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.

G. Noriega-Hevia*; J. Serralta*; A. Seco and J. Ferrer*.**

*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, València, Spain.

**CALAGUA – Unidad Mixta UV-UPV, Departament d'Enginyeria Química, Universitat de València, Avinguda de la Universitat s/n, 46100, Burjassot, València, Spain

Abstract

Nitrogen recovery technologies such as the hollow fibre membrane contactor are now being developed. However, an economic analysis is needed prior to their full-scale application in wastewater treatment plants. The aim of this study was to analyse the economic and environmental aspects of scaling-up this method. To achieve it, a full-scale 40,000 $m^3 \cdot day^{-1}$-wastewater treatment plant influent flow rate was simulated jointly with a membrane contactor plant to evaluate the minimum costs of optimum operating conditions of membrane contactors (pH, feed flow rate and membrane surface). The optimum conditions for treating 600 $m^3 \cdot day^{-1}$ of reject water was found to be 10 pH, 0.08 $m^3 \cdot s^{-1}$ feed flow rate and 10,580 m^2 of membrane surface, obtaining a 4% nitrogen ammonia sulphate solution. The results indicated capital (membrane modules and pumps) and operating costs (reagents and energy) of 0.0095 €$\cdot m^{-3}$ and a profit of 0.0090 €$\cdot m^{-3}$, including energy savings in terms of aeration and sales of the recovered ammonia sulphate, with the added benefit of reducing CO_2-eq by 10.3 tons per day.

Keywords

Nitrogen recovery; hollow fibre membrane contactor; global warming potential in wastewater treatment; membrane contactor modelling; economic analysis

1. Introduction

Nitrogen is present in the Earth in large quantities and different forms. The main source is the atmosphere, which has around 79% of stable N_2. There is a high demand for nitrogen, mainly as fertilizers in agriculture. Nitrogen in its reactive forms (ammonium, nitrite, and nitrate) is essential for plant growth, and its content is limited in soils. N_2 can be converted into ammonia by the Haber-Bosh process to produce fertilizers [1], although large amounts of energy are required. Razón [2] estimated this consumption at $6.4x10^{12} MJ \cdot year^{-1}$, which is equivalent to the energy consumed by 80,000,000 people in terms of global warming. Most of the nitrogen used in agriculture ends up in wastewater treatment plants (WWTPs), which are thus an important source of nutrients.

WWTPs have traditionally focused on organic matter and nutrient removal to avoid harmful effects on water bodies. However, new treatments, such as anaerobic membrane bioreactors (AnMBR), struvite recovery or nitrogen recovery processes, have been introduced to treat wastewater, produce energy and recover nutrients, phosphorous and nitrogen. The new approach seeks more sustainable wastewater treatment based on the circular economy to transform the classical WWTP into a source of nutrients and energy. Nitrogen is commonly removed by a nitrification-denitrification process which requires large amounts of energy for aeration (around 50-70% of the total energy consumption [3]). In these biological processes ammonium is transformed into N_2 gas, which is emitted to the atmosphere.

In this new framework, several alternative methods have been proposed to recover nitrogen, including air stripping, which is the conventional method, and others recently developed such as bioelectrochemical systems (BES), electrodialysis (ED) or the hollow fibre membrane contactor (HFMC). Air stripping consists of putting sulphuric acid in contact with free ammonia in two steps: stripping to separate the free ammonia and scrubbing to put the free ammonia in contact with the sulphuric acid, creating an ammonia sulphate solution. Although it is widely used in the industry, it also has some important drawbacks, such as high space, energy and reagent requirements [4]. In contrast, BES uses the electrons produced during microorganism-catalysed organic oxidation to produce energy and other value-added compounds, such as hydrogen [5]. These processes can separate free ammonia from the solution as gas. Although it is a promising technology, it has so far only been applied on a lab-scale, so more research is needed to scale it up. ED is another alternative based on the concentration of the dilute ions from a solution through ion migration from the anode to the cathode, crossing an anion exchange membrane. Although this technology is widely used for drinking water, it not often used for wastewater because of membrane fouling during nutrient recovery, for which electrodialysis reversal (EDR) is now being developed. This consists of the frequent reversion of the electrode polarities to mitigate fouling and breaking the aggregates on the membrane [6] improving ED applicability for nutrient recovery from wastewater.

HFMC is one of the most promising recent techniques for nitrogen recovery, which consists of a gas-permeable membrane, usually made of polypropylene (PP) or polyvinylidene fluoride (PVDF), in a hollow fibre configuration. A high pH nitrogen-rich solution (over 8.6), which works as the feed solution, is put in contact with an acid solution, usually sulphuric acid, which works as the draw solution, to transfer free ammonia to the acid solution in a single step. The hydrophobicity of the membrane favours the liquid-liquid extraction acting as a barrier to prevent the contact between both solutions. The process is driven by the different concentrations of free ammonia on both sides of the membrane. Once the free ammonia as gas crosses through the membrane, it is captured by the acid solution as ammonium, due to the ammonia-ammonium equilibrium. At the end of the process the draw solution is composed of ammonia sulphate (AmS), which can be marketed as a fertilizer source [7]. Although sulphuric acid is the most commonly used, Sancho et al. [8] used nitric and phosphoric acid producing other marketable subproducts with comparable efficiency. HFMC thus offers the prospect of being selective to ammonia removal, able to operate without a large energy input or big space (as in the case of air stripping) and is suitable for removing almost all the ammonium nitrogen [4].

