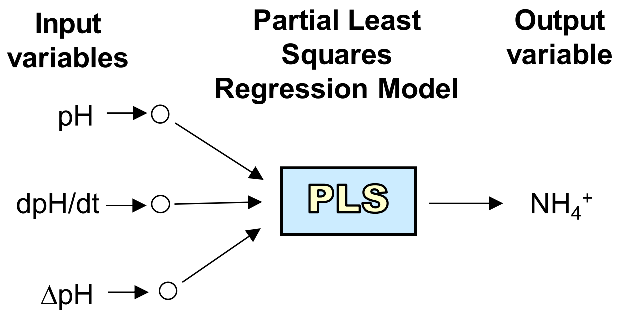


Fig. 5. Scheme of the fully specified architecture proposed for the NH_4^+ soft-sensor for the HFMC.

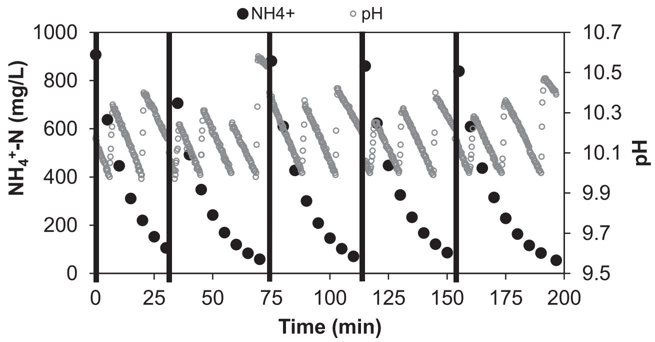


Fig. 6. TAN concentration and pH evolution along five different experiments. Each vertical black line indicates the beginning of a new experiment.

experiments) for testing its performance. According to cross-validation only two components resulted statistically significant. The models were well balanced, exhibiting in fit performance as well as in the prediction of the TAN concentration performance values higher than 90%. Fig. 7 shows the measured TAN concentration versus the estimation by the PLS-model. As can be seen in this figure, although an overall reasonable fit is achieved, the TAN concentration is systematically underestimated for values higher than 600 mg NH_4^+-N/L, while in the lower range (values lower than 300 mg NH_4^+-N/L) the TAN concentration is systematically overestimated.

The loading plot in Fig. 8a provides a graphical summary of the correlation between all the variables (X and Y). In this plot, highly correlated variables are plotted together, in the same quadrant when the correlation is positive and diagonally opposed quadrants when the correlation is negative. Thus, Fig. 8.a evidences that two variables, the slope of the pH (Slp) and the pH increment after each NaOH dosing (ΔpH) are highly correlated and that these variables are inversely correlated with the output variable, the TAN concentration (NH_4^+).

Variable importance in the projection (VIP) plot is also included in Fig. 8b to show the most important variables over the PLS model as a whole. The VIP parameter is a weighted summary of the loadings of all input variables across all the responses. Therefore, the higher the importance of given variable in a fitted PLS model, the higher its VIP value. It is interesting to point out that the extracted features from the pH resulted significantly more relevant than pH itself for the prediction of the ammonia concentration.

In order to improve the PLS model performance, model complexity was increased by incorporating as input variables the interaction terms as well as the quadratic and cubic forms of the three input variables shown in Fig. 5. As a result, the new PLS model had 12 input variables. Fig. 9 shows the measured TAN concentration versus the predicted concentration by the extended PLS-model. As can be seen in this figure, accurate predictions were possible in the entire range of values (from 0 to 980 mg NH_4^+-N/L) with this model. Therefore, this demonstrates that is possible to predict the TAN concentration evolution in a hollow fibre membrane contactor for nitrogen recovery, extracting primary information from the pH which is an easy-to-measure process variable. The predictions exhibit enough accuracy (RMSE = 37.67) to make decisions and actions on the process such as determining whether the desired nitrogen recovery level has been achieved. Thus, the proposed data-driven solution based on PLS unlocks a new dynamic approach in the HFMC process for process control and optimization.

