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membrane and electromembrane processes

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To encourage student participation at the conference and to feature excellent works, the organizers of the MEPRO 2020 conference are pleased to award the best student oral and poster presentations. Student Award ceremony will be the part of the Closing Ceremony.

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PREFACE

Dear colleagues,

You are opening the Book of abstracts of the Membrane and Electromembrane Processes Conference MELPRO 2020 which is organized by the Czech Membrane Platform in collaboration with AMCA.

The current covid-19 pandemic has significantly affected the organization of the conference MELPRO 2020. The original date of April 2020 had to be canceled due to the pandemic and the new date was set for November 2020. At the same time we started to prepare for the potential online conference but we were cautiously optimistic that MELPRO 2020 will be held as planned. However the situation does not allow us to organize in-person conference and MELPRO 2020 will take place online exclusively. You can attend the program via ZOOM application and connect with the speakers.

Main objective of the MELPRO 2020 is to provide space for presentation of new research results inside the academic community; it is also open to the exchange of information between the academic and industrial spheres. The organizing committee made the best effort to fulfill the expectations. Based on this target, the following structure of the MELPRO 2020 conference topics was put together:

New membrane materials

Gas, liquid and vapor separation

Pressure driven membrane processes

Electrochemical membrane processes

Membrane systems in water treatment, biotechnology and biomedical applications

Membrane operations in process engineering

Modelling and simulation in membrane systems

Membrane systems in the mining industry

Membrane systems in space

New trends in membrane applications

Membrane systems for new agriculture

We continue to look forward to meeting again in person at the next conference MELPRO. Until that time please register to join us at our first online conference.

Czech Membrane Platform

PLENARY LECTURES

FUNCTIONALIZED ULTRAMICROPOROUS POLYMERS FOR INDUSTRIAL GAS SEPARATION APPLICATIONS

Ingo Pinnau

Functional Polymer Membranes Group, Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

Abstract: Membrane-based gas separation is a rapidly emerging technology that has been well established for the purification hydrogen streams, nitrogen production from air and is showing an increasingly larger roles in natural gas sweetening and vapor/gas separations. One actively pursued strategy to generate new polymeric membrane materials with combinations of high permeability and high selectivity is the introduction of a bimodal distribution of microporosity (pores $< 20 \text{ \AA}$) and ultramicroporosity (pores $< 7 \text{ \AA}$) in the polymer matrix. It has been shown that rigid ladder-type chains comprising fused rings joined by sites of contortion pack inefficiently in the solid state to produce polymers of intrinsic microporosity (PIMs). Furthermore, the successful integration of monomers contorted by spirobisindane, ethanoanthracene, Tröger's base and triptycene moieties into polyimide structures has generated highly permeable intrinsically microporous polyimides (PIM-PIs). Some of these PIMs and PIM-PIs exhibited significantly enhanced performance for O_2/N_2 , H_2/N_2 , H_2/CH_4 and CO_2/CH_4 separations with properties located on the most recent permeability/selectivity upper bounds.^{1,2} Several series of PIM-PIs will be presented based on rigid and bicyclic moieties, which are solution processable to form mechanically robust films with high internal surface areas (up to $1000 \text{ m}^2 \text{ g}^{-1}$). Gas permeation and physisorption data indicate the development of ultramicroporous structures that are tunable for different gas separation applications. Specific emphasis will be placed on the potential use of hydroxyl- and carboxyl-functionalized PIM-PIs for energy demanding applications for natural gas treatment and olefin/paraffin separation. PIM-PIs with highly polar functional groups define the recently proposed 2018 mixed-gas polymer upper bound for CO_2/CH_4 separation.³ The potential use of PIM-PIs as matrix materials for hybrid polymer/MOF and microporous carbons will be demonstrated.

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POLYMER MEMBRANES FOR SEPARATION OF SMALL MOLECULES AND IONS

Young Moo Lee

Department of Energy Engineering, Hanyang University, Seoul, Korea

Abstract: Microporous polymers are a class of polymeric materials with high free volumes and large surface areas. Microporous polymers have received much attention for various energy-related applications in gas separation, gas storage, and for clean energy resources due to their easy processability as well as microporosity for high performance. As gas separation membrane materials, microporous materials exhibit high flux based on the fast gas transport through membrane matrix. Moreover, the easy processability of polymer materials has been a great advantage for expansion into industrial applications.

Reported rigid polymer membranes, so-called thermally rearranged (TR) polymer membranes have been developed from ortho-functionalized polyimides by a post thermal conversion process. They demonstrate bimodal cavity size of 0.3-0.4 nm and 0.7-0.9 nm and narrow cavity size distributions characterized by PALS measurement which is an efficient transport path for small molecules, especially for CO₂ molecules. As a result, TR polymer membranes exhibit both high permeability and high selectivity based on high diffusion of gas molecules. TR polymer membranes are also suitable for water treatment applications due to their microporous characteristics. In this presentation, we will report on the recent progress of thermally rearranged microporous polymer membranes for applications such as in energy and water.

In addition to microporous polymer membranes, polymer membranes with enhanced ion separation are very important to transport of ions for fuel cells and Li ion batteries and water hydrolysis. This presentation briefly introduces polymer membranes for separating ions.

Keywords: thermally rearranged polymer; gas separation; PRO; battery

ULTRAPERMEABLE COMPOSITE MEMBRANES BASED ON CARBON NANOTUBES AND GRAPHENE OXIDE: THE EFFECT OF METAL ION CONTENT ON H₂/CO₂ SEPARATION PERFORMANCE

D. Gardenö, D. Bouša, Z. Sofer, M. Lanč, S. J. Ashtiani, P. Číhal, K. Friess

University of Chemistry and Technology, Technická 5, Prague, 166 28, Czech Republic

Abstract: The outstanding H₂/CO₂ separation performance of novel composite membranes based on oxidized single-wall carbon nanotubes(SWCNT) [1] and graphene oxide [2] is presented. The SWCNT-GO membranes were prepared by the pressure-driven gravitation assembling method. The ultrapermeable character of SWCNT-GO membrane is given by its mesoporous SWCNT supporting layer and the selectivity of SWCNT-GO membrane increased after mild oxidation[1]. The remarkable separation efficiency of oxidized SWCNT-GO membranes was found after decoration with different amounts of metal ions. The tremendous separation performance was manifested by exceeding the corresponding Robeson 2008 upper bound for H₂/CO₂ (Fig. 1). Our results demonstrate the potential of composite SWCNT-GO materials and open a new promising route towards the fabrication of highly permeable, durable and efficient H₂-selective separation membranes for industrial application.

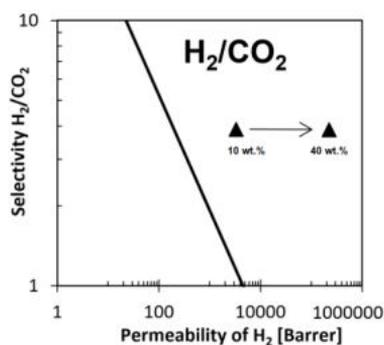


Fig. 1 The Robeson diagram for H₂/CO₂ gas pair* of SWCNT-GO composite membranes. The effect of metal ion content on permeability and selectivity is indicated by arrows. *Data taken from *J. Membr. Sci* 320, 390, 2008

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SELECTIVITY OF TRANSPORT PROCESSES IN ION-EXCHANGE MEMBRANES

D. V. Golubenko^{1,2}, I. A. Stenina^{1,2}, A. B. Yaroslavtsev^{1,2}

¹ *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991, Russia. (yaroslav@igic.ras.ru)*

² *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Academician Semenov av. 1, Chernogolovka, Moscow region, 142432, Russia.*

Abstract: Ion exchange membranes are widely used in different applications. Each of them has its own requirements. The presence of high ionic conductivity and selectivity of transport processes are basic/main requirements usually. Selectivity can be estimated by the ratio of transfer rates of coions (or gas molecules) and counterions. The purpose of this report is to describe the approaches used to design membranes which combine high selectivity of transport processes with high ionic conductivity. The structure of cation-exchange membranes can be described by the Gierke model. Hydrophilic functional groups with sorbed water form a system of pores and channels in the hydrophobic polymer matrix. Most of the cations are located in the Debye layer, near the negative charged pore walls. The transport in this layer determines the ionic conductivity of the membranes. The remaining pore volume is filled with an electrically neutral solution with low concentration of coions or gas molecules which determines their slow transfer and a decrease in membrane selectivity.

The large pores in heterogeneous membranes determine a decrease in their selectivity. Grafting polymerization of styrene inside an activated polymer film with subsequent sulfonation allows to obtain grafted membranes with the composition close to heterogeneous one, but the absence of secondary porosity makes them much more selective¹. It is possible to optimize the ionic conductivity and selectivity of membranes by varying the degree of grafting and crosslinking.

An increase in the ionic conductivity can be achieved by membrane doping by acidic nanoparticles. On the contrary, zirconia with basic properties can bind the part of the current carriers, decreasing membrane conductivity and water uptake and increasing its selectivity. In the case of acidic silica, negatively charged particles should be localized in the pore center. It results in the decrease in alcohol transfer and methanol crossover in fuel cells.

Acknowledgements: This work was supported by the Russian Science Foundation, project 17-79-30054.

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KEYNOTE LECTURES

PREPARATION AND PROPERTIES OF NOVEL HYBRID ORGANIC-INORGANIC MEMBRANES DOPED WITH RARE EARTH METAL OXIDES

W. Kujawski¹, P. Loulergue², J. Kujawa¹, A. Szymczyk², G. Li¹, P. Tomietto²

¹ Nicolaus Copernicus University in Torun, Faculty of Chemistry, 7 Gagarina Street, 87-100 Torun, Poland (wkujawski@umk.pl)

² Université de Rennes, Institute des Science Chimiques de Rennes – UMR 6226 CNRS, 263 Avenue du General Leclerc, Rennes 35042, France

Abstract: Membrane techniques are one of the fastest growing areas of separation methods. Nowadays, pervaporation and membrane distillation requiring hydrophobic membranes are gaining considerable interest. The aim of research was focused on the formation a new type of smart hybrid organic-inorganic separation materials – polymeric membranes (with inorganic filler – lanthanides oxide) possessing controlled physicochemical, tribological and separation properties. Mixed Matrix Membranes (MMM) were prepared by incorporating the inorganic fillers (chosen lanthanide oxides e.g. Gd₂O₃, Sm₂O₃, CeO₂, and Pr₆O₁₁) in polymeric matrix. Additionally, oxides were hydrophobized by octyltriethoxysilane - C6 and (1H,1H,2H,2H-perfluorooctyltriethoxy)silane - FC6. Polyvinylidene fluoride (PVDF) and renewable polymers from polyhydroxyalkanoates (PHA) family (i.e. poly(hydroxybutyrate-co-hydroxyvalerate) – PHBHV) were used as polymers for membrane preparation.

Pristine and modified oxides were characterized by using FTIR, Raman, XPS spectroscopies, as well as TEM and goniometric analysis. Membranes were evaluated in pervaporation of water-VOCs mixtures. It was found that pristine oxides are hydrophobic (contact angle $\approx 150^\circ$), however hydrophobization with FC6 allowed to prepare the superhydrophobic material (Fig. 1). The thickness of the grafted layer was in the range 3.4-3.6 nm (Fig. 2).

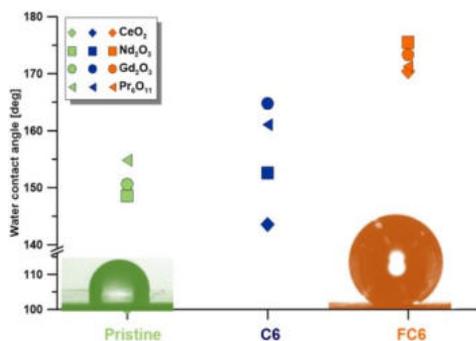


Fig. 1. Contact angle of pristine and modified oxides.

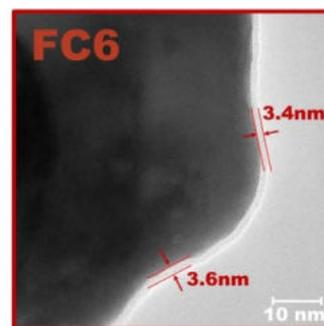


Fig. 2. TEM of modified oxide.

LIFE AT THE CELL'S EDGE: THE CELL SURFACE IS A PROGRAMMABLE MEMBRANE COMPOSITE

Satyajit Mayor

*National Centre for Biological Sciences, Tata Institute for Fundamental Research,
Bangalore, Karnataka, 560065, India*

Abstract: The membrane of the living cell acts as an interface between the cell and its external milieu. It serves as a dynamic conduit for information transduction and response, and well as a semi permeable barrier. It is composed of membrane lipids and protein in the form of a bilayer. Unlike an artificial membrane, the cell membrane is a highly organized system, with specific components in states that are far away from chemical equilibrium. I will present our current understanding of how the regulates this organization and discuss implications of how this organization inform the function of the living cell membrane. Insights gained from these studies have implications on designing programmable synthetic membranes for multiple functions.

BIOHYBRID, BIOMIMETIC, BIOINSPIRED, BIONIC (B4) SYSTEMS MEMBRANES AND THEIR POTENTIAL APPLICATIONS

L. Giorno, R. Mazzei, E. Piacentini, T. Poerio, G. Vitola, F. Bazzarelli, S. Regina, E. Drioli

*National Research Council of Italy, Institute on Membrane Technology CNR-ITM,
Via P. Bucci, CUBO 17C, 87036 Rende (CS) Italy*

Abstract: The development of artificial systems membranes able to reach the performance of natural systems membranes (in terms of selectivity, antifouling, self-cleaning, self-repairing, surface-to-volume ratio, processes integration, etc.) is still an open challenge.

On the other hand, the understanding of fundamentals and mechanisms in the field of interactions at molecular and supramolecular levels that govern hierarchical assembling at nanoscale and lead to target structures and functions, opens for breakthroughs in the field.

To design, tailor and fine-tune bio-artificial systems membranes it is possible to use the large variety of biomolecules, natural materials and processes. Besides, the biomimetic, bioinspired and bionic approaches offer the additional advantage of not being limited by nature-derived materials and processes tolerated by life.

This lecture aims to offer a picture on B4 systems membranes, including procedures and technologies for their fabrication, functionalization and characterization, and to present their properties and potential applications, with particular focus on the biotechnology, biomedicine, biorefinery, biosensor and water treatment areas contributed by the authors.

ADVANCED FLUOROPOLYMERIC MEMBRANES FOR WATER TREATMENT: FROM FUNDAMENTAL RESEARCH TO INDUSTRIALIZATION

Z. Cui

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China;

Abstract: Orienting to the major national demand of membranes with high performance for water treatment, aiming to solve the problems of membrane fouling during application and toxic solvents during the membrane preparation, a greener production technology was proposed, and the key problems such as designing of membrane microstructure and adjusting of membrane surface property were investigated. The technological bottleneck of highly-antifouling poly(vinylidene fluoride) (PVDF) membrane production was broken through, theory and method of greener polymeric membrane fabrication were developed, the accurate control of PVDF membrane pore size was realized, and its steady flux and permeate quality was significantly increased. The fabrication and modification theories of hydrophobic membrane materials for membrane contactor were investigated, and the hydrophobic porous membranes such as Hyflon AD and ECTFE membranes were explored. Their stability for long term run was obviously enhanced during the processes of membrane distillation, membrane crystallization and membrane condensation. Based on the above achievement, advanced PVDF hollow fiber membranes and reinforced membrane bioreactor (MBR) membranes were developed, as the main product of the spin-off company Nanjing Jiuying Membrane Corporation, and the large-scale production lines were built. The membranes have found wide applications in emission on standard, water reuse, zero-liquid discharge, and water purification.

TOWARD A MORE SUSTAINABLE APPROACH IN MEMBRANE FABRICATION

A. Figoli

¹ *Institute on Membrane Technology, CNR-ITM, Via P. Bucci 17c, 87036 Rende (CS), Italy (a.figoli@itm.cnr.it, www.itm.cnr.it)*

Abstract: Environmental protection and climate change are current issues at the heart of global economic growth. The awareness of the real risks connected with industrial membrane production sector has been the push towards the search of new, more sustainable, solvents and raw materials [1]. The 5th principle of Green Chemistry encourages the use of safer solvents and auxiliaries [2]. Solvents are the most common example of auxiliary substances for membrane preparation *via* phase inversion. They are needed for dissolving the selected polymer and their chemical-physical properties strongly influence the membrane formation too. Among the most widely used solvents, N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc) and N-methyl pyrrolidone (NMP), represent an excellent choice for dissolving sulfones polymers. However, since they are classified as highly reprotoxic and developmental harmful, their use should be avoided whenever possible. In this context, the use of alternative, less-toxic, diluents for making polymeric membranes open new perspectives for the sustainable membrane fabrication. Herein, case studies on the flat sheet membrane production via Non-solvent- coupled with Vapor- Induced Phase Inversion using different innovative non-toxic solvents, such as Dimethyl isosorbide (DMI) or Cyrene are presented [3-4]. These solvents are completely miscible with water and alcohols; their high boiling point make them a favorable alternative for dissolving fluoropolymers, such as polyether sulfone (PES) by using different coagulation bath. The possibility of tuning the morphology and pore size of the polymeric membranes produced by using these polymers will be reported too.

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SELECTIVE SEPARATION OF LITHIUM BY ION EXCHANGE MEMBRANES

Y. Zhao¹, B. Van der Bruggen^{1,2}

¹ *Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

² *Faculty of Engineering and the Built Environment, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa (bart.vanderbruggen@kuleuven.be, yan.zhao@kuleuven.be)*

Abstract: Currently, the main resources of lithium compounds are from limited rock reserves. The production of lithium from these rocks could cause environmental problems. On the other hand, the abundance of saline lakes as lithium resources (about 62% of the total worldwide lithium resources) has attracted people's attention to reinforce the exploitation of lithium. The application of membrane technology to separate and extract lithium has recently seen considerable growth as a research topic, driven by the growing demand for energy and the status of this technology as environmentally-friendly. In particular, ion exchange membranes (IEMs), which are the core elements of electrodialysis (ED), have unique advantages compared to membranes applied in pressure driven separations, in their ability to separate or extract ions in highly concentrated brines and avoid the scaling.

IEMs with selective separation properties for monovalent ions have been explored. In classical theories, the electrostatic repulsion effect between solution ions and the charged membrane surface and the size sieving effect between the hydrated ionic diameter and the membrane structure are the most important rules for preparation of the AEMs/CEMs with selective monovalent ion separation properties. For example, we controlled the tunable interlayer spacing and the functionalization of graphene oxide membranes by polyelectrolytes or by monomers allows for an efficient and selective separation of larger hydrated cations in ED.

However, based on the electrostatic repulsion effect, the coexistence of a large number of monovalent monovalent cations, such as Li⁺ and K⁺, with chemically similar properties is difficult to be selectively separated from each other. Furthermore, the size sieving effect may cause an inevitable low desalination efficiency, which leads to a high energy consumption. According to the classical mechanics of ion motion, the focus is usually only on the electric field effect in which ions move across IEMs in a perfect manner.

The quantum state of lithium in electric field can be used to describe the quantum mechanics of lithium in three dimensional states. Under the electric field, the lithium ion has its specific coherent superposition of waves and the wave function, so that the lithium is able to control the architecture of the multilayer. This electric field-based ionic control of selective separation layers shows great promise when applied to the fabrication of various other functional ion exchange membranes for extracting clean ion resources. Based on this mechanism, the potential for lithium purification from aqueous sources is presented.

CREATIVE FEED SPACER DESIGNS FOR MEMBRANE MODULES: HOW USEFUL AND PRACTICAL ARE THEY?

Hassan A. Arafat

Center for Membrane and Advanced Water Technology, Khalifa University, Abu Dhabi, United Arab Emirates

Abstract: Feed spacers constitute an indispensable component of membrane modules. In addition to their main function as space holders for feed within the module, they also provide mechanical support to the membrane and induce feed turbulence, thus suppressing both temperature and concentration polarization phenomena. However, commercial spacers have also been shown to constitute the point of origin for fouling within a membrane module, which is initiated at the dead zones created at the intersection of spacers filaments. These dead zones provide suitable sites for the deposition of organics, attachment of microbes for biofouling and nucleation for scaling.

In recent years, additive manufacturing, also known as three-dimensional (3D) printing, has been gaining momentum in several applications including aerospace, automotive industry and the medical field. Likewise, 3D printing has also gained attention as a promising fabrication pathway for several components of membrane-based systems for desalination and water treatment. The unique benefit of 3D printing over conventional manufacturing processes lies in its ability to fabricate structures with complex geometries that can be optimized for fluid flow, heat transfer, etc., based on the targeted application. Taking advantage of the advancements in 3D printing, several research groups around the world have designed and tested 3D-printed feed spacers with complex geometries for a range of membrane applications, including reverse osmosis (RO), ultrafiltration (UF) and membrane distillation (MD). The initial reported results from these groups were rather promising.

One class of complex geometries that were tested as designs for feed spacers are triply periodic minimal surfaces (TPMS). These geometries can be described mathematically such that they have no self-intersecting or enfolded surfaces. “Triply periodic” means that the structure can be patterned in the 3D space and “minimal surface” means that it locally minimizes surface area for a given boundary such that the mean curvature at each point on the surface is zero. Our research group has studied the use of these shapes as spacer designs for membrane applications over the last 4 years. We theorized that the interconnected maze-like pathways of TPMS structures would enhance turbulence through the feed channel, while the perfectly smooth minimal surface would minimize pressure drop, as well as reduce the available locations for the attachment of foulants. Our studies were carried out for both pressure-driven (RO and UF) and heat-driven membrane processes (MD). Selected TPMS spacer designs were fabricated via Selective Laser Sintering (SLS). We found that the use of TPMS spacers not only resulted

in enhanced mass transfer through the membranes, but it also led to significantly curtailed fouling and pressure drop in the feed channels. The ability of the TPMS spacers to improve flux while maintaining low pressure drop translates to lower energy footprint of the membrane system. Likewise, their ability to reduce scaling and biofouling and to improve the efficiency of membrane cleaning will lead to significant reduction in the use of chemicals, which has an impact on both process and environmental costs.

Our finding, as well as those of other groups, open up new avenues for further application of 3D printing of feed spacers in a wide range of membrane-based water (and wastewater) applications. Still, technical and economic aspects of the 3D printing process have to be managed carefully, but the potential for this application is massive.

ELECTRODIALYSIS APPLICATIONS USING DIFFERENT STACKS CONFIGURATIONS

T. Kotala

MemBrain s.r.o., Customer Application Department, Pod Vinicí 87, Stráž pod Ralskem, 471 27, Czech Republic, (tomas.kotala@membrain.cz, www.membrain.cz)

Abstract: Electrodialysis (ED) or bipolar electrodialysis (EDBM) as an electro-membrane separation method has excellent potential to face new environmental challenges and also helping in chemical species recovery. This work will be focused on lithium salt purification strategies, treating the wastewater from zeolite-based catalyst production. The different number of electrodialysis working loops allows for achieving various separation and purification levels.

The first example is a laboratory electrodialysis module with four working loops EDR-Z/4x5-0.8 working in the double replacement reaction mode. The ED module was used for lithium bicarbonate preparation. The electrodialysis module was treating two feed streams, such as lithium sulfate and sodium bicarbonate. The result in product streams was lithium bicarbonate and solution sulfate solution. The second example is laboratory electrodialysis modules with three working loops EDR-Z/3x5-0.8 and EDBM-Z/3x5-0.8. The modules were working in the partial anion replacement reaction mode. The different electrodialysis stacks configurations can be used to tetraalkylammonium hydroxides preparation. The EDR module was used for tetrapropylammonium bromide (TPABr) partial conversion. The electrodialysis module was treating a feed stream containing TPABr, sodium bromide, sodium silicate, and sodium hydroxide. The result in product streams was tetrapropylammonium hydroxide (TPAOH), depleted sodium hydroxide, and alkaline sodium bromide brine.

The lithium bicarbonate preparation first example using electrodialysis working in the double replacement reaction mode resulted in over 97.6 % purity. This intermediate purity is sufficient for final purification steps leading to battery-grade lithium carbonate. The purity was calculated as a ratio between lithium and lithium plus sulfur. The second example of tetrapropylammonium hydroxide recovery from waste TPABr zeolite synthesis wastewater allowed up to 70 % bromide removal. This approach can be generalized if the nitrogen species recovery near 50 % is required.

The electrodialysis stack setup for different applications depends on product purity requirements, desalination cut, or key species recovery specification. The exact configuration can also be affected by following waste streams management and process safety considerations. The correct electrodialysis setup can help save water, precious key chemical species, and help in commodity chemical production.

Acknowledgments: The research was funded using institutional support for the Long-term Conceptual Development of a Research Organization provided by the Ministry of Industry and Trade of the Czech Republic.

SURFACE MIMETICS OF REVERSE OSMOSIS MEMBRANES BY SELF-ASSEMBLED MONOLAYERS FOR SCALING AND FOULING STUDIES

K. Rathinam¹, D. Schwahn, W. Petry, Y. Oren¹, R. Kasher¹

¹ Department of Desalination and Water Treatment, Zuckerberg Institute for Water Research, The Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, 84990, Israel (kasher@bgu.ac.il, <http://in.bgu.ac.il/en/bidr/ziwr/dwt/Pages/staff/Kasher.aspx>)

² Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, D-85748, Garching, Germany.

Abstract: Silica scaling of membranes in reverse osmosis (RO) desalination of brackish groundwater causes severe problems, whereas during the recovery of domestic wastewater calcium phosphate is a major scaling factor that limits the process recovery. In this study mineral scaling in RO processes is investigated using self-assembled monolayers on gold surfaces. In experiments that simulate desalination of treated domestic wastewater we found that negatively-charged surfaces – especially surfaces that contain excess of carboxylic acid groups – promoted precipitation and scaling with calcium phosphate being the main scaling factor¹. On the other hand, in desalination of brackish groundwater quartz-crystal microbalance (QCM) analyses revealed that surfaces with positively-charged groups induced rapid silica precipitation², and the rate of silica precipitation followed the order $-\text{NH}_2 \sim -\text{N}^+(\text{CH}_3)_3 > -\text{NH}_2/-\text{COOH} > -\text{H}_2\text{PO}_3 \sim -\text{OH} > -\text{COOH} > -\text{CH}_3$. Force vs. distance AFM measurements showed that the adhesion energy between a silica colloid glued to AFM cantilever and the studied surfaces increased as the surface charge changed from negative to positive. The influence of the surface-exposed functional groups and the effect of the surface charge on scaling in RO desalination processes that were found here can be used to develop membranes with anti-scaling properties.

