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Cation selective membrane dialysis for ammonia removal from solutions of high salinity

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ABSTRACT

Ammonia represents frequent pollutant of water. Therefore various wastewater treatment technologies to remove ammonia are used. The traditional method is based on bacteria that convert ammonia to nitrate and in the second step to nitrogen gas. In several cases biological treatment is not applicable due to high salinity or toxicity of waste water. Thus an alternative method must be applied. Ammonia can be removed or decomposed by several methods such as air-stripping, membrane separation, breakpoint chlorination, and electrochemical oxidation. The danger of undesired organic byproduct formation during chlorination process restrict its applicability. Some separation process is required for selective separation of NH_4^+ ions from polluted stream.

For high salinity solutions the standard separation techniques as ion exchange, reverse osmosis or electrodialysis doesn't have desired efficiency. The dialysis process use as driving force the concentration gradient. In the case of similar salinity of the both sides of ion selective membrane the only one transported item is the NH_4^+ ion. The dialysis process was therefore studied as potential separation step in ammonia removal technology designed for solution of high salinity. The rate of ammonia separation in dependence of NH_4^+concentration was identified in lab scale dialyser equipped with cation selective membranes CM-PES Ralex (Mega a.s.). Diluate and concentrate solutions of various concentrations were tested. It was proved that dialysis process is capable to separate NH_4^+ ions from solution of high salinity.

Keywords: cation selective membrane dialysis, ammonia separation, waste water, high salinity

INTRODUCTION

Ammonia nitrogen can be considered one of the most hazardous water pollutants discharged into water bodies. The ammonia sources, which are municipal, agricultural and industrial, contribute to increased eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. Free ammonia (NH_3) and ionized-ammonia (NH_4^+) represent two forms of reduced inorganic nitrogen which exist in equilibrium depending upon the pH and temperature of the waters in which they are found. Nitrites and nitrates usually come into recipient from industrial effluents and also represents health risks when occur in high concentrations.

A variety of biological and physicochemical methods and technologies have been proposed for the removal of ammonia from wastewater like air stripping[1], ion exchange[2], breakpoint chlorination[2b, 3], and biological[4] nitrification-denitrification or nitritation-anammox processes. For anionic forms of nitrogen usually biological treatment is used. However in several cases also waste water of high salinity contaminated by ammonia have to be treated. In that case most of the standard methods lose its efficiency. And electrochemical advanced oxidation (EAOP) processes are considered as proper solution. Unfortunately chlorides and organic compounds traces are frequently present in wastewater. The danger of formation of toxic chlorinated hydrocarbons[5] prevents the application of EAOP directly in waste water stream.

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From that reason integrated solution with Donnan dialysis and break-point chlorination was proposed for ammonia removal from heavily polluted industrial effluents (eg. Landfill leachates).

The Donnan dialysis is based on concept of two solutions of different concentrations[6]. The concentration of the solutions used is limited by salt solubility but membrane selectivity are decisive for maximum operational concentrations in dialysis. Beside selectivity also osmotic drag of water from diluted stream to concentrated should be considered. Therefore for concentrated solutions treatment it is not possible to use concentrate of significantly higher concentration in comparison to diluate stream. In present work the dialysis process using the diluate of the same salinity like concentrate containing significantly lower content of NH_4^+ ions were studied. The aim of this work was to evaluate membrane dialysis process as separation technique for next possible integration with chlorination step.

EXPERIMENTAL

The lab scale dialyser of active membrane area 6 cm x 12 cm was constructed. The distribution frames of thickness 1.3 mm were prepared by 3D printing from ABS polymer. The net-like spacers were immersed into the frames to prevent membrane sticking. Four heterogeneous cation selective membrane RALEX® CM(H)-PES (Mega, Czech Republic) was assembled into the dialyser. Therefore total active area of dialyser was 288 cm^2. Prior the assembly the membranes were activated by alternating conversion of the membrane to the H^+ and OH^- form by exposing it to solutions of 1 mol dm^{-3} HCl and 1 mol dm^{-3} NaOH for 1 h. The alternation was made 4 times to ensure full transport properties. The last solution was 1 mol dm^{-3} NaCl.

As shown in Figure 1 the dialyser contains two concentrate chambers and three diluate chambers. The flow along membranes was kept at rate 10 cm s^{-1} to avoid insufficient mass transfer in the chambers.

Both concentrate (NH_4^+ contaminated solution) and diluate (pure solution) has volume 250 cm^3. Various concentrations of concentrate and diluate 0.5, 0.25 and 0.05 mol dm^{-3} NH_4^+ were tested. Identical concentrations and also asymmetric concentrations experiments were realized. For 1st evaluation NH_4NO_3 and $NaNO_3$ were used but other salts (KCl, K_2SO_4) were also used. To evaluate real conditions the NaCl solution of concentration 40 g dm^{-3} (0.68 mol dm^{-3}) contaminated by 0.9 g dm^{-3} NH_4^+ (i.e 0.05 mol dm^{-3}) were treated.

