Nitrogen recovery by Transmembrane Chemisorption process: pilot scale experiences

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Summary of key findings

In this work the feasibility of nitrogen recovery from high strength effluent was demonstrated using transmembrane chemisorption (TMCS). A low energy process combination: screw press, dynamic cross flow nanofiltration with ceramic membranes and reverse osmosis, was developed at industrial scale (by NEREUS), for treating the liquid stream from anaerobic digestion. The side stream (retentate) of reverse osmosis was treated in TMCS for extracting and concentrating ammonia, in order to produce ammonium sulphate $((NH_4)_2SO_4)$. The study reveals the influence of major parameters in order to provide recommendation for optimal design and operation.

Background and relevance

Technologies for nutrient recovery from wastewater bring world's attention today. Nitrogen removal in wastewater treatment plants (WWTPs) is generally carried out by nitrification/denitrification processes where nitrogen returns to the atmosphere as N_2 gas. Instead of that, a sustainable approach would be to convert ammonia into fertilizer for agriculture sector and transforming WWTPs into water resource recovery facilities (WRRFs) .Indeed fertilizer demand containing nitrogen and phosphorus increased by 600% in the last 50 years (1). International Fertilize Association predicts an increase of fertilizer demand by 1.5 % per year during 2014-2022 where global ammonia capacity is projected to expand by 8% over 2016, to reach 234 Mt NH_3 in 2021 (2). Furthermore, the traditional production of nitrogen fertilizer via the Haber-Bosch process and nitrification-denitrification in WWTPs are costly and energy intensive (1).

For ammonia recovery in WWTPs, air and steam stripping were until now the most common technology. These processes allow to treating ammonia rich supernatant which can reduce the N-load saving denitrification volume and improving nitrogen removal. Furthermore, they are applied to sludge from anaerobic digestion which has a high ammonium charge, representing until the 20 % of nitrogen effluent in WWTP (3) and producing fertilizer in form of ammonium sulphate. However, there is only around 10 pre-treatment stripping plants installed in Europe (4), partly because stripping process are less economically favourable than traditional processes due to high energy demand of the blowers and installation costs (1).

TMCS technique is a new attractive alternative for ammonia recovery as a fertilizer. In this process, free ammonia gas (NH_3) pass through a hydrophobic membrane from the liquid stream to an acid solution in which the low pH allow to convert all NH_3 gas to the form NH_4^+, producing ammonium sulphate solution. Due to high ammonia transfer rate compact system can be used. Because no air transport is necessary this technique has very low energy needs. There are few studies of TMCS technology at pilot scale; Boehler et al. got an overall ammonia removal of 80-99% from digested sludge with one pilot membrane contactor of 120 m^2 at WWTP Neugut. Two membrane contactors in series were also tested, the removal reached 75 % at WWTP Neugut and 80-85 % at WWTP Altenrhein. Similar performance were reported at WWTP Velon, whose N-NH_4 concentration in the sludge liquid was around 1035 mg/L (4). In addition, the installation at WWTP Yverson-les-Bains got an overall ammonia removal of 80% with an N-NH_4 concentration final product of 30-40 g/L. One crucial point was to prevent any risk of clogging by an efficient pretreatment of wastewater for suspend solids removal (settling, filtration, microfiltration). However most of the experiments reported were done with a unique membrane technology and poor information can be found on different membrane materials or technologies.

This work was performed in order to define design criteria and optimal operating conditions for a new TMCS module. Moreover an original strategy was applied by treating the concentrated stream of a reverse osmosis unit, allowing simultaneous nitrogen recovery and water reclamation.

Material & Methods

A pilot treating 2 m^3 h^{-1} by a combination of processes: screw press, dynamic cross flow nanofiltration with ceramic membranes and reverse osmosis was successfully operated with real high strength wastewater (coming from anaerobic digester of various liquid and solid wastes). A lab-scale TMCS unit was first used for treating the concentrate of the reverse osmosis step, i.e. an effluent with a concentration of 4.9 gN L^{-1}. TMCS module was formed by a microporous hydrophobic PTFE membrane (0.52 m^2 of surface) provided by POLYMEM. The sulfuric acid flowed inside the fibers of the module whereas the effluent flows through the shell-side of the membrane module decreasing the concentration gradient within the circuit. The pH of the effluent was increased by stripping carbon dioxide (CO_2) in a pre-aeration tank and by the addition of a base (NaOH or KOH) until reaching a pH value of 11. Then a settling phase was introduced to remove precipitates before entering into the TMCS module. Preliminary experiences were performed with ammonium chloride solution (4.5 gN L^{-1}, pH 11) for testing operating conditions before using the real effluent. Influence of temperature, pH of acid, as well as liquid flow and hydraulic retention time were determined. Ammonium removal efficiency, transfer rate and transfer coefficient (K_L) were systematically calculated.

