Smart fertiliser production from nitrogen recovery process

G. Noriega-Hevia*, A. González-Míguez*, A. Mayor*, L. Rodríguez-Hernández** and C.M. Castro-Barros*
* CETAQUA- Water Technology Centre. **VIAQUA
Presenting author email: guillermo.noriega@cetaqua.com
Keywords: Biofactory, hydrophobic membrane, ion exchange, nitrogen recovery, smart fertiliser.
Preferred presentation: oral. **Topic**: Recycling & resource recovery

INTRODUCTION

Nitrogen-based conventional fertilisers production is known to be a fossil-fuel dependent and energy-intensive process. Therefore, in the frame of Horizon 2020 WalNUT Project, CETAQUA proposes a technology for nitrogen-recovery from wastewater in two steps: 1) nitrogen concentration by an ion exchange system, 2) ammonium salt formation by hollow-fibre membrane contactors (HFMC) process. Concentration process was carried out in order to maximise the salt production and gas-permeable HFMC were selected as the recovery technology because of its low energy requirements, modularity, high ammonia selectivity and its hydrophobicity -which avoid the pass of hazardous substances such as heavy metals or organic micropollutants (Licon Bernal *et al*, 2016). Furthermore, recovering nitrogen from the reject water of Wastewater Treatment Plants (WWTPs) instead of removing it by conventional nitrification-denitrification process reduces the energy demand and the carbon footprint from WWTPs (Noriega-Hevia *et al*, 2021).

Although the ammonia salt produced by this recovery process is already marketable as fertiliser, the final aim of this project is to use ammonia-salt generated to produce a smart bio-based fertiliser (BBF) that makes possible an adaptative release of nutrient depending on the soil requirements by the addition of Plant Growth Promoting Bacteria (PGPBs).

MATERIAL AND METHODS

In order to try out, and optimise, the nitrogen-recovery technology proposed several trials were performed. Feedstock used was the rejected water from the full-scale Ourense WWTP, located in the Northwest of Spain, which contains an NH_4^+ concentration of 1307±146 NH_4^+-N mg and 2.3±0.3 g suspended solids · L^{-1}.

Concerning stage 1, nitrogen-concentration process, an ion exchange (IE) unit was applied. It was filled with natural zeolites (2-ZEOCAT 0-1mm) presenting a calculated bed volume (BV) of 1.06L. Activities for the optimization of stage 1 process consisted in a) defining the most-suitable pre-treatment for the recovery process, b) define optimal hydraulic retention time (HRT) for the adsorbent and WW used, c) select the type of regenerant used and its optimal concentration for the desorption process and d) delimit 2-ZEOCAT 0-1mm lifespan. To do so, sedimentation and filtration were tested as pre-treatments, several HRT were tested in duplicate for the adsorption step, NaOH concentration as regenerants, and lifespan was calculated by adsorption-desorption cycles.

Concurrently, stage 2 optimization took place by putting to test several flowrates and types of acid in a two-modules Liqui-Cel® 3M HFMC system with a unitary surface of 1.4m². For HFMC assays, nitrogen-rich permeate obtained from desorption of zeolite was used as influent.

Regarding the BBF production process, four PGPB strains were define as the optimal bacteria for smart BBF fabrication. Three different fertilisers and mixed-strain bacteria inoculum were mixed for the BBF making and shaking conditions at room temperature were maintained for 0-7 days. Optical density, as a measure of bacteria growth, was selected as the succeed criteria.

RESULTS AND DISCUSION

Filtration was selected as the most suitable pre-treatment, as it eliminated almost 40% of the total suspended solids (TSS) of the feedstock, compared with 5% when decantation was used. Later, 15.14 min was determined as the optimal HRT compared with other tested, as it allows to reduce the HRT without compromising adsorption capacity (Figure 1). Adsorption performance of zeolite is shown in Figure 1 as the volume of feedstock needed, expressed as accumulated BV, to achieve zeolite saturation -defined as the moment where adsorption-desorption equilibrium was achieved- and the kinetics stabilize. Regarding the desorption step to provoke the ammonia release, different concentration of NaOH was tested as it is shown in shown in Figure 2, determining that 0.35M was the best NaOH concentration for N desorption.

Figure 3 shows how cation exchange capacity (CEC) evolved with every adsorption-desorption cycle, where each point represent maximum CEC obtained per adsorption assay and is align with the amount of accumulated volume of feedstock treated when that CEC value was achieved. Low CEC value in assay number one may be explained by an incomplete zeolite activation at the beginning of the trials, finished when first desorption process took place. Afterwards, it's captured an obvious CEC decay within usage. Lifespan assays were considered finish when a significant CEC decay between cycles was observed. At this point, zeolite had recovered during cycles

239.82 g NH_4^+-N, which means that depletion of CEC was observed after 104.43 mg NH_4^+-N was recovered per gram of zeolite. During these experiments, 96% of the nitrogen adsorbed was recovered.

