

University of Groningen

Ion-selective membranes for the recovery of ammonium and potassium

Casadella Muni, Anna

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:
2016

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Casadella Muni, A. (2016). *Ion-selective membranes for the recovery of ammonium and potassium*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

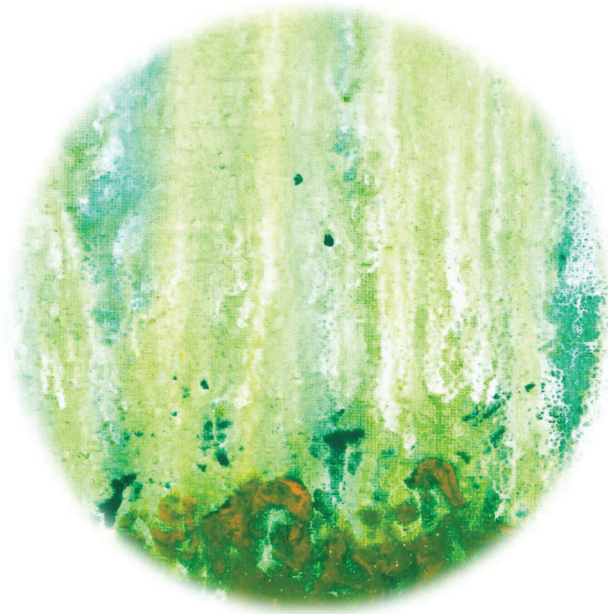
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Chapter 6

General discussion

Outlook



Abstract

A discussion of the main conclusions of the research on the production and characterization of ion-selective membranes for the recovery of potassium and ammonium from a matrix similar to urine is developed in this Chapter. Furthermore, this Chapter discusses considerations and challenges for the future of nutrient recovery based on membrane technology.

6.1 General discussion and Outlook

The previous chapters of this thesis provided motivation, methodology, results and discussions on how this research was conducted to achieve selective membranes for the recovery of ammonium and potassium nitrate. These two compounds are essential nutrients for plant growth and are therefore necessary in fertilizers.

In this Chapter, the work presented in this thesis is placed in perspective while limitations and possible future research directions are presented.

6.1.1 General discussion

Considering the scarcity of potassium in certain areas of the world [1, 2] and the current high energy costs for the synthesis of ammonia/ammonium [3], the necessity of finding technologies that can separate and recover them from natural sources (no synthesis) arises. In our work we focused on urine as natural source it is rich in both nutrients [4]. An efficient separation and recovery system should be capable to provide high selectivity and to process high volumes of feed solution (e.g. urine) in short times.

Selectivity

The achievement of high selectivity among cations is related to the chemical interaction between the target cation and the substance providing the selectivity so the host-guest chemistry [5].

In the case of mixed matrix membranes (MMMs) (*Chapter 2*), the selectivity is provided by the clinoptilolite embedded in the polymeric matrix. However, clinoptilolite is a natural zeolite and its selectivity is dependent on its origin (where it is collected), so its affinity may vary slightly [6]. Therefore, adsorption tests are recommended before the embedding of the clinoptilolite in the polymeric matrix. For efficient ion adsorption capacity of the MMM, the

interfacial contact between the membrane (and the zeolite) and the solution permeating is crucial [7]. Therefore, an optimal flux across the membrane needs to be investigated for the optimal adsorption capacity of the MMM. High contact times are inefficient for the process but low contact times are not enough for the adsorption to take place. However, a higher volume process of the feed solution ($> 100\text{mL}$) should not alter its chemical structure and therefore its selectivity as already fluidized beds proved [8-11].

When a MMM is made according to all these factors, its performance is now dependent on the interface between the solution and the membrane. There, convection phenomena (advection plus diffusion) take place so the ion is transported and adsorbed into the pore structure of the adsorbent [12]

In the case of polymer inclusion membranes (PIMs) (*Chapter 3* and *Chapter 5*), the selectivity is provided by the ionophore blended in the polymeric matrix. In our research we have proven that the composition of the membrane (ionophore, plasticizer and polymer) does not imply the formation of further bonds and therefore the ionophore that provides the selectivity remains unaltered and so is its selectivity. However, the composition does alter the affinity of the cations to the membrane bulk and therefore the flux in passive diffusion. In the case of the application of an electric field across the PIM (*Chapter 4*), the selectivity is almost negligible. This is caused by the strong driving force across the membrane that could be stronger than the complexation of the cation to the ionophore. Therefore, it is not favourable to apply a current density across a PIM for preserving the selectivity.