In laboratory and pilot scale several authors have reported that the system works well with different streams. Seco et al. [9] applied HFMC to treating the centrate from anaerobic co-digestion of primary sludge and microalgae with higher than 90% efficiency. It has also been applied to industrial wastewater [10], manure [11] or landfilled leachate [12] with similar recovery efficiencies. On a larger scale, Boehler et al. [13] and Richter et al. [14] applied it in different WWTPs at 28.8 $m^3 \cdot day^{-1}$ and 360 $m^3 \cdot day^{-1}$, respectively, maintaining the high lab-scale efficiency. These results suggest the technology is feasible on an industrial scale from a technical point of view.

Apart from the technical feasibility, the economic aspects of these processes in full-scale WWTPs also need to be studied. Some authors have reported interesting economic data on new energy production systems (AnMBR [15]) or phosphorous recovery (struvite precipitation [16]) in WWTPs, but few studies have been made on nitrogen recovery. Only Dube et al. [17], who applied these membranes to swine manure, considered some economic aspects. The aim of the present study was thus to evaluate the economic aspects of HFMC in recovering nitrogen from anaerobic supernatant in a full-scale Spanish WWTP. The capital (CAPEX) and operating costs (OPEX) of different operating conditions were evaluated, plus the likely profits from their application (aeration energy savings, production of a fertilizer solution and reduced greenhouse gas emissions). For this, models were used to simulate the WWTP and HFMC performance in search of the optimum operating conditions as regards reagents, energy, and membrane surface, estimating costs, savings and Global Warming Potential (GWP).

2. Method

The method described in the following sections was applied to evaluate the economic aspects of scaling up HFMC technology and optimize the operating parameters. Figure 1 shows the scheme followed.

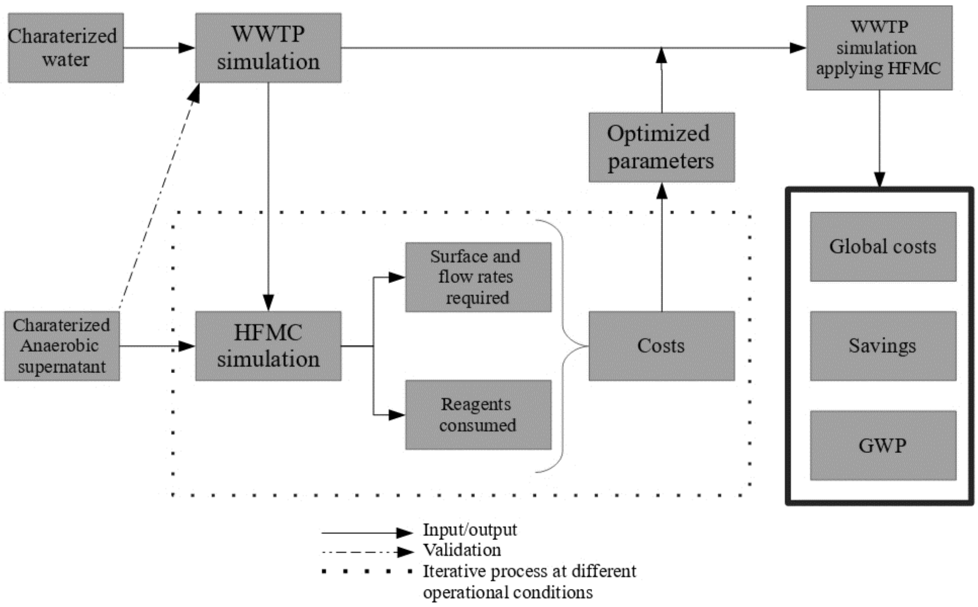

Figure 1. Scheme of the methodology followed to evaluate the economic aspects of HFMC.

Characterized influent wastewater from the Conca del Carraixet WWTP in Valencia (Spain) was used to simulate the whole plant (mainstream and sidestream). The results obtained were validated by comparison with experimental data, mainly from the effluent and the previously characterised anaerobic digestion supernatant. The results obtained, especially those of the ammonia load and flow rate of the anaerobic digestion supernatant, were used to simulate the performance of the HFMC in the full-scale WWTP. Simulations were carried out considering different membrane surfaces, flow rates and pH values to evaluate the costs and benefits of the different options looking for the optimum conditions in economic terms. The WWTP was simulated again assuming the optimum HFMC conditions after the anaerobic digestion to assess its influence of aeration and nitrogen load on the plant. All these data were used to analyse costs, savings and the GWP impact of the parameters.