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NEW METHOD FOR ENERGY HARVESTING FROM SALINITY GRADIENT

A. Siekierka¹, K. Smolinska-Kempisty¹, M. Bryjak¹, N. Kabay²

¹ *Wroclaw University of Science and Technology, Faculty of Chemistry, Wroclaw, Poland (e-mail: marek.bryjak@pwr.edu.pl)*

² *Ege University, Faculty of Engineering, Izmir, Turkey (e-mail: nalan.kabay@ege.edu.tr)*

Introduction

Blue energy or salinity difference energy (SGE) deals with harvesting energy released when two different solutions are mixed. Several SGE technologies were developed to convert the entropic energy to electricity. Among them, pressure retarded osmosis (PRO) or reverse electrodialysis (RED) have been prototyped. In the case of PRO, osmotic membrane is placed between two solutions and osmotic flow feeds a turbine. In the case of RED, the pairs of ion exchange membranes are used and ion transport constitutes electricity. To these two methods, one has to add capacitive mixing (CAPMIX) that was developed lately¹. The process is based on mixing of two solutions and allows to obtain an electrical current by switching periodically high- and low-saline solutions. When ion-exchange membranes are used, the energy is generated by Donnan potential. Hence, electrodes accumulate cations and anions without any need for external voltage. When the external solution is changed, ions move back.

Two approaches can be used for assembling the electrode with ion-exchange barriers: i) wrapping electrodes with ‘polymeric’ ion-exchange membranes and ii) depositing of polyelectrolytes on the electrodes. The first assembly forms ‘hard’ electrode, while the second – ‘soft’ electrode.

Material and Methods

All electrodes for CAPMIX system were prepared from YP-50F (Kuraray Chem. Com.) activated carbon with poly(vinyl chloride) as a binder.

Cation and anion exchange membranes were obtained from interpolymer polyethylene/styrene-co-divinylbenzene thick films. They were chlorosulfonated and hydrolyzed to obtain cation exchange membranes or aminated to obtain anion exchange membranes.

Poly(acrylic acid), PAA MW 50 kDa, was adsorbed on the electrode surface to obtain a cation-exchange layer. That layer was modified with excess of poly(ethylene imine), PEI MW 25 kDa to get an anion-exchange layer.

1. Results and Discussion

The essence of the CAPMIX process is to select the best ion-exchange membranes. After optimization of the process, the highest energy was obtained when both ion-exchange membranes were made from interpolymer crosslinked with 2% of DVB. The best salt gradient was 80 g/L and 4 g/L as highest and lowest concentrations on NaCl, and 3 min for charging and 3 min for discharging. Finally we were able to extract energy of 125 mW/m² for that system. When time for charging/discharging steps was reduced to 1 min, the system offered 188 mW/m² of energy. In the case of polyelectrolytes and the 3 min charge/discharge runs, the best CAPMIX system appeared to be comprised of PAA and PAA/EDA electrodes. The system was able to extract 220 mW/m² of energy. When the time of charging/discharging runs was reduced to 1 min, the system generated 290 mW/m² of energy.

When one compares the energy harvested by CAPMIX method to other SGE systems, one realizes that PRO and RED are more efficient. They offer almost 10 W/m² (PRO) and 1 W/m² (RED)². However, the capacitive mixing is still at the beginning of its development and our results show that this process is a perspective one. It can be combined with capacitive deionization to merge two processes: water desalination and energy harvesting.

2. Conclusions

1. The best conditions of the CAPMIX process are as follows: highest salinity 80 g/L, lowest salinity 4 g/L, time of charging/discharging 1 min.
2. In the case of polymer membranes prepared from inter-polymer of polyethylene//styrene-co-divinylbenzene, the best polymer matrix is formed when polystyrene is crosslinked with 2% of divinylbenzene.
3. In the case of deposited polyelectrolytes, the best system was assembled of electrodes covered by poly(acrylic acid) and poly(acrylic acid modified with ethylene diamine).
4. Soft electrodes were more productive in energy harvesting than their hard counter-partners.

Acknowledgements: This research has been financially supported by bilateral collaboration program (TUBITAK-NCBR-2549) between Turkey and Poland

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FROM BLACK BOX TO MACHINE LEARNING: A JOURNEY THROUGH MEMBRANE PROCESS MODELLING

C. F. Galinha¹, J. G. Crespo¹

¹ LAQV-Requimte, Department of Chemistry, FCT-NOVA University of Lisbon, Campus de Caparica, 2829-516 Caparica, Portugal (jgc@fct.unl.pt)

Abstract: The synthesis of fundamental process models is many times impracticable due to the high development time and cost, the lack of measurement techniques of key properties, and, more importantly, the lack of fundamental knowledge about key aspects of the process. The main goal in this lecture is to illustrate how non-mechanistic modelling techniques can be applied with advantage to such complex membrane processes. These approaches may be applied to different situations where other mathematical approaches fail or, at least, do not provide a sufficiently powerful solution.

The first situation deals with cases where the existing mechanistic models are not able to describe correctly the problem under study. This may happen when the phenomena/processes investigated are rather complex in their character and, therefore, mechanistic models supported on the relation between a limited number of variables, sometimes with a high degree of interdependence, are not able to fully capture the variance of the data observed. There are several phenomena which, due to their complexity, are not fully described by mechanistic models. This is the case of the development of reliable models for the processing of solvent mixtures by using solvent-resistant nanofiltration (NF) membranes. The common approaches fail to predict the permeability of NF membranes when processing solvent mixtures, using permeability data of individual solvents.

The second situation refers to cases where relevant information about the process under study is available in the form of images (i.e., obtained by microscopy techniques) and spectra (from different complementary spectroscopic techniques). Traditionally, the information acquired by these characterization techniques is deconvoluted and interpreted, supported on our knowledge about the material observed and the technique employed. This deconvolution approach aims at reducing this complex information to parameters with a physical meaning, which may then be integrated in deterministic models, offering a totally diverse approach for the use of this information: the raw data acquired in an image or in a spectrum are firstly vectorized; once in a numeric form this information may be integrated as input data in a model and related with relevant operating or performance process parameters. When following this approach, the original data are not preprocessed by our “biased knowledge” but, otherwise, this modelling approach allows for a complete use of the information acquired: the identification of the relevant information embedded in these images or spectra is dictated by the relations established between input and output data within the model. This approach will be illustrated in this lecture for modelling of membrane processes using information acquired by two-dimensional (2D) fluorescence.

NON-PALLADIUM MEMBRANES FOR HYDROGEN SEPARATION AND THEIR APPLICATIONS IN NUCLEAR FUSION AND HYDROGEN ENERGY

A. I. Livshits

Bonch-Bruевич Saint-Petersburg State University of Telecommunications, 22/1 prospekt Bolshevikov, St. Petersburg 193232, Russia

Abstract: Hydrogen is the base of future energy. (1) Hydrogen isotopes are the fuel for nuclear fusion energy. First deuterium and tritium will serve as such a fuel, and then the nuclear fusion reactor will be able to work on deuterium, whose reserves on Earth are unlimited. (2) Hydrogen is an environmentally friendly energy carrier and, at the same time, a fuel for the efficient conversion of chemical energy into electricity with fuel cells. Membrane technologies are very promising for both direction of energy development. However the Pd alloy membranes that are usually used for the separation of hydrogen from gas mixtures are very expensive while not very productive and the lecture will be focused on alternative new materials.

As to the nuclear fusion reactors, the problem that can be solved with the membrane methods is the separation of nuclear fuel (D and T) from the product of nuclear reaction, i.e. from He. The membranes superpermeable for suprathemal hydrogen particles are proposed to employ for this purpose. The superpermeable membranes are made of group 5 metals, e.g. of V and their permeability for suprathemal hydrogen approaches its conceivable limit: the permeability of an opening of the same area. The superpermeable membranes are impermeable to any other gases including He and capable to automatically compress permeating hydrogen (D and T) by orders of magnitude.

As for the hydrogen energy, the membrane technology can be used for the extracting ultrapure hydrogen from the gaseous products of hydrocarbon fuel conversion. For this purpose seamless thin-walled self-maintained membranes of tubular shape, made of vanadium alloys with a thin Pd-coating on their inner and outer sides were fabricated (Fig. 1). In view of reliable and highly productive operation of such V-alloy membranes as well as of their absolute selectiveness, the assembly from these membranes was fabricated to use it in the fuel processor feeding a 1kW PEM FC and providing up to 16 slpm of ultrapure hydrogen by the steam conversion of light and heavy hydrocarbons including diesel.

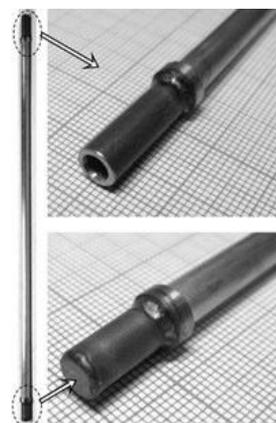


Fig. 1.

NANOSTRUCTURED MATERIALS FOR GAS MANAGEMENT

P. Vacca, M. Mudu, G.M. Calderoni, A. Nuzzo, M. Riva

Group Research Labs, SAES Getters S.p.A., viale Italia 77, Lainate 20020 (MI)
(paolo_vacca@saes-group.com)

Abstract: Nanostructured materials have gained increasing interest due to their ability to be modified in fundamental properties as the size of their constituent grains or phases decreases to the nanometer scale. These materials offer unique and entirely different optical, mechanical, and gas adsorption properties compared to conventional micro-size materials. In particular, gas interaction on nanostructured materials can sustain the definition of new strategies for the gas management in a variety of industrial applications where SAES technology platform based on Specialty Chemicals, a new class of functional composites, can play a relevant role. Engineered nanozeolites, submicro metal-oxides, nanoporous polymers and polymer capsules area adopted to allow new functional properties in terms of solid-gas interaction for both VOC adsorption/releasing and gas permeation. Innovative synthetic routes [1,2] have been developed to allow high flexibility in materials designing. Submicro zeolites are obtained through sol-gel hydrothermal synthesis at room temperature without any adoption of organic templates. Moreover emulsification assisted process is currently adopted as a flexible route to integrate new functionalities in organic submicro-beads and –capsules.

These functional materials represent today a tremendously versatile and promising platform to prepare mixed matrix membranes where a strong interaction between fillers and organic binders is obtained through a fine tuning of surface characteristics able to ensure high affinity and to preserve core material properties. Obtained systems find application in different industrial sectors from organic electronics (e.g. sensitive devices) to advanced packaging (e.g. food packaging) where a deep control in gas permeation and internal atmosphere are strongly requested.

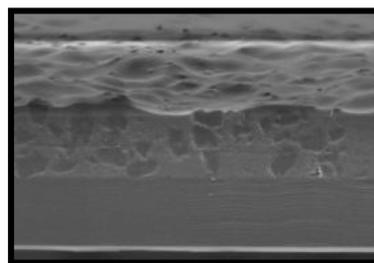


Fig. 1. Mixed matrix membrane based on functional fillers

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SHORT LECTURES

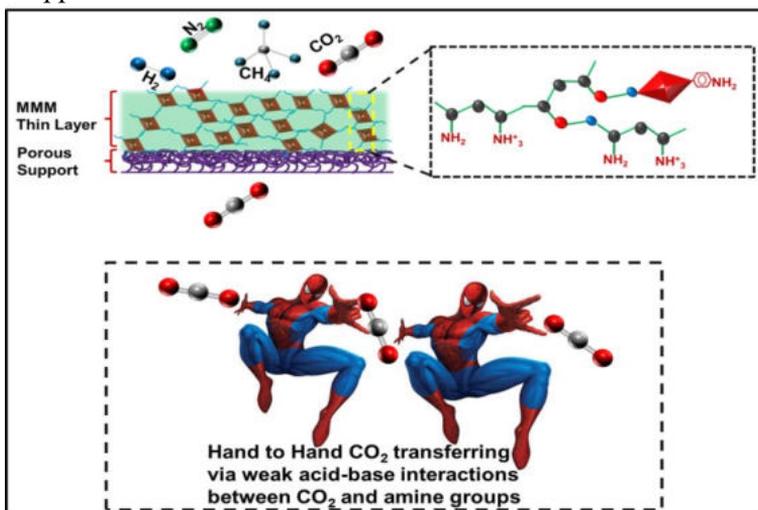
INTERFACIAL DESIGN OF MIXED MATRIX MEMBRANES VIA PVA GRAFTING ON UiO-66-NH₂ TO ENHANCE GAS SEPARATION PERFORMANCE

S. Jamali Ashtiani¹, M. Khoshnamvand², K. Friess¹

¹ Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 16628 Prague 6, Czech Republic

² University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Defect-free facilitated transport mixed matrix membrane (MMM) with high loading amount of UiO-66-NH₂ nanoparticles as metal-organic frameworks (MOFs) was fabricated. The MOFs were covalently bonded with Poly (vinyl alcohol) (PVA) to incorporate into poly (vinylamine) (PVAm) matrix solution. Uniform UiO-66-NH₂ dispersion even up to 50wt% was observed without precipitation and agglomeration after one month which is attributed to the high covalent interaction at interphases of UiO-66-NH₂ and PVAm which provided by PVA as a functionalized organic linker. The CO₂ permeance and CO₂/N₂, CO₂/CH₄ and CO₂/H₂ selectivity were significantly enhanced for the MMM by using optimal fabrication parameters. This improvement in gas performance is due to the strengthen impact of solubility and decreasing in influence of diffusion in membrane to promote CO₂ transport with a bicarbonate reversible reaction. The prepared MMM were characterized by XRD, DSC and FTIR to study the MMM chemical structure and polymers MOFs-particles interactions. Cross-sectional and surface morphology of the MMM were observed by SEM-EDX to detect the dispersion into the polymer matrix and explore their interfacial morphology. This approach can be extended for variety of polymer-filler interfacial designee for gas separation applications.



Key words: UiO-66-NH₂, high MOF loading, MMM, polymer-filler interaction, gas separation.

DEVELOPMENT OF UNPRECEDENTED POROUS MATRIMID®5218 MEMBRANES WITH A SUSTAINABLE APPROACH

F. Russo¹, R. Castro-Muñoz^{1,2}, F. Galiano¹, A. Figoli¹

¹ Institute on Membrane Technology (ITM-CNR), Via P. Bucci 17/c, 87036 Rende (CS), Italy (*a.figoli@itm.cnr.it)

² University of Chemistry and Technology Prague, Technická 5, 166 28, Prague 6, Czech Republic

Abstract: The focus of the research was the preparation, for the first time, of porous Matrimid® 5218 membranes by employing a combination of vapour induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) technique. The sustainable work plan was developed by using a green solvent (Rhodiasolv® Polarclean), according to the Green Chemistry principles and pursuing the systemic approach of the circular economy. The feasibility of preparing membranes was demonstrated by comparing the prepared membranes using green solvent with a traditional toxic solvent, such as N-methyl-2-pyrrolidone -NMP. Rhodiasolv® Polarclean solvent respects most of the parameters required in order to identify the green solvent for membrane preparation, including biodegradability, high boiling point, total solubility in water, low carbon footprint and low risks for human health. Matrimid® 5218 is one of the most commercially thermoplastic polymers used in gas separation for its properties such as high chemical resistance and good thermal stability; it is obtained by polycondensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and a mixture of two cycloaliphatic monomers (BTDA-DAPI). The preliminary studies of Hansen solubility parameters were carried out, followed by the ternary phase diagrams with both solvents. The exposure time to humidity (0, 2.5 and 5 minutes) and the effect of polymer concentration (8, 10 and 12 wt.%) on membrane morphology and properties were evaluated. The resulting membranes were characterized in terms of morphology, shrinkage propensity, thickness, porosity, mechanical properties, pore size, contact angle and water permeability (PWP). All the prepared membranes were porous with predominance of a sponge-like structure (with Rhodiasolv® Polarclean) and a macrovoid structure (with NMP). The membrane pore size was in the range from 0.05 to 0.73 µm in line with the porosity values (from 57 to 82%)¹. The PWP (~1000-35000 L/m²hbar) test confirmed the potential application of the membranes in ultrafiltration (UF) and microfiltration (MF) water treatment processes.

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CHEMICAL MODIFICATION OF ELECTROSPUN NANOFIBER MEMBRANES FOR SPECIFIC FUNCTIONS

P. Čapková¹, P. Ryšánek¹, E. Štěpanovská¹, O. Benada¹, M. Syrový¹,
M. Kormunda¹, M. Munzarová²

¹ J.E. Purkyně University, Faculty of Science, České mládeže 8, 400 96 Ústí nad Labem, Czech Republic

² Nanovia, Ltd, Podkrušnohorská 271, 436 03 Litvínov - Chudeřín, Czech Republic

Abstract: Electrospun nanofiber membranes PA6, PAN, PVDF have been manufactured using needleless electrospinning (*Nanospider* technology). Functionalization of membranes has been carried out by 2 different ways: (1) chemical modification using one pot synthesis (modifying agent directly in spinning solution) and (2) after-treatment of electrospun membranes using plazma supported chemical modification. Molecular modeling (force field calculations) has been used as necessary prerequisite of functionalization to predict stability of composite: nanofiber/modifying agent. Prepared functionalized membranes have been characterized as to the structure, morphology, phase composition, stability of chemical composition and their functionality using XPS spectroscopy, HRSEM microscopy, electrokinetic measurements and XRD analysis. The effect of chemical modification on structure, morphology and properties of nanofibers was illustrated on PA6 and PVDF membranes modified by three types of antimicrobial agents: Chlorhexidine (CHX), 1-dodecyltrimethylammonium bromide (DTAB) and benzyltrimethylammonium bromide (BTAB)^{1,2}. Results proved the stability of chemical composition and antimicrobial activity after long lasting air filtration tests of membranes. Present analysis revealed also the effect of charge distribution in crystal structure of piezoelectric polymers PAN and PVDF on morphology of electrospun nanofibers³. Layered crystal structure of these polymers with tendency to strip-shaped electrospun fibers together with asymmetric charge distribution on flat nanofibers leads to the longitudinal roll-up of nanofibers creating hollow fibers. Hollow nanofibers prepared by electrospinning may bring a new functionality of these membranes like high surface area for consequent chemical modification, sound insulation capabilities etc....

Acknowledgements: This work was supported by several projects: ERDF/ESF project "UniQSurf - Centre of biointerfaces and hybrid functional materials" (No. CZ.02.1.01/0.0/0.0/17_048/0007411), project NanoEnviCz No: LM2015073 and UJEP SGS project 2020 "nanofiber membranes for specific functions".

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NOVEL THIN FILM COMPOSITE MEMBRANES WITH UNPRECEDENTED STABILITY UNDER EXTREME PH

A. Tashvigh, N. Benes*

¹ *Films in Fluids Group, Membrane Science and Technology Cluster, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands (n.e.benes@utwente.nl)*

Abstract: Separation in aqueous mixtures at extreme pH is challenging but inevitable in industrial wastewater treatment. Thin film composite (TFC) membranes could be a sustainable solution for processing such wastewaters. TFC membranes are commonly made through an interfacial polymerization (IP) reaction, where a polyamide selective layer is deposited on a substrate. Unlike the nearly perfect stability of the polyamide-based membranes in harsh organic solvents, they quickly lose their performance upon contact with alkaline solutions. The main cause for such instability is the existence of carbonyl groups in the polyamide structure that can be easily influenced by OH⁻ ions.

For the first time, by carefully engineering the structure of the monomers we report the preparation of a polyamine based TFC membrane made from IP without the carbonyl groups in the polymer network, leading to an unprecedented stability in both acidic and alkaline conditions.

Figure 1 shows the morphology of the TFC membranes after 4 weeks immersion in highly acidic or alkaline solutions.

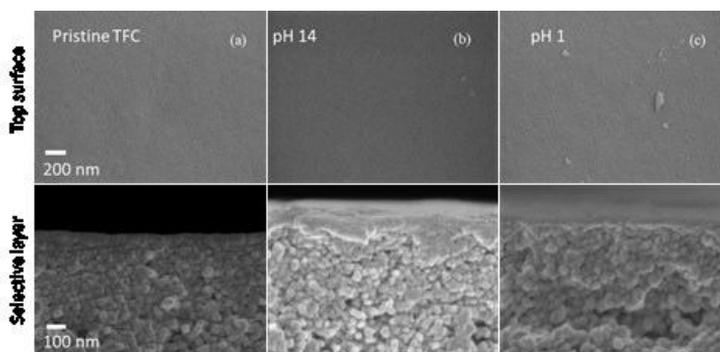


Figure 1. Morphology of the (a) pristine membrane, (b) the membrane after 4 weeks immersion in 1 M NaOH and (c) 0.1 M HNO₃

As shown in Figure 1, the newly developed polyamine membranes are reasonably stable in both acidic and alkaline conditions and no obvious structural change was detected. It can be concluded that, by carefully designing the monomer structures, the carbonyl groups in the final TFC membrane were eliminated and a highly pH stable membrane was fabricated. Given the ease of fabrication (i.e., IP) this work represents a step forward in producing pH-stable membranes for industrial wastewater treatment.

RINGING THE CHANGES ON PIM-1

P.M. Budd¹, A.B. Foster¹, M. Tamaddondar¹

¹ *Department of Chemistry, University of Manchester, Manchester M13 9PL, UK*

Abstract: The prototypical polymer of intrinsic microporosity PIM-1 (**Fig. 1a**) has attracted much attention as a membrane material for gas separation, pervaporation, nanofiltration and other separation processes. Defects arising during synthesis (**Fig. 1b**) give rise to a variety of PIM-1 topologies, including linear, cyclic, tadpole, branched and network structures (**Fig. 1c**), which have a profound influence on membrane properties.¹ Network structures can also be achieved through the introduction of a multifunctional monomer (**Fig. 1d**). In the case of a very tightly-crosslinked network, a nanosheet morphology is obtained (**Fig. 1e**), which can be utilized as a filler in mixed-matrix membranes with PIM-1 itself.² This illustrates how a basic PIM structure may be adapted to tailor the performance of a membrane.

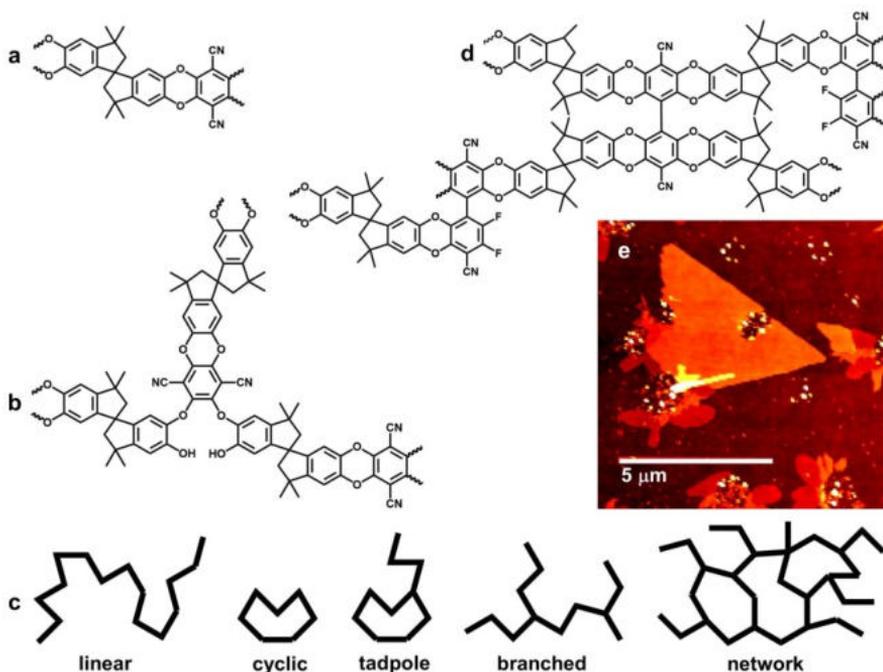


Figure 1. (a) PIM-1 repeat unit. (b) PIM-1 fragment with branch arising from chain defect. (c) Illustration of polymer topologies. (d) Network-PIM-1 fragment formed when tetrafluoro- monomer is replaced by octafluoro- monomer. (e) Atomic force microscope image of network-PIM-1 nanosheets.

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GLASS/AU COMPOSITE MEMBRANES WITH GOLD NANOPARTICLES INSIDE PORES FOR SELECTIVE ION TRANSPORT

D.V. Lebedev¹, M. O. Novomlinsky¹, M.S. Panov¹, I.N. Anfimova²,
V.A. Kochemirovsky¹, I.I. Ryzhkov³, T.V. Antropova²

¹ Saint Petersburg State University, 13B Universitetskaya Emb., St Petersburg 199034, Russia (denis.v.lebedev@gmail.com)

² Grebenshchikov Institute of Silicate Chemistry (ISCh) RAS, 2 Adm. Makarova emb., St Petersburg, 199155, Russia

³ Institute of Computational Modelling SB RAS, 50/ 44, Akademgorodok, Krasnoyarsk, 660036, Russia

Abstract: Hybrid or composite membranes containing various nanoparticles have been actively studied during the last decade. It was previously shown that the presence of different inorganic particles in the membrane structure can significantly affect its ionic selectivity and transport properties. The current work is aimed at the synthesis of glass membranes with gold nanoparticles inside the pores and investigation of their selective properties. Porous glass (PG) samples in the form of plane-parallel polished plates $10 \times 10 \times 1.0 \text{ mm}^3$ in size have been prepared in the ISCh RAS (project № 0097-2019-0015) by chemical etching of phase-separated sodium borosilicate glass with two-frame structure [1] in HCl and KOH solutions consistently as described in [1, 2]. The PG's porosity and average pore diameter are $0.5 \text{ (cm}^3/\text{cm}^3)$ and 25 nm, respectively [2]. The method of laser-induced metal deposition from solution was used for the formation of a new type of Glass/Au composite membranes [3]. Porous glass was impregnated with HAuCl_4 water solution. Then the sample was exposed by a pulsed laser with a wavelength of 355 nm. The potentiometric method was implemented for studying the selective properties of membranes. 2D Space Charge Model based on the Navier-Stokes, Nernst Planck and Poisson equations was utilized for interpreting the experimental results [4]. As part of the work, the selective properties of obtained membranes in model solutions of KCl salts were investigated. It was shown that the formation of particles inside membrane pores essentially affects its ion-selective properties. The results obtained can be widely used in various technologies. Specify what technologies, otherwise it the sentence looks very general.

Acknowledgment: This work is supported by the Russian Science Foundation under grant № 19-79-00095. The authors also express their gratitude to the resource center of SPBU “Optical and Laser Materials Research” and “Interdisciplinary Resource Centre for Nanotechnology”.

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STABILITY OF LBL COATED MEMBRANES AGAINST HIGH IONIC STRENGTH SOLUTIONS

J. Stumme, B. Wendler, M. Ernst

DVGW Research Centre TUHH, Am Schwarzenberg Campus 3, 21073 Hamburg, Germany, (jakob.stumme@tuhh.de)

Abstract: This study focuses on transforming the rejection properties of PES hollow fiber membranes from ultrafiltration to nanofiltration performance by Layer by Layer (LbL) modification. During the modification, the membrane is exposed alternately to polyelectrolyte (PE) solutions with positive and negative charges. Due to electrostatic interaction and the release of counterions during the exposition of electrolyte solutions, the PE adsorb on the membrane building up a film layer. The ionic strength of storage and filtration solutions might play an important role on the conformation of these films. If the ionic strength of these solutions is too high, an overcompensation of the intrinsic charges within the PE film might occur. Our study shows the influence of the storage solution on LbL-coated membranes when exposed to different NaCl solutions (0 M, 0.1 M, 0.5 M) for 8 double layer coated membranes (1 g/L PDADMAC/PSS in 0.1 M NaCl).

