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## Ion-selective membranes for the recovery of ammonium and potassium

Casadella Muni, Anna

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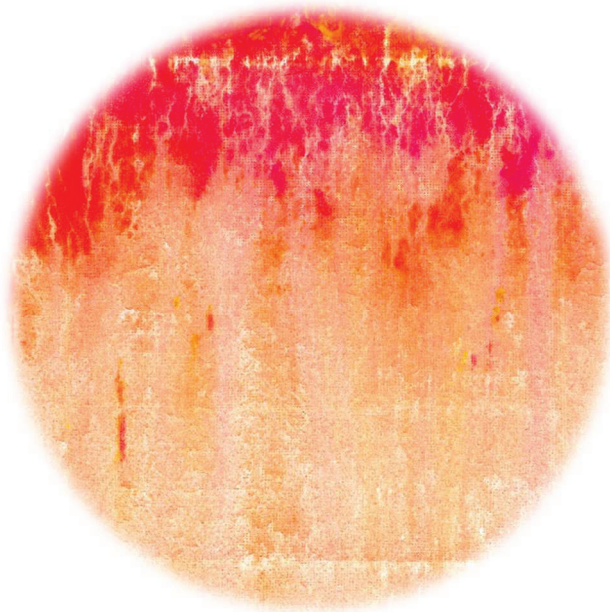
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## Introduction



## 1.1 Motivation

In 2010, at the start of this research, the news agency IRIN (Integrated Regional Information Networks) published an eye-catching article: “NEPAL: lack of fertilizer hampers food security” [1]. In this article it was reported that the United Nations World Food Programme (UN-WFP) estimated 3.6 million people to be food insecure in Nepal in 2010. Nepalese farmers and their government could not afford chemical fertilizers as they had to be imported and the ones from natural type (e.g. manure) were not sufficient.

This is not an isolated case; our planet is expecting a population growth in the coming years leading to an increased demand of food production (i.e. crops) that will require higher crop yields [2]. Therefore, the demand of fertilizers (chemical or natural) is going to increase. These fertilizers contain at least one, but preferably more of the essential elements necessary for plant growth (nutrients): phosphorus, nitrogen and potassium.

Urine is more and more considered as source of nutrients [3-6], therefore development of technologies to recover them from urine is important, as it will help closing the chain of use and re-use of resources. In other words, recovery of nutrients closes a chain based on the use of fertilizers, the human uptake and discharge of nutrients (alimentation and excretion) and the recovery of these nutrients to produce fertilizer (Figure 1).

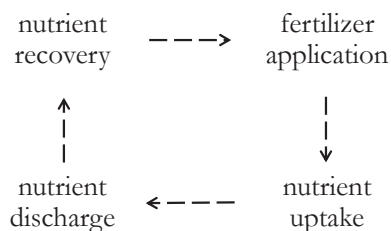


Figure 1. Simplified scheme of the sustainable nutrient cycle.

The recovery of phosphorus (P) is currently a trending research topic [7]. One of the most popular methods used for its recovery from urine is by struvite precipitation [8]. The main cations present in urine (prior to urea hydrolysis) are: 49.0% sodium ( $\text{Na}^+$ ), 38.5% potassium ( $\text{K}^+$ ), 8.76% ammonium ( $\text{NH}_4^+$ ), 2.15% calcium ( $\text{Ca}^{2+}$ ) and 1.59% magnesium ( $\text{Mg}^{2+}$ ) [9]. Due to the high financial and energetic costs of  $\text{NH}_4^+$  production [10, 11], studies on its recovery from urine [12-14] at low costs will become of increasing economic interest in the near future. Another cation that is interesting to recover from urine is  $\text{K}^+$  as it is not always an available nutrient [15] and it is vastly used in fertilizers. The most abundant cation in urine is  $\text{Na}^+$  but it is usually not required or even unwanted:  $\text{Na}^+$  concentration higher than 36mM NaCl in soil is toxic and could lead to death of crops [16].

In order to base the fertilizers on the needs of each crop, it is necessary to individually recover  $\text{K}^+$  and  $\text{NH}_4^+$  and separate them from  $\text{Na}^+$ . These three cations have the same charge (+1), very similar hydrated radii [17] and a very similar diffusion coefficient [18], which renders separation by charge, size and mobility exclusion unsuitable for the separation process (Table 1). Thus, a need of a technology capable to selectively separate these cations from urine arises.

**Table 1. Comparison of hydrated radii and diffusion coefficients in water of main metal ions present in urine [17, 18].**

	<b>Hydrated radii (Å)</b>	<b>Diffusion coefficient (<math>10^{-5} \text{ cm}^2 \text{ s}^{-1}</math>)</b>
$\text{K}^+$	3.31	1.96
$\text{Na}^+$	3.58	1.33
$\text{NH}_4^+$	3.31	1.96

## 1.2 Means to selectivity

Semantically, selectivity has its origin in *seligo*, which in Latin means “to choose” or “to select”. So, to be selective can mean “tending to choose” and selectivity, “the state or quality of being selective”.