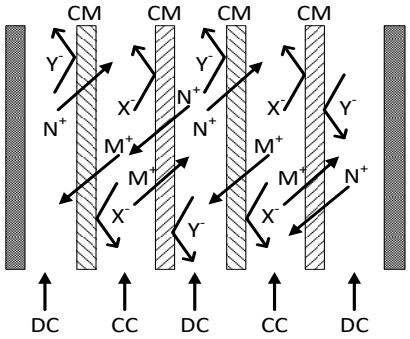

Figure 1 *Schematic diagram of dialysis unit with 4 cation selective membranes (CM), concentrate stream (CC), diluate stream (DC), cations N^+, M^+, anions Y^-, X^-.*

RESULTS AND DISCUSSION

The selected membrane CM(H)-PES is commercially used in electrodialysis process. In electrodialysis the driving force is realized by electric potential gradient applied between side electrodes. In our case in dialysis process the only one driving force is concentration gradient due to the different NH_4^+ concentrations in diluate and concentrate. Reciprocally to keep electroneutrality complementary cation must penetrate through membrane from diluate to concentrate.

The rate of ion diffusion through membrane at various concentrations was evaluated by equal combination of NH_4NO_3 in concentrate and $NaNO_3$ in diluate. As shown in Figure 2 the relative concentration course is almost identical independently on initial concentrations.

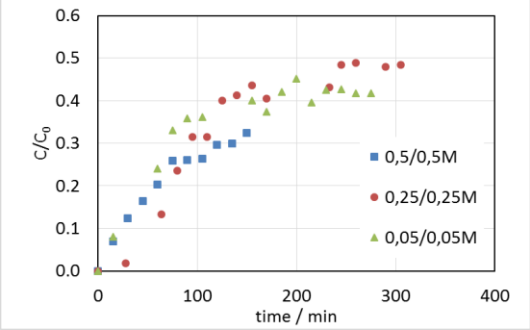

Figure 2 *The relative concentration course of NH_4^+ in diluate for various initial concentrations. Identical salinity in concentrate (NH_4NO_3) and diluate ($NaNO_3$), concentrations in mol dm^{-3} are identified in legend. $V_{conc.} = V_{diluate} = 250$ cm^3. 25°C.*

If the volume and initial concentrations are the same for both solutions the maximum reachable NH_4^+ is ½ of starting concentration in concentrate. This limit was in all cases reached after approx. 5 h of operation.
It is obvious, that the rate of NH_4^+ penetration into diluate is influenced by complementary cation transported in opposite direction from diluate to concentrate. At higher concentrations also dissociation can play role and thus influence of counter anions were tested. As it follows from Figure 3 divalent CO_3^{2-} or monovalent Cl^- didn't show any difference in dialysis rate and only negligible rate increase can be observed for K^+.

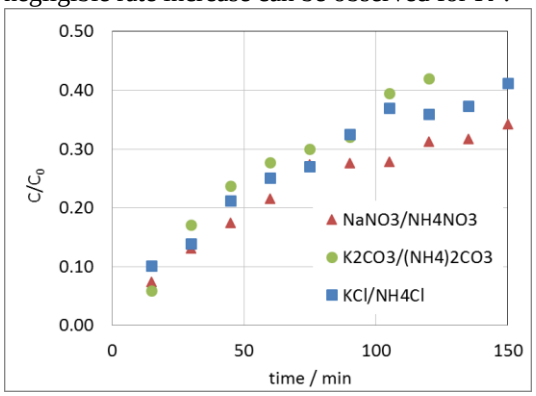

Figure 3 *The relative concentration course of NH_4^+ in diluate for various initial concentrations. Identical cation molarity in concentrate (0.5 mol dm^{-3} NH_4NO_3 or 0.5 mol dm^{-3} NH_4Cl or 0.25 mol dm^{-3} $(NH_4)_2CO_3$) and diluate (0.5 mol dm^{-3} $NaNO_3$ or 0.5 mol dm^{-3}KCl or 0.25 mol dm^{-3} K_2CO_3), solution types are identified in legend. $V_{conc.}$ =$V_{diluate}$=250 cm^3. 25°C.*

It just confirms independence on treated water composition with respect to the rate of ammonia removal from concentrate stream to diluate.
Another situation represents asymmetric salinity on membrane sides. The concentrate consisting of 0.25 mol dm^{-3} NH_4NO_3 and 0.25 mol dm^{-3} $NaNO_3$ was placed against diluate of concentration 0.05 mol dm^{-3} $NaNO_3$. Surprisingly the NH_4^+ concentration reached almost full cations concentration in diluate (Figure 4). This unexpected behavior is not in agreement to the theory of Donnan dialysis[6] and thus another phenomenon should be considered. The simplest explanation is in the permeation of anions into the diluate stream. The producer of CM(H)-PES membrane declares transport number > 0.95. Therefore final salinity of diluate is significantly higher than at the beginning of experiment. It was confirmed by experiment with distilled water as diluate and 0.5 mol dm^{-3} NH_4NO_3 as concentrate. Linear increase of NH_4^+ in diluate was observed and 0.04 mol dm^{-3} was reached within 3 hours. If more diluted concentrate was used the penetration of anions through membrane decreases significantly. It identifies, that dialysis with asymmetric concentrations are limited by selectivity properties of used membrane.