Process of the feed solution

The process of high volumes of feed solution in short times can be translated in high adsorption/desorption processes in the case of mixed matrix membranes (MMMs) and in high fluxes in the case of polymer inclusion membranes (PIMs).

In the case of mixed matrix membranes (MMMs) (*Chapter 2*) a discussion on the permeability arises. In our research we worked at $17.8 \text{ mL}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}\cdot\text{bar}^{-1}$, by applying a higher pressure ($>0.5 \text{ bar}$) this permeability and therefore a higher volume of feed solution could be forced across the system in a shorter time. However, the contact time between the target cation and the membrane matrix is decisive for the adsorption process to occur – diffusion and convection phenomena need to take place in order to achieve adsorption [7, 12]. If these phenomena do not occur, the adsorption of the target cation does not occur either and the high permeability is counterproductive. Therefore, an optimal permeability needs to be investigated in order to achieve sufficient contact at the interface.

In the case of polymer inclusion membranes (PIMs) (*Chapter 3* and *Chapter 5*) the flux was in the order of $\times 10^{-3} \text{ mmol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. Although this magnitude of flux is common in such membranes [13], it is relatively low if compared with ion-exchange membranes (IEMs) that are in general used for salt separation (desalination) with a higher volume of feed solution [14]; although only selective for either cations or anions. The higher flux of IEMs is due to (a) the lower chemical barriers the cations need to overcome compared to PIMs (e.g. complexation with selective ionophore) and (b) the difference in driving forces between IEM (electric field) and PIMs (passive diffusion). IEMs and PIMs have different transport mechanism regardless the driving force; for IEMs the mechanism is ion-exchange [15] and for PIMs is co-transport (*Chapter 3*). Therefore, the application of an electric field to increase the flux across a PIM is counterproductive, as the target cation in PIMs is transported together with its anion. In an electric field where the transport of the cation (+) is promoted, the transport of the anion (-) is not favorable and therefore the system is unsuitable.

It can be concluded that MMMs are a successful approach for separation and recovery of potassium and ammonium together in two steps (adsorption

and desorption) and PIMs are a valid approach for the separation and recovery of ammonium and potassium separately in a one-step process (transport across the membrane).

6.1.2 Outlook

The future research directions for the recovery of nutrients using ion-selective membranes are broad. For example, we have shown that composition and operating conditions of the membrane are key parameters to further optimize the system. Therefore, future directions for membrane composition should include:

1. The *polymer* is the component that was not extensively studied yet, but it is essential for membrane productions. Studies on the effect of the dipole moments and dielectric constants of the polymer are of great interest. A hypothesis is that a greater dipole moment and dielectric constant (negative charge density) can lead to a higher cation transport as it will present a higher affinity to the membrane. However, the opposite effect could also be expected. This attraction could lead to an accumulation of the cation in the membrane diffusion layer and therefore uptake (either adsorption or transport) is reduced. Two good polymers to assess in the future are polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF) with a dipole moment of 1.6D and 2.1D correspondingly [16].

2. A *plasticizer* is generally used in PIMs to reduce the intermolecular forces among the polymeric matrix and enhance the flux. It is usually a big organic molecule that can tune the general hydrophobicity of the membrane. This organic compound presents a high toxicity and ecological persistence once leached out of the membrane into the environment. Studies on alternatives to plasticizers based on green chemistry should be conducted. Alternative green plasticizers should be designed to be biodegradable, to minimize their use and their generation of hazardous substances. An approach for the development of

such plasticizers is to synthesize compounds with structural properties as the harmful plasticizer. For example, an alternative could be the substitution for phthalate for maleic acid which is the *cis*-isomer.