In nature, selectivity is present. It can be translated into many interactions, the main ones being: a) biochemical (immunochemical or enzymatic), b) chemical reactions, c) formation of associates, d) adsorption to surfaces, e) inclusion phenomena and, f) electrochemical reactions [19]. For separation and especially for recovery selective processes, it is necessary that the interaction is reversible and with low thermodynamic (e.g. feasible at room temperature) and slow kinetic (e.g. in a short period of time) requirements.

From the above mentioned interactions adsorption and inclusion phenomena are the most advantageous because, in general, they do not imply a change in the chemical structure (therefore in the properties) of the component to be separated and recovered. These two processes are based on the selective transfer of a target molecule from the fluid phase to the solid phase where an active group or molecule (insoluble in the fluid) binds it. In literature, examples of separation and recovery processes based on adsorption to surfaces are systems containing activated charcoal [20] or zeolites [21] and, on inclusion phenomena, for example systems containing ionophores [22]. In this research, zeolites and ionophores are at the core of the research because of the extended literature available on their interactions with cations.

### 1.2.1 Zeolites

In 1756 the scientist Axel Fredrik Cronstedt established the name “zeolite” because of his findings in water uptake and release from stilbite [23]. He named the material zeolite, from the Greek *ζέω*, meaning "to boil" and *λίθος*, meaning "stone". Most of zeolites are naturally available.

Zeolites are defined as aluminosilicates with open 3-dimensional framework structures (micropores) composed of corner-sharing  $\text{TO}_4$  tetrahedra, where T is Al or Si [24]. Cations that compensate the charge of the anionic framework are generally associated with the framework oxygens, and the remaining pore volume is filled with water molecules. The non-framework cations are generally exchangeable and the water molecules removable.

The chemical conformation of the zeolite determines the selective adsorption in its cavities. It has been demonstrated [25-29] that ion-exchange using natural zeolites is an alternative method for the removal (adsorption in the zeolite) and recovery (desorption from the zeolite) of  $\text{NH}_4^+$  and  $\text{K}^+$  from wastewater, two of the cations under study here. For instance, clinoptilolite is an inexpensive abundant natural zeolite in the form of aluminosilicate minerals with ion sieving properties and high cation-exchange capacity (CEC). The generic chemical formula of clinoptilolite is  $(\text{Na,K,Ca})_6(\text{Si,Al})_{36}\text{O}_{72}\cdot 2\text{H}_2\text{O}$ . Clinoptilolite is composed by a three-dimensional framework of  $\text{SiO}_4$  and  $\text{AlO}_4$  forming tetrahedral ring channels that provide ion sieving properties. The ion-exchange capacity of clinoptilolite results from its chemical composition.  $\text{Al}^{3+}$  generally occupies the position in the centre of the tetrahedron of four oxygen atoms, the isomorphous replacement of  $\text{Al}^{3+}$  with  $\text{Si}^{4+}$  (common in silicates) provides a negative charge in the inner part of the structure (lattice) [30]. Therefore, each replacement of  $\text{Al}^{3+}$  with  $\text{Si}^{4+}$  requires a cation (e.g. alkali metal ions) to maintain the overall electroneutrality in the lattice. Clinoptilolite has a natural affinity for  $\text{K}^+$  and  $\text{NH}_4^+$  due to its structure, therefore these two cations are preferably adsorbed by exchange with the ions already adsorbed in the structure of clinoptilolite [28, 31].

## 1.2.2 Ionophores

An ionophore is as a chemical species that binds ions in a reversible fashion. However, literally it means *ion carrier* because most ionophores are hydrophobic compounds that transport ions across a cell membrane. In nature, usually synthesized by microorganisms, there are two possible classifications of ionophores [32]:

a) Ionophores binding a specific ion (hydrophilic) and compensating for the charge with its charged density. The ion being part of the ionophore - ion complex (hydrophobic) can therefore pass across the membrane because of its higher affinity to the membrane.

b) Ionophores forming a hydrophilic channel across the membrane so the ion can pass and does not need to interact with the hydrophobic membrane matrix.

The most commonly used ionophores in ion transport research are the ones forming the ionophore - ion complex [32, 33].

In 1964, Moore and Pressman [34] observed that the natural antibiotic valinomycin has the capacity to uptake  $K^+$  into the mitochondria and consequently to release  $H^+$  from the mitochondria. This fact encouraged further research, and, for example, Simon and Stefanac [33] developed hydrophobic thin films doped with antibiotics that gave similar responses in terms of selectivity as biological systems.