2.1. WWTP

The simulated plant, with a daily flow rate of 40,000 $m^3 \cdot day^{-1}$, was the Conca del Carraixet WWTP, located in Valencia, Spain. This plant has an activated sludge (AS) process in the main line to remove organic matter and nitrogen by nitrification-denitrification. Phosphorous is removed by ferric chloride chemical precipitation. Primary and waste sludge are thickened separately and digested in an anaerobic reactor at mesophilic temperature to stabilise and recover energy. The treated sludge is dewatered by separating the reject water, which is recirculated to the biological reactor, and the solid fraction. This reject water is the most suitable WWTP stream to recover nitrogen because of its high concentration of nitrogen in the form of ammonia and its low solid content. The proposed HFMC plant was therefore designed to be fed with reject water as the source of ammonia.

The influent wastewater, the WWTP model's main input, was characterized. Table 1 gives the overall values. The most remarkable were the daily flow rate, which represented the size of the full-scale plant and its total nitrogen load, which was the amount of potentially recoverable nitrogen. The total nitrogen load was 2,112 $kg \cdot d^{-1}$. Alkalinity was also important in terms of alkali requirements for working at different pH.

Table 1. Influent characterization.

	Average ± S.D
Flow rates ($m^3 \cdot d^{-1}$)	40,000
COD (g COD$\cdot m^{-3}$)	510 ± 80
N-NH_4 (g N$\cdot m^{-3}$)	42.8 ± 3.4
P-PO_4 (g P$\cdot m^{-3}$)	5.5 ± 0.3
N_T (g N$\cdot m^{-3}$)	52.8 ± 4.8
P_T (g P$\cdot m^{-3}$)	10.2 ± 2.1
TSS (g$\cdot m^{-3}$)	342 ± 65
Alkalinity (mg $CaCO_3 \cdot m^{-3}$)	453 ± 29

2.2. WWTP simulation

The software DESASS [18] was used to simulate the full-scale plant based on the previously described wastewater characterization. The Biological Nutrient Removal Model Nº 2S (BNRM2S) [19] was the model implemented. This model considers the most important physical, chemical and biological processes and simulates the whole plant's performance plus the interactions of the different streams. The units and dimensions of the full-scale plant as well as the influent wastewater characterization were entered in the software. All the data were used to achieve a complete and reliable representation of the plant to evaluate the effect of HFMC focusing on the influence of reducing the nitrogen load on the biological reactor and the aeration energy requirements in both situations.

2.3. HFMC plant

An HFMC plant was designed to evaluate its effect on nitrogen recovery in a WWTP. The set-up is shown in Figure 2. Reject water passes through two different tanks for pre-treatment before feeding the membrane. To prepare the reject water, it is firstly stored in a closed tank to reduce stripping losses where the pH is adjusted. Therefore, the solids formed are removed in the settler to avoid membrane clogging. The reject water is sent to the feed tank to pass through the different membrane contactor units. The selected pH is maintained in the feed tank by means of NaOH addition. Acid solution is replaced when the pH reaches values near 6-7 because at this point there is no more acid available, free ammonia concentration in the acid solution increases and the driving force is significantly reduced. Reject water is pumped into the shell side while the acid solution is pumped into the lumen side to reduce clogging. Both streams are re-circulated and fed counter-currently. pH and temperature are monitored in each tank.

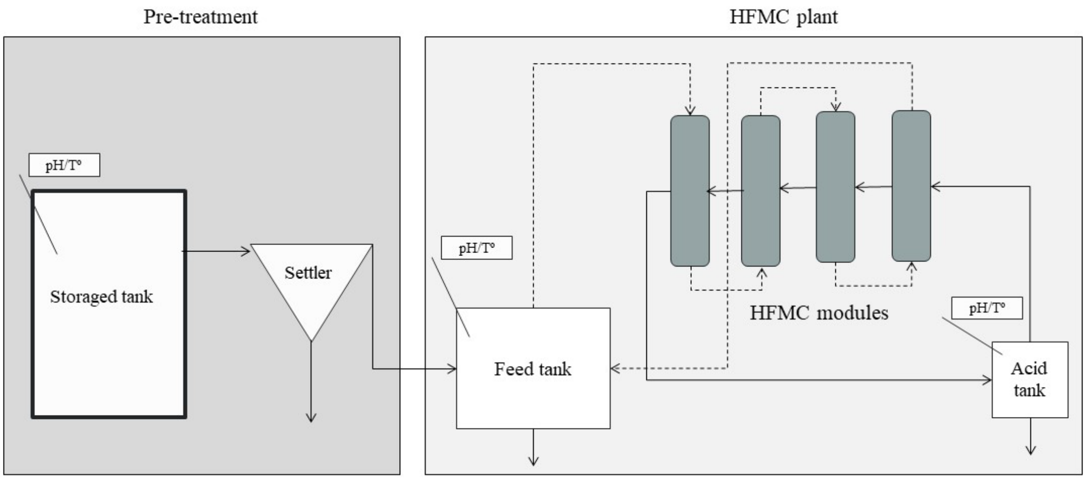

Figure 2. HFMC set-up.

2.4. HFMC plant simulation

The model described in [20] was used to simulate HFMC application. This model can reproduce the evolution of Total Ammonia Nitrogen (TAN) in the membrane and reagent consumption required to maintain pH. The model incorporated in MATLAB-Simulink®, includes the kinetic-governed process (gas stripping across the membrane) and the equilibrium-governed process (acid-based reactions). The latter process provides a framework to predict the variations in OH^- concentration (alkali addition) needed to raise and maintain pH during the process and can be used to analyse this reagent's requirements during long-term operations.