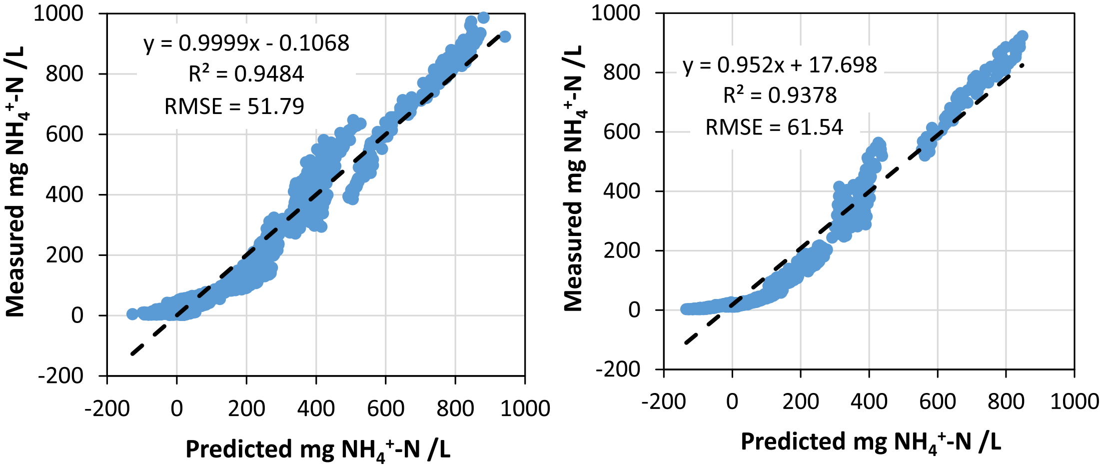
The loading plot shown in Fig. 10a provides a graphical summary of the correlation between all the variables of the PLS extended model. As can be seen in this Figure, the correlation structure among the main variables is the same as before. The cubic terms are in the opposite quadrant to the other expanded terms (interactions and quadratic forms). To know and visualize the importance of each input variable in the extended data-driven model, the variable over the projection is shown in Fig. 10b. Again, the extracted features from the pH resulted significantly more relevant than pH itself, thus, highlighting the importance of the feature engineering process to develop useful artificial intelligence solutions.

It should be highlighted that the developed soft-sensor only uses the pH, the extracted features from the pH, and their interaction and exponential forms as input variables, thus, offering an inexpensive opportunity to extract primary information on the TAN concentration.

The soft-sensor works very well because during the nitrogen recovery process, the pH of the feed solution decreases due to free ammonia stripping, and increases when caustic soda is added to boost the amount of nitrogen present in the feed solution as free ammonia (to enhance the nitrogen recovery rate). The pH measurement carries information in its own value, in its slope and in the variations it shows when NaOH is added to raise its value. This close and causal relationship between both variables, allows to obtain these nice results.

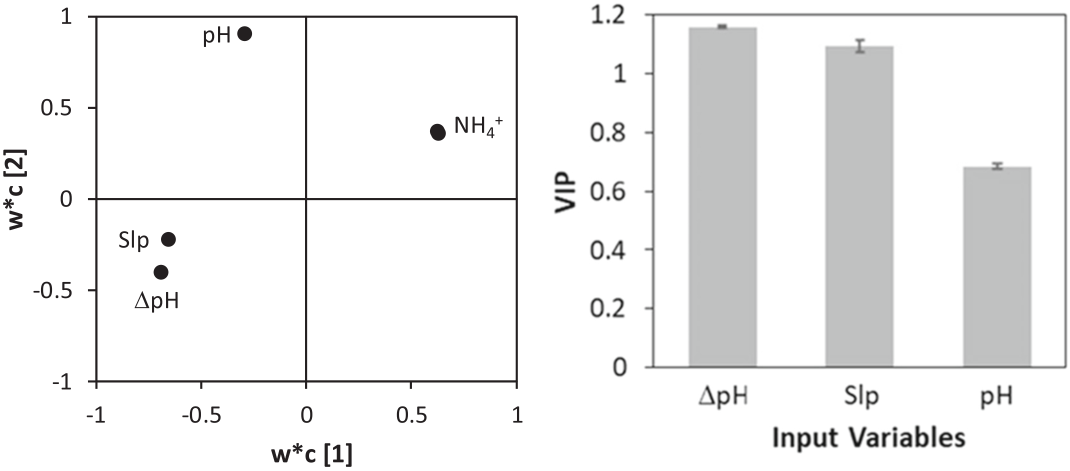
The estimation of the TAN concentration that can be carried out with the soft-sensor presented in this study could be very useful for implementing this technology at full-scale WWTPs. One of the main bottlenecks for HFMC process optimization is the development of a control system for determining the end of each N-recovery cycle. The acid solution should be replaced when the pH raises over neutrality and the feed solution should be replaced when nitrogen concentration reaches the desired value. Considering the drawbacks of on-line ammonium sensors commented in the introduction section, the soft-sensor based on pH measurements could provide valuable information for control system development.