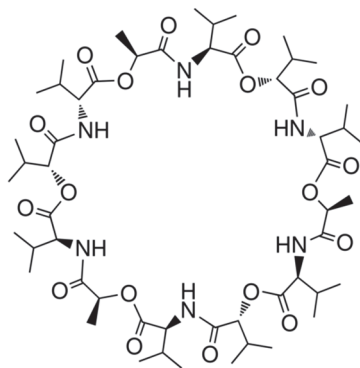


Figure 2. Chemical structure of valinomycin.

In the same decade, in 1967, Charles J. Pedersen developed the synthesis and characterization of cyclic polyethers (crown ethers) that are selective for metal ions such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and many more [35]. For this development, he won the Nobel Prize in Chemistry in 1987. This type of chemistry, which is an inclusion phenomenon, is known as host-guest (H-G) chemistry. It involves molecular recognition (selectivity) and non-covalent bonding interactions. It is based on complexes that are built of two or more molecules or ions that are held together in specific structural relations by non-covalent forces [36]. In the case of a hydrophobic host (H) (e.g. ionophore) and a hydrophilic guest (G) (e.g. ion), the selective complex is dependent on the charge, the volume, and the energy of formation [37]. As mentioned before, the ionophore should be capable to compensate for the charge of its target ion so that the complex net charge is neutral and the ion can be transported in a hydrophobic matrix. The available volume the ionophore has and the volume the ion occupies need to be optimal for the combination. For example, if the volume is too big compared to the volume of the ion, the chemical interaction will be weak. The complex ionophore–ion (host–guest, H-G) is formed because is thermodynamically favorable; their interaction should result in a lower overall Gibbs free energy (Figure 3).



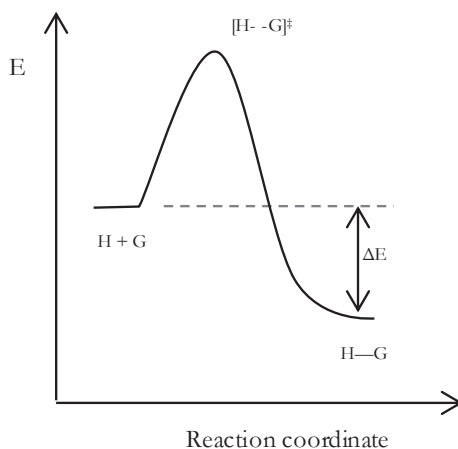


Figure 3. Free energy diagram of host-guest (H-G) complex formation.

### 1.3 State-of-the-art of selective membranes

The general definition of a membrane is “a selective barrier that separates and/or contacts two adjacent phases and allows or promotes the exchange of matter, between the phases” (Figure 4) [38]. Phase 1 is commonly considered as the feed side and Phase 2 is considered the permeate side or the receiving phase. The separation process occurs as a result of the membrane specific properties that allow the transport of one or more components from Phase 1 and excludes the transport of other components. In general, this transport takes place due to various transport mechanism such as concentration gradient ( $\Delta C$ ), pressure gradient ( $\Delta P$ ), temperature gradient ( $\Delta T$ ) or electrical gradient ( $\Delta E$ ) [38].

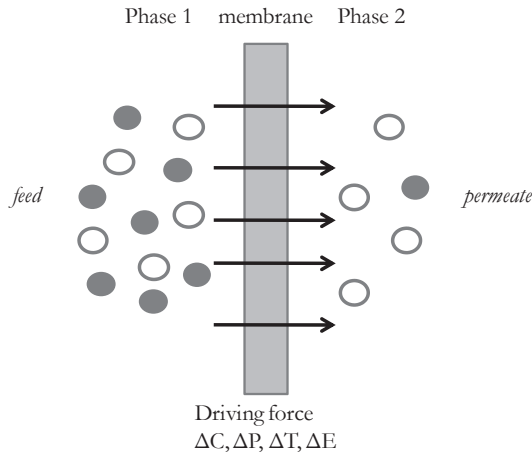


Figure 4. Schematic representation of a two-phase system separated by a membrane (adapted [38]).

In general terms, membranes can be classified in biological or synthetic. Our body and living creatures in general are formed by cells which contain hydrophobic (lipid) membranes (biological membranes) to transport nutrients in the cell that blood vessels transport along the body. Nowadays, we have the knowledge and tools to mimic nature to certain extent and create membranes to transport and recover specific substances (synthetic membranes). Synthetic membranes are subdivided into inorganic (ceramic or metal) and organic (polymeric or liquid) membranes. In this research the focus is on organic membranes.

On a microscopic level, there are two types of membranes based on their structure: non-porous (dense) and porous. Their structure and characteristics are dependent on the process in which a polymer is transformed in a controlled manner from a liquid to a solid. This process is called phase inversion [38].