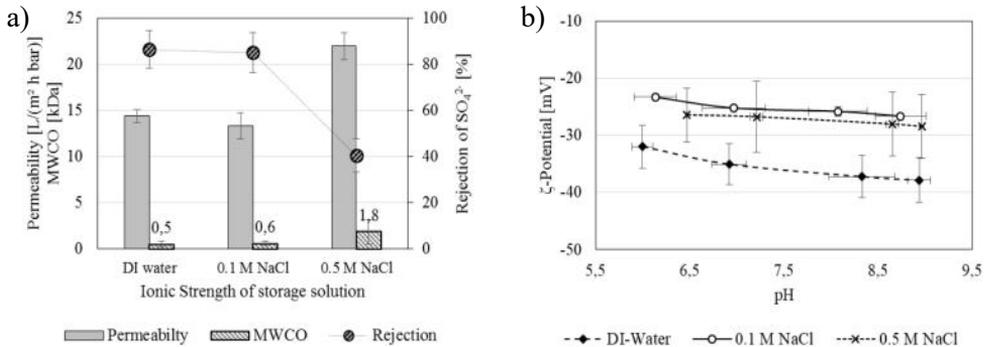


Figure 1: Influence of the storage solution on a) permeability, MWCO, SO_4^{2-} rejection and b) zeta potential of membrane active layer

Figure 1 exhibits that although the ZP is slightly less negative when the membrane is exposed to 0.1 M NaCl for 48 h at a typical pH range of drinking waters, there is no drastic change in sulfate rejection and MWCO. The results are different when the membranes are stored in 0.5 M NaCl, the MWCO and consequently the permeability increase drastically while the rejection for SO_4^{2-} collapses. These results suggest that steric rejection mechanism (measured by MWCO) might be more relevant for sulfate rejection than electrostatic effects (measured by ZP). Reasons for the change in structure may be attributed to the overcompensation of the charges as mentioned above. Further research investigates the influence of model solutions and real waters on the filtration behavior, stability and therefore applicability and limits of LbL-membranes for water treatment. Results are obtained within the SULEMAN project (03ET1574A), funded by BMWi and DVGW.

CHARGED NANOPOROUS MEMBRANES AS AN ALKALINE-RESISTANT SEPARATOR FOR ELECTROCHEMICAL CO₂ REDUCTION

K. V. Petrov¹, D. A. Vermaas¹

¹ Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands

Abstract: The electrochemical reduction of CO₂ could allow to use renewable energy from wind and solar directly for the production of sustainable fuels and chemicals. Two of the current issues in CO₂ electrolysis are that the ion-exchange membranes (IEMs) are not stable in the alkaline conditions in which the electrolytic CO₂ reduction cells often operate, and that these membrane cause a substantial ohmic loss. Therefore, there is a demand for improved IEMs, which are chemically stable, highly selective and conductive.

This project aims to tackle these issues using the novel concept of a self-supported ultrathin nanoporous inorganic IEM (Figure 1). It has recently been proven that these materials can be used as an alternative to polymeric IEMs and provide ion-selectivity based on the charge of the double layer¹. In our work, the relationship between pore size, surface charge and ion-selectivity of an inorganic nanoporous material is studied using anodized aluminium oxide substrates.

Ultimately, the large-scale production of a self-supported alkaline resistant IEM could make the scale-up of a CO₂ conversion process possible and economically viable. These materials can also be a major advantage to other electrochemical applications since they have the potential to increase charge density in comparison to polymeric membranes, as the charge density is no longer bound to a trade-off in ion exchange capacity and swelling. This could allow the membrane to remain selective at higher concentrations, which in turn, could mean an increase of the overall productivity of a process.

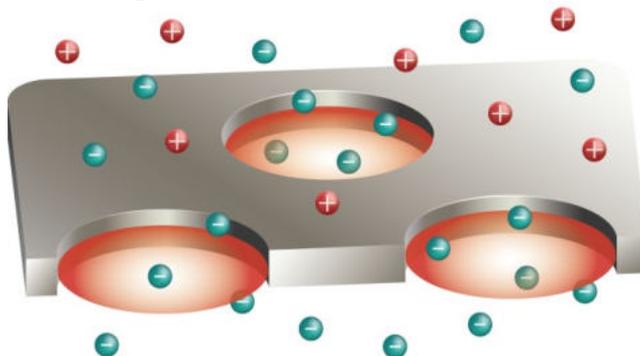


Figure 1: Concept of selective ion transport through a positively charged nanoporous membrane.

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NEW TWO-DIMENSIONAL BASED MEMBRANES FOR ULTRAFAST AND EFFICIENT MEMBRANE DISTILLATION AND MEMBRANE CRYSTALLIZATION

M. Frappa¹, F. Macedonio¹, A. Gugliuzza¹, E. Drioli¹

¹*Research Institute on Membrane Technology-National Research Council (CNR-ITM)
Via Pietro Bucci 17C, 87036 Rende (CS), Italy*

Abstract: This work focuses on the design of advanced hydrophobic functional membranes for highly productive and efficient water desalination¹. Considered the increasingly demand of fresh and reusable water, our intent is to identify new materials membranes for making water desalination much more productive and efficient through two eco-sustainable membrane operations such as membrane distillation (MD) and membrane crystallization (MCr)². We confine exfoliated few-layers graphene³ and/or transition metal dichalcogenides (TMDs) in PVDF membranes with spherulitic-like morphology^{4,5}. A significant increase in the productivity as well as high NaCl rejection are achieved when we operate synthetic seawater (NaCl 0.6 M) as a stream solution in a direct contact (DCMD) mode configuration. Also, we demonstrate how 2D materials, confined in membranes equipping MCr devices, stimulate quicker crystal nucleation and growth rate; as a result, we obtain better-quality NaCl crystals, which are more uniform in size and shape. Here, we discuss experiments carried out under different operating conditions as well as relationships between exfoliated few-layer materials and membrane properties. We examine the great potential of these new functional interfaces in developing MD and MCr on scale in order to supply a larger amount of fresh water and high-quality minerals in a logic of eco-sustainability and global societal growth.

Acknowledgements

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PECTIN AS NEW CROSSLINKING AGENT FOR POLYVINYL ALCOHOL MEMBRANES

S. Regina, R. Mazzei, T. Poerio, L. Giorno

National Research Council of Italy, Institute on Membrane Technology (CNR-ITM), Via P. Bucci 17/C, 87036 Rende (CS), Italy (s.regina@itm.cnr.it)

Abstract: Considerable work has been carried out in searching for new and non-toxic crosslinking agents¹ in order to improve the microbial and the physico-chemical stability of biopolymers such as cellulose, chitosan, polyvinyl alcohol (PVA), polylactic acid and others, that represents a eco-friendly alternative to petroleum-derived-materials for membrane manufacturing.

The purpose of this work was to carry out the crosslinking of PVA-based membranes by using for the first-time pectin (PEC), a heteropolysaccharide that represents a waste in juice fruit processing²; then its recovery and re-use is highly desired.

The crosslinked membranes were prepared with different mass ratio PVA/PEC by using Evaporation-Induced Phase Separation (EIPS) technique and these have been characterized as described below. Fourier Transform Infrared (FTIR) spectroscopy analysis confirmed the successful of crosslinking reaction pointing out the presence of absorption bands of ester groups, not present in PVA membrane spectra, and by using Thermogravimetric Analysis (TGA) a higher degradation-onset temperature for PVA/PEC (485 °C) respect to PVA membranes (285 °C) was observed, which depends on the crosslinked structure that confers greater thermal resistance. Besides, the crosslinking degree (70%) obtained by acid-basic titration was a further confirmation of the formation of covalent ester bonds between PVA-hydroxyl and PEC-carboxyl groups. Properties such as water uptake, microbial and chemical stability, antiradical and antibacterial activity were also determined. All these properties were compared with those obtained from PVA membranes crosslinked with citric acid (PVA/CA)³.

Results demonstrated that the prepared membranes showed good performance in terms of water uptake, resistance to soil bacteria, stability to the tested pH (3, 7 and 11), and high antiradical and antibacterial activity (against *E. coli*, *S. aureus*, *E. faecalis*, *B. subtilis*, *P. aeruginosa*).

Thanks to all these new acquired properties, the use of these membranes can be different (e.g., enzyme immobilization, membrane separation, biomedical application) and, moreover, these can be prepared ad hoc based on application.

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NANOSTRUCTURED MICROFILTRATION MEMBRANES FOR WASTE WATER TREATMENT

D. Kimmer¹, I. Vincent¹, L. Lovecka¹, M. Kovarova¹, D. Vesela¹,
L. Musilova¹

¹ *Centre of Polymer Systems, Tomas Bata University in Zlin, trida Tomase Bati 5678, 76001
Zlin, Czech Republic (email address: kimmer@utb.cz)*

Abstract: Preparation of homogeneous modified nanofiber structures with the desired morphology and properties by means of electrospinning process^{1,2} and consequent exploitations in liquid filtration³ are presented.

Applications of nanostructured materials made from nanofibers are limited markedly by their mechanical properties. Their improvement by selection of suitable polyethylene terephthalate support materials and the influence on filtration properties of microfiltration membranes are discussed. Filters prepared from polyethylene terephthalate nonwoven support and layer of nanofibers possesses excellent flux and can be washed repeatedly with retention of high almost initial flow properties.

Application of nanostructures modified against biofouling can improve the utility properties and the lifetime of microfiltration membranes.

Very high microfiltration efficiencies of used membranes are proved by measuring of particle size distributions by means of laser diffraction and dynamic light scattering before and after filtration process.

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DOPED LASER-INDUCED GRAPHENE CATALYTIC FILTERS AND MEMBRANES FOR WASTEWATER TREATMENT

A. Kumar¹, S. Santoki¹, S. P. Singh^{1,2*}

¹ *Environmental Science and Engineering Department (ESED), Indian Institute of Technology Bombay, Mumbai-400076, India*

² *Centre for Research in Nanotechnology & Science (CRNTS) Indian Institute of Technology Bombay, Mumbai-400076, India*

Abstract: Fouling and selectivity permeability tradeoff are the leading challenges in the membrane-based desalination and wastewater treatment technology. Laser-induced graphene (LIG) is a three-dimensional porous electrically conductive graphene material printed on the polymer substrates with a 10.6 mm CO₂ laser in a single step and chemical free process.^{1,2,3} A single step conversion of metal and metal oxides doped PES membranes to LIG filters and further UF membrane has been demonstrated with the excellent catalytic and anti-biofouling properties. These electrically conductive filters and membranes achieved 6-log removal of mix culture of bacteria with applied voltage along with the generation of H₂O₂. These conductive membranes can be tuned for the in-situ selective removal of the contaminants. The “catalytic mechanisms of these doped LIG filters will be explained, including the 3D texture effect of LIG. These filters and membranes (single step laser printed) have great potential in desalination and wastewater treatment.

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FROM BULK TO THIN-FILM — AN EXPERIMENTAL OVERVIEW OF THERMODYNAMIC AND KINETIC EFFECTS RELEVANT FOR GAS TRANSPORT IN POLYMER MEMBRANES

G. Genduso, I. Pinnau

Advanced Membranes, and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. (giuseppe.genduso@kaust.edu.sa)

Abstract: The quantification and understanding of thermodynamics (*i.e.*, competitive sorption) and kinetic (*i.e.*, plasticization) phenomena allow the design of tailored polymers for membranes with CO₂/CH₄ permeability selectivities higher than 40. This value permits substantial economic return during the pretreatment of natural gas, which production was ~ 4000 billion cubic meters during 2017. Based on experimental observations, we describe how the thermodynamics of sorption advantages the permeability selectivity of both polymer and carbon molecular sieve films (we present selected experimental sorption case studies at 35 °C). Independently from the concentration at equilibrium, CO₂ vs. CH₄ mixed-gas solubility coefficients trend was linear, and mixed-gas solubility selectivities increased with equilibrium pressure. Moreover, from experimental observations of bulk- and thin-film sorption, we found that gas-gas-polymer interactions reduce the uptake of mixtures in comparison with the ideal value.

In the second half of this work, we discuss how CO₂-induced plasticization hampers the selectivity of advanced and conventional membrane materials. The mixed-gas diffusion coefficients of CO₂ were determined from experimental solubility and permeability coefficients and were not significantly affected by the presence of methane. Methane diffusion, instead, was enhanced by carbon dioxide revealing the implication of CO₂-induced plasticization on polymer films. The ratio between mixed- and pure-methane diffusion coefficients was used to quantify membranes' plasticization revealing that intra-chain rigidity (*i.e.*, restricted chains' building blocks mobility) is not beneficial against plasticization. Conventional polymer films resisted better to plasticization and were more selective than relevant polymers of intrinsic microporosity (PIMs).

FLUE GAS PURIFICATION BY NON-POROUS MEMBRANES

P. Stanovsky^{1,2}, A. Žitková¹, J. C. Jansen³, B. C. Gándara⁴,
N. B. McKeown⁴, P. Izak^{1,2,5}

¹ *Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojova 135, 165 02 Prague 6 – Suchbátka, Czech Republic*

² *Institute of Environmental Technology VSB-TUO, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic*

³ *Institute on Membrane Technology, CNR-ITM, Via P. Bucci 17/C, 87036 Rende (CS), Italy*

⁴ *EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, Midlothian, Scotland*

⁵ *Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, Prague 6, 166 28, Czech Republic*

Abstract: This work presents flue gas purification on ultrapermeable membrane made from polymer of intrinsic microporosity based on tetramethyltetrahydronaphthalene unit combined with bicyclic triptycene (PIM-TMN-Trip). Permeation experiments were performed on laboratory developed permeation units for pure gases and for flue gas mixtures. Measurement with model mixture of flue gas the PIM-TMN-Trip membrane has shown high permeability for sulfur dioxide SO₂ but mixed gas selectivity from CO₂ was low, in order of units. Permeability of SO₂ from air-CO₂ mixture was very high (18-25.104 barrer) but selectivity was small (around 1.5) but comparable with other thermally rearranged membranes which also have shown superior separation properties for CO₂/CH₄.

This interesting polymer membrane was also tested by pervaporation where organic compounds (hexane, toluene), which contaminate water can be effectively removed.

Keywords: Fluids purification, gas permeation, pervaporation, polymer with intrinsic microporosity, membrane gas separation

Acknowledgements: The financial support of the Czech Science Foundation (grant no. 18-05484S) is greatly appreciated.

INCORPORATION OF MOF-808 TO ENHANCE EFFICIENCY OF PDMS BASED MEMBRANES APPLIED FOR ORGANIC SOLVENT SEPARATION

K. Knozowska¹, R. Thür², J. Kujawa¹, I. Vankelecom², W. Kujawski¹

¹ Nicolaus Copernicus University in Toruń, Faculty of Chemistry, 7 Gagarina Street, 87-100 Toruń, Poland (katkno@doktorant.umk.pl, www.chem.umk.pl)

² Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, Celestijnenlaan 200F, Box 2454, 3001 Heverlee, Vlaams-Brabant, Belgium

Abstract: Pervaporation (PV) can be utilized for the dehydration of organic solvents, the removal of organics from water, as well as the separation of organic-organic mixtures. An advantage of pervaporation is the possibility of the separation of close-boiling mixtures, breaking the azeotropes, and separation of molecules possessing similar shape or molecular weight. Further development of organic-organic pervaporation requires preparation of membranes possessing satisfactory separation properties and long-term stability during the process. Preparation of heterogeneous Mixed Matrix Membranes (MMMs) is an interesting solution to develop membranes with enhanced transport and separation properties[1].

The aims of this work were: 1) modification of MOF-808, 2) preparation and modification of membranes based on poly(dimethylsiloxane) (PDMS), 3) investigation of physicochemical properties of prepared membranes, 4) examination of pervaporation properties of native and modified PDMS based membrane applied for separation of binary organic mixtures.

The physicochemical properties of prepared membranes were determined by applying SEM, AFM, TGA analysis. SEM analysis proves the formation of the dense membrane. TGA analysis showed that membranes are thermally stable up to 300°C. Pervaporation results were analyzed implementing separation factor (β), and thickness normalized Pervaporation Separation Index (PSI_N). Incorporation of nanoparticles caused an increase of β and PSI_N . The best efficiency during the separation of ethyl acetate/ethanol (EtOAc/EtOH) was found for membranes modified by incorporation MOF-808-TFA (10 wt%).

This work was supported by PRELUDIUM 13 grant (2017/25/N/ST5/01097) from The National Science Center (NSC). The NSC PhD scholarship for Katarzyna Knozowska within the frame of ETIUDA 6 project (2018/28/T/ST5/00411) is kindly acknowledged.

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WATER-SWOLLEN MEMBRANE FOR FLUE GAS SEPARATION

A. Žitková, M. Kárászová, P. Stanovský, P. Izák, Z. Petrusová

Institute of Chemical Process Fundamentals, Czech Academy of Sciences, 165 02 Prague 6, Czech Republic (petrusova@icpf.cas.cz, www.icpf.cas.cz)

Abstract: We have shown that CO₂ and SO₂ can be removed from a mixture of model flue gas by water-swollen membrane in a one-step process. The continuous experiments were carried out by our permeation apparatus described in a detail in Žitková *et al.* [1]. It was found that this membrane is highly permeable for both SO₂ (Fig. left) and CO₂. It results in the real selectivity of SO₂/CO₂ close to 1 (Fig. left). Generally, membrane separation is able to compete with the currently used amine scrubbing when the gas permeability and its corresponding selectivity is high enough [2, 3]. Our membrane seems to be suitable for the purification of a real flue gas as can be seen from the comparison of our data with published data by Scholes *et al.* [4] (Fig. right). The membrane is suitable when the wetting and swelling of the thin selective layer is homogeneous and stable [5].

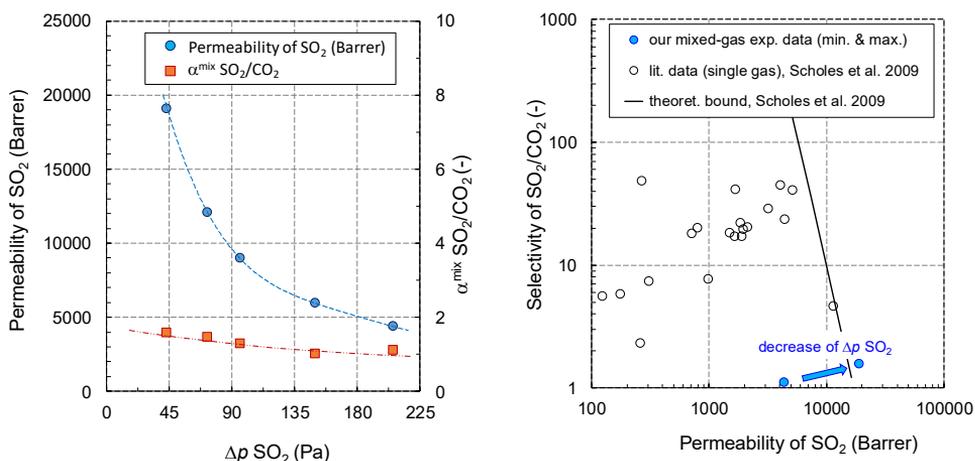


Figure: Permeability of SO₂ and mixed-gas SO₂/CO₂ selectivity as the function of SO₂ partial pressure differences (left) and the comparison of our experimental data with published data by Scholes *et al.* (right) [1]

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SOFT CONTROL OF MATERIAL PROPERTIES VIA NON-COVALENT INTERACTIONS IN SYNTHETIC POLYMERS

J.V. Kostina¹, Yu.G. Bogdanova², A.Yu. Alentiev¹

¹ *A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Pr., 119991, Moscow, Russia (julia@ips.ac.ru, www.ips.ac.ru)*

² *M.V.Lomonosov Moscow State University, Chemistry department, Leninskie Gory, 1, 119991, Moscow, Russia*

Abstract: Non-covalent interactions and their influence on the structure and properties of synthetic polymers are a new trend in modern chemistry. The effect of a solvent, including a polymer non-covalently bound to functional groups, has been discussed in the literature over the past decade. Both monographs [1] and thematic conferences [2] are devoted to non-covalent bonds and their influence on the properties of chemical objects.

Vibrational spectroscopy is one of the most important methods for studying non-covalent interactions. The combination of experimental (high-temperature IR spectroscopy) and theoretical (quantum-chemical modeling) data makes it possible to find out how the structural characteristics of macromolecules change and how these changes affect the properties of the polymer object as a whole.

If we understand the mechanism of change, we can specifically introduce a small additives to change the geometric, electronic, and energy characteristics of the functional groups. However, the simplest way is to use a solvent as such the small additive. We can to change the solvent and to regulate the conformational changes in the elementary unit of the polymer. Thereby we control the changes in the physicochemical properties of the polymer object (coating, film, membrane).

If we change the arrangement of functional groups in the polymer, we can:

- change the gas separation properties of films of amorphous glassy polymers;
- change the temperature of the thermochemical reaction of polyimide films were obtained for polyimides containing hydroxyl groups in the diamine fragment in the ortho- position to the nitrogen atom of the imide group;
- control the content of functional groups on the surface of the films to change the surface energy.

Acknowledgements: *This work was carried out within the State Program of TIPS RAS and Russian Science Foundation, № 19-19-00614*

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CHAINS PACKING ORDERING AND GAS SEPARATION PROPERTIES OF X-RAY AMORPHOUS AND SEMI-CRYSTALLINE GLASSY POLYMERS

A.Yu. Alentiev¹, R.Yu. Nikiforov¹, I.S. Levin¹, S.V. Chirkov¹,
N.A. Belov¹, A.Yu. Nikolaev², A.S. Kechekyan³, P.A. Kechekyan³

¹ *Topchiev Institute of Petrochemical Synthesis RAS, 29 Leninsky pr., 119991, Moscow, Russia (E-mail: alentiev@ips.ac.ru)*

² *Nesmeyanov Institute of Organoelement Compounds RAS, 28 Vavilova str., 119334, Moscow, Russia*

³ *Enikolopov Institute of Synthetic Polymeric Materials RAS, 70 Profsoyuznaya str., 117393, Moscow, Russia*

Abstract: The gas permeability and selectivity of films and membranes obtained from polymer solutions mostly depends on the method of their preparation or treatment. In some cases, it is possible to make significant modification of the gas separation parameters by the treatment without chemical transformations. Typically, for amorphous polymers these effects are associated with changes in chains packing ordering in the polymer matrix. We have shown that for x-ray amorphous glassy polymers a quantitative estimation of the changes in chains packing ordering is possible by analyzing the diffusion coefficients of gases with different molecular sizes for films with different histories of their formation or treatment [1]. The most important experimental parameter characterized the ordering of the polymer matrix is the diffusion selectivity. In the present work, the structural changes of 7 glassy polymers for membrane gas separation after annealing, uniform biaxial deformation, treatment with non-solvents, supercritical CO₂, etc. are evaluated. It is shown that the investigated polymers can be divided into 3 classes according to the degree of ordering: (1) completely amorphous (polysulfone, AF2400), (2) x-ray amorphous partially ordered (polyetherimides, polyhexafluoropropylene, PIM-1) and (3) semi-crystalline (polyphenylene oxide – PPO). For polyetherimides, polyhexafluoropropylene and PIM-1, various treatments significantly affect the chains packing ordering of the amorphous polymer matrix. For completely amorphous polymers and PPO, the effect of treatment on the ordering of the amorphous polymer matrix is not detected. However, for the semi-crystalline PPO, the main parameter that affects transport parameters is the degree of crystallinity, with the permeability of the crystal phase being significantly higher than the amorphous one.

Acknowledgements: *This work was supported by Russian Science Foundation (Grant No. 19-19-00614).*

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IN SITU FTIR SPECTROSCOPY STUDY OF POLYBENZIMIDAZOLE MEMBRANE SWELLING INDUCED BY SORPTION OF METHANOL

V. Loianno¹, M. Galizia², G. Mensitieri¹, P. Musto³

¹ Chemical, Materials and Production Engineering Department, University of Naples "Federico II", P.le Tecchio 80, Naples, NA, 80125, Italy

² School of Chemical, Biological and Materials Engineering, The University of Oklahoma, 100 E. Boyd Street, Norman, OK, 73019, United States

³ Institute on Polymers, Composites and Biomaterials, National Research Council of Italy, Via Campi Flegrei 34, Pozzuoli, NA, 80078, Italy

Abstract: Organic solvent nanofiltration based on polymeric membranes is an attractive alternative to thermal separation processes due to the low capital and operational costs. Polybenzimidazoles (PBI) are a promising candidate for this application because they have high thermal stability and are insoluble in almost any solvent but dimethylacetamide and dimethyl sulfoxide¹. In this work, *in situ* FTIR spectroscopy in the transmission mode is applied to study simultaneously methanol sorption in PBI films and the resulting membrane swelling. A major advantage of this approach is the evaluation of multiple thermodynamic parameters of the polymer-penetrant mixture with a single experiment.

Stepwise sorption tests are performed at 25°C and up to 0.7 activity. Sorption of methanol in PBI is measured from the intensity of the methanol peak at 1028 cm⁻¹ corresponding to the $\nu(\text{C-O})$ mode, whereas swelling is measured from the PBI peak at 1175 cm⁻¹. Solubility and dilation data are modelled with the *dual mode* approach. Interestingly, a PBI doublet at 704 – 690 cm⁻¹ displays an *isosbestic point* at 694.0 ± 0.5 cm⁻¹. This effect is related to the disruption of the H-bonding network (N–H---N) present in the pristine membrane, and to polymer swelling. Time-resolved spectra are recorded to measure the sorption kinetics: relaxation of the polymeric matrix is confirmed by the observed *dual stage* behavior. The adopted experimental approach has proven to be accurate and reproducible.

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BASIC IONIC LIQUIDS FOR SIMULTANEOUS CATALYTIC CONVERSION OF GLYCEROL TO GLYCEROL CARBONATE AND REMOVAL OF BY-PRODUCTS

D. Nikolaeva¹, J. Estager², D. Debecker³, P. Luis¹

¹ *Materials & Process Engineering (iMMC-IMAP), Université catholique de Louvain, Place Sainte Barbe 2, 1348 Louvain-la-Neuve, Belgium (daria.nikolaeva@uclouvain.be)*

² *Certech, Centre de Ressources Technologiques en Chimie, Rue Jules Bordet, Zone Industrielle C, 7180 Senefte, Belgium*

³ *Institute of Condensed Matter and Nanoscience (IMCN), Université catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain la-Neuve, Belgium*

Abstract: Transesterification reaction between glycerol (GLY) and dimethyl carbonate (DMC) offers a straightforward approach for biodiesel waste valorization¹⁻². This reaction is catalyzed by basic sites and presents a thermodynamic equilibrium that can be influenced by preferential removal of by-product, namely methanol (MeOH)³. However, when conventional distillation is applied, DMC and MeOH form an azeotrope that should be broken. This effort can be sparred by pervaporation, which allows to reduce energy consumption and intensify the separation process. In addition, membranes used for pervaporation may employ the ionic liquids with basic sites which will facilitate the reaction between GLY and DMC⁴.