Simulations were carried out in different operating conditions. pH was varied from 9 to 11 and feed flow rates between 0.02 to 0.117 $m^3 \cdot s^{-1}$ to evaluate optimum feed flow rate, the required membrane surface and reagent consumption at the minimum cost. It should be noted that the feed flow rate was the flow rate pumped into the units and recycled. After obtaining the optimum conditions, the whole plant was simulated again on DESASS with a reduced nitrogen load recycled from the sludge dewatering system to assess the influence of HFMC on the WWTP.

2.5. Economic evaluation

The different consumption values obtained in the simulations were used to determine the optimum values of each parameter. The cost associated with each item was taken into account, also the membrane and pumps as CAPEX costs, while the reagent consumption (sodium hydroxide, citric acid and sulphuric) and pumping energy were included as OPEX. Table 2 shows the unit cost of sodium hydroxide, sulphuric acid, citric acid pumping energy and membrane surface costs.

Table 2. Data used for economic evaluation.

Reagents Consumed	Units	Value	References
NaOH	$€\cdot kg^{-1}$	0.1225	[21]
H_2SO_4	$€\cdot L^{-1}$	0.1281	[22]
$C_6H_8O_7$	$€\cdot kg^{-1}$	0.56	[23]
Energy	$€\cdot kWh^{-1}$	0.09	[24]
Membrane surface	$€\cdot m^{-2}$	49	Based on manufacturer’s data
Ammonia Sulphate	$€\cdot kg\ N^{-1}$	0.77	Based on manufacturer’s data

Furthermore, the following general assumptions were made to calculate the costs:

- 10-year pump and membrane lifespan [17] and 20 years for the settler.
- Moderate cleaning with a sodium hydroxide solution of 6 wt% and citric acid solution of 10 wt% once a month. This is the cleaning procedure recommended by membrane manufacturers.
- Nitrogen recovery efficiency 90 %.
- 20 working hours per day to cope with reject water peak flow rates and maintenance.

- Membrane surface requirements were increased by 15 % to cope with reject water peak flow rates.
- 4% nitrogen-rich ammonia sulphate solution (based on experimental results (data not shown)).

The CAPEX and OPEX costs were evaluated. CAPEX comprises pumps, the settler and membrane surface, being this latter the most important parameter. OPEX comprises the requirements of sodium hydroxide, sulphuric acid, citric acid and energy for pumping. The points are energy and sodium hydroxide which are closely related to pH and flow rate. Control and automation costs as well as OPEX associated to the settler are considered negligible.

The savings achieved were also evaluated in the simulation. Nitrogen recovery from the AD supernatant, which is recycled to the mainstream, considerably reduced the nitrogen load and the aeration required to remove it. The production of ammonium sulphate was also considered to benefit from the application of this technology. The nitrogen concentration in the product in comparison with the AmS fertilizers and their market prices were the main aspects analysed.

In the environmental analysis, different GWP aspects were considered. Firstly, the nitrification process emits N_2O, which has a remarkable GWP of 298 ton CO_2-eq·ton N_2O^{-1}[25], so that reducing the nitrogen load reduces these emissions. As the savings in aeration also have an impact on the plant's carbon footprint, the industrial AmS process was also included to evaluate the GWP of the nitrogen recovery process.

3. Results and discussion

3.1. WWTP simulation

The WWTP simulation was based on the wastewater characterization and the plant description. Table 3 compares the model predictions and experimental values. As can be seen, the mathematical model faithfully reproduced the experimental values. The most important values for designing the HFMC plant were the AD supernatant flow rate and the ammonia concentration in this stream. A nitrogen load of 424.7 kg N·day^{-1} was obtained and the aeration energy consumption of the process was around 5,860 kWh·day^{-1}.

Table 3. Real and simulated characterization of the AD supernatant and effluent.

	AD Supernatant		**Effluent**	
	Real ± S.D	Simulated	Real ± S.D	Simulated
Flow rates ($m^3 \cdot d^{-1}$)	-	567.94		
COD (g COD·m^{-3})	842.6 ± 25.3	821.90	62.3 ± 5.2	68.5
N-NH_4 (g N·m^{-3})	741.5 ± 35.1	738 .00	1.35 ± 0.2	1.40
P-PO_4 (g P·m^{-3})	-	-	1.18 ± 0.2	1.22
N_T (g N·m^{-3})	750.7 ± 37.2	747.84	9.65 ± 0.4	9.80
P_T (g P·m^{-3})	-	-	2.08 ± 0.2	2.13
Alkalinity (g $CaCO_3$·m^{-3})	2,825.8 ± 165.3	2,897.80	198.5 ± 10.5	200.83