Since during the recovery process there are also variations in the concentration of the ions present in the feed solution, the conductivity, which is another inexpensive process variable, could also offer information related to the TAN concentration and, thus, if this process variable is available it could be then tested as input variable of a soft-sensor.



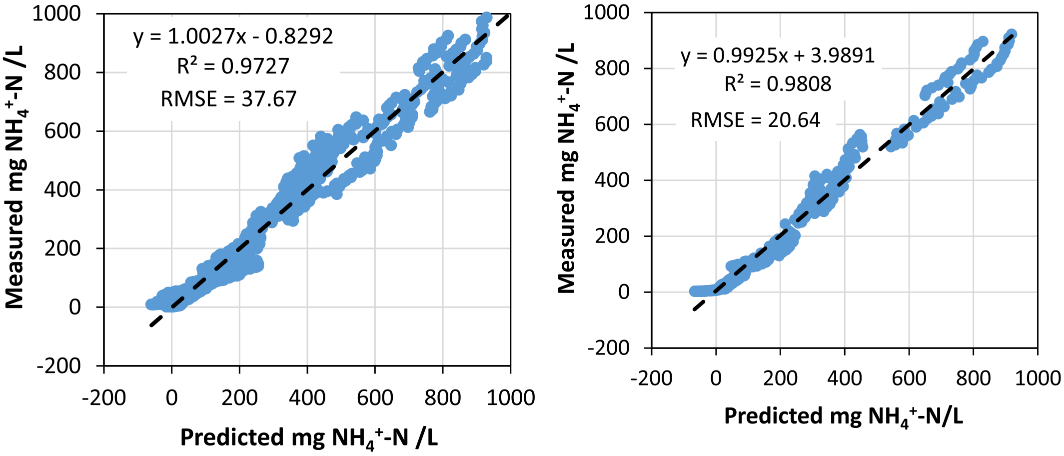
(a) (b)

Fig. 7. Observed NH_4^+-N concentration versus the predicted values by the PLS-model with 3 input variables: (a) model fitting (b) model test. The linear regression equation, the determination coefficient of the fitting and the RMSE are also shown to visualize and assess the data-driven model performance.



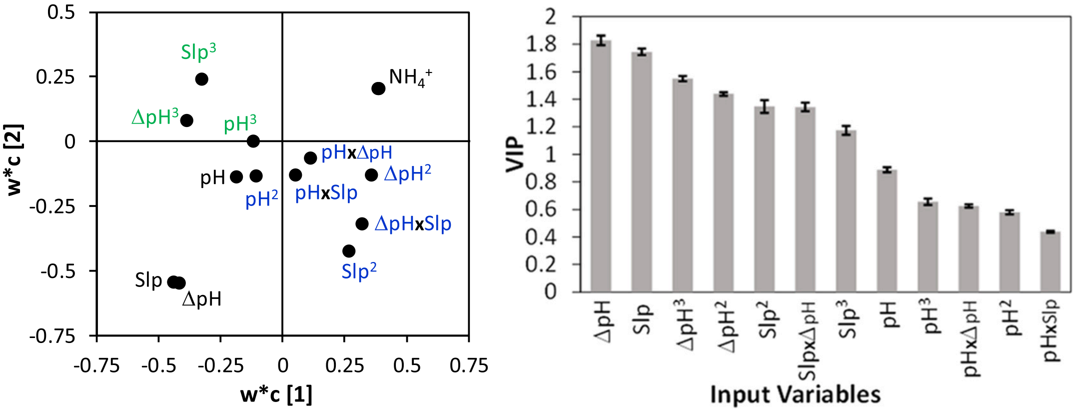
(a) (b)