Dense membranes are prepared by solvent evaporation. A polymer solution is casted on a suitable support which may be porous (e.g. non-woven polyester) or non-porous (e.g. glass plate). The solvent is then allowed to evaporate under an inert atmosphere (e.g.  $N_2$ ) as to avoid water vapor. Alternatives to casting are dip coating or spraying followed by solvent evaporation.

Porous membranes can be prepared by immersion precipitation. A polymer solution is casted on a suitable support (same as with dense membranes) and immersed in a coagulation bath filled with a non-solvent (e.g. water). The solidification occurs due to the exchange of solvent and non-solvent. Therefore, the membrane structure is based on the mass transfer between solvent and non-solvent and the phase inversion.

Ion-exchange and polymer inclusion membranes are examples of dense membranes, while mixed matrix membranes are an example of porous membranes.

### **1.3.1 Ion-Exchange Membranes**

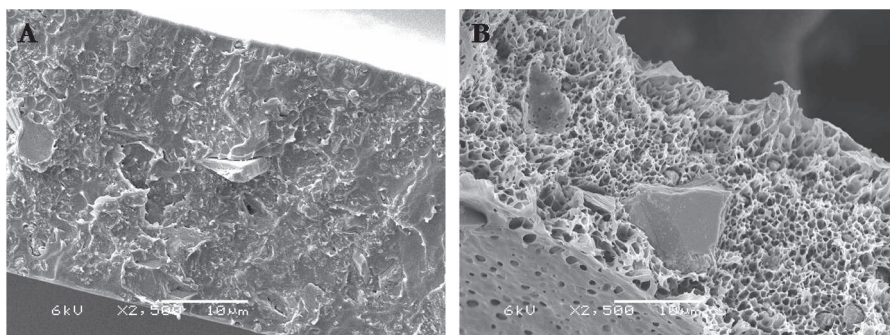
Membranes carrying charged groups are called ion exchange membranes (IEMs). Regarding the charge of the groups of the membranes (positive or negative), two types of ion exchange membranes are defined: a) cation exchange membranes (CEMs) which contain negatively charged groups fixed to the polymer matrix and, b) anion exchange membranes (AEMs) which contain positively charged groups fixed to the polymer matrix. In a CEM, cations are transported whereas anions are retained because of their charge, which is the same as that of the fixed charges in the polymer matrix. In a AEM, anions are transported and cations excluded because the fixed charges are positive in the polymer matrix. The fact that only the ions with the opposite charge of the membrane (counter-ions) are able to permeate, while the ones with the same charge (co-ions) are excluded is known as Donnan exclusion [39].

Besides the charge of the membrane and the ions, the mobility of the ions in the membrane mainly depends on steric effects such as the hydration radius and the membrane chemistry (e.g. the crosslinking density of the membrane). As a general rule, the counter-ions with a higher valence and a smaller hydrated radius have a higher permeability in an IEM than ions with lower valence and

larger hydrated radius [39]. IEMs are not capable yet to distinguish and to selectively transport ions, especially when the ions have the same valence.

### 1.3.2 Mixed Matrix Membranes

Mixed matrix membranes (MMMs) are characterized to embed functionalized particles (dispersed) in their polymeric matrix (dense or porous). The polymeric matrix is used to provide support to the functionalized particles without interfering with the properties of the particles. These particles can be porous (zeolites, metal-organic frameworks (MOFs), etc.), solid nanoparticles, or catalysts.



**Figure 5.** Cross-section images of a dense MMM (A) and a porous MMM (B) containing both clinoptilolite in a polysulfone polymeric matrix.

Most of the MMM research in literature describes pervaporation of aqueous mixtures or gas separation processes [40]. One of the first reports on mixed matrix membranes was performed by Raul and Kemp in 1973 [41]. They compared the relation between permeability, diffusion and selectivity of theoretical results and developed mixed matrix membranes using different materials. Nowadays, besides being widely applied in the gas separation field, mixed matrix membranes are used in diverse matrix separation processes as well, such as blood or enzymes [42-44] which are closer to the purpose of this research.

In general, there are several factors that are important in the design of a mixed matrix membrane [45]:

a) The affinity of each of the components of the membrane and the solution in terms of their hydrophobicity/hydrophilicity and chemical stability. In addition, it is crucial that the solid phase has the right selectivity for the aimed separation.

b) The resulting composite material must have good processing capabilities. The addition of the solid phase should not change the polymer morphology making it more difficult for the solution to permeate into a membrane.

c) The particle size is related to the desired membrane thickness. Smaller particles have higher surface area/volume ratios that normally enhance mass transfer between the phases.

d) The particle distribution within the mixed matrix should avoid the formation of agglomerates. This effect increases the diffusion distance within the solid phase and generates gaps among the particles that minimize their effectiveness.

e) The interfacial contact between the solid and polymer phase should be sufficient to eliminate any gap between the phases but not block access to the solid phase surface or porous structure.