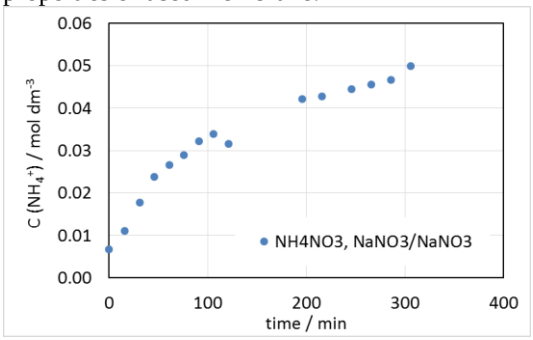

Figure 4 *The concentration course of NH_4^+ in diluate at asymmetric initial concentrations. Molarity in concentrate (0.25 mol dm^{-3} NH_4NO_3 and 0.25 mol dm^{-3} $NaNO_3$) and diluate (0.05 mol dm^{-3} $NaNO_3$) $V_{conc.}$ =$V_{diluate}$=250 cm^3. 25°C.*

Finally the conditions close to real application was tested. As model contaminated water the water of composition 40 g dm^{-3} NaCl and 1 g dm^{-3} NH_4^+ (in the form NH_4Cl) was used as concentrate. NaCl solution of concentration 40 g dm^{-3} was used as diluate. As shown on **Figure 5** the dialysis process is capable to separate NH_4^+ ions at comparable rate to previous experiments without significant influence of high NaCl content. The diluate is free of organic compounds and thus the ammonia removal by chlorination e.g. by use of electrolysis unit connected on the diluate output is possible. Treated diluate can be again recycled to dialyser.

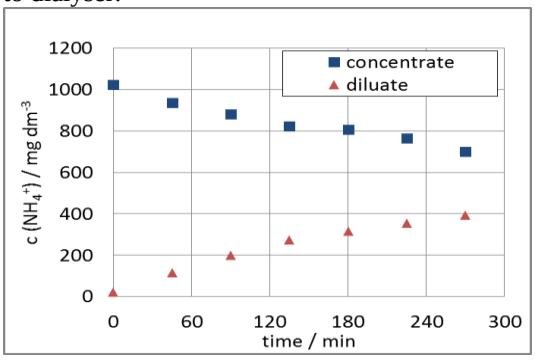

Figure 5 *The concentration course of NH_4^+ in diluate and concentrate at simulated real conditions. Concentrate 40 g dm^{-3} NaCl and 1 g dm^{-3} NH_4^+ (in the form NH_4Cl) and diluate 40 g dm^{-3} NaCl $V_{conc.}$ =$V_{diluate}$=250 cm^3. 25°C.*

CONCLUSIONS

The possibility of NH_4^+ ions removal by dialysis process was evaluated. It was shown that NH_4^+ ions are transferred through cation selective membrane into diluate. Due to high salinity of model waste water, the classical concept of Donnan dialysis is not applicable. The use of low salinity diluate is limited by selectivity of membrane at high concentrations. The treatment of model waste solution of high NaCl content is possible without any deterioration effect. The main benefit of proposed process is separation of ammonia from stream containing other impurities like organic compounds which prevents direct application of chlorination process. To reach lower concentration of ammonia in concentrate more dialysis units connected in series can be used.

Acknowledgments

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REFERENCES

1. US EPA *Wastewater Technology Fact Sheet Ammonia Stripping*; U.S. Environmental Protection Agency, Office of Water: Washington, D.C., 2000.
2. (a) Demir, A.; Günay, A.; Debik, E., Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA* **2002,** *28* (3), 329-335; (b) Huang, H.; Yang, L.; Xue, Q.; Liu, J.; Hou, L.; Ding, L., Removal of ammonium from swine wastewater by zeolite combined with chlorination for regeneration. *J. Environ. Manage.* **2015,** *160*, 333-341.
3. Pitter, P., *Hydrochemistry*. Praha: SNTL: Prague, 1990; p 568.
4. Henze, M.; van Loosdrecht, M. C.; Ekama, G. A.; Brdjanovic, D., *Biological wastewater treatment*. IWA publishing: 2008.
5. Dong, S.; Masalha, N.; Plewa, M. J.; Nguyen, T. H., Toxicity of Wastewater with Elevated Bromide and Iodide after Chlorination, Chloramination, or Ozonation Disinfection. *Environmental Science and Technology* **2017,** *51* (16), 9297-9304.
6. Miyoshi, H., Donnan Dialysis with Ion-Exchange Membranes. I. Theoretical Equation. *Separation Science and Technology* **1996,** *31* (15), 2117-2129.