3.2. HFMC plant design

The HFMC plant was designed to treat 600 m^3·day^{-1} to cope with peak flow rates. Simulations under different operating conditions were carried out using the HFMC mathematical model to find the optimum conditions. Figure 3 shows the membrane surface requirements to achieve a 90% efficiency of nitrogen recovery at different pH values (9-11) and feed flow rates (0.02-0.117 m^3·s^{-1}). At low flow rates the membrane surface required to treat the same flow rate of AD supernatant increases. When the feed flow rate is increased from 0.02 m^3·s^{-1} to 0.05 m^3·s^{-1}, around 46% a smaller membrane surface is required at different pH. However, when the flow rate is increased between 0.05 and 0.1 m^3·s^{-1} it is only reduced by 10% due to the boundary layer effect. At low flow rates the boundary layer resists ammonia transfers due to the low turbulence around the fibre. However, when both the flow rates and turbulence increase, the resistance gradually falls to the minimum. Flow rates lower than 0.02 m^3·s^{-1} were not evaluated due to the high membrane surface requirements, while the higher flow rates were not included because they do not significantly reduce membrane requirements.

Significant differences in the membrane requirements were obtained for pH, especially between pH 9 and the other values. Working at a pH of 10 reduces the membrane surface by around 57 % and at pH 11 by 63% less than at pH 9. The reason for this is that at pH 10 almost 85% of the nitrogen is free ammonia at 25º degrees while, at the same temperature the percentage of free ammonia at pH 9 is around 30%. Thus, this large amount of free ammonia available to be transferred makes that the contact time between the stream and the membrane can be reduced maintaining the same flux.

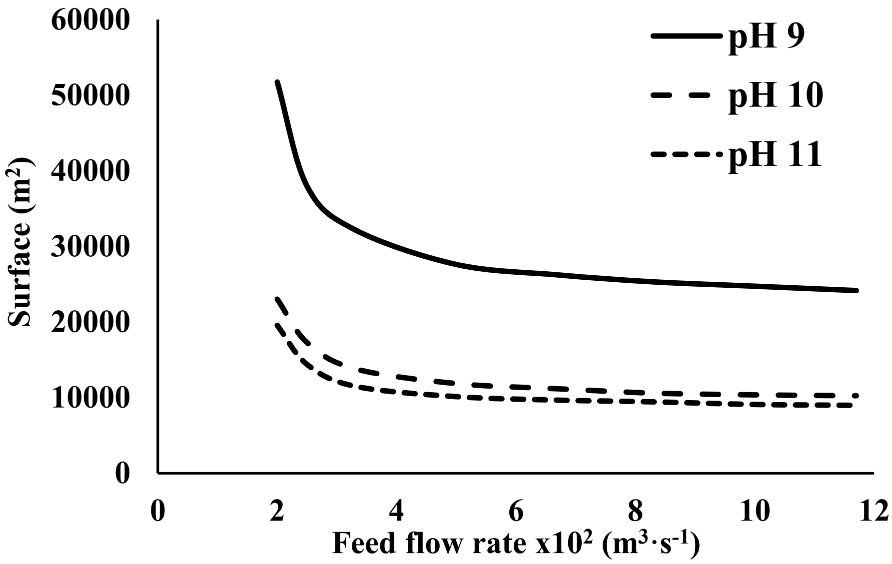

Figure 3. Membrane Surface requirements to treat 600 $m^3 \cdot d^{-1}$ at different pH and flow rates.

pH affects not only the membrane surface requirements but also reagent consumption, especially NaOH. Figure 3 shows that higher pH reduces the membrane surface requirements but increases sodium hydroxide consumption. Figure 4 gives the daily NaOH consumption at different pH values and that 13 m^3(1M) of sodium hydroxide are needed to treat 600$m^3 \cdot d^{-1}$ at pH 9, which increases to 50% at 10 and to 140% at pH 11. The economic analysis thus determines the optimum pH.

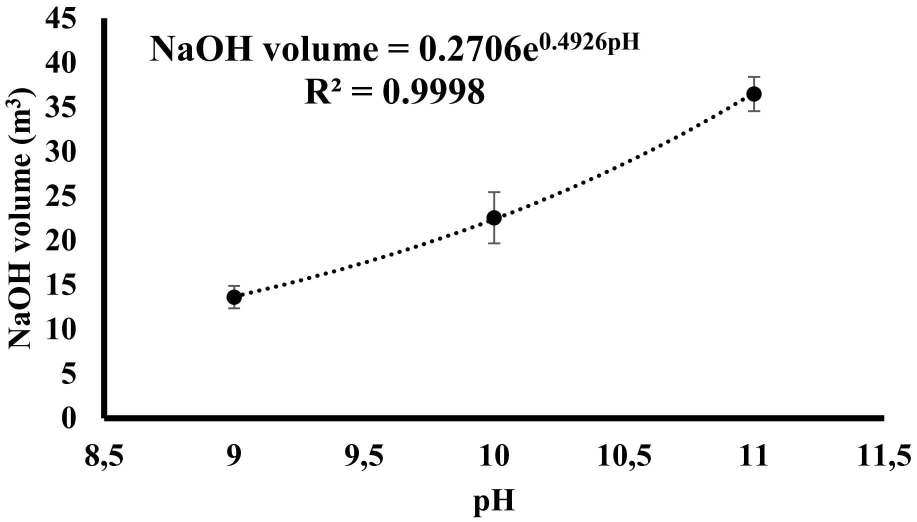

Figure 4. Daily NaOH (1M) required to raise the pH of the AD supernatant.