Hereby we report on synthesis and characterization of basic ionic liquids (ILs) used for catalytic conversion of GLY to glycerol carbonate (GC)⁵. The basicity of ILs is measured by pH in water and dimethyl sulfoxide, and polarity is measured based on Kamlet-Taft solvatochromic parameters⁶. The catalytic performance is evaluated based on kinetic experiments with subsequent GLY concentration evaluation by HPLC. Our objective is to confirm the catalytic activity of the synthesized ILs based on the reaction conversion.

The authors **acknowledge** the Fonds européen de développement régional (FEDER) as well as the Wallonia (Belgium) for their financial supports via the "INTENSE4CHEM" projects (projects N° 699993-152208).

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DEVELOPMENT OF ZIRCONIUM-BASED MOF_s MIXED MATRIX MEMBRANES FOR HIGH-PRESSURE CO₂/CH₄ SEPARATION

M.Z. Ahmad^{1,2}, T.A. Peters³, V. Fila¹

¹ Department of Inorganic Technology, University of Chemistry and Technology, CZ

² Current address: Department of Chemistry, University of Manchester, UK

³ SINTEF Industry, P.O. Box 124, Blindern, N-0314 Oslo, NORWAY,
(mohdzamidi.ahmad@manchester.ac.uk)

Abstract: The gas separation properties of highly permeable 6FDA-DAM mixed matrix membranes (MMMs) with zirconium-based metal-organic frameworks, MOFs (UiO-66, UiO-66-NH₂, UiO-66-NH-COCH₃; ca. 40 nm) were investigated. All MOFs and membranes were characterized systematically. Compared to UiO-66, the CO₂ uptake of the two functionalized UiO-66s were improved by 44% and 58%, respectively, at 10 bar. The atomistic modeling for the MOF/polymer interface was consistent with a moderate MOF surface coverage by 6FDA-DAM, which did not play a detrimental role in the membrane performance. Their gas separation performances were evaluated by feeding CO₂/CH₄ equimolar mixtures at 2 bar pressure difference at 35 °C. CO₂ permeability (P_{CO_2}) of pristine 6FDA-DAM ($P_{CO_2} = 997 \pm 48$ Barrer, $\alpha_{CO_2/CH_4} = 29 \pm 3$) increased by 92% with 20 wt.% UiO-66 loading, while maintaining the CO₂/CH₄ selectivity. Improvements of 23% and 27% were observed for P_{CO_2} with the same 20 wt.% loading of UiO-66-NH₂ and UiO-66-NH-COCH₃, respectively. The α_{CO_2/CH_4} was improved up to 16% using both functionalized UiO-66 type MOFs. Succeeding, the gas separation performance at high feed-pressure (2–20 bar) was also conducted with a variation of CO₂ feed content (10–50 vol.%) between 35–55 °C. Moreover, the plasticization, competitive sorption effects, and separation of an acid gas hydrogen sulfide (H₂S) were investigated in a tertiary feed mixture of CO₂:H₂S:CH₄ (vol.% ratio of 30:5:65) at 20 bar and 35 °C. The Zr-MOFs improved not only the 6FDA-DAM gas separation properties but also deterred CO₂-induced plasticization and swelling. Additionally, in the presence of high H₂S content (50,000 ppm in feed mixture) at high total pressure, both CO₂- and H₂S-induced plasticization were suppressed and only presented a reversible competitive sorption effect.

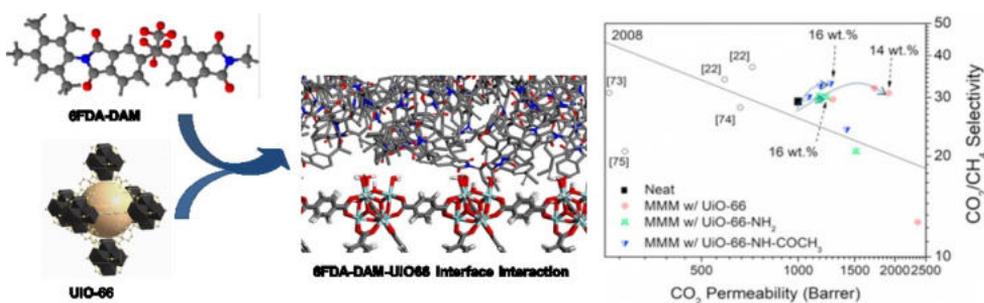


Figure 1: Graphical abstract.

CO₂ SEPARATION USING COMPOSITE MEMBRANES BASED ON PIM-1

H. Schwarzová¹, C. Antonelli², D. Quémener², M. Bernauer¹, R. Castro-Muñoz¹, V. Fíla¹

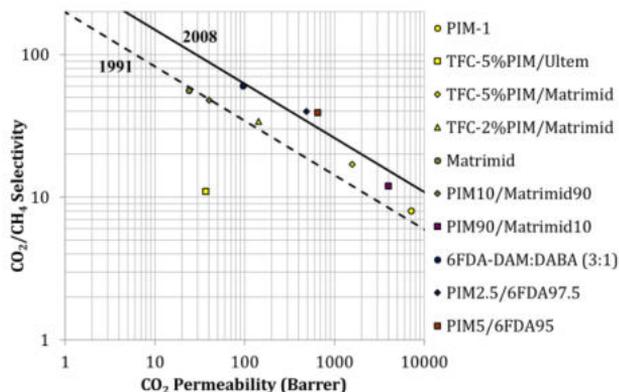
¹ *University of Chemistry and Technology Prague, Technická 5, 16628 Prague 6, Czech Republic (filav@vscht.cz)*

² *Institut Européen des Membranes (IEM) Université de Montpellier, 2 Place Eugène Bataillon, 34095 Montpellier cedex 5, France*

Abstract: Membrane gas separation presents an alternative technology to the traditional gas separation processes. Polymers of intrinsic microporosity (PIMs) exhibit high CO₂ permeability and moderate CO₂/CH₄ selectivity. The main disadvantage of PIM-1 is its relatively high price. The preparation of PIM-1-based composite membranes presents an opportunity to reduce the amount of PIM-1 used per unit area of the membrane and improve the gas separation performance.

The different approaches reducing the PIM-1 amount per unit membrane area have been tested in this work. The novel i) blended dense PIM-1/Matrimid®5128 and PIM-1/6FDA-DAM:DABA (3:1) membranes, and ii) thin-film composite membranes composed of cross-linked Matrimid®5128 or Ultem®1000 porous support and PIM-1 layer were synthesized. The gas separation performance and stability of prepared membranes were evaluated at several feed pressures using binary CO₂/CH₄ 1:1 feed mixture. Moreover, the FTIR, SEM, TGA and DSC methods have been used for membrane characterization.

The addition of PIM-1 in 6FDA-DAM:DABA (3:1) provides outstanding CO₂/CH₄ separation results. The introduction of low PIM-1 loadings brings an important increase of mixed-gas permeability without losing the separation factor. The performance of these membranes surpasses the Robeson limit from 2008.



Part of this work was supported by the Operational Program Prague – Competitiveness (CZ.2.16/3.1.00/24501) and “National Program of Sustainability“(NPU I LO1613) (MSMT-43760/2015)

REDEFINITION OF THE CO₂/N₂ AND CO₂/CH₄ UPPER BOUNDS USING 2D ULTRAPERMEABLE POLYMERS OF INTRINSIC MICROPOROSITY (PIMS)

A. Fuoco¹, B. Comesaña-Gándara², J. Chen², C.G. Bezzu², M. Carta³, I. Rose², M.C. Ferrari⁴, E. Esposito¹, J.C. Jansen¹ and N.B. McKeown²

¹ Institute on Membrane Technology, CNR-ITM, Italy. (a.fuoco@itm.cnr.it)

² EaStCHEM, School of Chemistry, University of Edinburgh, UK.

³ Department of Chemistry, Swansea University, UK.

⁴ Institute for Materials and Processes, School of Engineering, University of Edinburgh, UK.

Abstract: Membrane technology is a mature technology for several industrial applications such as oxygen or nitrogen separation from air, hydrogen or vapours recovery, natural gas treatment, and biogas upgrading. Nevertheless, the synthesis of novel polymers with enhanced gas transport properties is essential to make more cost-effective and promote membrane gas separation technology for CO₂ capture and removal. Recently, we have reported a series of ultrapermeable PIMs, based on benzotriptycene units, showing similar permeability ($P_{CO_2} > 20000$ Barrer) to the well-known poly(trimethylsilylpropyne) (PTMSP) but with substantially higher selectivity.¹ Their enhanced gas transport properties are attributable to their 2D polymeric chains which lead to a very inefficient packing resulting in large and well interconnected free volume elements. We will show the role of the substituents on the later chains, which act as spacer, in tailoring the permeability, diffusivity and solubility and their associated selectivities. Ageing data and the effect of the temperature on the transport properties will be also discussed.² Finally, we will show that the outstanding CO₂/CH₄ and CO₂/N₂ permselectivity properties of these benzotriptycene PIMs allow the introduction of the new upper bounds to define the current state-of-the-art.

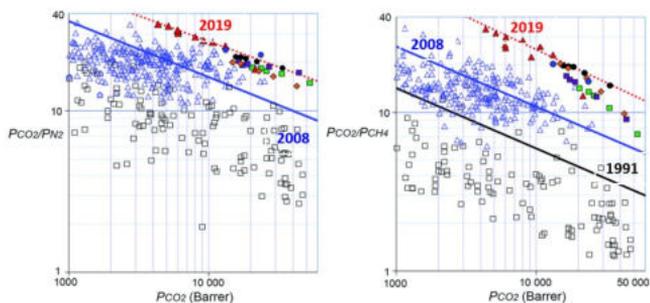


Figure 1 The 2019 upper bounds for CO₂/N₂ and CO₂/CH₄ gas pairs.

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CHARACTERIZATION OF FOULING-INDUCED CHANGES IN MEMBRANE POROSITY BY BRUNAUER–EMMETT–TELLER (BET) GAS ADSORPTION TECHNIQUE

T. Virtanen¹, L. Puro¹, K. Kakko¹, M. Mänttari¹, Mari Kallioinen¹

¹ *Department of Separation Science, LUT University, Yliopistonkatu 34, 53850 Lappeenranta, Finland*

Abstract: Porosity is an essential property of membranes and defines the permeability and rejection properties of the membrane together with hydrophilicity and charge of the membrane material. Size distribution of the selective pores and available surface area play important roles also in the membrane fouling because in several cases only foulants with certain size can access the pores of the membrane and block them. Thus, collecting information on the fouling-induced changes in membrane porosity and on the relationship of porosity properties and fouling tendency of the membrane may help to gain deeper understanding on the mechanisms of the fouling. We have investigated the applicability of Brunauer-Emmett-Teller (BET) gas adsorption/desorption method for characterization of organic membrane fouling¹.

In our recent studies, BET has been applied to characterize changes in the porosity of different kind of polymeric membrane samples after fouling caused by wood hot-water extracts², lake water³ and orange juice⁴. The studied samples have covered both flat sheet and hollow fiber ultrafiltration membranes, and the membrane materials have included polyethersulfone, cellulose acetate and polyvinylidene fluoride. Samples were pretreated by degassing and the applied conditions were selected based on the membrane materials and presence of volatile foulants. BET calculations were used to get both cumulative values and pore size distributions for pore areas and pore volumes in meso-pore (2–50 nm) and macro-pore (>50 nm) regions. The total amount of micro-pores (<2 nm) was also determined. In general, BET has been able to reveal pore narrowing and pore blocking as changes in pore volumes and pore area distributions in meso-pore region, and build-up of porous fouling layers as increases in porosities in macro-pore region.

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INFLUENCE OF SUPPORT CHARACTERISTICS ON MEMBRANE PERFORMANCE IN DISTILLATION TEST

M. Pagliero¹, A. Comite¹, C. Costa¹

¹ *membrane&membrane Research Group, Department of Chemistry and Industrial Chemistry, University of Genoa, 16146 Genoa (Italy)*

Abstract: In this work, polyvinylidene fluoride (PVDF) in dimethylformamide solutions were used to prepare hydrophobic membranes using the non-solvent induced phase separation technique. Based on previous works, ethanol was used as non-solvent to create a peculiar morphology that enhances the hydrophobic character of the membranes¹. PVDF membranes need to be supported on a stronger material in order to achieve the mechanical properties required for their operation. However, the support used can affect the final membrane performance². In this work, some commercial non-woven (NW) supports made of PP/PE or polyester were employed as a support to cast the membranes, and the influence of their thickness, porosity and morphology on membrane performance was investigated. Further membranes were prepared using some reverse osmosis spacer nets (permeate side) as a support. Membrane characterization was performed using scanning electron microscope, liquid entry pressure of water (LEP) and gas permeation (nitrogen) while their performance in vacuum membrane distillation (VMD) processes was assessed.

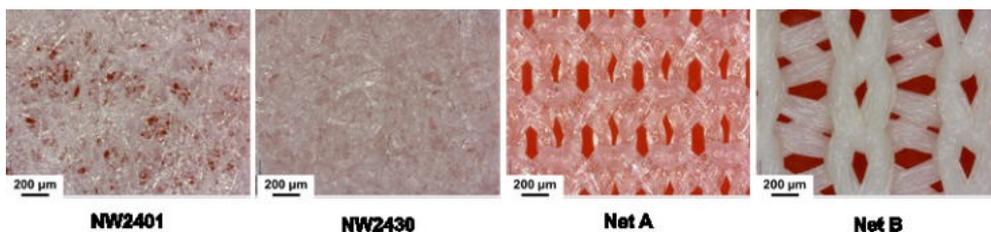


Figure 1: Optical microscope image of two non-woven and two nets used.

The differences in the main structure of the two kind of tested supports played a major role on the overall characteristics and performance of the finished membranes. In fact, when using the nets as support, the PVDF solution can diffuse inside the mesh of the net creating a thicker polymeric layer. This results in higher LEP values (almost 5 bar) but also in lower water flux during VMD operation.

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BIPOLAR MEMBRANE ELECTRODIALYSIS FOR ELECTROCHEMICAL CO₂ CAPTURE FROM OCEAN

R. Sharifian^{1,2}, M. Wagterveld¹, D.A. Vermaas²

¹Wetsus, European Centre of Excellence for Sustainable Water Technology, Netherlands

²Delft University of Technology, Department of Chemical Engineering, Netherlands

Abstract: Honoring the Paris agreement, to achieve a net zero CO₂ emission by the end of this century, strategies for CO₂ emission reduction *and* CO₂ capture both need to be employed¹. The CO₂ concentration in the ocean (as dissolved inorganic carbon, DIC) is more than 160x times higher than that in the atmosphere. Furthermore, lowering DIC concentration in the ocean, pulls additional CO₂ from the air (i.e., carbonate equilibrium); Making Ocean an interesting source for CO₂ capture. Capturing the carbonic species from seawater is possible via bipolar membrane electrodialysis (BPMED), through a pH-swing approach². The existing process is, however, rather energy intensive.

By creating an acidic pH in BPMED, the CO₂ (aq) concentration rises above its solubility and can be removed in the gaseous form, Figure 1. A bipolar membrane dissociates water into H⁺ and OH⁻ when a current is applied, with a required energy of approximately 2.5x less than that for water electrolysis (for a ΔpH=14). This energy consumption can be brought down even further by using lower pH gradients; as the Nernstian behavior predicts a lower membrane voltage for lower ΔpH over the BPM, shown in previous work³. In the present work, we investigate effect of flow direction, rate and current to achieve an efficient ΔpH_{BPM} for CO₂ recovery from aqueous sources. The results can be used to optimize ocean CO₂ capture as well as other applications of BPMED.

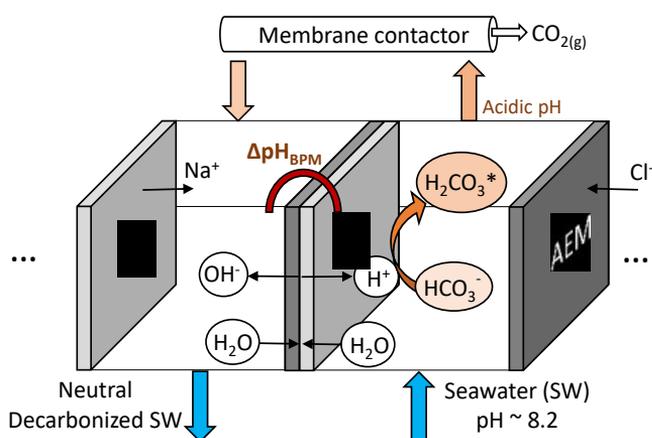


Figure 1: one cell pair of BPMED for CO₂ capture from seawater. $[H_2CO_3^*] = [CO_2^*(aq)]$ can be as high as 2.5mM when $pH \leq 4$, enabling recovery of 51 liter CO₂ (g)/m³ SW.

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INTERACTIONS OF CATIONIC ENTITIES OF VARIOUS SIZE AND CHARGE WITH ION-EXCHANGE RESINS IN DC ELECTRIC FIELD

P. Polezhaev¹, T. Bellon¹, Z. Slouka^{1,2}, L. Vobecka¹

¹ *University of Chemistry and Technology, Prague, Czech Republic*

² *University of West Bohemia, New Technologies - Research Centre, Pilsen, Czech Republic*

Introduction

Within the framework of our current research project, we study experimentally the interactions of various ionic entities with both anion- and cation exchange systems under the influence of DC electric field to: (i) determine characteristic internal dimensions of the ion-exchange systems dividing the studied ions into easily exchangeable ions and potential foulants (too large to be exchanged), (ii) describe the effect of ion size and charge on proceeding reaction-transport processes potentially leading to fouling, and (iii) establish the possibility of electrostatically enhanced fouling leading to creation of a bipolar junction splitting water. This contribution is focused on the homologous series of quaternary alkylammonium cations of various size and charge.

Methods

The experiments employ electrochemical measurements (current-voltage curves - CVC, chronoamperometry - CA) and simultaneous video capture of the reaction-transport phenomena in the vicinity of single ion-exchange resins in polycarbonate microcells. These microcells are fabricated according to the in-lab developed methods.

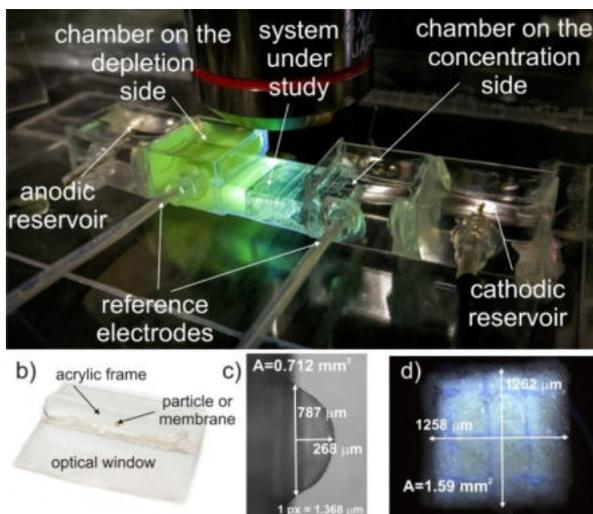


Fig. 1. Fabrication of a minifluidic electrochemical cell.

Results and Discussion

Current-voltage curves of the cation-exchange resin being the functional component of Ralex membranes (Mega a. s., Czech republic) in the solutions of quaternary ammonium cations display strong dependence on the hydraulic diameters of the used counterions (Fig. 2). The characteristic internal dimension of the ion-selective system corresponds to the one of tetrabutylammonium (green hexagons), which significantly deviates from the CVCs of smaller counterions (black, red and purple curves). Larger counterions such as tetrapentylammonium cations (blue curve) display negligible conductivity (navy stars) and their transport is hindered due to steric effects.

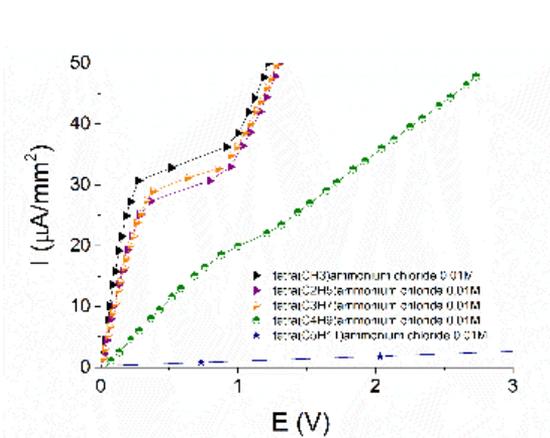


Fig. 2. Current-voltage curves for aqueous solutions of $\text{R}_4\text{N}^+\text{Cl}^-$.

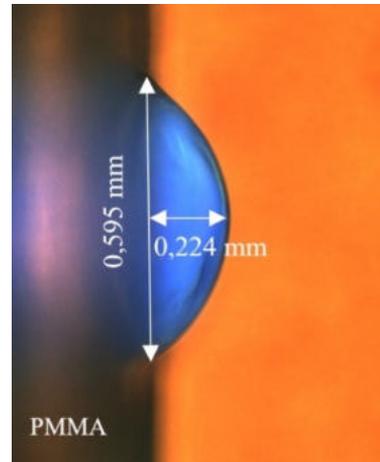


Fig. 3. Pristine cation-exchange resin used as a functional component in heterogenous cation-exchange Ralex membranes.

The size of counterions leads to development of significantly different electroconvective patterns. Small enough counterions allow strong electroconvection to develop while large counterions attenuate the electroconvective vortices. None of the counterions was able to create a bipolar junction splitting water. Large counterions fouled the membrane allowing only very small current to pass through the system.

LABORATORY AND BENCH SCALE TESTING OF BIPOLAR MEMBRANE ELECTRODIALYSIS FOR SULFATE RECYCLING IN METALLURGICAL INDUSTRY.

Kuldeep¹, H. Pajari², P. Kauranen¹, L. Murtomäki

¹ School of Chemical Engineering, Aalto University, PO Box 16100, 00076 Aalto, Finland

² VTT

(kuldeep.kuldeep@aalto.fi, www.aalto.fi)

Abstract: Demand for nickel and cobalt sulfates is expected to increase due to the rapidly growing Li-battery industry needed for the electrification of road transport. This is leading to increasing production of sodium sulfate waste, the discharge of which to natural waters is strictly regulated. Reduction of water discharges and reuse of the side streams are needed to make the battery industry more sustainable. Na₂SO₄ can be split into NaOH and H₂SO₄ using bipolar membrane electro dialysis (BPED). The acid and base produced can be reused in the metal processing/battery chemical industry. The economics of the BPED process depend on the CAPEX and OPEX of the system as well as possible pre- and post-treatments needed to reach sufficient purity and concentration for the BPED process and chemical reuse.

We have studied and optimized the BPED process at laboratory and bench scale. The laboratory setup consists of a five-chamber single repeat unit (membrane area 3.14 cm²) and the bench-scale system of a short stack of 10 repeat units (membrane area 280 cm²). The membranes and stack hardware were supplied by SUEZ Water Technologies & Solutions. The experimental systems have been operated using both pure Na₂SO₄ solutions and industrial sulfate-containing waste stream.

The promising results are encouraging our industry partners to proceed with further scale up to a pilot installation within the Finnish metal refining industry.

Acknowledgement



This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

NITRATE SELECTIVE ANION EXCHANGE MEMBRANES PREPARED BY USING DISCARDED REVERSE OSMOSIS MEMBRANES AS SUPPORT

A. Lejarazu-Larrañaga^{1,2}, S. Molina¹, J. M. Ortiz¹, E. García-Calvo^{1,2}

¹ IMDEA Water Institute, Avenida Punto Com, 2, 28805. Alcalá de Henares, Madrid, Spain (amaia.ortiz@imdea.org, www.water.imdea.org)

² Chemical Engineering Department, University of Alcalá, Ctra. Madrid-Barcelona Km 33.600, 28871. Alcalá de Henares, Madrid, Spain

Abstract: Membrane separation using ion exchange membranes represents an economical and environmentally friendly alternative to recover and reuse nitrogen from wastewater. However, its current limitations in terms of selective separation ability and membrane high cost hinder its application. In this work, nitrate-selective heterogeneous anion exchange membranes (AEMs) were prepared by coating method, using a recycled pressure filtration membrane as mechanical support. Three different anion exchange resins were tested. The effects in the separation efficiency of i) the type of anion exchange resin, ii) the use of the recycled membrane support and iii) the employed current density were studied.

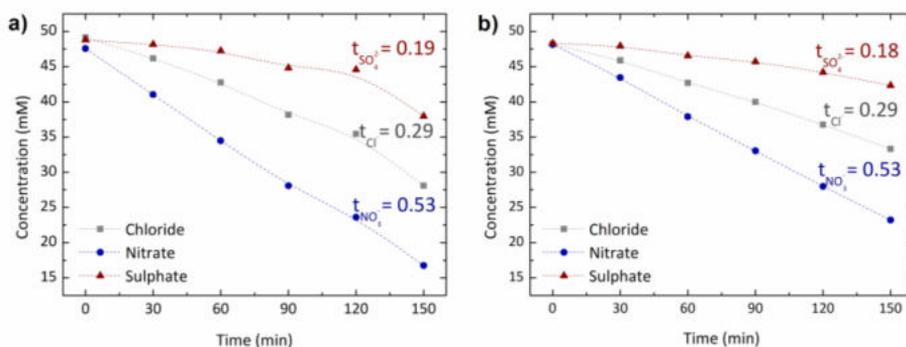


Figure 1. Selective separation at $5 \text{ mA}\cdot\text{cm}^{-2}$; a) AEM without mechanical support, b) AEM with recycled membrane, “t” transport number.

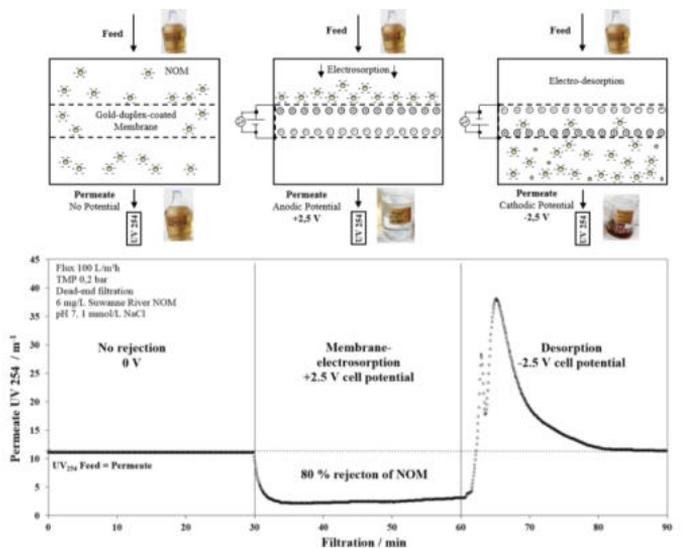
Results revealed that prepared membranes can effectively facilitate the transport of nitrates over other monovalent and multivalent anions. The use of the recycled membrane support did not increase the ion fractionation efficiency; however it provides mechanical stability to the prepared membranes. Finally, the use of low current density significantly improves the separation efficiency and facilitates the transport of nitrates through the membrane. This work shows a simple, low cost and scalable method to prepare nitrate-selective AEMs. The selectivity of the membranes for target ions could be easily tuned up by selecting the appropriate ion exchange resin.