Fig. 8. PLS model to predict ammonium concentration in the reactor: (a) weight plot of the two latent variables, and (b) variable importance in the fitted PLS model (VIP) with its error bar. The VIP parameter is a weighted summary of the loadings of all X-variables.



(a) (b)

Fig. 9. Observed NH_4^+-N concentration versus the predicted values by the PLS-model with 3 input variables: (a) model fitting (b) model test. The linear regression equation, the determination coefficient of the fitting and the RMSE are also shown to visualize and assess the data-driven model performance.



(a) **(b)**

Fig. 10. Expanded PLS model to predict ammonium concentration in the reactor: (a) weight plot of the two latent variables, and (b) variable importance in the fitted PLS model (VIP) with its error bar. The VIP parameter is a weighted summary of the loadings of all X-variables.

4. Conclusions

In this work a data-driven soft-sensor solution based on PLS has been proposed to extract primary information on the TAN concentration evolution in the HFMC from the pH time-evolution profile. The main conclusions that can be drawn from this study are:

- The HFMC process allows high N-recovery efficiencies treating the supernatant of anaerobic digesters of municipal WWTPs.
- The pH is an inexpensive and easy-to-measure process variable that carries relevant information on TAN concentration in the feed tank.
- The developed PLS-based soft-sensor is able to predict with high accuracy the TAN concentration evolution in hollow fibre membrane contactors for nitrogen recovery.
- This soft-sensor uses the pH and extracted features (its derivative and increments) as input variables offering an inexpensive opportunity to extract primary information on the TAN concentration.
- The pH derivative and the pH increment after each reagent dosing were more relevant for TAN concentration prediction than the pH value itself.
- Feature extraction based on technical knowledge of the process was key to make the development of a reliable data-driven PLS soft-sensor possible.
- This study highlighted the potential of the developed data-driven soft-sensor solution based on PLS to unlock a new dynamic approach in optimization and control of the HFMC process as well as decision making in troubleshooting.

Declaration of competing interest

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

Acknowledgements

This research was financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO projects CTM2014-54980-C2-1/2-R and CTM2017-86751-C2-1/2-R) with the European Regional Development Fund (ERDF) as well as the Universitat Politècnica de València via a pre-doctoral FPI fellowship to Guillermo Noriega.

References

[1] L.F. Razon, Life cycle analysis of an alternative to the haber-bosch process: non-renewable energy usage and global warming potential of liquid ammonia from cyanobacteria, Environ. Progr. Sustain. Energy 33 (2014) 618–624, https://doi.org/10.1002/ep.11817.

[2] A. Robles, D. Aguado, R. Barat, L. Borrás, A. Bouzas, J.B. Giménez, N. Martí, J. Ribes, M.V. Ruano, J. Serralta, J. Ferrer, A. Seco, New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the circular economy, Bioresour. Technol. 300 (2020), 122673, https://doi.org/10.1016/j.biortech.2019.122673.

[3] C. Vaneeckhaute, V. Lebuf, E. Michels, E. Balia, P. Vanrolleghem, F.M. Tack, E. Meers, Nutrient recovery from digestate: systematic technology review and product classification, Waste Biomass Valoriz. 8 (2017) 21–40, https://doi.org/10.1007/s12649-016-9642-x.

[4] G. Noriega-Hevia, J. Serralta, A. Seco, J. Ferrer, Economic analysis of the scale-up and implantation of a hollow fibre membrane contactor plant for nitrogen recovery in a full-scale wastewater treatment plant, Separation and Purification Technology 275 (2021) 119128, https://doi.org/10.1016/j.seppur.2021.119128.