The economic analysis should also include the energy savings and profits obtained from nitrogen recovery. The maximum concentration obtained experimentally by the present authors was a 4% nitrogen-rich AmS solution, which is similar to that obtained by Richter et al [14]. This is equivalent to a subproduct of 188 g AmS $\cdot L^{-1}$.

3.3. OPEX/CAPEX

This section gives the OPEX and CAPEX costs. OPEX included the NaOH required to increase the pH and cleaning, the sulphuric acid needed to extract the free ammonia from the feed solution, citric acid for membrane cleaning and pumping energy consumption. The CAPEX studied were membrane surface requirements, the settler and the pumps. All the costs are related to the WWTP influent flow rate (WWinf), which is 40,000 $m^3 \cdot day^{-1}$.

3.3.1. OPEX

3.3.1.1. Consumption of NaOH

Reagent consumption is the main input of the OPEX costs, with sodium hydroxide the main reagent used in this process since pH must be raised to at least 9 to enhance free ammonia transfer through the membrane. To raise the pH of 600 $m^3 \cdot day^{-1}$ to 9, 547 kg $NaOH \cdot day^{-1}$ (99% richness) are needed, with an economic impact of 67 €$\cdot day^{-1}$, or 0.002 € per cubic meter of influent wastewater (0.002 €·m^{-3} WWinf). However, when pH was set at 10 or 11 the NaOH consumption rose to 895 and 1464 kg·day^{-1}, respectively, which represents a cost of 110 €·day^{-1} (0.0028 €·m^{-3} WWinf) and 180 €·day^{-1} (0.0045 €·m^{-3} WWinf) respectively. Although raising pH reduces the membrane surface required, it also increases the reagent costs.

Regarding to the sodium hydroxide consumption associated to membrane cleaning (a solution of 6 wt% NaOH), which is related with the membrane surface required, is 3.2×10^{-5}€·m^{-2} per cleaning.

3.3.1.2. Consumption of acids

Sulphuric acid is used to capture free ammonia and convert it to ammonium, producing an AmS solution. To obtain a 4% nitrogen-rich final product, 1,512 kg H_2SO_4 ·day^{-1} (99% richness) is needed due to the stoichiometric relationship between sulphate and ammonia to create ammonia sulphate (ratio of 3.5 kg H_2SO_4·kg N^{-1}). Sulphuric acid requirements are, in monetary terms, 107 €·day^{-1} or 0.003 €·m^{-3} WWinf. It should be noted that this value is constant in all conditions, since a 90% recovery efficiency was obtained under all the operating conditions evaluated.

Citric acid, which is applied for membrane cleaning once a month, is also constant. The costs associated to a citric acid solution of 10 wt%, which depends on the membrane surface required, is 0.03 €·m^{-2} per cleaning.

3.3.1.3. Energy consumption

The energy consumed depends on the feed flow rate, which varied between 0.02 and 0.117 m^3·s^{-1}. The energy cost depends on the energy required to pump the feed at a given flow rate and the price per kWh, which was set at 0.09 €·kWh^{-1}. The required power was calculated by fixing a head loss of 2 m and an efficiency of 75% for the pump and the motor.

The outcomes showed a cost of 1.5 €·day^{-1} and 3.77×10^{-5} €·m^{-3} WWinf for a feed flow rate of 0.02 m^3·s^{-1}. In contrast, at a feed flow rate of 0.117 m^3·s^{-1} the costs would be 8.8 €·day^{-1} and

$2.2x10^{-4}$ €·m^{-3} WWinf. The cost associated with the highest flow rate studied is nearly 6 times higher than that of the lowest.

A fixed acid solution flow rate of 0.03 $m^3 \cdot s^{-1}$ was used for all the conditions studied at a cost of 5.65 $x10^{-5}$ €·m^{-3} WWinf.

3.3.2.CAPEX

3.3.2.1. Membrane requirements

As can be seen in Figure 3, the membrane requirements depend mainly on the flow rate and pH chosen. The following assumptions were made to estimate the capital cost of the membrane: 10-year lifespan, an increase of 15% in the membrane requirements to cope with reject water peak flow rates, a recovery efficiency of 90% and 20 working hours per day. According to these parameters and a price of 49 €·m^{-2}, which was based on the manufacturer's data, membrane costs varied from 2,535,750 € (51,750 m^2) to 439,530 € (8,970 m^2), which is equivalent to 0.017 €·m^{-3} WWinf (at a pH of 9 and a feed flow rate of 0.02 $m^3 \cdot s^{-1}$) to $3.0x10^{-3}$ €·m^{-3} WWinf (at pH 11 and a feed flow rate of 0.117 $m^3 \cdot s^{-1}$).

3.3.2.2. Pumps

A feed pump with a flow rate of 0.015 $m^3 \cdot s^{-1}$ at a price of 3,223 € was selected to estimate pump costs. The number of pumps vary according to the feed flow rate. The cost of these pumps is equivalent to $1.0x10^{-4}$ €·m^{-3} WWinf for a flow rate of 0.02 $m^3 \cdot s^{-1}$ and $3.34x10^{-4}$ €·m^{-3} WWinf for a flow rate of 0.117 $m^3 \cdot s^{-1}$.