POSITIVELY CHARGED ELECTRICALLY CONDUCTING MEMBRANE: E-SORPTION OF NOM

T. Mantel, M. Ernst

University of Technology Hamburg, Institute for Water Supply and Water resource, Am Schwarzenberg Campus 3, 21073 Hamburg, Germany, (tomi.mantel@tuhh.de)

Abstract: Recent studies showed that electrically conductive ultrafiltration membranes exhibit several advantages regarding fouling and rejection behavior due to the application of a cathodic electrical potential onto the membrane surface. A repulsive force is induced when the membrane is charged negatively due to the likewise negative charge of most dissolved organic water compounds such as natural organic matter (NOM). We used sputter deposition of ultra-thin gold layers (15 nm) to generate an electrically conducting gold-polymer-gold flat sheet membrane by coating the active and the support layer of a commercial polymer membrane (pore size ~ 50 nm, pure water permeability 1200 L/(m² h bar)). The novel approach of this study is the application of positive charge (+2.5 V anodic cell potential) to the active layer to induce electrosorption of NOM onto the membrane surface. Desorption of the NOM is achieved by changing the potential periodically (e. g., after 30 min filtration) to negative charge (-2.5 V cathodic cell potential). The present results showed that UV254 reduction of Suwannee River NOM is achieved to an extent of 80% whereas no reduction of flux of the membrane was observed. Application of negative potential led to desorption of NOM. Due to a low current density of 0.6 A/m², the additional energy consumption of electrosorption and desorption process was low with 0.01 kWh per m³ permeate. By the novel approach of membrane-electrosorption, an electrical conduction membrane with energy consumption between microfiltration and ultrafiltration is achieving the NOM rejection of nanofiltration and is so breaking the selectivity-permeability trade-off.



DESALINATION AND REUSE OF VISCOUS POLYMER-FLOODING PRODUCED WATER

P.A., Sosa-Fernandez^{1,2}, J.W. Post¹, H. Bruning², F.A.M. Leermakers³, H.H.M. Rijnaarts²

¹ *Wetsus, Centre of excellence for sustainable water technology. P.O. Box 1113 8911 CC Leeuwarden, NL*

(paulina.sosafernandez@wetusus.nl, www.wetusus.nl; paulinaa.sosa@gmail.com)

² *Wageningen University, Department of Environmental Technology. P.O. Box 8129, 6700 EV Wageningen, NL*

³ *Wageningen University, Laboratory of Physical Chemistry and Colloid Science. P.O. Box 8038, 6700 EK, Wageningen, NL*

Abstract: Polymer-flooding produced water (PFPW) is an abundant stream generated during oil extraction through polymer flooding. Reusing PFPW to confect fresh polymer solution would result threefold beneficial since it would minimize fresh water and polymer consumption, reduce problems related to PFPW disposal, and guarantee a reliable supply of water for enhanced oil recovery projects. However, since the reuse of PFPW is limited by its salt content, a partial desalination of the stream is required, for example via electro dialysis.

Although electro dialysis (ED) is a promising option to treat PFPW for reuse, the presence of charged polymers makes the desalination step more challenging, since they might increase concentration polarization and foul the membranes. Indeed, thick gel layers of polymer have been observed on the diluate side of the anion exchange membranes (AEMs), which cause a notorious increase of membrane resistance and scaling formation¹.

Varied strategies have been experimentally explored to minimize the fouling and improve process performance. These include operating in intermittent mode (pulsed electric field), utilizing AEMs with different physico-chemical properties, and operating in the ED reversal mode. Water recovery, energy consumption, and required membrane area have been taken into account to select the best process conditions, under which ED shows to be a highly feasible process to desalinate PFPW.

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FIRST EXPERIMENTS WITH MULTICHAMBER SHOCK ELECTRODIALYSIS UNIT

J. Čížek¹, J. Marek^{1,2}, P. Cvejn¹, D. Tvrzník³, J. Zlámal¹, J. Korytář¹

¹ Institute of New Technologies and Applied Informatics, Faculty of Mechatronics, Technical University of Liberec, Studentská 1402/2, 461 17, Czech Republic

² Institute for Nanomaterials, Advanced Technologies and Innovations (CxI), Technical University of Liberec, Studentská 1402/2, 461 17, Czech Republic, email: jaromir.marek@tul.cz

³ Membrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic

Abstract: In previous works we published optimization of one chamber shock electro dialysis unit – optimization of all components including membranes, electrodes, spacers and porous material towards functional and more effective scalable shock electro dialysis unit. The other aspect of the work was design of shock electro dialysis unit built up from common, available materials with reasonable price. After successful optimization exhibiting more than 99% desalination on single-chamber device, a unit with multiple desalination chambers was developed to examine the scalability of the SED processes. Further optimizations, regarding sealing of the unit, balancing the internal pressure, separation of the diluate and concentrate as well as the choice and treatment of the porous material needed to be done in order to achieve desirable performance in terms of flow rates and desalination.

In this work we compare the performance of the multi-chamber device with previous SED unit generations as well as with mathematical models developed based on theoretical principles and results obtained on single-chamber SED unit. We discuss the advantages, pitfalls and future prospects of shock electro dialysis as a method for water desalination.

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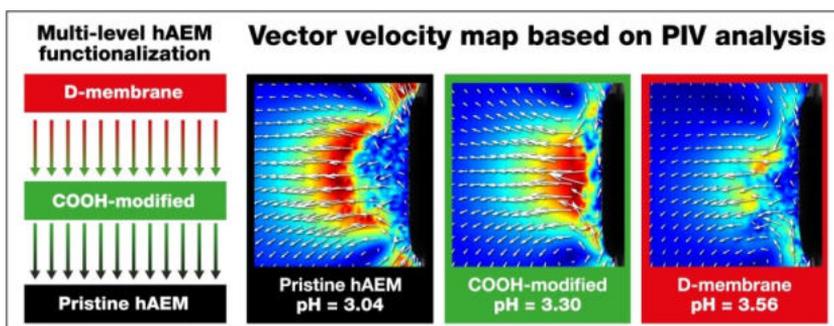
OVERLIMITING BEHAVIOR OF A SURFACE-MODIFIED HETEROGENEOUS ANION-EXCHANGE MEMBRANE

T. Bellon¹, Z. Slouka^{1,2}

¹ University of Chemistry and Technology, Prague, Chemical Engineering Dep.,
Technická 5, 166 28 Praha 6, Czech Republic

² University of West Bohemia, New Technologies Research Centre, Univerzitní 8,
306 14, Pilsen, Czech Republic (tomas.bellon@vscht.cz, zdenek.slouka@vscht.cz,
www.forancephoto.com)

Abstract: Electrochemical and electrokinetic behavior of ion-exchange systems as a result of electrostatic interactions between the fixed charge and the ionic species present in the electrolyte can significantly vary with the type of electrolyte and the membrane composition. In this paper, we studied experimentally the effect of surface modification of a heterogeneous anion-exchange membrane on its properties and overlimiting behavior. The surface modification of the anion-exchange membrane included carboxylation of its surface through benzophenone-based photochemistry followed by covalent linkage of single stranded DNA molecules. Such surface chemistry produced a molecular layer of negative charge on the positively charged membrane surface. We investigated the membrane samples with different levels of surface modification on their exposure either to KCl solutions or solutions containing a biopolymer serving as a model membrane foulant. The surface modification results in larger membrane resistances that are especially pronounced in the limiting and overlimiting region. The overlimiting current density was almost 50% smaller for the modified membrane than that for the pristine one. The anion exchange membrane was shown to split water efficiently at overlimiting conditions no matter what the status of surface modification was. The electroconvection, as another mechanism driving overlimiting current, tracked by the PIV method was largely suppressed upon surface modification. Soaking the membranes with different levels of surface functionalization in a solution of a model membrane foulant with the opposite charge to that fixed in the studied membrane showed that the pristine membrane is the most prone for electrostatically enhanced fouling.



Differences between various level of functionalized systems based on PIV analysis.

DECREASE IN SELECTIVITY OF CATION-EXCHANGE MEMBRANES DURING ED DESALINATION OF CALCIUM-CONTAINING SOLUTIONS

N.D. Pismenskaya, V.D. Titorova, S.A. Mareev, V.V. Nikonenko

Membrane Institute, Kuban State University, 149 Stavropolskaya st., Krasnodar, Russia

Abstract: Electrochemical behavior of homogeneous (CMX, Astom) and heterogeneous (MK-40, Shchekinoazot) cation-exchange membranes during electro dialysis desalination of 0.01÷0.1 eq/L NaCl, CaCl₂ and NaCl + CaCl₂ solutions was studied. It was found that in the case of calcium-containing solutions, the section of the inclined plateau of the current-voltage curves (CVC) of the membranes lengthens; the limiting current determined by the intersection of the tangents to this and the initial CVC section increases (Fig. 1a), water splitting rate grows. A maximum is recorded on chronopotentiograms, which is more and more noticeable (Fig. 1b) with increasing duration of membrane operation under electric field. Reduction of membrane selectivity and suppression of electroconvection due to a decrease in the ion exchange capacity and the surface charge of the membranes cause these changes in the membrane electrochemical characteristics. Apparently, the reason is in increasing specific interactions of calcium ions with sulfonic fixed groups when an electric current flows. This result explains qualitatively the lower current efficiency of desalination in the case of electro dialysis of calcium-containing solutions compared with NaCl solution.

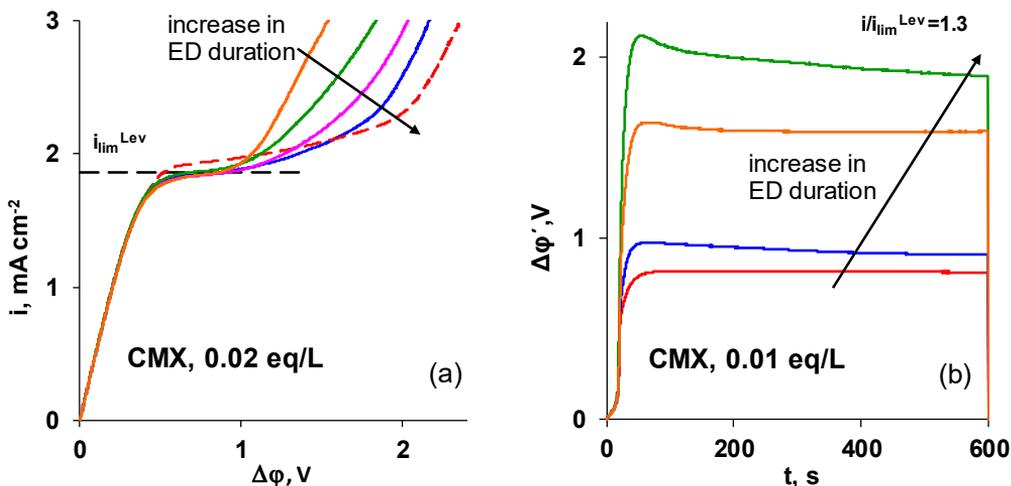


Figure 1. Current-voltage curves (a) and chronopotentiograms (b) of CMX membrane depending on the ED duration of CaCl₂ solution desalination.

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OVERLIMITING MECHANISMS OF ION EXCHANGE SYSTEMS

T.Belloň¹, P.Polezhaev¹, L. Vobecká¹, Z.Slouka^{1,2}

¹ University of Chemistry and Technology Prague, Dept. of Chemical Engineering, Technická 3, Prague 6, 16628, Czech Republic

² University of West Bohemia, New Technologies – Research Centre, Univerzitni 8, Pilsen, 30614, Czech Republic (sloukaz@vscht.cz)

Abstract: Ion-exchange systems exhibit an interesting current-voltage curve which has nonlinear character and displays three easily distinguishable regions (Fig. 1). These regions are usually referred to as ohmic (underlimiting), limiting, and overlimiting ones. The occurrence of the overlimiting part is unique to ion exchange systems [1]. It is not observed at any other membrane separation processes in which an increase in the driving force does not result in the increase of the transmembrane flux upon reaching the limiting conditions. From this perspective, the operation of electromembrane separation processes in the overlimiting region offers a relatively easy way of process intensification. However, a full understanding of the mechanisms driving the overlimiting current is necessary. In this contribution, we will present our experimental approach to study electroconvection and water splitting reaction appearing on various ion-exchange systems under overlimiting conditions. The observations can be summarized in several general points: (i) electroconvection occurs on both cation and anion exchange systems [2], [3], (ii) electroconvection is the dominant overlimiting mechanism at cation exchange systems (Fig. 1) [2], (iii) anion exchange systems also show significant extent of water splitting reaction (under review), (iv) natural convection occurs simultaneously to electroconvection after polarization of the membrane (in preparation), (v) overlimiting mechanisms are strongly affected by the presence of fouling agents especially if possessing charge opposite to that one fixed in the ion-exchange system [3], [4].

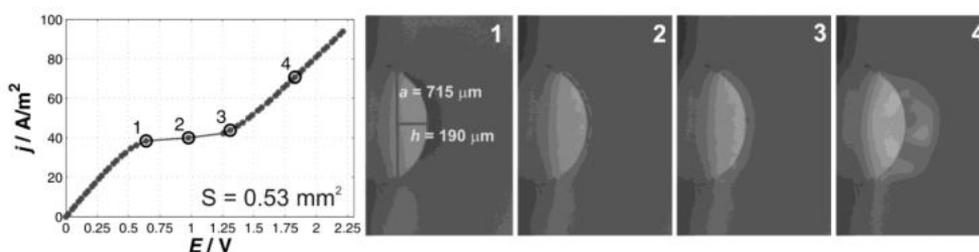


Figure 1: Current voltage curve measured on a cation exchange resin particle and a set of images capturing the occurrence of electroconvection.

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NOVEL STANDARD GRADE AND MONOVALENT-SELECTIVE ANION-EXCHANGE MEMBRANES

D. Golubenko^{1,2}, A. Yaroslavtsev^{1,2,3}

¹ *Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, 119991, Moscow, Russia*

² *Institute of Problems of Chemical Physics of Russian Academy of Sciences, 142432, Chernogolovka, Russia*

³ *National Research University Higher School of Economics, 101000, Moscow, Russia*

Abstract: Despite the fact that there are many commercial ion-exchange membranes on the market, the development of new materials and optimization of existing approaches is actively ongoing [1]. It is closely related to the emergence of new polymers or methods of their preparation, which open up new possibilities for researchers. The present study is devoted to the development of standard anion-exchange membranes (AEM) and membranes with a selective surface layer based on a new grafted copolymer of polystyrene and UV-activated polymethylpentene [2,3].

Standard AEM have been manufactured by chloromethylation and subsequent quaternization of polystyrene within a graft copolymer film. Particular attention is given to the kinetics of chloromethylation and the influence of the reaction conditions on the properties of the anion-exchange membranes. By means of variation of the polystyrene content and its cross-linking degree, we have obtained membranes that have an ion-exchange capacity ranging from 1.1 to 2.9 mmole g⁻¹, anion transport numbers between 91.0 and 95.6 % and specific ionic conductivities ranging from 2 to 25 mS cm⁻¹ (Fig.). It is estimated that the use of the developed materials will increase the efficiency of reverse electrodialysis energy production by 8-10% compared to the state of the art membranes.

An AEM with monovalent selectivity and antifouling properties was obtained by adding the step of surface sulfonation with sulfuric acid into the scheme for the preparation of standard AEM. The best surface-sulfonated membrane obtained has a low specific/surface ionic resistance of 89.3 Ohm cm/0.69 Ohm cm² and a high Cl/SO₄-selectivity of up to 6.5. Surface-modified membranes do not absorb humic acids. The effect of surface sulfonation of AEM on diffusion permeability, potentiometric transport numbers, and current-voltage characteristics was studied. It is shown that the Cl/SO₄ selectivity of sAEM membranes depends on the specific current. The obtained selectivity values are interpreted using mathematical modeling methods.

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POLY (PHENYLENE OXIDE)-BASED ANION EXCHANGE MEMBRANE WITH IMPROVED POWER DENSITY AND ENERGY EFFICIENCY NEUTRAL AQUEOUS ORGANIC REDOX FLOW BATTERY

M.T. Tsehaye^a, X. Yang^{b,c,d}, T. Janoschka^d, F. Alloin^a, C. Iojoiu^a

^a Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38 000 Grenoble, France

^b Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena, Germany

^c Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

^d JenaBatteries GmbH, Otto-Schott-Strasse 15, 07745 Jena, Germany
Email: misgina-tilahun.tsehaye@grenoble-inp.fr

Abstract: Neutral pH aqueous organic redox flow batteries (AORFB) employing water-soluble dimethyl viologen (MV) and *N,N,N*-2,2,6,6-heptamethylpiperi-dinyl oxy-4-ammonium chloride (TMA-TEMPO) molecules have been demonstrated as a high-performing RFB^{1,2}. The membrane allows the transport of counter ions while preventing the intermixing of the active molecules of the electrolyte solutions. However, despite being of crucial importance, there is a lack of appropriate membranes designed for the system as it is usually overlooked in many studies³. Therefore, synthesis of a suitable membrane, which shows a high (chloride) conductivity and selectivity, optimized water uptake, adapted mechanical strength, is required⁴.

In this work, a series of flexible and conductive AEMs composed of Poly (phenylene oxide) with six carbon side chain ended with quaternary ammonium (DABCO or TMA) were fabricated via casting and tested in a 5 cm² TMA-TEMPO/MV-based AORFB. The AEM with optimized

properties exhibited much higher peak power density than a well-performing commercial membrane (FAA-3-50@Fumatech) (388 vs 244 mW/cm²) (Figure 1).

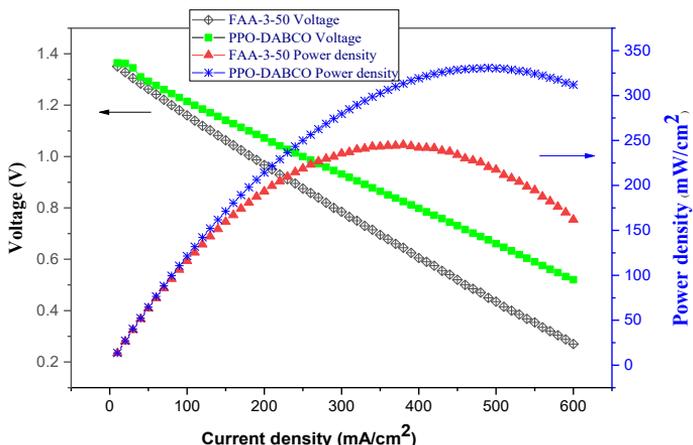


Figure 1: Polarization curve of FAA-3-50 and PPO-DABCO membranes

Moreover, our membrane permitted to obtain excellent coulombic efficiency (>99%) and a high energy efficiency (80% vs. 78%) than the commercial membrane. Our results show a promising membrane candidate for AORFBs.

Funding: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement no. 765289.

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CASE STUDIES ON THE APPLICATION OF NEW ION EXCHANGE MEMBRANE MATERIALS FOR BIOELECTROCHEMISTRY

L. Koók¹, J. Žitka², R. Cardeña³, P. Bakonyi¹

¹ *Research Institute on Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem str. 7, Veszprém, H-8200, Hungary (kook@almos.uni-pannon.hu)*

² *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*

³ *Laboratory for Research on Advanced Processes for Water Treatment, Instituto de Ingeniería, Unidad Académica Juriquilla, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, Querétaro, Qro. 76230, México*

Abstract: Bioelectrochemical systems (BES) can be considered as promising alternatives for sustainable energy (microbial fuel cell, MFC) and value-added chemicals such as hydrogen (microbial electrolysis cell, MEC) production from renewable sources (mainly wastewater) by using the bioelectrochemical activity of exoelectrogenic microbes¹⁻². These systems consist of two electrode chambers separated by an ion exchange membrane³. The architectural engineering of MFCs and MECs followed the scheme of classical polymer electrolyte membrane fuel cells, employing proton exchange membranes (PEM), such as Nafion. However, the specific biological and ionic nature of the electrolytes in BES shortly made it clear that PEM fails to ensure efficient operation. Therefore, significant research work has been done recently on the investigation of alternative membrane materials, such as ion exchange membranes, ceramics, low-cost materials and ionic liquids. Moreover, it has been concluded that anion exchange membranes can be advantageous in BES from the energy losses point of view.

This work presents case studies on the application of alternative anion exchange membranes in BES for electricity and hydrogen production. It was observed that PSEBS DABCO membranes could outperform Nafion membrane in MFC in aspects of energy yields and internal resistance. Moreover, this membrane proved to be comparable and in some aspects more advantageous than commercially available anion exchange membranes.

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THE EFFECT OF DIFFERENT THICKNESSES AND OF DIFFERENT DESIGNS OF FEED SPACERS IN RO MEMBRANES, UNDER VARIOUS TEMPERATURE-PRESSURE-CONDITIONS, ON THE EFFICIENCY OF A SKIM MILK CONCENTRATION PROCESS

M. Weiland, C. Zscherpe, C. Weissgerber, S. Schwermann

University of Applied Sciences and Arts Hannover, Faculty II, Department of Bioprocess Engineering, Heisterbergallee 10 a, 30453 Hannover, Germany (saskia.schwermann@hs-hannover.de, www.hs-hannover.de)

Abstract: In the current political climate, the reduction of the energy consumption gained a significant importance. This is all the more true for dairy companies¹. The production of milk concentrate is a significant cost factor in dairy companies due to its high energy requirements. The energy consumption of evaporation processes can be reduced through pre-concentration of the milk to up to 25 % dry matter² via RO.

Commonly used spiral wound modules (SWM) are equipped with a feed spacer. They are essential, as they keep the membrane envelopes apart and therefore create a flow channel for the fluid and promote turbulences that reduce concentration polarization and hereby, enhance the mass transfer. To gain high flux, feed spacers should be as thin as possible, as a greater membrane area and a higher flow velocity of the fluid promote a better mass transfer. On the other hand, they should be as thick as necessary, to reduce the pressure drop and thereby, the energy consumption of the SWM³. These two counterparts, flux and energy consumption, can be combined to determine the efficiency of the process.

This paper compares SWM with feed spacers of different thicknesses (31 & 46 mil) and different feed spacer design (diamond & ladder type, both 31 mil). These SWM were used to concentrate skim milk to up to 24 % dry matter at transmembrane pressure (TMP) of 25/30/35 bar and temperatures of 10/15 °C.

The results show that the efficiency of the process (flux/energy consumption) is the highest at 15 °C & 25 bar and the lowest at 10 °C & 35 bar for 31 and 46 mil feed spacer. Furthermore, the design of the feed spacer considerably influences the pressure drop and therefore energy consumption. The efficiency of the process is with up to 55 % significantly lower for the ladder type spacer.

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USE OF ADVANCED VARIABLE MEMBRANE TECHNOLOGY FOR INDUSTRIAL WASTEWATER TREATMENT

M. Johnova¹, L. Dvorak¹, J. Krivankova², D. Vilim²

¹ *Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Bendlova 1409/7, 461 17 Liberec, Czech Republic*

² *ENVI-PUR Ltd., Na Vlcovece 13/4, 160 00 Praha 6, Czech Republic*

Abstract: Main goal of this study was to develop and evaluate an advanced treatment technology consisted of two main segments, i.e. efficient pre-treatment step and membrane separation unit allowing an effective treatment of industrial wastewaters. Entire technology is designed with respect to its variability and flexibility enabling easy process and operation modifications based on the character of incoming wastewaters.

The developed membrane unit was tested on hardly biodegradable wastewaters coming from the engineering industry (production of aluminum castings). The quality of the raw wastewater varied greatly in the influent COD ranging from 1200 to 24400 mg·L⁻¹ as well as in concentration of total petroleum hydrocarbons (TPH) ranging from 90 to 600 mg·L⁻¹. The raw wastewater was firstly pretreated using rotary sieve (diameter 2 mm), and then through deemulgation by FeCl₃ at an optimum pH value of 6.5 with corresponding dose of 150-200 mg·L⁻¹ Fe³⁺. The resulting sludge was separated in a lamella settlement tank (2.1 m³). Pretreated wastewater then flowed into aerated activation tank (3.0 m³) which was coupled with separate membrane chamber (1.7 m³). Membrane chamber was equipped with submerged flat-sheet ceramic membrane module (pore size of 0.1 μm, total area of 1.8 m², silicon carbide, 12 pieces). Since the raw wastewater was poor for nutrients, urea and AMOFOS NP fertilizer was dosed in the activation tank. Operational phases differed in permeate flows (net flux 0.02 – 0.05 m³·h⁻¹), hydraulic retention time (7 - 10 d) and organic (COD) sludge loading (0.1 – 0.24 kg·kg⁻¹·d⁻¹) during pilot plant operation. In all phases, hydraulic performance and treatment efficiency was investigated.

Compared to the current industrial WWTP which involves deemulgation by FeCl₃ at pH value of 5 without sedimentation, followed by biological treatment and sedimentation tank, the permeate from advanced membrane unit achieved on average about 70% lower COD concentration and about 96% lower TPH concentration.

Acknowledgment: Project No. TH04030037 supported by Technological agency of the Czech Republic is gratefully acknowledged.

DIRECT MEMBRANE FILTRATION FOR WASTEWATER TREATMENT – PILOT SCALE EXPERIENCES FROM NORWAY AND SWEDEN

F. Lipnizki¹, T. Hey², Å. Davidsson¹, M. Cimbritz¹

¹ *Department of Chemical Engineering, Naturvetarvägen 14, 221 00 Lund, Sweden*

² *COWI Norway,*

Abstract: Direct membrane filtration (DMF) is a relative new concept for treating municipal wastewater with membranes. In contrast to the widely accepted membrane bioreactor (MBR) concept which combines membrane filtration with aerobic or anaerobic biology, the DMF is independent of biology, which leads to a reduced energy and space consumption.

In this presentation, the results from two Scandinavian pilot studies of DMF are presented and compared. The first installation is in Lund (Sweden), while the second installation is in Fredrikstad (Norway). Both installations are equipped with 0.2 µm polyvinylidene difluoride (PVDF) microfiltration membranes in flat sheet configuration (Alfa Laval, Denmark). In both cases precipitation with coagulant and polymer in combination with pre-filtration using a micro-screening (100 µm) is applied as pre-treatment to ensure a stable operation of the DMF unit. Furthermore, while the installation in Fredrikstad is one of the largest DMF installation in the world, the installation in Lund consisted of a forward osmosis unit using seawater for further polishing of the DMF permeate before discharge to demonstrate that the DMF concept has the potential to match current and future discharge limits for municipal wastewater.