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 [43].

### 1.3.3 Polymer Inclusion Membranes

Polymer inclusion membranes (PIMs) are characterized to be selective dense membranes for the transport of organic molecules, cations or anions depending on the nature of the carrier.

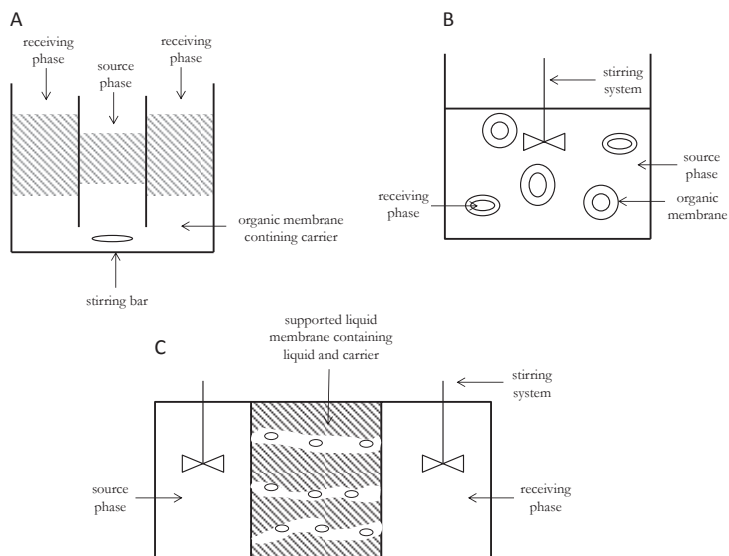
The development of PIMs is linked to the evolution of extracting techniques. Recently, several studies have shown the possibility to recover cations using solvent extraction as well as the transport through liquid membranes (LMs) [46-49]. LMs can be found in different forms *i.e.*: bulk (BLMs), emulsion (ELMs) and supported (SLMs) liquid membranes. A scheme of their operational set-ups can be found in Figure 6.

Despite their many advantages such as selectivity and simple operating set-ups, they present poor stability (few turnovers) and low flux of ions. Therefore, membrane technology evolved towards polymer inclusion membranes (PIMs) [22, 50]. PIMs can separate and recover small organic molecules from an aqueous mixture as well as transport metal ions with higher selectivity and higher flux as compared to LMs. For example, Schow *et al.* [51] showed that the flux of a PIM was three orders of magnitude higher than for a SLM under the same conditions.

The composition of the PIM is one of the main factors. PIMs are composed of a) polymer, b) plasticizer and c) carrier (ionophore) [22]:

a) Polymers (mainly thermoplastics) provide mechanical strength to the membrane. They consist of linear polymer strands with no cross-links among the strands and therefore are soluble in a suitable organic solvent. The mechanical strength of these polymers renders in a combination of intermolecular forces and the process of entanglement [52]. The intermolecular forces among the atoms of the polymer determine the flexibility of the membrane, resulting in a rigid membrane when these forces are high and a flexible membrane when these forces are low. The entanglement process takes

place in the formation of the membrane, when the solvent evaporates and the flexible polymer strands accommodate randomly. The most common polymers used for preparing PIMs are cellulose triacetate (CTA) and poly(vinyl chloride) (PVC) due to their high solubility in organic solvents.



**Figure 6. Schematic set-ups of BLM (A), ELM (B) and SLM (C).**

b) Plasticizers are generally used to increase the ion flux across the membrane and to provide flexibility to the membrane. Plasticizers intercalate into the polymer molecules and their polar groups interact with the polar groups of the polymer resulting in charge neutrality or they simply increase the distance between the polymer molecules and therefore reduce the strength of the intermolecular forces [53].

c) Carriers (ionophores) are found in different types: basic (e.g. quaternary amines [54]), acidic and chelating (e.g. sulfonic acids [55]), neutral (e.g. phosphoric acid esters [56]), macrocyclic and macromolecular (e.g. imidazole azothiacrown ethers [57]). For the transport of alkali metals (e.g.  $K^+$ ), macrocyclic and macromolecular crown ethers (Figure 7) are commonly used as

carriers [58]. They have a specific host-guest complexation behavior which allows the transport of the target ion across the PIM.