The acid solution pumps had a flow rate of 0.011 $m^3 \cdot s^{-1}$ and an individual price of 1,285€. As the acid flow rate is fixed at 0.03 $m^3 \cdot s^{-1}$ in all the simulations, its cost is constant. Three pumps plus one for leeway were considered which involves an investment of 4,913 € over 10 years, which is equivalent to $3.36x10^{-5}$ €·m^{-3} WWinf.

3.3.3.Settler

The settler cost, which is required to remove the solids of the feed solution is also considered. Attending to the feed flow rate, a settler of approximately 70.3 m^3 of volume (surface of 21.7 m^2 and a high of 3.25 m) is required. It is estimated, based on different prices of settlers, that the construction cost is 100 €·m^{-3}. Thus, the cost associated to the settler is 7,030 €, which is equivalent to 2.4×10^{-5} €·m^{-3} WWinf.

3.3.4. Overall results

Figure 5 shows the overall cost of implementing the HFMC plant in the Carraixet WWTP per cubic metre of influent wastewater at different pH and flow rates. All the items previously discussed in Sections 3.2.1 and 3.2.2 were considered. As can be seen, pH 9 is the most expensive component, regardless of the flow rate chosen. The reduction in sodium hydroxide requirements is not enough to compensate for the larger membrane surface required at this pH. However, increasing the flow rate, which considerably reduces the membrane surface requirements, would reduce the overall cost from 0.022 to 0.013 €·m^{-3} WWinf.

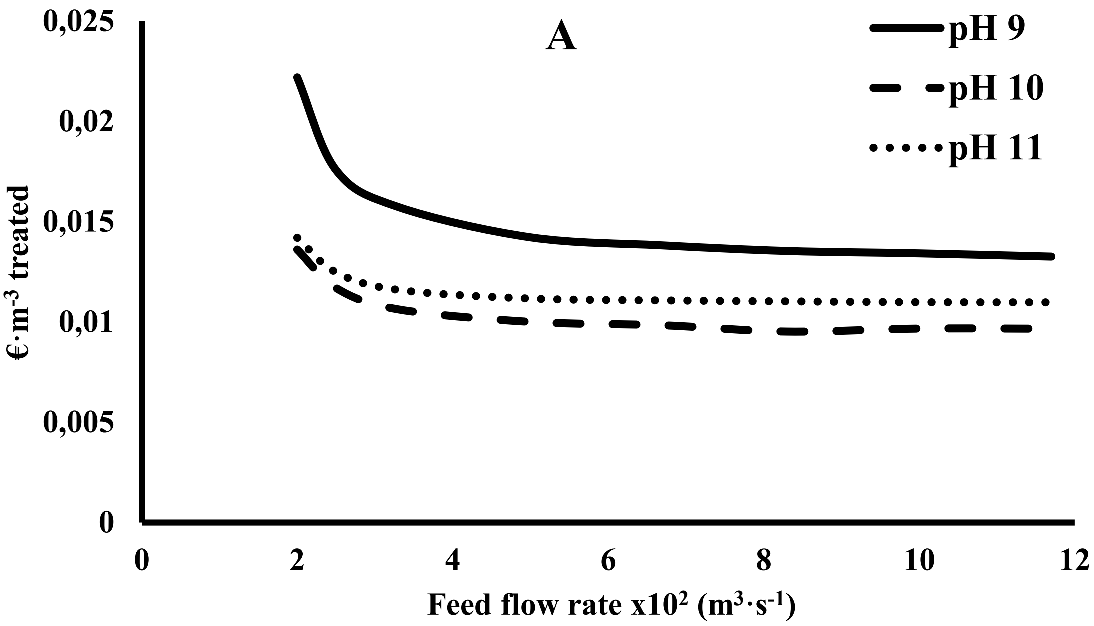

Figure 5. Costs under different operating conditions:(A) at a pH of 9, 10 and 11 and (B) zoom of costs at pH 10.

The costs obtained in the simulations carried out at pH 10 are slightly lower than those obtained at pH 11. Although the membrane surface was less at pH 11 (see Figure 3) the cost of the sodium hydroxide needed to reach this pH is greater than the reduced membrane. As can be seen in Figure 5.A, pH 10 is the best option as regards the overall costs and the minimum costs are obtained at a flow rate of 0.08 $m^3 \cdot s^{-1}$(Figure 5.B) which is equivalent to 10,580 m^2 of membrane. The costs at higher flow rates are slightly higher because the savings in the membrane surface are similar to the higher pumping cost for the higher flow rate. The minimum overall cost was 0.0095 €·m^{-3} WWinf, while the average wastewater treatment cost in this region is 0.35 €·m^{-3} [26].

Table 4. Cost associated to each item at the optimum conditions.