[5] M. Darestani, V. Haigh, S.J. Couperthwaite, G.J. Millar, L.D. Nghiem, Hollow fibre membrane contactors for ammonia recovery: current status and future developments, J. Environ. Chem. Eng. 5 (2) (2017) 1349–1359, https://doi.org/10.1016/j.jece.2017.02.016.

[6] A. Bayrakdar, R.Ö. Sürmeli, B. Çalli, Dry anaerobic digestion of chicken manure coupled with membrane separation of ammonia, Bioresour. Technol. 244 (2017) 816–823, https://doi.org/10.1016/j.biortech.2017.08.047.

[7] F. Wäeger-Baumann, W. Fuchs, The application of membrane contactors for the removal of ammonium from anaerobic digester effluent, Sep. Sci. Technol. 47 (2012) 1436–1442, https://doi.org/10.1080/01496395.2011.653468.

[8] G. Noriega-Hevia, J. Serralta, L. Borrás, A. Seco, J. Ferrer, Nitrogen recovery using a membrane contactor: modelling nitrogen and pH evolution, J. Environ. Chem. Eng. 8 (2020), https://doi.org/10.1016/j.jece.2020.103880.

[9] M.C. Garcia-González, M.B. Vanotti, Recovery of ammonia from swine manure using gas-permeable membranes: effect of waste strength and pH, Waste Manag. 38 (2015) 455–461, https://doi.org/10.1016/j.wasman.2015.01.021.

[10] J. Nagy, J. Kaljunen, A.J. Toth, Nitrogen recovery from wastewater and human urine with hydrophobic gas separation membrane: experiments and modelling, Chem. Pap. 73 (2019) 1903–1915, https://doi.org/10.1007/s11696-019-00740-x.

[11] L. Richter, M. Wichern, M. Grömping, U. Robecke, J. Haberkamp, Nitrogen recovery from process water of digested sludge dewatering with membrane contactors, in: 3rd IWA Resour. Recover. Conf., Venize, 2019, 2019, pp. 13–14.

[12] N. Zhao, X. Li, X. Jin, I. Angelidaki, Y. Zhang, Integrated electrochemical-biological process as an alternative mean for ammonia monitoring during anaerobic digestion of organic wastes, Chemosphere 195 (2018) 735–741, https://doi.org/10.1016/j.chemosphere.2017.12.139.

[13] P.M.L. Ching, Richard H.Y. So, T. Morck, Advances in soft sensors for wastewater treatment plants: a systematic review, J. Water Process Eng. 44 (2021) 102367, https://doi.org/10.1016/j.jwpe.2021.102367.

[14] H. Haimi, M. Mulas, F. Corona, R. Vahala, Data-derived soft-sensors for biological wastewater treatment plants: an overview, Environ. Model Softw. 47 (2013) 88–107, https://doi.org/10.1016/j.envsoft.2013.05.009.

[15] A.M. Nair, B.M. Gonzalez-Silva, F.A. Haugen, H. Ratnaweera, S.W. Østerhus, Real-time monitoring of enhanced biological phosphorus removal in a multistage EBPR-MBBR using a soft-sensor for phosphates, J. Water Process Eng. 37 (2020), 101494, https://doi.org/10.1016/j.jwpe.2020.101494.

[16] B. Li, W. Yu, H.M. Huang, E. Lim, I. Boiarkina, B. Young, Struvite image analysis and its application for product purity prediction, J. Environ. Chem. Eng. 7 (5) (2019), 103349, https://doi.org/10.1016/j.jece.2019.103349.

[17] APHA, 22nd edition, 2012. Washington DC, USA.

[18] R.E. Moosbrugger, M.C. Wentzel, G.A. Ekama, G.v.R. Marais, A 5 pH point titration method for determining the carbonate and SCFA weak acid/bases in anaerobic systems, Water Science and Technology. 28 (1993) 237–245, https://doi.org/10.2166/wst.1993.0112.