Results and discussion

Results indicate that effluent flowrate and HRT were the parameters with the highest impact on performance. Ammonium removal efficiency increased when liquid flow decreased. Theoretically the flow influences both the turbulence and the retention time in the module. Observation shows that the removal efficiency increase due to increase of the contact time between the liquid and the membrane interface. Highest removal efficiency in the module was 75% for 25 min of retention time. On the contrary the total ammonium transfer rate decreased with the decrease of flow rate (increase of HRT) which means that the optimal design would depend on a compromise between removal efficiency and productivity. Higher HRT allows increasing the removal but the final product concentration substantially decreases (fig 2).
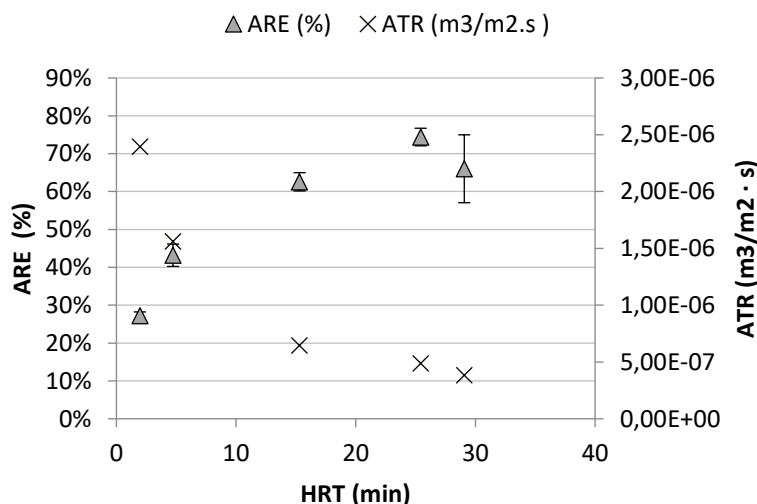

Figure 1. Ammonia removal efficiency (ARE) and ammonia transfer rate (ATR) obtained for different effluent flow rates, as a function of retention time, at 23 ± 2 ºC, with H_2SO_4 solution (0.5M, pH 0.8 - 1)
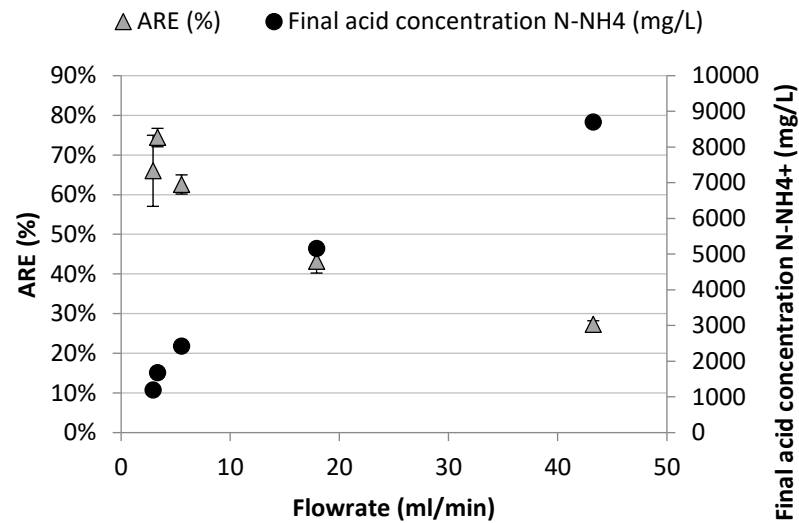
Figure 2. Ammonium removal efficiency (ARE) and outlet ammonium concentration in acid solution for different flow rates.

Results showed that the pH at the side of the acid solution also affects the mass transfer. Experiences were performed at pH lower than 1 and the acid outlet pH were constant with values ranging from 1 to 1.9. When the pH reached above 2.4, the NH_3 transfer rate decreased by more than 25%. These results confirmed those of Bohler and al 2016 (4), and the membrane material does not influence significantly that effect. It was also shown that the acid solution outflow can reach pH values around neutral with an on-going recirculation, a pH value appropriate for further production solution as fertiliser.

With the real effluent comparable ARE was achieved (but slightly lower than synthetic solution): about 61% removal, for HRT of 15 minutes. The reason for the slight decrease of performance with real effluent still needs to be clarified. The presence of multiple chemical species and ions in this effluent may explain that difference. Indeed ionic strength modifies the acid/base equilibrium constants and also constitutes contaminant for gas/liquid interface which could decrease the transfer coefficient.

Conclusion

The feasibility of the TMCS technology coupled with RO is now demonstrated. The technique is able to reach adequate ammonium removal efficiency (75%) with very low energy consumption, and recovering ammonium sulphate fertilizer.

For optimal design, regarding the influence of flow rate on performance, it can be suggested to use multiple membrane module in series. This can improve the ARE, but a much lower ATR in the second module should be expected. Economical calculation would help to design the optimal length and number of module depending on the influent concentration and rejection constraints.

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