	€·m^{-3} WWinf	**Percentage (%)**
NaOH	2.70x10^{-3}	29.1
Sulphuric Acid	2.67x10^{-3}	28.1
Citric acid	2.30x10^{-4}	2.4
Pumping	2.13x10^{-4}	2.2
Pumps	5.05x10^{-5}	0.5
Settler	2.41x10^{-5}	0.4
Membrane	3.55x10^{-3}	37.3
TOTAL	0.0095	100

The percentage contribution of each item to the overall cost is shown in Table 4. The membrane (37.3%) has the highest impact on the costs, with NaOH being 29.1% of the total and sulphuric acid 28.1%. The other costs (pumps, settler, citric acid and energy consumption) are around 5.5% of the total. These results highlight the importance of feed solution pH because it determines not only the NaOH consumption, also the membrane surface, which together make up 66.4% of the total cost.

3.4. Positive effects

The application of this technology in a WWTP also has positive effects that could provide economic and environmental benefits. Firstly, the recovery of ammonia from the AD supernatant reduces the amount of nitrogen in the mainline. The simulation results show that 424.7 kg N are recycled daily to the mainline, which represents 20% of the total nitrogen load in the influent wastewater. The reduction in the reactor ammonia load has a positive impact on the aeration requirements for nitrification. The simulations showed that a reduction of 10% could be achieved in aeration energy consumption with similar effluent composition, which is equivalent to 0.0013 €·m^{-3} WWinf.

AmS can be marketed obtaining economic benefits. Free ammonia production is based on the Haber-Bosh process, which requires an energy consumption of 19.3 kWh·kg N^{-1} [27], a stripping process and crystallization. Although, traditionally AmS was used as a solid fertilizer, it is now increasingly sold in liquid form. Diluting the nitrogen content to 6%, it can be sold to farmers at around 0.77 €·kg N^{-1}. The simulation showed that approximately 400 kg N·day^{-1} could be recovered by HFMC (at 90% efficiency) producing an AmS solution with a nitrogen content of 4% (a daily production 9.96 m^3AmS solution). The profits from the sale of this solution would thus be 308 €·day^{-1}, or 0.0077 €·m^{-3} WWinf. As the 4% nitrogen-rich solution is suitable for direct fertilizer use, a costly evaporation process is not required.

To sum up, the economic benefits of applying HFMC are 0.0013 €·m^{-3} due to aeration energy savings of 0.0077 €·m^{-3} from AmS sales for a total of 0.009 € ·m^{-3} WWinf, which is like the total costs (CAPEX and OPEX) of this technology, showing considerable savings over the traditional Haber-Bosch process.

3.5. Global Warming Potential

The new technology considerably reduces the carbon footprint. Nitrous oxide (N_2O) emissions from nitrification have a big impact on GWP and represent 26% of the greenhouse gas footprint in WWTPs [1], even bigger than CO_2 (298 kg CO_2-eq·kg N_2O^{-1} [25]).

Although different values can be found in the literature for WWTP, N_2O emissions (between 0-14.6% of total nitrogen load), 4% is a representative value [28]. Assuming that the nitrogen recovered and therefore not recycled to the main line is 400 kg N·day^{-1}, this avoids 16 kg of N_2O emissions (4,768 kg CO_2-eq·day^{-1}). In addition, raising the COD/N ratio in the wastewater entering the biological reactor helps to reduce total N_2O emissions [29].

Reducing the required aeration energy also has a positive impact on the plant's GWP. The average Spanish CO_2 emissions from electricity generation is 0.43 kg $CO_2 \cdot kWh^{-1}$ [30]. Reducing the nitrogen load of the nitrogen recovery process will reduce the aeration energy requirements by 10%, or 5,292 $kWh \cdot day^{-1}$, which means a reduction of 2,275.56 kg CO_2-eq per day. Furthermore, the energy consumption of the HFMC plant means an increase of 106 $kWh \cdot day^{-1}$ which is 45.7 kg CO_2-eq per day.

The total GWP reduction in the simulated WWTP is 6,997.3 kg CO_2-eq per day, or 2,554 tons CO_2-eq per year. Moreover, the nitrogen recovered reduces the ammonia produced by the Haber-Bosch process which has an important carbon footprint. The industrial production of the same daily amount of nitrogen (400 kg N per day) would require an energy consumption of around 7,720 $kWh \cdot day^{-1}$, which means approximately 3.3 ton CO_2-eq per day in terms of GWP. Thus, the total GWP reduction would be of 10.3 ton CO_2-eq per day.

4. Conclusions

The following conclusions can be drawn from the results obtained:

- The total costs of scaling up HFMC for nitrogen recovery at the Carraixet WWTP are estimated to be 0.0095 $€ \cdot m^{-3}$ of influent wastewater, with reagents (57.2%) and membrane surface (37.3%) composing 94.5% of the total costs.
- The optimum operational conditions are a pH of 10 and a feed flow rate of 0.08 $m^3 \cdot s^{-1}$ which lead to a membrane surface of 10,580 m^2 .
- The application of HFMC creates a benefit of 0.009 $€ \cdot m^{-3}$ WWinf due to the sales of AmS and the energy savings related to the nitrification process.
- A reduction of 10.3 ton CO_2-eq per day was estimated.: 6,997.3kg CO_2-eq per day due to the reduced N_2O emissions and energy consumption and 3.3-ton CO_2-eq per day because of the AmS production without the application of Haber-Bosch.

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