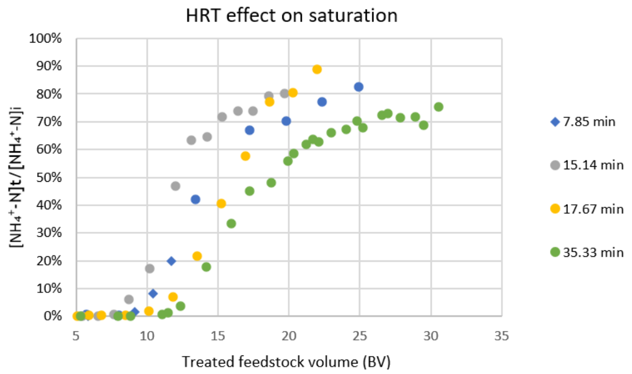

Figure 1. Operational HRT tested in duplicate: 7.85 min, 15.14 min, 17.67 min and 35.33 min.

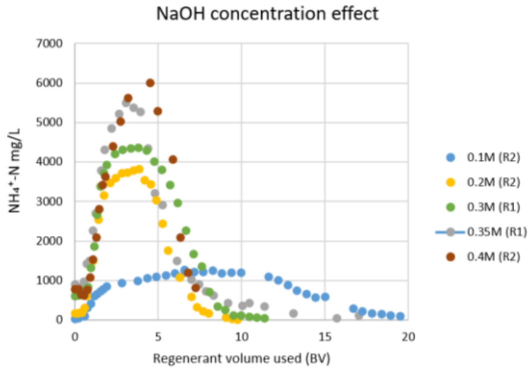

Figure 2. NaOH concentration effect on nitrogen desorption.

Concurrently, HFMC test showed that no differences were observed when nitrogen-rich-permeate flowrate increase over 400 mL·min^{-1} (Figure 4) and acid flowrate variation didn´t affect the recovery rate or efficiency either (data not shown). On the other hand, type of acid used did affect the recovery capacity, as total amount of nitrogen recovered was slightly lower when using nitric acid than when using sulfuric acid (data not shown). HFMC achieved 91% nitrogen recovery in ammonium salt form.

Finally, *Pseudomonas putida*, *Bacillus megaterium*, *Azospirillum brasilense* and *Pseudomonas aeruginosa* were selected as optimal PGPB and BBF trials showed that bacteria growth was more successful when alkaline fertilizers were used (data not shown).

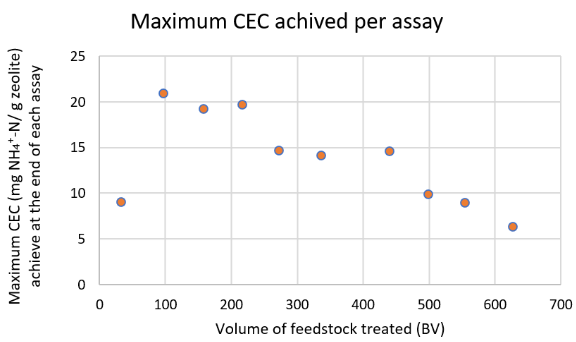

Figure 3. CEC evolution within assays performed.

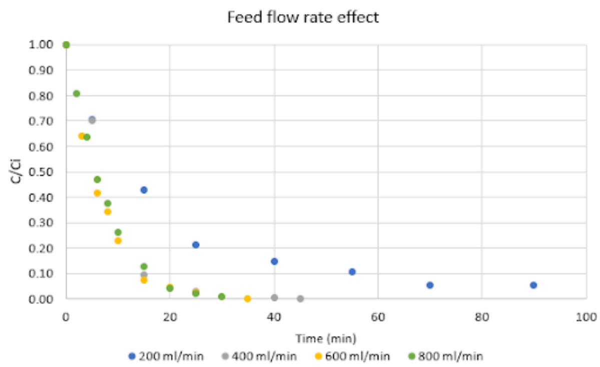

Figure 4. Flow rate effect over ammonia salt production kinetics.

CONCLUSIONS

CETAQUA's proposed technology has proven to be both, a worthy alternative for N-elimination process and an environmental-pleasant way to use that N to produce smart BBF. High recovery efficiencies (91%) were reached concerning ammonium salt production and preliminary BBF fabrication trials were favourable. However, scale-up optimization must be done in order to produce the final Smart BBF.

REFERENCES

Licon Bernal, E.E,. Maya, C., Valderrama, C., Cortina, J.L. 2016 Valorization of ammonia concentrates from treated urban wastewater using liquid-liquid membrane contactors. Chem. Eng. J. **302**, 641-649.

Noriega-Hevia, G., Serralta, J., Seco, A., Ferrer, J. 2021 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. Sep. Purif. Technol. **275**, 119128.

ACKNOWLEDGEMENTS

The authors are grateful to the European Commission, specifically to the Horizon 2020 Programme, which funds WalNUT project (H2020-RUR-2020-2 101000752).