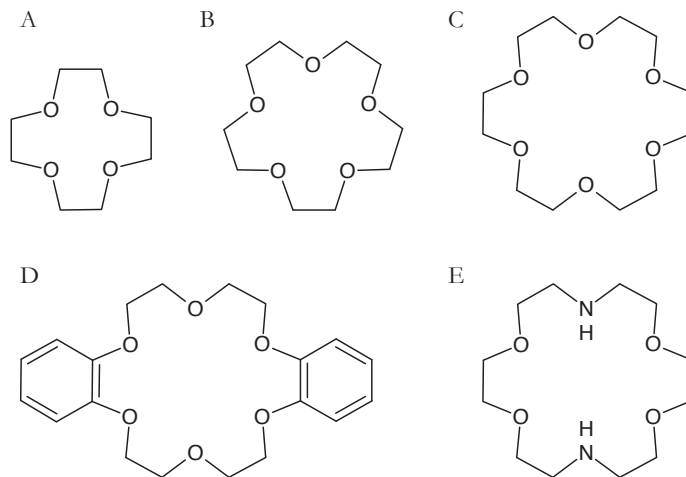


Figure 7. Chemical structure of the most researched crown ethers: 12-crown-4 (A), 15-crown-5 (B), 18-crown-6 (C), dibenzo-18-crown-6 (D) and diaza-18-crown-6 (E).



## 1.4 Scope of the thesis and structure

This thesis focuses on the development and characterization of membranes selective for the separation and recovery of ammonium and potassium, essential nutrients for plant growth. This research proposes a membrane-based technology as it can be operated in continuous systems and because of the possibility to incorporate selective phases (zeolites and ionophores) to the polymer matrix.

According to the motivation at the beginning of this Chapter, it is necessary to separate and recover  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  from a sustainable source – urine in our case. The separation of  $\text{Na}^+$  is necessary so that it does not negatively affect the application of fertilizers on crops (**Chapter 2**). The separation and recovery of  $\text{K}^+$  and  $\text{NH}_4^+$  is valuable as these nutrients present a great contribution in the crops yield increase (**Chapter 2, 3, 4 and 5**). These three cations have the same charge (+1), very similar hydrated radii [17] and very similar diffusion coefficients [18] (Table 1) which makes it hardly possible to separate them by charge, size, and mobility. Thus, a need of a technology capable of selectively separate these cations from urine arises.

**Chapter 2** describes the synthesis and characterization of a mixed matrix membrane (MMM) that selectively excludes  $\text{Na}^+$  and adsorbs  $\text{K}^+$  and  $\text{NH}_4^+$  using clinoptilolite as the selective solid phase. It starts with the description of the synthesis and characterization of a dense mixed matrix membrane and its drawbacks to accomplish the goal, the separation and recovery of  $\text{K}^+$  and  $\text{NH}_4^+$ . Later, the chapter describes the synthesis and characterization of a porous mixed matrix membrane that accomplished the established goal. Two conditioning methods were compared to reach the highest static adsorption capacities and exclusion of  $\text{Na}^+$ . The MMM was applied in a dead-end filtration

cell (dynamic adsorption) to further increase the adsorption capacities compared to static conditions. Synthetic solutions and urine samples were compared and results indicated that MMM is a promising method for the recovery of  $K^+$  and  $NH_4^+$  directly from urine. The desorption (recovery) of  $K^+$  and  $NH_4^+$  from the MMM is described as well.

**Chapter 3** describes the properties of polymer inclusion membranes (PIM) regarding their selective recovery of  $K^+$  over competitive ions typically present in urine ( $Na^+$  and  $NH_4^+$ ). The influence of the membrane composition was studied in terms of ion transport and selectivity. It was also studied whether the transport mechanism occurring in the membrane system was based on co-transport of a counter-ion or ion-exchange using two different receiving phases. Results on transport mechanisms suggest that co-transport of cation and anion is taking place across the PIMs.

**Chapter 4** compares the application of two driving forces across the PIM developed in Chapter 3. The study was based on the comparison of ion transport and selectivity across a polymer inclusion membrane (PIM) containing dicyclohexano-18-crown-6 ( $K^+$  selective) under two driving forces: concentration gradient (diffusion) and potential gradient (migration).

**Chapter 5** describes the synthesis and characterization of a polymer inclusion membrane (PIM) selective for  $NH_4^+$ . An  $NH_4^+$  selective ionophore based on substituted benzene was synthesized and blended in a polymeric matrix also containing plasticizer. We investigated the interactions of each of the components and their effect on the membrane transport and selectivity in the presence of competitive cations.

**Chapter 6** provides a discussion on all results and conclusions from the research chapters of this thesis. This chapter also includes an outlook with respect to further research questions as well as suggestions for the continuation of this research line.