The outcome of the studies demonstrated that the DMF concept can achieve very high rejection rates of carbon (COD, SS) and total phosphorus. Additionally, the increased rejection of high carbon rejection can result in a higher biogas production which brings the concept closer to an energy neutral or even energy plus municipal wastewater treatment plant.

In general, DMF is a very compact and low energy municipal wastewater treatment technology, which could be of particular interest for the upgrade of wastewater treatment plants in areas with a high population.

PARTIAL DESALINATION OF SALINE GROUNDWATER BY PRESSURE DRIVEN AND ELECTROCHEMICAL TECHNOLOGIES

H. Rosentreter¹, M. Walther^{2,3}, A. Lerch¹

¹ Chair of Process Engineering in Hydro Systems, Technische Universität Dresden, 01062 Dresden, Germany (hanna.rosentreter@tu-dresden.de, www.tu-dresden.de/bu/umwelt/hydro/isi/hvt)

² Department of Environmental Informatics, Helmholtz-Centre for Environmental Research GmbH – UFZ Leipzig, 04318 Leipzig, Germany

³ Chair of Contaminant Hydrology, Technische Universität Dresden, 01062 Dresden, Germany

Abstract: Coastal aquifers are often characterized by a high salt concentration resulting from natural salt deposits or saltwater intrusion processes [1]. Saline groundwater usually consists of high monovalent ion concentrations as sodium and chloride as well as high divalent ion concentrations as calcium and sulfate. In general, the concentrations of sodium, chloride and sulfate in saline groundwater exceed the recommended concentrations for drinking water or irrigation guidelines. Since the treatment of saline groundwater is more expensive than for fresh groundwater, saline groundwater is seldom used for domestic, agriculture or industrial use.

Usually, thermal driven, pressure driven or electrochemical desalination technologies are the chosen standard processes used for desalination of seawater and saline groundwater [2]. However, a total demineralization of saline groundwater is depending on the use and is often not necessary. Especially for managed aquifer recharge, demineralized water for injection may not be required. In our study, the suitability of nanofiltration (NF), brackish water reverse osmosis (BWRO), seawater reverse osmosis (SWRO) and membrane capacitive deionization (MCDI) for partial desalination of saline groundwater was examined. Therefore, partial desalination of slightly saline groundwater, moderately saline groundwater and very highly saline groundwater was investigated by experiments and simulations in order to comply with the thresholds for freshwater, irrigation and drinking water guidelines. Moreover, the operating and capital expenses of the presented desalination scenarios were calculated.

Especially NF and MCDI are both energy efficient desalination technologies for partial desalination, whereby the preference for one of these desalination technologies depends on the composition and temperature of saline groundwater.

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PROTOTYPE OF HOLLOW FIBRE MEMBRANE MODULE FOR DIFFUSION DIALYSIS

M. Bobák¹, D. Malý¹, M. Kout¹

¹ MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic (marek.bobak@membrain.cz, www.membrain.cz)

Abstract: Our objective was to develop a prototype of the industrial diffusion dialysis membrane module for regeneration of acids from spent pickling baths. High-alloy steels are usually pickled in mixtures of HNO₃ and HF. The waste pickling bath contains more than half of the original, unreacted acids, which can be separated and returned to the pickling bath by diffusion dialysis process. Thus the composition of the bath is maintained and the pickling performance is stable. Moreover the recycling saves the fresh acids and reduces the production of the waste.

The first part of the development focused on the new type of ion-exchange membrane (IM) in the form of hollow fiber. We have found optimal IM composition in terms of the binder and anion-exchange resin. The process of the hollow fiber production was optimized in order to achieve required productivity and quality (ion-exchange capacity, swelling, chemical and mechanical resistance). Membrane was tested using both model solutions and real spent pickling solutions. Selected membrane has the yield of the free acids up to 90 % and the rejection of the Fe ions was above 80 %. Those results were achieved by lab-scale membrane modules with flow-rates of 200 ml/h.

The next stage of the development was the scale-up of the membrane module. Our target flow-rate range was 6 – 12 l/h. We designed the module including the procedure of hollow fiber potting and optimization of potting material. The final outer diameter of the module prototype is 110 mm. This dimension was identified as maximal due to prevent possible defects caused by swelling of potting materials in aggressive environment of the working solutions.

The performance of the membrane module prototype was tested on the pilot unit processing real spent pickling bath. Industrial scale module achieved the yield of free acids 70 % and metal (Fe) rejection of 75 %. Although these values are somewhat lower than in the lab-scale experiment, it is still a very good result for practical application.

SPIRAL MEMBRANE MODULES FOR RECOVERY OF ACIDS AND METAL USING DIFFUSION DIALYSIS

B. Spasova¹, T. Weimer¹, L. Šeda², L. Čopák²

¹ *Spiraltec GmbH, Heinzenberger Weg 34, 74343 Sachsenheim, Germany*
(bspasova@spiraltecgmbh.de, www.spiraltecgmbh.de)

² *Membrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic*

Abstract: Industrial activities contribute to Europe’s economic growth and provide employment. But they also have a significant impact on the environment. In waste management recycling loops lead to reduction as well in waste and raw material demand.

In many different chemical processes acid solutions are used which must be partially or completely replaced with significant amounts of free acid. Such purge solutions must be neutralized. An alternative to decrease salt content in the waste water and to reduce acid demand is the recovery of free acid from the purge by using diffusion dialysis (DD). The process using Spiral Membrane Modules (SMM) for acid and/or metal recovery is presented in Fig. 1.

In this work an innovative and economic Spiral Membrane Modules (SMM) for diffusion dialysis in countercurrent flow regime for acid recovery is presented. This technology was evaluated for three different industrially sectors: (i) surface treatment (anodizing baths), (ii) printed circuit board (PCB) and (iii) glass fiber.

In comparison with the “state-of-the-art” technology SMM achieves a higher acid recovery up to 95 %, metal retention up to 95 % and shows a significant reduction of volume waste water. In addition, metal recovery is feasible from a low acidic waste water. Therefore, this optimized diffusion dialysis with SMM can be extended to zero-liquid discharge (ZLD) processes in many applications.

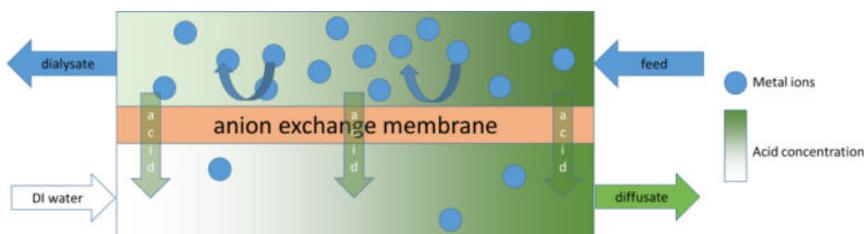


Fig. 1. Working principles of diffusion dialysis (DD) in Spiral Membrane Modules (SMM).

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NANOFILTRATION CONSIDERED AS REPLACEMENT OF DIALYSES IN THE SODIUM HYDROXIDE RECOVERY FROM VISCOSE STEEPING LYE

K. Schlackl¹, R. Herchl², K. Fackler², W. Samhaber³

¹ Kompetenzzentrum Holz GmbH, Altenberger Straße 69, A-4040 Linz, Austria
(k.schlackl@wood-kplus.at)

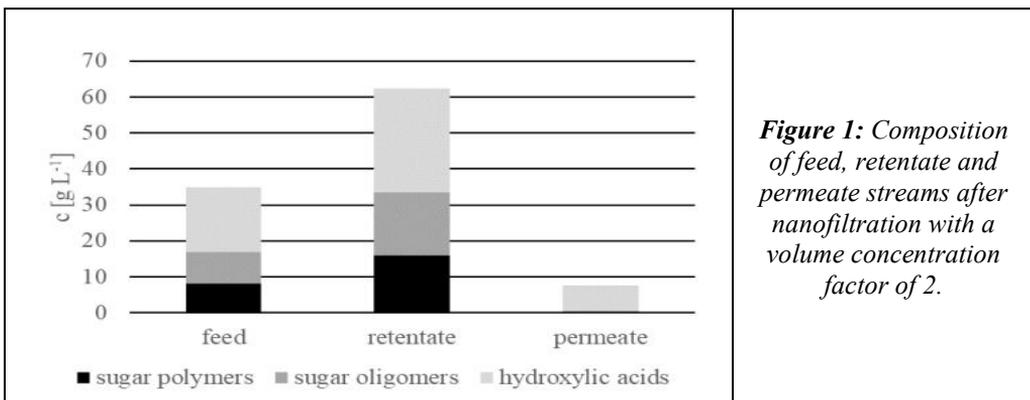
² Lenzing AG, Werkstraße 1, A-4860 Lenzing, Austria

³ Institute of Process Engineering, Johannes Kepler University Linz, Altenberger Straße 69, A-4040 Linz, Austria

Abstract: Highly concentrated sodium hydroxide solutions are used in several process steps during the production of wood-based cellulose fibers, therefore its recovery is important for economical and ecological reasons. Recovery means cleaning the sodium hydroxide solution from wood degradation products like sugar oligomers and polymers as well as from more degraded components like hydroxylic acids. The purification is usually be done via dialysis process in which treated vellum is used as membrane. Replacing the dialysis process with a pressure driven membrane process would increase process efficiency, since the recycled hydroxide solution is not diluted and can be reused more versatile.

Different commercial and highly caustic stable polymeric nano- and ultrafiltration membranes were tested in lab-scale. Different streams from the industrial steeping process as well as mixtures of model compounds were used as feed.

The retention behavior of the membranes was examined with regard to different component classes such as polymer sugar, sugar oligomers and hydroxylic acids with different chain lengths. In addition, the interactions of highly-retained sugar polymers with oligomers and hydroxyl acids were examined in more detail. The formation of secondary filtration layers was studied using different polymeric ultrafiltration membranes with a molecular weight cut off in the range from 1,000 to 50,000 g mol⁻¹. The sodium hydroxide concentration was varied from 2 to 5 mol L⁻¹



AN INTEGRATED APPROACH FOR HCL AND METALS RECOVERY FROM WASTE PICKLING SOLUTIONS: PILOT PLANT DESIGN AND OPERATIONS

R. Gueccia¹, D. Winter², S. Randazzo¹, J. Koschikowski², A. T06 / SL32Cipollina¹, G. Micale¹.

¹ *Dipartimento di Ingegneria, Università di Palermo – Viale delle Scienze ed.6, 90128 Palermo, Italy (rosa.gueccia@unipa.it)*

² *Fraunhofer Institute for Solar Energy Systems ISE Heidenhofstraße 2, 79110 Freiburg, Germany*

Abstract: Pickling is one of the key steps in the hot-dip galvanizing process, where HCl solutions are largely used to remove metal oxides from metallic surfaces, thus generating spent waste liquors containing high concentrations of metals and acid. Disposal of the industrial pickling waste dramatically affects the hot-dip galvanizing industry economics and environmental footprint. Thus, reducing strong acid waste disposal is one of the most beneficial steps to enhance the process sustainability.

Moreover, the continuous regeneration of pickling solutions enhances pickling rate and process performance, also minimizing industrial wastewater disposal and chemicals consumption promoting the circular use of such raw materials.

In this work we propose the recovery and recycling process of valuable substances (e.g. acid, metals and aqueous streams) from pickling solutions by coupling two innovative cutting-edge membrane technologies: diffusion dialysis (DD)¹ and membrane distillation (MD)².

A pilot-scale unit was designed and build following extensive experimental and simulative campaigns carried out the ReWaCEM project³. The Demo system consists of a DD module, where HCl is recovered from the waste pickling acid solution, a MD module, where the recovered HCl is concentrated, and a reactive precipitation section, where Fe ions, exiting with the metals-rich retentate brine from the diffusion dialysis, is recovered as iron hydroxide. In this latter stage, also an ammonium hydroxide/zinc chloride solution is produced, to be reused in the fluxing bath of the hot-dip galvanizing plant.

The fully-automatized pilot unit is able to operate in continuous, guaranteeing the operation at the optimal pickling conditions in terms of HCl and Fe concentration. Moreover, the use of waste heat (for MD operation) further contributes to enhance process sustainability.

The main results of the on-site pilot plant operation are presented. Several experiments were carried out to assess the system operability and the feasibility of fully reducing spent pickling solution disposal and recovering valuable materials. Results have shown that high recovery of acid (80%) can be achieved in the Diffusion Dialysis unit since the presence of iron ions in solution further increases

acid recovery, although significant Zn leakage occurs through the membrane. On the other side, the performance of MD is good when operating in the lower range of metals concentration, while it suffers when metal salts are present in large quantities (due to poorer rejection in the DD unit) due to the lower water vapor pressure. On the basis of this first pilot campaign an optimized configuration for the system has been developed and will be tested in the next months.

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NUCLEATION AND GROWTH OF NANOCRYSTALS ON PVDF SURFACES

E. Tocci¹, M. L. Perrotta¹, F. Macedonio¹, A.G. Bruno², W. Jin³, Z. Cui⁴, E. Drioli^{1,4}

¹ *Institute on Membrane Technology, CNR-ITM, Via P. Bucci 17/C, 87036 Rende (CS), Italy (e.tocci@itm.cnr.it, www.itm.cnr.it)*

² *Dept. of Physics and Astronomy, University of Leicester, Leicester, UK*

³ *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China*

⁴ *Engineering Research Center for Special Separation Membrane, Nanjing Tech University, Nanjing, 210009, China*

Abstract: Membrane assisted crystallization (MCR) is a well-known technology where microporous hydrophobic membranes are used to promote the water vapor transfer between phases inducing supersaturation in solution¹. Membrane crystallization is an efficient process for production, purification and/or recovery of solid materials with interesting advantages in comparison to traditional crystallization techniques, such as well-controlled nucleation and growth kinetics and fast crystallization rates and reduced induction time². It is generally difficult to monitor the growth mechanisms of crystals formation however, molecular modelling helps to investigate the mechanism of nucleation and crystals growth^{3,4}.

Our contribution was aimed at analyzing the crystal nucleation and growth of sodium chloride in contact with hydrophobic polyvinylidene fluoride (PVDF) surfaces (amorphous together with α and β phases) at a supersaturated concentration of salt.

The results show that salt nucleation is faster with amorphous PVDF model than α and β PVDF. Molecular models confirm the highly efficient packing of the α and β polymer chains, in comparison to the amorphous one resulting in greater diffusion of water molecules

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ANALYTICAL APPROXIMATION OF THE HYDRODYNAMIC PERMEABILITY FOR GLOBULAR MEMBRANES

D. Khanukaeva

Department of Higher Mathematics, Gubkin Russian State University of oil and gas, Leninskiy Avenue, 65-1, Moscow, Russia

Abstract: The membrane hydrodynamic permeability is a characteristic which can be both measured in an experiment and calculated theoretically. Being a macro characteristic the hydrodynamic permeability depends on micro properties of a membrane material and a permeate. So, it is important to understand how these parameters influence the hydrodynamic permeability.

The Happel and Brenner cell model technique is well developed and verified in the membrane flows simulations. Fibrous membranes are represented by cylindrical cells, globular membranes can be modeled by spherical cells. Each cell consists of a solid or porous or combined core and liquid shell. The flow problem is considered in a single cell, the influence of the surrounding cells being taken into account via the boundary conditions. The solutions of boundary value problems in the framework of a cell model are known and presented in analytical form for the cases of simple and composite cells in Newtonian and micropolar flows. They allow to obtain an analytical expression for the hydrodynamic permeability in an explicit form as a function of the membrane and permeate characteristics. Nevertheless, these expressions are so cumbersome that they are never given in any paper. It makes this result almost inapplicable for the engineering and experimental purposes.

The present work is devoted to the derivation of as simple as possible analytical approximation of the hydrodynamic permeability as a function of the membrane and permeate parameters. For the common solid-liquid cell model of a membrane the dependence is found as a function of the membrane porosity. For a model of a degraded membrane with porous core of the cell the permeability of the porous medium is introduced in the dependence. For composite cells the fraction of porous material presents in the approximation. For the case of the micro structured liquids filtration, the dependence of the hydrodynamic permeability on the fluid characteristics is also taken into account in the approximation.

All of the formulas are presented in the most simple explicit analytical form, suitable for direct calculations. The approximation is obtained in the least squares sense.

The work is supported by the RFBR (grant N 19-08-00058).

THE CELL MODEL OF ION-EXCHANGE MEMBRANE

A. N. Filippov

Department of Higher Mathematics, Gubkin University, Leninskii prospect 65-1, Moscow, 119991, Russia (a.filippov@mtu-net.ru, <http://kvm.gubkin.ru/filippov.html>)

Abstract: In this work, we applied the developed cell model^{1,2} to the characterization of perfluorinated cation-exchange MF-4SC membranes made by cast in the pristine (pure) state, as well as their samples modified with halloysite nanotubes, functionalized with Pt or Fe nanoparticles³ and placed in HCl solution of different concentrations. Due to the cell method, a membrane is considered as an ordered assemblage of porous charged particles of spherical shape, placed in spherical shells filled with electrolyte solution. Theoretical study is conducted within the framework of irreversible thermodynamics on the base of Onsager's approach and the result is calculation of electrokinetic coefficients. Experimental dependences of electroosmotic permeability, electrical conductivity and diffusion permeability of all mentioned membranes on electrolyte concentration were simultaneously and quantitatively described using exact analytical formulas based on same set of physicochemical and geometrical parameters, like coefficients of distribution and of ion diffusion in a bulk solution and in a membrane itself, porosity, exchange capacity and specific hydrodynamic permeability of an ionite grain (gel). Based on the least squares method and specially developed linked optimization procedure, the physicochemical and geometrical parameters of the cell model were found, which allowed acceptably describing the available experimental results. These parameters give an opportunity to evaluate their changes during the modification process from the unified theoretical point and predict transport properties of new membranes. The cell model was also successfully tested using experimental data on the electrical conductivity and electroosmotic permeability of the extrusion MF-4SC membrane at given current density and concentration of the 1 : 1 electrolytes HCl, NaCl, KCl, LiCl, and CsCl⁴.

The possibility of calculating the electroosmotic flux of water/water transport numbers using finite algebraic formulas derived here with parameters that have a clear physical meaning is important not only in electromembrane processes (i.e. fuel cells, sensors, electrolyzers etc.), but also in calculations of electroosmotic pumps in microfluidics, in determination of water content in food products during their long-term storage, and analysis of reduction of fluid transport through concrete, since excessive moisture leads to corrosion of metal reinforcement and premature degradation of concrete.

This study was financially supported by RFBR (project No. 20-08-00661).

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ASSESSMENT OF THE POTENTIAL OF MEMBRANE TECHNOLOGY TO REDUCE CO₂ EMISSIONS IN THE STEEL INDUSTRY

M. Sarić¹, J. W. Dijkstra¹, Y. C. van Delft¹, E. de Coninck²

¹ TNO, The Netherlands

² Arcelor Mittal, Belgium

Introduction

The present work is related to the project aims at using advanced membrane technology for carbon dioxide (CO₂) emission reduction in the steel and cement industry. In this work potential of two types of membrane separation technologies: IPOSS (interfacial polymerization polyhedral oligomeric silsesquioxane) membranes for H₂ separation, and MOF (Metal Organic Framework) membranes for CO₂ separation in the steel industry is quantified. Two concepts presented in the Figure1 evaluating CO₂ emission reduction by re-using residual steel gases by means of CO₂ or H₂ separation were considered. In the first concept H₂ is separated from coke oven gas by IPOSS membrane. Separated hydrogen is used in heat production or exported e.g. for methanol production. The CO₂ rich retentate stream is used in the plasma torch to produce syngas that is recycled to the blast furnace. In the second concept, CO₂ after separation from a blast furnace gas by MOF membrane is sent to the plasma torch, while the retentate CO stream is used for either heat of Fischer Tropsch-based fuel production.

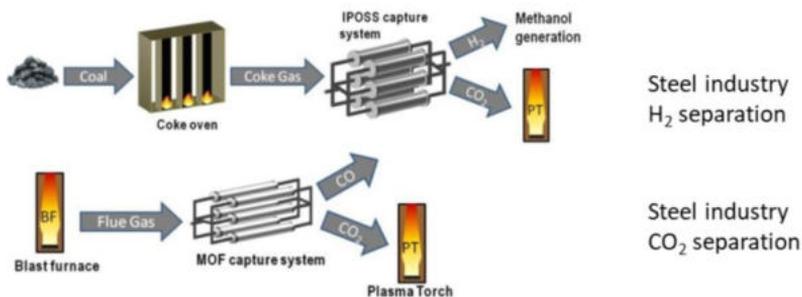


Figure1. Concepts considered in study

Methodology

Key Performance Indicators (KPI's) were defined to compare membrane with the reference technology. As a reference technology for hydrogen separation Pressure Swing Absorption is used, and for CO₂ separation CO₂ capture in Mono Ethanol Amine solution was used. The most important KPI is SPECCA (The Specific Primary Energy Consumption for CO₂ Avoided). In addition, a cost estimate for the CO₂ capture was used for the assessment and benchmarking. To account for the uncertainty in membrane costs a sensitivity analysis was performed.

Results and discussion

The presented membrane based processes were be simulated and optimized in the Aspen Plus simulation program. Integration with a steel mill was be done iteratively, as an impact of produced syngas from plasma torch on the blast furnace performance was calculated by a model developed by the steel industry. Once optimized, processes were be benchmarked against the reference plants. The results were also be compared to similar studies of membrane-based CO₂ capture processes.

Acknowledgment: The work presented was part of the Genesis project. This project has received funding from European Union's Horizon 2020 research and innovation programme under grant agreement No 760899.

SEPARTION OF SUCCINIC ACID: DONNAN-STERIC PARTITIONING-MODEL ON A SYNTHETIC AND REAL FERMENTATION BROTH

E. Mancini¹, P. Ramin¹, S. S. Mansouri¹, K. V. Gernaey¹, J. Luo^{2*}, M. Pinelo^{1**}

¹ *Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark;*

² *State Key Laboratory, Institute of Process Engineering, CAS, Beijing, China. * No. 1 North Second Street, Zhongguancun, Haidian District, 100190, Beijing, China. ** Søtofts Plads, Building 227, 2800 Kgs. Lyngby, Denmark.*

Abstract: The downstream of fermentation products, such as succinic acid (SA), accounts for about 60-70% of the total production costs. A key step in the downstream is the separation of succinic acid from other organic acids in the fermentation broth¹. To predict the separation performance of SA, both the membrane charge density and the properties of the solution to be filtered must be defined. We investigated the charge and steric hindrance phenomena in nanofiltration of organic acids for final separation of succinic acid from a synthetic fermentation broth. Repulsive forces between SA and the membrane are higher at pH 7.0 than at 2.2 for all four tested commercial nanofiltration (NF) membranes, increasing the rejection from 60 to more than 80% (up to 94% rejection with NF270 - Fig. 1A). However, the rejection difference between solution at pH 7.0 and 2.2 becomes very small for non-diluted SA solutions (10 times dilution - Fig. 1B), with a maximum of $15.5 \pm 2.2\%$ of SA rejection with NTR7450, indicating that the diffusion force becomes stronger than the repulsive forces between succinate and the membrane. Despite the low rejection, the filtration time increases dramatically for the concentrated broth, from less than 1h (pH 7 and 5 g L^{-1}) up to more than 8h (pH 7 and 50 g L^{-1}). An exception is NTR7450 for which, no filtration time difference was observed from the solutions. The obtained experimental results from a real and a synthetic fermentation broth are used to simulate SA separation via NF using the donnan-steric-partitioning model². The model is used to evaluate different mechanisms driving the NF namely, convection, diffusion and Electromigration, under various tested conditions.

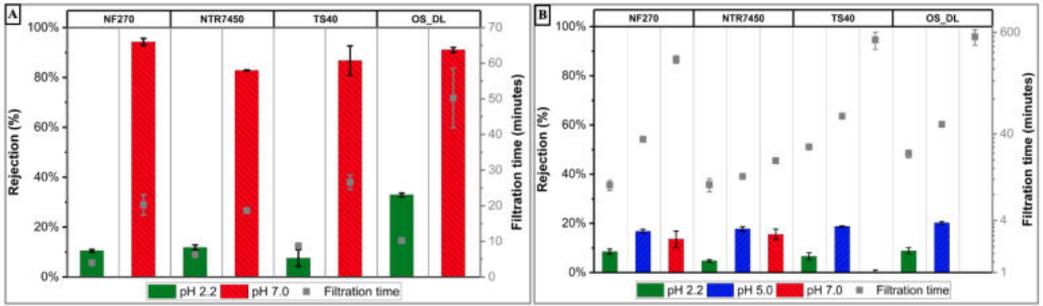


Figure 1. rejection (bars) and filtration time (dots) of [A] 5 g L⁻¹ SA solution and [B] 50 g L⁻¹.

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CAPILLARY FLOW INSIDE THE MEMBRANE PORE: TRACKING THE INTERFACE

H. Chamani, T. Matsuura, D. Rana, C. Lan.

Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur Private, Ottawa, Ontario K1N 6N5, Canada

Abstract: Replacement of liquid with gas and replacement of gas with liquid in membrane pores occur during membrane preparation and characterization processes. Bubble point method [1], porometry [2], liquid entry pressure (LEP) [1], etc. are some examples of this kind of flow inside the membrane pore. For instance, LEP, a parameter related to wetting characteristics of hydrophobic membranes, is defined as the minimum transmembrane pressure causing liquid feed to overcome the hydrophobic forces and enter the pores [3]. When liquid enters the pore, liquid replacement with air occurs. In most of the research conducted in this field [4-7], the focus was on transmembrane pressure required for the liquid entry into the pore. However, in this study, the movement of the liquid/gas interface was tracked and consequently the pressure and velocity at the interface and the required time for replacement were studied. The model was developed in accordance with the governing equations applicable for liquid and gas flows inside the membrane pore.

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A VALIDATED MULTI-SCALE MODEL OF A NOVEL ELECTRODIALYTIC ACID-BASE FLOW BATTERY

A. Culcasi, A. Zaffora, A. Cosenza, M. Di Liberto, L. Gurreri,
A. Tamburini, A. Cipollina, G. Micale

Dipartimento di Ingegneria, Università degli Studi di Palermo (UNIPA) - viale delle Scienze Ed.6, 90128 Palermo, Italy (luigi.gurreri@unipa.it)

Abstract: Electrical energy storage is crucial for a deeper penetration of intermittent renewable energies, e.g. solar and wind. The Acid/Base Flow Battery (AB-FB) is a novel, sustainable, environmental-friendly storage technology with high energy density¹. The process is based on reversible electrochemical techniques that convert the electrical energy in the chemical energy associated to pH gradients and *vice versa*. The bipolar membrane electrochemical process operates in the charge phase, while the bipolar membrane reverse electrochemical in the discharge phase. The stack consists of repetitive units, called triplets, made up of an anion-exchange membrane, a bipolar membrane, and a cation-exchange membrane, separated by spacers forming the channels where the acid, base and salt solutions flow.