3. The use of *ionophores* and *zeolites* for the selective performance of the membranes is key. In case of ionophores, their low solubility in the polymeric matrix is a drawback. Studies on covalent attachment of the ionophores to the polymeric matrix need to be conducted. With this, precipitation and leaching will be avoided and the amount of selective compounds in the membrane increases and so might the flux. The covalent attachment could be based on an elongation of an aliphatic chain of the ionophore, a selectivity test before the attachment (the chain could alter the properties of the ionophore) and finally the covalent bond formation. In case of zeolites, its natural condition allows a broad variety of selectivity and properties. Studies on the chemical modification of the needed zeolite towards a standard zeolite would be beneficial for the scale-up of the MMM process. For example, the study of the temperature and pressure effect on the conditioning process with NaCl.

The use of undiluted urine and the effect of such a complex matrix on the membrane performance will provide valuable knowledge for future membrane systems.

6.2 References

1. D. Korstick, Minerals Handbook, United States Geological Survey, 2005.
2. S. Zhang, C.Y. Lim, C.-L. Chen, H. Liu, J.-Y. Wang, Urban nutrient recovery from fresh human urine through cultivation of *Chlorella sorokiniana*, *Journal of Environmental Management*, 145 (2014) 129-136.
3. M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.W. Kim, M. Hara, H. Hosono, Ammonia synthesis using a stable electrode as an electron donor and reversible hydrogen store, *Nature Chemistry*, 4 (2012) 934-940.
4. K. Diem, C. Lentner, *Documenta Geigy: Scientific tables*, 7 ed., Georg Thieme Verlag Stuttgart, 1975.
5. A.B. Harvey Lodish, Chris A. Kaiser, Monty Krieger, Matthew P. Scott, Anthony Bretscher, Hidde Ploegh, Paul Matsudaira, *Molecular Cell Biology*, 4th edition ed., New York, 2000.
6. S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, *Chemical Engineering Journal*, 156 (2010) 11-24.
7. R. Mahajan, W.J. Koros, Mixed matrix membrane materials with glassy polymers. Part 1, *Polymer Engineering & Science*, 42 (2002) 1420-1431.
8. G. Xuejun, Z. Larry, J. Xin, Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite, *Journal of Environmental Sciences*, (2013) 954.
9. A.e.C.e.e. Erbil, E. Soyer, B. Beler Baykal, Ammonium Ion Removal with a Natural Zeolite in Monodispersed and Segregated Fluidized Beds, *Industrial & Engineering Chemistry Research*, 50 (2011) 6391-6403.
10. İ. Tosun, Ammonium Removal from Aqueous Solutions by Clinoptilolite: Determination of Isotherm and Thermodynamic Parameters and Comparison of Kinetics by the Double Exponential Model and Conventional Kinetic Models, *International Journal of Environmental Research and Public Health*, 9 (2012) 970-984.
11. J. Gallant, A. Prakash, L.E.W. Hogg, Fluidization and hydraulic behaviour of natural zeolite particles used for removal of contaminants from wastewater, *The Canadian Journal of Chemical Engineering*, 89 (2011) 159-165.
12. M.-E. Avramescu, M.r. Gironès, Z. Borneman, M. Wessling, Preparation of mixed matrix adsorber membranes for protein recovery, *Journal of Membrane Science*, 218 (2003) 219-233.
13. A.J. Schow, R.T. Peterson, J.D. Lamb, Polymer inclusion membranes containing macrocyclic carriers for use in cation separations, *Journal of Membrane Science*, 111 (1996) 291-295.

14. T. Xu, Ion exchange membranes: State of their development and perspective, *Journal of Membrane Science*, 263 (2005) 1-29.
15. A.H. Galama, J.W. Post, M.A. Cohen Stuart, P.M. Biesheuvel, Validity of the Boltzmann equation to describe Donnan equilibrium at the membrane–solution interface, *Journal of Membrane Science*, 442 (2013) 131-139.
16. D.R. Lide, *Handbook of Chemistry and Physics*, 85 ed., CRC Press, 2004.