**Chapter 7** is an extensive Summary that includes all highlights and core findings of this thesis.

## 1.5 References

1. IRIN, NEPAL: Lack of fertilizer hampers food security, in, <http://www.irinnews.org/report/90539/nepal-lack-of-fertilizer-hampers-food-security>, 2010
2. FAO, Global agriculture towards 2050, in, Food and Agriculture Organization of the United Nations, Rome, 2009.
3. 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.
4. K.M. Udert, M. Wächter, Complete nutrient recovery from source-separated urine by nitrification and distillation, *Water Research*, 46 (2012) 453-464.
5. J.A. O'Neal, T.H. Boyer, Phosphate recovery using hybrid anion exchange: Applications to source-separated urine and combined wastewater streams, *Water Research*, 47 (2013) 5003-5017.
6. R.C. Tice, Y. Kim, Energy efficient reconcentration of diluted human urine using ion exchange membranes in bioelectrochemical systems, *Water Research*, 64 (2014) 61-72.
7. P. Wilfert, P.S. Kumar, L. Korving, G.-J. Witkamp, M.C.M. van Loosdrecht, The Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from Wastewater: A Review, *Environmental Science & Technology*, 49 (2015) 9400-9414.
8. M. Ronteltap, M. Maurer, W. Gujer, Struvite precipitation thermodynamics in source-separated urine, *Water Research*, 41 (2007) 977-984.
9. K. Diem, C. Lentner, *Documenta Geigy: Scientific tables*, 7 ed., Georg Thieme Verlag Stuttgart, 1975.
10. J. Rockstroem, W. Steffen, K. Noone, A. Persson, F.S. Chapin, E.F. Lambin, T.M. Lenton, M. Scheffer, C. Folke, H.J. Schellnhuber, B.O. Nykvist, C.A. de Wit, T. Hughes, S. van der Leeuw, H. Rodhe, S. Sorlin, P.K. Snyder, R. Costanza, U. Svedin, M. Falkenmark, L. Karlberg, R.W. Corell, V.J. Fabry, J. Hansen, B. Walker, D. Liverman, K. Richardson, P. Crutzen, J.A. Foley, A safe operating space for humanity, *Nature*, 461 (2009) 472-475.
11. 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.
12. P. Kuntke, T.H.J.A. Sleutels, M. Saakes, C.J.N. Buisman, Hydrogen production and ammonium recovery from urine by a Microbial Electrolysis Cell, *International Journal of Hydrogen Energy*, 39 (2014) 4771-4778.

13. P. Kuntke, K. Śmiech, H. Bruning, G. Zeeman, M. Saakes, T. Sleutels, H. Hamelers, C. Buisman, Ammonium recovery and energy production from urine by a microbial fuel cell, *Water Research*, 46 (2012) 2627-2636.
14. M. Maurer, P. Schwegler, T.A. Larsen, Nutrients in urine: energetic aspects of removal and recovery, *Water Science and Technology*, 48 (2003) 37-46.
15. D. Korstick, *Minerals Handbook*, United States Geological Survey, 2005.
16. E.N. Bui, Soil salinity: A neglected factor in plant ecology and biogeography, *Journal of Arid Environments*, 92 (2013) 14-25.
17. E.R. Nightingale, Phenomenological Theory of Ion Solvation. Effective Radii of Hydrated Ions, *The Journal of Physical Chemistry*, 63 (1959) 1381-1387.
18. D.R. Lide, *Handbook of Chemistry and Physics*, 85 ed., CRC Press, 2004.
19. J. Bassman, Stefan R.I., Van Staden J.F., Danzer K., Lindner W., F.A. Burns D.T., Müller H., Poster: Selectivity in Analytical Chemistry. Recommendations for its Use, in: IUPAC Congress/General Assembly, Brisbane (Australia), 2001.
20. Metcalf&Eddy, *Wastewater Engineering: Treatment and Reuse*, 4th ed., McGraw-Hill Education, 2003.
21. D. Bastani, N. Esmacili, M. Asadollahi, Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 375-393.
22. L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S.D. Kolev, Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), *Journal of Membrane Science*, 281 (2006) 7-41.
23. L.D. Rollmann, E.W. Valyocsik, R.D. Shannon, Zeolite Molecular Sieves, in: *Inorganic Syntheses*, John Wiley & Sons, Inc., 2007, pp. 227-234.
24. W.M. Meier, Zeolites and zeolite-like materials, *Pure and Applied Chemistry*, 58 (1986) 1323-1328.
25. A.R. Rahmani, A.H. Mahvi, A.R. Mesdaghinia, S. Nasser, Investigation of ammonia removal from polluted waters by Clinoptilolite zeolite, *International Journal of Environmental Science & Technology*, 1 (2004) 125-133.
26. 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.
27. S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, *Chemical Engineering Journal*, 156 (2010) 11-24.
28. A. Hedström, Ion Exchange of Ammonium in Zeolites: A Literature Review, *Journal of Environmental Engineering*, 127 (2001) 673-681.