This work presents for the first time an experimentally validated AB-FB process model along with a sensitivity analysis. The model is based on a multi-scale simulation strategy, where four different dimensional scales are integrated within a comprehensive simulation tool with distributed parameters. The lowest hierarchical level concerns the channels. It includes CFD simulations for the estimation of polarization phenomena and pressure losses, and the correlations for the physical properties of the solutions. The middle-low hierarchical level simulates the triplets, by computing mass balances, membrane fluxes, electrical resistance and electromotive force. The middle-high scale simulates the stack by an electrical sub-model intended to compute the shunt currents, and by a hydraulic sub-model to calculate pressure losses. Finally, the highest hierarchical level simulates the external hydraulic circuit including dynamic mass balances in the tanks.

The model was validated against an original experimental campaign, showing a good agreement. A broad sensitivity analysis was performed in order to explore the behavior of the battery under several scenarios. The model outcome illustrates how stack geometry, operating parameters and battery layouts (e.g. open-loop vs closed-loop operations) can affect the process performance. By adopting some measures to tackle the shunt currents and taking thermodynamic advantages from open-loop operations, the round trip efficiency reached values up to 70%. This original model will orient the identification of optimized and competitive AB-FB systems.

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MODELLING AND EXPERIMENTAL INVESTIGATION OF A NOVEL ION EXCHANGE MEMBRANE CRYSTALLIZER FOR MAGNESIUM RECOVERY

D. La Corte¹, C. Morgante¹, F. Vassallo¹, G. Battaglia¹, A. Cipollina¹, M. Micari², A. Tamburini^{1,3}, G. Micale¹

¹ *Dipartimento di Ingegneria, Università di Palermo – Viale delle Scienze ed.8, 90128 Palermo, Italy*

² *German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*

³ *ResourSEAs SrL, viale delle Scienze Ed.16, 90128 Palermo, Italy*

Abstract: The selective transport properties of ion exchange membrane has recently raised a significant interest towards the development of processes here a selective passage of ions between solutions can be the key of success for the obtainment of a desired product. Within this context, reactive crystallisation processes often require the addition of ionic species into a reacting environment, yet limiting as much as possible the direct mixing of feed solutions.

On the basis of the above idea, a novel ion exchange membrane crystallizer (CrIEM¹) was developed for the valorisation of saline natural or industrial waste streams by means of magnesium and other valuable minerals recovery.

In particular, in a CrIEM reactor, the presence of an Anion Exchange Membrane, separating a brine and an alkaline solutions, allows the passage of hydroxyl ions from the alkaline to the brine compartment, where crystallization of magnesium hydroxide occurs, yet avoiding a direct mixing between the solutions feeding the reactor. This enables the use of low-cost reactants (e.g. Ca(OH)₂) without the risk of co-precipitation of by-products and contamination of the final crystals.

An experimental campaign was carried out treating two types of feed solutions, namely: 1) Mediterranean seawater, collected from North Sicilian coast (Italy), and 2) a waste industrial brine from the Bolesław Śmiały coal mine in Łaziska Górne (Poland). The Mg²⁺ concentration in the feed solutions ranges from 0.7 to 3.1 g/L. The CrIEM was tested in two configurations: batch and feed & bleed.

Interestingly, a magnesium hydroxide purity between 95 and 99% can be obtained, while the anionic membrane has not suffered performance drops throughout the 80 hours of operation. Furthermore, a mathematical model was purposely developed to simulate the performance of the crystallizer, based on the Donnan Dialysis equilibrium and transport mechanism. The model was implemented using Python and numerical simulations of the experimental runs were successfully carried-out, thus providing a good validation of the modelling tool.

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ENHANCEMENT OF ELECTRODIALYSIS USING PULSE ELECTRIC FIELDS

V.V. Nikonenko¹, M.K. Urtenov¹, A.V. Kovalenko¹, S.A. Mareev¹,
D.Y. Butylskii¹, S. Mikhaylin², L. Bazinet²

¹ Membrane Institute, Kuban State University, 149 Stavropolskaya st., Krasnodar, Russia
(v_nikonenko@mail.ru, www.kubsu.ru)

² Institute of Nutrition and Functional Foods (INAF), Dairy Research Center (STELA),
Laboratory of Food Processing and Electro-Membrane Processes (LTAPEM), Food
Science Department, Université Laval, Québec, QC, Canada

Abstract: During last twenty year, there are more and more evidences in the literature about the positive effect of pulsed electric fields (PEF) on the performance of electrodialysis (ED). It was established that this ED mode allows mitigation of membrane fouling and scaling, it increases the mass transfer rate and reduces the undesirable water splitting. Moreover, PEF improve specific permselectivity, i.e. the selectivity in the transfer of certain specific ions compared to the transfer of other ions with the same sign of charge. Understanding of the mechanisms behind the above effects is still not sufficiently clear. However, there is no doubt about the crucial role of electroconvection (Fig.). There is a certain interplay between the kinetics of the formation of concentration profiles and the effect of enhanced electroconvection affected by PEF. Our contribution is aimed at reviewing the known experimental results on mass transfer, fouling, water splitting and specific permselectivity in ED, as well as at an analysis of the mechanisms of the observed effects. We believe that a better understanding of these effects will contribute to a faster transition of the PEF mode ED from laboratory scale to industrial scale.

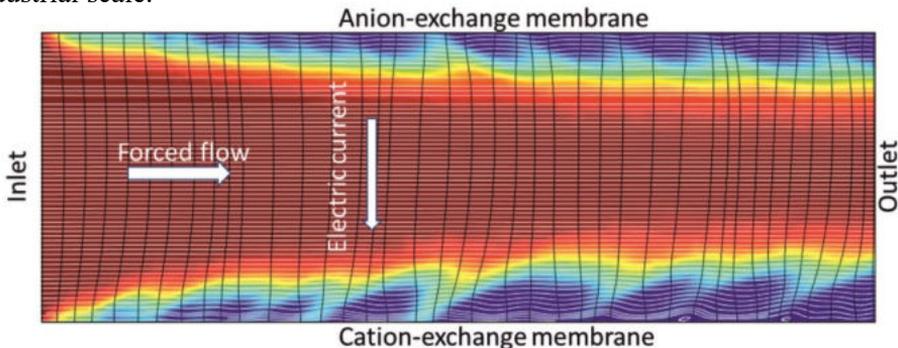


Fig. Distribution of salt concentration (shown with different colors), electric current (black lines) and fluid velocity streamlines (white lines) in an ED desalination compartment of length $L=4$ mm and intermembrane space $h=1$ mm. Electroconvective vortices appearing 0.01 s after reapplying a voltage of 2 V following a pause of 0.5 s.

We are grateful to Russian Foundation for Basic Research (project #20-58-12018) and NSERC, Canada (Grant IRCPJ 492889-15 to Laurent Bazinet) for financial support.

HYBRID MATERIALS BASED ON NAFION AND ELECTRICALLY CONDUCTIVE POLYMERS FOR DETERMINATION OF DRUGS IN PHARMACEUTICALS

T. Titova¹, P. Yurova¹, T. Kolganova², G. Z. Habtemariam²,
A. Parshina², I. Stenina¹, O. Bobreshova², A. Yaroslavtsev¹

¹ Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia
(titova_tatyana@mail.ru)

² Voronezh State University, Voronezh, Russia

Introduction. Nowadays the use of hybrid materials in electrochemical sensors for drugs determination is increasing [1]. Previously the possibility of using Nafion-type membranes with inorganic nanoparticles in multisensor systems to determine various analytes was shown [2]. Conducting polymers such as poly-3,4-ethylenedioxythiophene (PEDOT) also attract researchers' attention as dopants do [3]. The purpose of this work is to develop systems of potentiometric cross-sensitive DP-sensors (DP – Donnan potential) based on Nafion/PEDOT hybrid materials for determination of procaine, lidocaine and bupivacaine cations in aqueous solutions and pharmaceuticals.

Experiments. Nafion/PEDOT materials are synthesized by *in situ* oxidative polymerization. The membranes are sequentially kept in solutions of an oxidizing agent and then in a monomer. The initial monomer concentrations (0.01 and 0.002 M) and the ratio of monomer to oxidizer concentrations (1/1.25 and 1/2.5) are varied. The characteristics of DP-sensors are determined in solutions of procaine, lidocaine, bupivacaine hydrochlorides, HCl and NaCl ($1.0 \cdot 10^{-4}$ - $1.0 \cdot 10^{-2}$ M) and in pharmaceutical solutions.

Results and Discussion. The relationship between the equilibrium and transport properties of Nafion/PEDOT materials and the characteristics of DP-sensors in polyionic solutions of anesthetics and inorganic electrolytes is revealed. Membrane compositions are selected in such a way in order to provide an increase in the anesthetics' determination accuracy and reproducibility in aqueous solutions and pharmaceuticals. With the use of a DP-sensor based on the Nafion/PEDOT membrane (0.002 M, 1/2.5) the relative error in the active substance determination in the "Novocain" preparations is 0.4%. An array of DP-sensors based on Nafion and Nafion/PEDOT membranes (0.002 M, 1/1.25) is used to determine bupivacaine hydrochloride and sodium chloride in the "Markain® Spinal" preparations with an error of 11 and 6%, respectively. The stability of characteristics in time, the analysis without the use of reagents and with a relatively low dilution of the drug, as well as ease of analysis are advantages of the proposed sensor systems for the analysis of pharmaceuticals.

The reported study was funded by RFBR, project number 19-38-60045.

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SELECTIVE EXTRACTION OF SINGLY CHARGED IONS USING A NEW METHOD OF ELECTROBAROMEMBRANE SEPARATION

D.Y. Butylskii¹, V. Ignatenko¹, S.A. Mareev¹, A. Kisly¹,
N.D. Pismenskaya¹, P.Y. Apel², V.V. Nikonenko¹

¹ Membrane Institute, Kuban State University, 149 Stavropolskaya st., Krasnodar, Russia
(dmitrybutylsky@mail.ru, www.kubsu.ru)

² Joint Institute for Nuclear Research, 6 Joliot-Curie St., Dubna, Moscow region, Russia

Abstract: The electrobaromembrane separation method is a new step in the development of membrane processes. The separation of the ions of the same sign of charge occurs under the action of simultaneously applied gradients of electric potential and pressure across a membrane. The electric and mechanical forces are applied in the opposite directions. The separation is due to the different mobility of different ions.

We have successfully conducted preliminary experiments on the separation of K^+ and rhodamine ($Rh6G^+$) ions with a PET Hostaphan® track-etched membrane. When a voltage of 1V is applied across the membrane, it is sufficient to set the oppositely directed pressure gradient of 0.1 bar to stop the flow of $Rh6G^+$ ions (Fig).

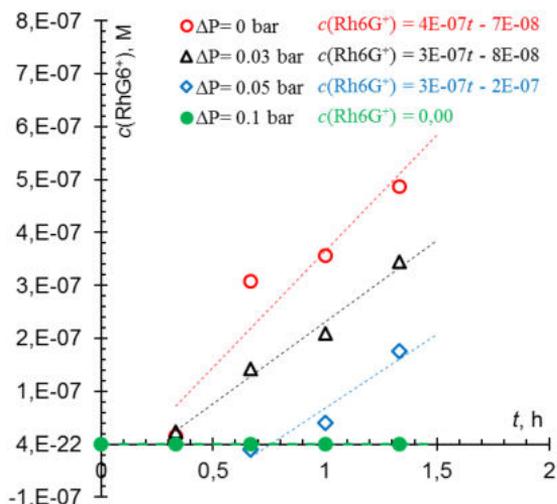


Fig. Kinetics of the increase in the concentration of $Rh6G^+$ in the concentration chamber at a voltage of 1 V and different pressure drops across a PET Hostaphan® membrane

We are grateful to Russian Science Foundation (project #19-19-00381) for financial support.

NEW APPROACH FOR THE IDENTIFICATION OF SUSPENDED SOLIDS INTERACTIONS DURING ORANGE JUICE MICROFILTRATION: RHEOLOGY AND PARTICLES SIZE FRACTIONATION

C. Demoulin¹, M. Delalonde², L. Dahdouh¹, J. Ricci¹, C. Wisniewski²

¹ CIRAD, UMR Qualisud, F-34398 Montpellier, France.

² Qualisud, Univ Montpellier, CIRAD, Montpellier SupAgro, Univ d'Avignon, Univ de La Réunion, Montpellier, France.

Abstract: Microfiltration is used during fruit processing to ensure the stabilization, concentration or clarification of fruit juices. However, the performance of this technique is greatly hampered by membrane fouling leading to significant decay of the filtration performance. The evaluation of the filtration performance is generally done through long and expensive pilot scale experiments. Indeed, few predicting tools are proposed to evaluate adequately fruit juices filterability and subsequently anticipate filtration performance. During microfiltration of fruit juices, suspended solids are concentrated in the membrane vicinity due to various interactions between juice particles and membrane surface. The interactions between juice suspended solids close to the membrane are not yet well identified and studied. New approaches have to be developed to provide new knowledge and tools to anticipate membrane fouling during fruit juices microfiltration.

The objective of this study was to propose a rheological approach for a better comprehension of the interactions between different size-classes of particles involved in membrane fouling during orange juice microfiltration.

Methodologies of fractioning and mixing specific size-classes of orange juice particles were proposed, notably by using a mixture design. Rheological measurements (oscillatory tests) were performed to evaluate the viscoelastic properties of the different size-classes of particles. Meanwhile, the fouling propensity of each size-class of particles was estimated through an original methodology. The fouling resistance of cakes containing particles with specific sizes was evaluated in pressurized filtration cell (25°C, 1.5 bar). To do so, mixtures of particles with specific sizes were used as fouling layers spread on an organic membrane (PES, pore diameter 0.1µm) to evaluate the fouling resistance of these layers (water fluxes).

Results showed that the particles network strength and juice viscoelastic behaviour are due to complex interactions between all juice particles. Moreover, interactions between different size-classes of particles had a significant role in the solid-like behaviour and the fouling resistance of suspended solids. For example, the presence of large particles enhanced the solid-like behaviour of suspended solids while reducing their fouling propensity. This knowledge could be useful in predicting and controlling membrane fouling during fruit juices microfiltration process.

NEW SPECIALTY MEMBRANE PRODUCTS FOR CHALLENGING INDUSTRIAL WASTEWATERS

C.R. Bartels, R.N. Franks

Hydranautics, Oceanside, CA USA

Abstract: Over the past 30-40 years, water reclamation from municipal wastewater has become a common practice and has greatly supplemented water supplies in water-stressed areas, such as southern California, Singapore, and the Middle East. Plants such as the 378 MLD Orange County Reclamation Facility have implemented ultrafiltration (UF), reverse osmosis, (RO) and ultra violet (UV) technologies to reclaim 80-85% of the water, having very high quality for industrial or indirect potable reuse. Reclamation of industrial wastewater has also been employed during this period, but has been limited to smaller systems, much more varied processes and treating very complex wastewaters. In addition, regional issues have forced some industries to fully reclaim their wastewater to achieve zero liquid discharge (ZLD). Recent issues regarding the disposal challenges for industrial wastewaters have put significant stress on these industries to find more economical treatment processes to comply with ZLD requirements.

Industrial wastes are often characterized as having high organic content that can come from solvents, oils, fats, greases, and other materials used or derived in industrial processing. These wastes can also have a variety of dissolved salts and metals, which make treatment difficult due to issues with scaling and osmotic pressure. Typical treatment processes utilize particle filtration technology, softening, RO, evaporation and crystallization to achieve ZLD; however, this can be a very complex treatment process and the evaporation and crystallization processes are very expensive. Also, the resulting solid waste will have a mixture of salts and may not be easily disposed in a landfill.

Through recent developments in fouling resistant membranes, these high organic content wastewaters can be treated with better stability. Another key development has been salt-selective nanofiltration membranes which can separate the salts into chloride rich and sulfate rich streams so that the resulting brine can be potentially reused. Finally, new ultra-high-pressure membranes have been developed which allow economical brine volume reductions and minimize the use of expensive evaporation processes. This paper will report on three case studies where newly developed membranes have been demonstrated in these processes. The results show that the low fouling membrane reduces flux decline by as much as 20%, compared to conventional polyamide membranes. The second case study shows how

extra selective NF membranes are used to concentrate sodium sulfate for reuse in a tannery waste, and finally, new extreme pressure RO membranes are demonstrated in textile waste treatment to reach TDS values as high as 146,000 mg/l.

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SPIRAL MEMBRANE MODULES FOR RECOVERY OF ACIDS AND METAL USING DIFFUSION DIALYSIS

B. Spasova¹, T. Weimer¹, L. Šeda², L. Čopák²

¹ *Spiraltec GmbH, Heinzenberger Weg 34, 74343 Sachsenheim, Germany*
(bspasova@spiraltecgmbh.de, www.spiraltecgmbh.de)

² *Membrain s.r.o, Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic*

Abstract: Industrial activities contribute to Europe’s economic growth and provide employment. But they also have a significant impact on the environment. In waste management recycling loops lead to reduction as well in waste and raw material demand.

In many different chemical processes acid solutions are used which must be partially or completely replaced with significant amounts of free acid. Such purge solutions must be neutralized. An alternative to decrease salt content in the waste water and to reduce acid demand is the recovery of free acid from the purge by using diffusion dialysis (DD). The process using Spiral Membrane Modules (SMM) for acid and/or metal recovery is presented in Fig. 1.

In this work an innovative and economic Spiral Membrane Modules (SMM) for diffusion dialysis in countercurrent flow regime for acid recovery is presented. This technology was evaluated for three different industrially sectors: (i) surface treatment (anodizing baths), (ii) printed circuit board (PCB) and (iii) glass fiber.

In comparison with the “state-of-the-art” technology SMM achieves a higher acid recovery up to 95 %, metal retention up to 95 % and shows a significant reduction of volume waste water. In addition, metal recovery is feasible from a low acidic waste water. Therefore, this optimized diffusion dialysis with SMM can be extended to zero-liquid discharge (ZLD) processes in many applications.

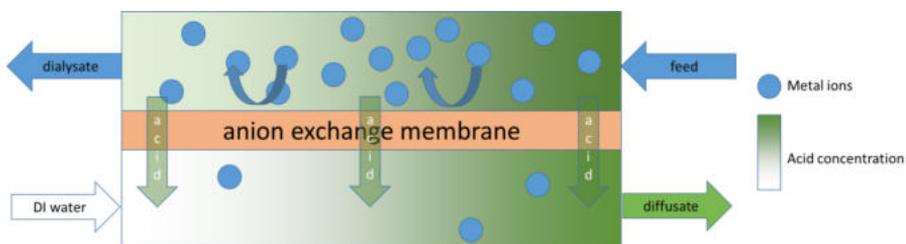


Fig. 1. Working principles of diffusion dialysis (DD) in Spiral Membrane Modules (SMM).

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THE NEW FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION HORIZON EUROPE

Petr Pracna

Technology Centre CAS, Prague, Czech Republic

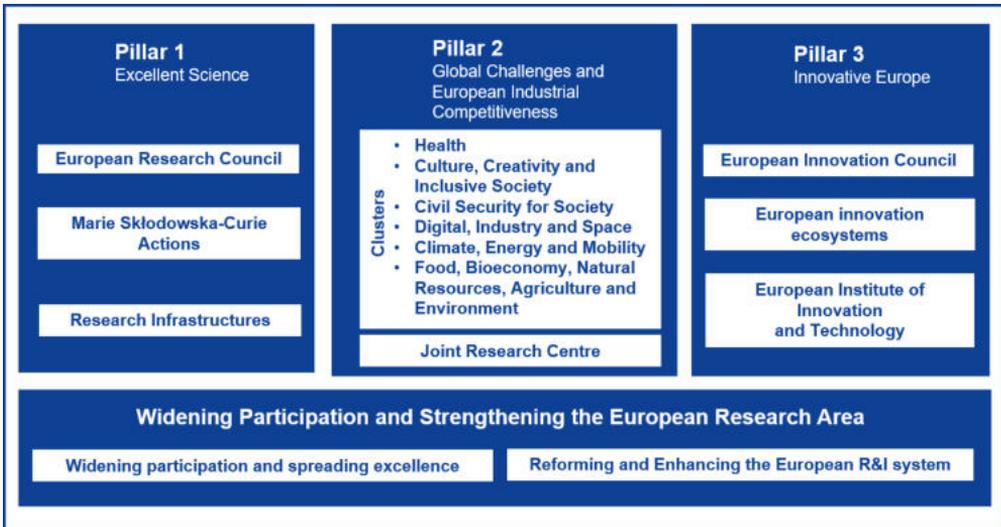
Horizon 2020, the EU Framework program (FP) for research and innovation, is in its final phase and preparations of the subsequent FP Horizon Europe for the period 2021-2027 are under way. The talk will present in brief the changing structure of the new FP and its three pillars – Excellent Science, Global Challenges and Industrial Competitiveness, and Innovative Europe.

Pillar I (Excellent Science) is the one that becomes changed the least. Its subprogrammes follow the structure of Horizon 2020, except the Future and Emerging Technologies programme which has already been moved as FET Pathfinder into the European Innovation Council (EIC) Pilot in H2020 for the period 2018-2020 and will remain its integral part in Horizon Europe. The other major part of the EIC pilot has incorporated the transformed SME Instrument programme as the EIC Accelerator.

Pillar II (Global Challenges and European Industrial Competitiveness) is a merge of programmes formerly constituting the Industrial Leadership and Societal Challenges pillars of H2020. It is tentatively divided into 6 clusters, as shown in the figure below, and incorporates further formally also the Joint Research Centre. The clusters of Pillar II will be interlinked through **Partnerships** which are intended to rationalize the European R& landscape by improving their openness and transparency. The other novelty of Pillar II is the concept of **Missions** which will relate EU's research and innovation to society and citizens' needs, with strong visibility and impact.

Pillar III (Innovative Europe) will have the EIC programme as its core together with the Knowledge and Innovation Communities (KICs) of the European Institute of Innovation and Technology (EIT) and support of the European innovation ecosystems.

The **Widening Participation and Strengthening the European Research Area** part of the new FP aims at optimizing the impact and attractiveness of the European Research Area and foster excellence-based participations from all Member States, including low-performing, and to facilitate collaborative links in European research and innovation.



The presentation will briefly outline the expected adoption timeline of the Horizon Europe work programme and describe in more detail the mobility part of Pillar I – the Marie Skłodowska-Curie Action.

POSTERS

POLYSEBS MEMBRANES BEARING MEGLUMINE AS A CHIRAL SELECTOR

M. Otmar¹, J. Gaálová², J. Žitka¹, L. Brožová¹, P. Cuřínová²,
M. Kohout³, Š. Hovorka⁴, P. Izák²

¹ Institute of Macromolecular Chemistry of the CAS, v.v.i., Heyrovského nám. 1888/2, 162 06 Prague 6, Czech Republic (otmar@imc.cas.cz)

² Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojová 135/1, 165 02 Prague, Czech Republic

³ Department of Organic Chemistry, University of Chemistry and Technology Prague, Technická 1905/5, 166 28 Prague, Czech Republic

⁴ Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 1905/5, 166 28 Prague, Czech Republic

Abstract: Preparation of chiral compounds remains a challenging task, despite a great progress in asymmetric syntheses and separation techniques. Nowadays, there is a strong tendency to use enantiomerically pure drugs to reduce the burden of the other ineffective or even harmful enantiomer in the patient's organs¹. Therefore, many chiral drugs have been reformulated as single enantiomers. During more than a half century of development, a number of industrial techniques were established for the separation of pure enantiomers. Their drawback is, however, a high financial cost. To the contrary, enantioseparation using polymer membranes seems to be a promising technique combining an acceptable effectivity and a relatively low cost².

Recently, we prepared polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (polySEBS) membranes bearing covalently anchored (*S*)-(-)- α -methylbenzylamine as a chiral selector. In preferential sorption experiments these membranes exhibited a higher affinity to *L*-tryptophan and (*R*)-(-)-ibuprofen than to their enantiomeric counterparts³. Motivated by these results, we were interested if another covalently anchored chiral selector on the polySEBS membrane can cause a similar enantiomeric enhancement of a racemic analyte. Therefore, we chose *N*-methyl-*D*-glutamine (meglumine) as an alternative chiral selector and prepared a chiral functionalized polySEBS membrane in analogy with the previous. In preferential sorption experiments the meglumine membrane also exhibited a higher affinity to *L*-tryptophan than to *D*-tryptophan as that in the previous case. These results indicate that the polySEBS membranes bearing chiral selectors are worth to further study.

Acknowledgement: The authors gratefully acknowledge Czech Science Foundation, Grant No. 20-06264S, for financial support.

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MODIFIED NANOFIBER MEMBRANE FOR CLEANING OF OILY WASTEWATER

F. Yalcinkaya¹, A. Siekierka², J. Hruza¹, J. Maryska¹, M. Bryjak²

¹ Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Studentska 1402/2, 46117 Liberec, Czech Republic (fatma.yalcinkaya@tul.cz)

² Faculty of Chemistry, Wrocław University of Science and Technology, 27 Wybrzeże Stanisława Wyspińskiego, 50-370 Wrocław, Poland

Abstract: Nanofiber technology has gained huge interest in various industrial applications recently due to its high specific surface area, porous structure, interconnected nanoscale pore size, pore size distribution, and chances for alteration of surface properties. Fiber-based membranes can provide advantages for the separation of oily wastewater. Nevertheless nanofibers unique properties; there is no real industrial application for the oil/water separation systems. The main reason is the low mechanical properties of nanofibers. Another reason is low wettability because of the polymeric structure. Herein, we focus on these two problems. First, the mechanical strength of the nanofiber membranes was improved using a special lamination method. Second, the surface of the various polymeric membranes was modified to improve membrane wettability. Polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and polyamide 6 (PA6) nanofibers was selected for the membrane preparation. A two-step modification was done using Ar plasma treatment and methacrylic acid (MAA) grafting, respectively. According to results, modification significantly improved membrane permeability as shown in Figure 1. Moreover, the membranes showed hydrophilic and oleophobic properties after modification.