29. L.R. Weatherley, N.D. Miladinovic, Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite, *Water Research*, 38 (2004) 4305-4312.
30. D.W. Breck, Crystalline molecular sieves, *Journal of Chemical Education*, 41 (1964) 678.
31. S.E. Jorgensen, O. Libor, K. Lea Graber, K. Barkacs, Ammonia removal by use of clinoptilolite, *Water Research*, 10 (1976) 213-224.
32. E. Bakker, P. Bühlmann, E. Pretsch, Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics, *Chemical Reviews*, 97 (1997) 3083-3132.
33. P. Bühlmann, E. Pretsch, E. Bakker, Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 2. Ionophores for Potentiometric and Optical Sensors, *Chemical Reviews*, 98 (1998) 1593-1688.
34. C. Moore, B.C. Pressman, Mechanism of action of valinomycin on mitochondria, *Biochemical and Biophysical Research Communications*, 15 (1964) 562-567.
35. C.J. Pedersen, Cyclic polyethers and their complexes with metal salts, *Journal of the American Chemical Society*, 89 (1967) 7017-7036.
36. 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.
37. P. Atkins, *Physical Chemistry*, 6th ed., 2001.
38. M. Mulder, *Basic Principles of Membrane Technology*, 2nd ed., Springer Science & Business Media, 1996.
39. H. Strathmann, *Membrane science and technology ion-exchange membrane separation Processes*, 1st ed., Elsevier, 2004.
40. R.D. Noble, Perspectives on mixed matrix membranes, *Journal of Membrane Science*, 378 (2011) 393-397.
41. D.R. Paul, D.R. Kemp, The diffusion time lag in polymer membranes containing adsorptive fillers, *Journal of Polymer Science: Polymer Symposia*, 41 (1973) 79-93.
42. M.-E. Avramescu, Z. Borneman, M. Wessling, Dynamic behavior of adsorber membranes for protein recovery, *Biotechnology and Bioengineering*, 84 (2003) 564-572.
43. 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.
44. Saiful, Z. Borneman, M. Wessling, Enzyme capturing and concentration with mixed matrix membrane adsorbers, *Journal of Membrane Science*, 280 (2006) 406-417.

45. B.W. Rowe, L.M. Robeson, B.D. Freeman, D.R. Paul, Influence of temperature on the upper bound: Theoretical considerations and comparison with experimental results, *Journal of Membrane Science*, 360 (2010) 58-69.
46. J.P. Shukla, A. Kumar, R.K. Singh, Macrocyclic-mediated selective transport of plutonium(IV) nitrate through bulk liquid and supported liquid membranes using dicyclohexano-18-crown-6 as mobile carrier, *Separation Science and Technology*, 27 (1992) 447-465.
47. J. Tomar, A. Awasthy, U. Sharma, Synthetic ionophores for the separation of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  metal ions using liquid membrane technology, *Desalination*, 232 (2008) 102-109.
48. N.E. Belkhouche, M.A. Didi, R. Romero, J.A. Jönsson, D. Villemin, Study of new organophosphorus derivatives carriers on the selective recovery of M (II) and M (III) metals, using supported liquid membrane extraction, *Journal of Membrane Science*, 284 (2006) 398-405.
49. S.S. Madaeni, H.R.K. Zand, Selective transport of bismuth ions through supported liquid membrane, *Chemical Engineering and Technology*, 28 (2005) 892-898.
50. M.I.G.S. Almeida, R.W. Cattrall, S.D. Kolev, Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs), *Journal of Membrane Science*, 415-416 (2012) 9-23.
51. 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.
52. R.P. Wool, Polymer entanglements, *Macromolecules*, 26 (1993) 1564-1569.
53. J.K. Sears, J.R. Darby, *Technology of Plasticizers*, John Wiley & Sons, New York, 1982.
54. M.I. Vázquez, V. Romero, C. Fontàs, E. Anticó, J. Benavente, Polymer inclusion membranes (PIMs) with the ionic liquid (IL) Aliquat 336 as extractant: Effect of base polymer and IL concentration on their physical-chemical and elastic characteristics, *Journal of Membrane Science*, 455 (2014) 312-319.
55. M.I.G.S. Almeida, A.M.L. Silva, R.W. Cattrall, S.D. Kolev, A study of the ammonium ion extraction properties of polymer inclusion membranes containing commercial dinonylnaphthalene sulfonic acid, *Journal of Membrane Science*, 478 (2015) 155-162.
56. O. Arous, M. Amara, M. Trari, A. Bouguelia, H. Kerdjoudj, Cadmium (II) and lead (II) transport in a polymer inclusion membrane using tributyl phosphate as mobile carrier and  $\text{CuFeO}_2$  as a polarized photo electrode, *Journal of Hazardous Materials*, 180 (2010) 493-498.

57. M. Ulewicz, J. Szczygelska-Tao, J.F. Biernat, Selectivity of Pb(II) transport across polymer inclusion membranes doped with imidazole azothiacrown ethers, *Journal of Membrane Science*, 344 (2009) 32-38.
58. K.L. Thunhorst, R.D. Noble, C.N. Bowman, Properties of the transport of alkali metal salts through polymeric membranes containing benzo-18-crown-6 crown ether functional groups, *Journal of Membrane Science*, 156 (1999) 293-302.