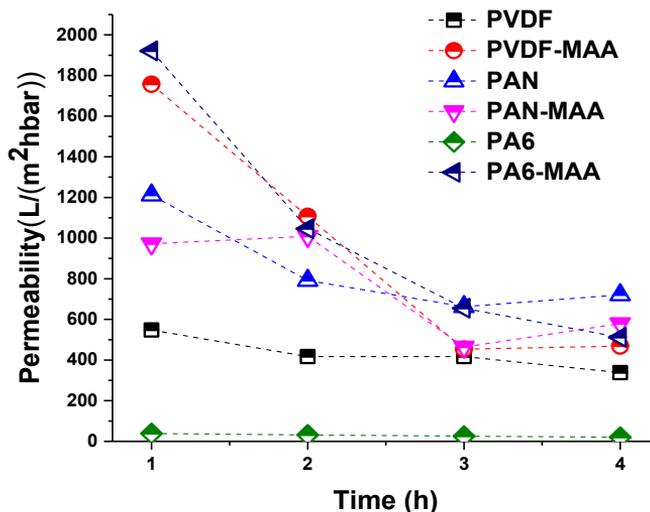


Figure 1. Permeability of modified and un-modified nanofiber webs in time

IONS DISTRIBUTION INSIDE ANION EXCHANGE MEMBRANES FROM DFT AND MD SIMULATIONS

J. Luque Di Salvo¹, G. De Luca², A. Cipollina¹, G. Micale¹

¹ *Dipartimento di Ingegneria (DI), Università degli Studi di Palermo– viale delle Scienze Ed.6, 90128 Palermo (PA), Italy.*

² *Institute on Membrane Technology, ITM-CNR, Via P. Bucci 17/C, 87036 Rende (CS), Italy.*

Abstract: The effect of the water uptake (W_U) and Ion Exchange Capacity (IEC) on the hydroxyl diffusion in polysulfone-tetramethylammonium (PSU-TMA) anion exchange membranes was studied through combined *ab-initio* calculations, in the framework of Density Functional Theory (DFT), and Molecular Dynamics (MD) simulations¹. The following results were highlighted: (1) The W_U computed from DFT modelling was in good agreement with experimental data up to when membrane swelling is observed; (2) OH^- diffusion coefficients (D) increased nonlinearly with increasing IEC; (3) the computed D values, calculated either by MD simulations or by analytical obstruction models, showed a very similar trend. Based on these encouraging results¹ this DFT/MD combined approach¹ was then used to study the ions distribution inside hydrated PSU-TMA membranes counter-balanced with chloride ions. In particular, an analysis based on the N-Cl distances through the MD trajectories (Figure 1) was performed. The results showed that, on average, the fraction of Cl^- counter-ions not condensed to the fixed charge groups (α) was higher as IEC decreased, in good agreement with experimental data². These findings provide important insights on the crucial effect of water on the interacting forces that affect molecular diffusion³, since considering ion-pair association as the only factor that slows down diffusion is not enough to explain the opposite behaviour of low D at low IEC, high α at low IEC. Thus, water adsorption and its distribution inside the membrane are the main factors affecting diffusion.

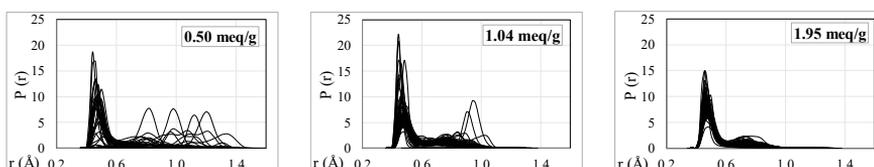


Figure 1. Probability distribution curves of the minimum Nitrogen – Chloride distances accumulated through the 100 ns NVT trajectories for each single Cl^- counter-ion.

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GAS SEPARATION PROPERTIES AND FREE VOLUME OF PIM-1 UNDER DIFFERENT TREATMENT CONDITIONS

A.Yu. Alentiev¹, L.E. Starannikova¹, R.Yu. Nikiforov¹, N.A. Belov¹, I.I. Ponomarev², I.V. Blagodatskikh², A.Yu. Nikolaev², V.P. Shantarovich³, Yu.P. Yampolskii¹

¹ *Topchiev Institute of Petrochemical Synthesis RAS, 29 Leninsky pr., 119991, Moscow, Russia (E-mail: alentiev@ips.ac.ru)*

² *Nesmeyanov Institute of Organoelement Compounds RAS, 28 Vavilova str., 119334, Moscow, Russia*

³ *Semenov Institute of Chemical Physics RAS, 4 Kosygina str., 119991, Moscow, Russia*

Abstract: One of the promising materials for membrane gas separation is amorphous highly permeable polymer of intrinsic microporosity PIM-1. The gas separation characteristics and free volume of PIM-1 strongly depend on the method of films preparation and treatment. In the present work, PIM-1 with a high molecular weight (about 90 kDa) was prepared by precipitation polycondensation in DMSO. The permeability coefficients of He, H₂, O₂, N₂, CO₂, CH₄ were measured by chromatographic method at a temperature of 22±2 °C. The free volume was characterized via positron annihilation life-time spectroscopy. The following ways of film treatment were used for the PIM-1 samples: treatment with ethanol and supercritical carbon dioxide (sc-CO₂), annealing in a helium atmosphere in the strained and free-standing state. Changes in the properties of PIM-1 films and ethanol-treated films during physical aging were studied. Physical aging and annealing, particularly in the strained state, was shown to lead to a decrease in permeability and a sharp increase in selectivity. The rate of physical aging was estimated, which was significantly lower than previously published data [1]. It was observed that the sizes of free volume elements obtained by the positron annihilation method ($d \sim 10.4 \text{ \AA}$) practically did not change during physical aging. Ethanol treatment results in an increase of the permeability and size of free volume elements ($d \sim 11.0 \text{ \AA}$), and in a decrease in selectivity. Treatment with sc-CO₂ leads to an increase both in permeability and selectivity. So, the current investigation demonstrates the possibility of controlling the properties of PIM-1 by means of various methods of film treatment that change the chains packing ordering.

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INVESTIGATION ON GAS SEPARATION PROPERTIES OF POLYPHENYLSULFONE (PPSU) MEMBRANES FOR BIOGAS UPGRADING

G. Li¹, W. Kujawski¹, B. V. Bruggen², N. Pedišius³, J. Tonkonogij³, A. Tonkonogovas³, A. Stankevičius³, J. Šereika³, J. Kujawa¹

¹ Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100, Torun, Poland

² Department of Chemical Engineering, Catholic University of Leuven, Oude Markt 13, 3000 Leuven, Belgium.

³ Lithuanian Energy Institute, Breslaujos st. 3, LT-44403 Kaunas, Lithuania

Abstract: To mitigate carbon dioxide emissions and pollution issues, biogas has gained significant interest. Moreover, as a renewable energy, it might be a promising alternative to conventional fossil fuel^{1,2}. Membrane based gas separation technology is of great importance in many industrial processes, e.g. carbon dioxide (CO₂) is removed from natural gas or biogas to improve the energy quality³. In this study, different types of polyphenylsulfone (PPSU) membranes were investigated by scanning electron microscope, thermal gravimetric analysis and derivative thermogravimetry to obtain the structure properties and thermal properties. Moreover, the permeability of CO₂ and CH₄ through membranes were measured by a laboratory-made set-up for gas permeation measurements. It was found that all the membranes possess a support layer with micropores which can reduce the resistance of gas transport and a dense selective layer with granular structure on the outer surface. The TGA data showed all the membranes possess desirable thermal stability. The gas permeation data revealed that membranes possessed high CO₂ permeability and the ideal selectivity (CO₂/CH₄) was in the range of 2 – 3.

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METAL DOPING OF POLYMERS OF INTRINSIC MICROPOROSITY (PIM_S) FOR CO₂ SEPARATION

M.Z. Ahmad¹, E. Asuquo¹, S. Rico-Martinez², A.F. Foster¹,
P.M. Budd¹

¹ The University of Manchester, Oxford Road M13 9PL, United Kingdom

² IU CINQUIMA, Universidad de Valladolid, Paseo Belén 5, Valladolid, Spain
(mohdzamidi.ahmad@manchester.ac.uk)

Abstract: We investigated the gas separation properties of several high molecular weight PIMs with various network contents of between 4.6 to 83.5 wt.% (PIM-1(a), $M_w = 208$ kDa; PIM-1(b), $M_w = 750$ kDa; PIM-PY, $M_w = 196$ kDa). The polymers were characterized by multiple detector SEC, NMR, DLS, and elemental analysis to exemplify their significant structural differences, produced under different synthesis conditions. Single gas measurement was conducted by feeding CO₂, N₂ and CH₄ at a constant feed pressure of ~35 psia, at 25 °C. The results indicated a comparable performance to 2008 CO₂/CH₄ and CO₂/N₂ Robeson upper bounds. Subsequently, the polymers were doped with Pd and Fe salts, through both solid-state and liquid-state doping procedures, and characterized using TGA, FTIR, UV-fluorescence and SEM-EDX. The metal-doped membranes showed significant CO₂/CH₄ and CO₂/N₂ separation selectivity improvements up to 26%. Mixed gas measurement (CO₂/CH₄ 50:50 vol.%, at 35 psia, 25 °C) was conducted on both pristine and metal-doped membranes to determine their aging behavior. See Figure 1 for pristine membrane aging. The best-performing membranes after ~100 days of aging are the Fe-doped PIM-1(a) ($P_{CO_2} = 4,404$ Barrer, $\alpha_{CO_2/CH_4} = 17.8$) and Fe-doped PIM-1(b) ($P_{CO_2} = 1,233$ Barrer, $\alpha_{CO_2/CH_4} = 22.6$), showing an outstanding selectivities above the upper bound and translated into 60% and 104% improvement, respectively.

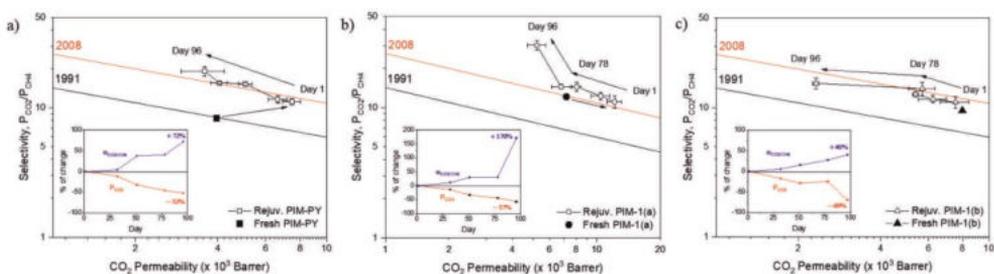


Figure 1: CO₂/CH₄ separation performances of fresh (a) PIM-PY, (b) PIM-1(a), and (c) PIM-1(b) against 2008 Robeson upper bound and their respective aging profile up to ~100 days.

WATER-SWOLLEN MEMBRANE FOR FLUE GAS SEPARATION

A. Žitková, M. Kárászová, P. Stanovský, P. Izák, Z. Petrusová

Institute of Chemical Process Fundamentals, Czech Academy of Sciences, 165 02 Prague 6, Czech Republic (petrusova@icpf.cas.cz, www.icpf.cas.cz)

Abstract: CO₂ and SO₂ can be removed from a mixture of model flue gas by water-swollen membrane in a one-step process. The continuous experiments were carried out by our permeation apparatus described in a detail in Žitková *et al.* [1]. It was found that this membrane is highly permeable for both SO₂ (Fig. left) and CO₂. It results in the real selectivity of SO₂/CO₂ close to 1 (Fig. left). Generally, membrane separation is able to compete with the currently used amine scrubbing when the gas permeability and its corresponding selectivity is high enough [2, 3]. Our membrane seems to be suitable for the purification of a real flue as can be seen from the comparison of our data with published data by Scholes *et al.* [4] (Fig. right). The membrane is suitable when the wetting and swelling of the thin selective layer is homogeneous and stable [5]. Moreover, we have to also pay the attention to the potential aging [6] accompanying by the changes of transport and separation properties.

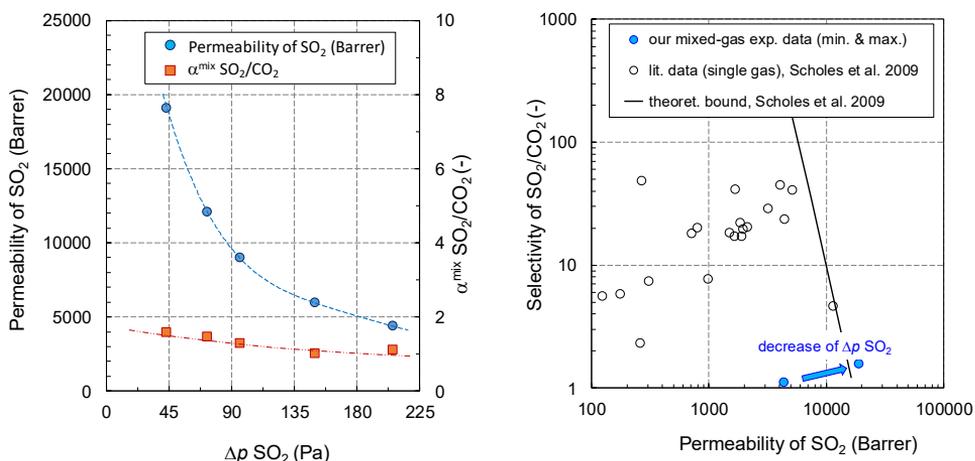


Figure: Permeability of SO₂ and mixed-gas SO₂/CO₂ selectivity as the function of SO₂ partial pressure differences (left) and the comparison of our experimental data with published data by Scholes *et al.* (right) [1]

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DESALINATION OF SALINE GROUNDWATER FOR HYDRAULIC BARRIERS

H. Rosentreter¹, M. Walther^{2,3}, A. Lerch¹

¹ *Chair of Process Engineering in Hydro Systems, Technische Universität Dresden, 01062 Dresden, Germany (hanna.rosentreter@tu-dresden.de, www.tu-dresden.de/bu/umwelt/hydro/isi/hvt)*

² *Department of Environmental Informatics, Helmholtz-Centre for Environmental Research GmbH – UFZ Leipzig, 04318 Leipzig, Germany*

³ *Chair of Contaminant Hydrology, Technische Universität Dresden, 01062 Dresden, Germany*

Abstract: Fresh groundwater is the most often used water resource for domestic, irrigation and industrial use in (semi-) arid coastal regions. However, due to over-pumping and declining groundwater levels, the intrusion of saltwater decreases the groundwater quality by higher sodium and chloride concentrations exceeding the thresholds for irrigation and drinking water [1]. Hydraulic barriers can be used as managed aquifer recharge method to counteract saltwater intrusion. However, water in appropriate quality and quantity is often not available in (semi-)arid regions for managed aquifer recharge. Therefore, desalinated saline groundwater can be used within the Abstraction-Desalination-Recharge (ADR) methodology for remediation of saline aquifers [2]. The sustainable realisation of this ADR methodology bases thereby on cost efficient desalination technologies.

In our study, we examined the suitability of different desalination technologies for various saline groundwater qualities and various infiltration concentrations. Since a total demineralisation of saline groundwater is not needed for infiltration, we examined pressure-driven and electrochemical membrane processes showing a high removal rate for sodium and chloride concentrations within a recovery rate of approximately 50 %. Especially for slightly and moderately saline groundwater, membrane capacitive deionisation and nanofiltration have proven to be cost efficient desalination technologies with a specific energy requirement of 10 Wh/m³ to 1 kWh/m³ infiltrated water. In contrast, highly saline groundwater cannot be sufficiently desalinated by nanofiltration or membrane capacitive deionisation. Therefore, brackish water or seawater reverse osmosis membranes needs to be applied using a pressure up to 35 bar resulting in an energy requirement up to 1.4 kWh/m³ infiltrated water.

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SEPARATION OF MULTICOMPONENT MODEL SOLUTIONS BY REVERSE OSMOSIS

K. Jastřembská, H. Jiráňková , P. Mikulášek

*Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology,
University of Pardubice, Studentská 573, Pardubice 2, 53210, Czech Republic
(karolina.jastrembska@student.upce.cz)*

Abstract: Generally, reverse osmosis as a technique for production of potable water is widespread and well known. Other uses of reverse osmosis, such as separation of organic compounds, are considered in recent years¹.

In this research, four model solutions consisting of selected organic compounds (ethanol, *n*-propanol, *i*-propanol and maltose) were investigated.

Aqueous mixtures of these substances were prepared with concentration of organic compounds below 2.0 g L⁻¹.

The main objective of this study was to determine the possibility of separation of the organic compounds. The effects of the pressure differences and concentration of the organic substances on the rejection coefficient and the permeate flux were investigated as well.

Rejection coefficient of organic compounds at the various applied pressure differences was studied. In the case of ternary solutions, the lowest value of rejection coefficient was observed for ethanol, while the highest value was achieved for *i*-propanol. Rejection coefficients obtained in the case of multicomponent solution measurements were lower, especially for more polar compounds. Several theories are suggested for the explanation of this phenomenon. They are based on the interactions between organic compounds and membrane and on concentration polarization phenomenon².

Permeate flux was influenced negatively by presence of organic compounds. The realized experiments showed that the lowest permeate flux was found for multicomponent model solution with higher concentration of organic matter.

This research was supported by University of Pardubice under grant SGS_019_001.

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HYDROGELS PRODUCING FROM WHEY AND ITS DERIVATIVES BY MEMBRANE PROCESSES

J. Drbohlav, A. Šalaková, M. Borková, J. Peroutková, V. Bár, V. Dráb

*Dairy Research Institute – Ke Dvoru 12a, Prague 6, 160 00, Czech Republic
(www.vumlekarensky.cz)*

Abstract: This paper gives information about further possibilities of using whey and its derivatives from ultrafiltration and electrodialeses.

The aim of the whole project is to design the production of hydrogels and propose their application for soil protection purposes. Hydrogels are three-dimensional networks of natural or synthetic polymers capable to bind and to release water.

Whey is one of the commonly available raw materials in the dairy industry. It is mainly a by-product of cheese, cottage cheese production. Depending on the type of milk coagulation it is possible to obtain whey from cheese, usually sweet or acid whey from curd. Sweet whey finds good further use. Acid whey for lactic acid bacteria content and high lactic acid content has mostly been used only for fattening pigs. Sources of acid whey from the production of cottage cheese in the Czech Republic are relatively small; it also does not contribute to their more efficient use.

Similarly, the by-products - whey derivatives - permeate from milk or whey ultrafiltration and the whey electrodialeses concentrate produced by the whey demineralization are poorly used.

These three hardly economically viable by-products – (waste materials) - have been analysed and found to be useful for the production of hydrogels which, in addition to the growing substrate, will not only be able to bind and release water for plants but carry, bind and release added nutrients and nutrients - minerals contained in processed waste material.

Hydrogels formed by binding these materials with carboxymethyl cellulose or another thickener, not crosslinked or crosslinked with a suitable agent such as citric acid or urea, will be mixed with a relatively inert material such as crushed straw or peat to produce a product that will preferably cyclically bind and release water, and added to the plant growth substrate. This will improve the cultivation substrate and improve plant production.

Presented research is a part of the project “Environmentally friendly soil conservation materials for the crop production intensification based on renewable resource” within the National Agency for Agricultural Research (NAZV) No. QK 1910392 and DKRVO (NAZV) 2019.

THE EFFECT OF ZINC AND MANGANESE ON THE CRYSTALLIZATION KINETICS AND MORPHOLOGY OF CALCIUM SULFATE DIHYDRATE

M. Šír, J. M. Budatala

Department of Environmental Chemistry, University of Chemistry and Technology Prague, Technická 5, Prague 6 – Dejvice, 166 28, Czech Republic

Abstract: Main aim of this study was to investigate the influence of trace metal ions on the crystallization process of calcium sulphate dihydrate, which is a major inorganic scalant in membrane process of reverse osmosis within desalination plants.

Calcium sulphate solutions at different concentrations under the influence of zinc and manganese metal ions were analyzed by means of beaker tests for conductivity curves, and crystallization rates were determined from the changes recorded over time. The metal ions were added in the amounts corresponding to the proposed molar ratios (50:1, 100:1, 200:1), relative to the calcium sulphate solution concentrations. The results showed a trend of decrease of induction time of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystallization on the addition of Zn and Mn. A particular phenomenon was observed in all cases where smallest dosage (200:1) had the immediate and higher degree of influence in comparison to higher amount (50:1).

The morphology of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal samples collected were studied under SEM. In the first step the morphological study distinguished between *rod-like* and *flaky* crystal structures corresponding to lower and higher calcium sulphate solution concentrations respectively. Subsequently it was shown that the morphology was significantly altered by the addition of zinc and manganese metal ions, which was noticeable from the formation of different needle like structures.

The data obtained will help to better set the process of reverse osmosis, where working with supersaturated solutions. This would facilitate in better understanding the influence of trace elements on membrane scaling and make necessary improvements.

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SURFACE MODIFICATION OF HETEROGENEOUS ION-EXCHANGE MEMBRANES WITH PERFLUOROSULFONIC ACID POLYMER FILM CONTAINING TITANIUM OXIDE

V. Gil, M. Porozhnyy, D. Butylskii

*Membrane Institute, Kuban State University, 149, Stavropolskaya str., Krasnodar, 350040, Russia
(violetta_gil@mail.ru)*

Abstract: In the course of electrodialysis of dilute solutions, the surface properties of ion-exchange membranes affect significantly the performance of the separation process. In particular, the membrane surface parameters have a strong impact on the intensity of electroconvection (EC). EC ensures that the current exceeds the limiting diffusion current severalfold, moreover, EC hinders fouling. In this regard, to improve membrane performance, it is enough to carry out a surface modification.

A batch of membranes based on the MK-40 heterogeneous membrane (Shchekinoazot) and different in surface properties (thickness of the modifying film and the mass fraction of TiO₂ nanoparticles embedded in it) were produced. It is found that changes in surface characteristics conditioned by such modification lead to an increase in the experimental limiting current density, i_{lim}^{exp} , due to the stimulation of EC, which develops according to the mechanism of electroosmosis of the first kind. The greatest increase in the current compared to the pristine membrane can be obtained by modification with the film being 20 μm thick and containing 3 wt% of TiO₂ (Table 1). The sample containing 6 wt% of TiO₂ provides higher mass transfer in overlimiting current modes (characterized by the current-voltage curve's plateau length and slope) due to the development of nonequilibrium EC.

Table 1. Some parameters of current-voltage curves.

Sample	Modifying film thickness, μm	Mass fraction TiO ₂ in the film, wt%	i_{lim}^{exp} , mA cm ⁻²	Plateau length, V	Plateau slope, mS cm ⁻²
MK-40	-	-	1.57	1.43	0.61
MK-40 ₂₁	21±2	-	1.81	0.60	1.58
MK-40 _{21+3%}	21±2	3	2.19	0.85	1.08
MK-40 _{21+6%}	21±2	3	1.97	0.50	1.33
MK-40 _{33+3%}	33±2	6	2.01	1.03	0.78
MK-40 _{33+6%}	33±2	6	1.71	1.25	0.62

A 1.5-fold increase in the thickness of the modifying film reduces the positive effect of introducing TiO₂ nanoparticles due to (1) partial shielding of the nanoparticles on the surface of the modified membrane; (2) a decrease in the tangential component of the electric force, which affects the development of electroconvection.

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BILAYER ION EXCHANGE MEMBRANES IN ELECTROMEMBRANE PROCESSES. DEVELOPMENT, ELECTROCHEMICAL PROPERTIES AND PROSPECTS FOR APPLICATION

S. S. Melnikov¹, E. D. Melnikova¹, E. N. Nosova¹

¹ *Physical chemistry department, Kuban state university, 149 Stavropolskaya, Krasnodar, Russia*

Abstract: Multilayer membranes with improved physicochemical and operational properties are widely used in such fields of membrane science and technology as reverse osmosis, nano- and ultrafiltration, as well as in gas separation processes.

In our work, we present a bilayer membrane consisting of two ion-exchange layers, one of which is much thinner than the other. This thin layer provides new features of the original membrane, such as specific ionic selectivity, the ability to accelerate the dissociation of water, or thermal and chemical stability. The authors of this work have developed a method that makes it possible to obtain an asymmetric bipolar membrane possessing high mechanical, chemical and physical stability. A mechanically robust heterogeneous anion-exchange membrane and an MF-4SC (Nafion analog) solution (5% MF-4SC in isobutyl alcohol) can be used to obtain asymmetric bipolar membranes via casting method. The ability to apply thin layer on the membrane-substrate allows the relatively easy introduction of various catalyst additives.

The electrochemical behavior of asymmetric bipolar membrane depends on its structure (the thickness of the cation-exchange layer) as well as on the conditions of its use (the current density and external solution concentration). In dilute solutions, the process of water splitting at the bipolar boundary of the membrane prevails, and an asymmetric bipolar membrane is similar in its properties to a classical bipolar membrane. At low current densities in a more concentrated solution, the asymmetric membrane behaves like a monopolar membrane, i.e., the primary process is the transfer of salt ions.

As for the practical aspect, the most interesting mode is the mixed mechanism of ion transport, in which the desalting process can proceed simultaneously with the water-splitting reaction. The role of such processes in the practice of electromembrane technologies is quite high, for example, in the preparation of water for the needs of heat power generation, in the stabilization of juices, wines and other products of the food industry, in the separation of biologically active substances that are sensitive to the pH value.

This work was supported by the Russian Foundation for Basic Research, grant № 19-08-01172_a.

SIMULTANEOUS DESALINATION AND pH ADJUSTMENT OF STRONG ELECTROLYTE SOLUTION USING BILAYER MEMBRANES WITH WATER SPLITTING CATALYST

E. N. Nosova¹, S. S. Melnikov¹

¹ *Physical chemistry department, Kuban state university, 149 Stavropolskaya, Krasnodar, Russia*

Abstract: The currently produced ion-exchange membranes are either too expensive or created for the processing of strong electrolytes, and their characteristics do not meet the new requirements. The solution to these problems can be the creation of anisotropic ion-exchange membranes by applying modifying layers to the surface of the substrate membrane, that is, by creating bilayer and multilayer ion-exchange membranes.

Taking into account the current trend aimed at sustainable development and the desire to create technological processes with a minimum discharge of wastes, the demand for membrane processes, and electromembrane techniques, in particular, has increased. One can note electrodialysis with bipolar membranes (BMED), as a technology that allows obtaining acid and alkali from salt solution without formation of by-products. The BMED technology is in demand not only for the synthesis of acids and bases from salt solutions but also for the reagent-free adjustment of pH of technological solutions and natural waters in water treatment, chemical and food industries.

Unlike acid and alkali production, pH adjustment does not require bipolar membranes with high selectivity. Moreover, it is convenient to combine the desalination process with a simultaneous pH adjustment. However, the flux of salt ions through the bipolar membrane is very low. This circumstance limits the use of bipolar membranes in the process of desalting with the simultaneous adjustment of the pH of the solution. At the same time, it is possible to obtain a bipolar membrane in which the cation and anion-exchange layers have different thicknesses. Use of asymmetric membrane allows controlling the ion fluxes passing through the membrane by changing the thickness of the monopolar layers (CEL and AEL), the current density, and the solution concentration

In the present work we have studied the process for simultaneous desalination and pH adjustment of NaCl solution using bilayer (asymmetric bipolar) membranes with and without catalyst. We used the two-chamber electrodialysis setup with bilayer and cation-exchange membranes. We have found that integral characteristics of the process depend on the transport properties of the cation-exchange membrane in a greater way than on the ability of bilayer membrane to split water. The main feature that determines the process parameters is the specific permselectivity of the cation-exchange membrane towards hydrogen ion.

This work was supported by the Russian Foundation for Basic Research, grant № 19-08-01172_a.

INCREASING THE PERFORMANCE OF ANION EXCHANGE MEMBRANES PREPARED FROM DISCARDED REVERSE OSMOSIS MEMBRANES

A. Lejarazu-Larrañaga^{1,2}, S. Molina¹, J. M. Ortiz¹, G. Riccardelli^{1,3}, E. García-Calvo^{1,2}

¹ IMDEA Water Institute, Avenida Punto Com, 2, 28805. Alcalá de Henares, Madrid, Spain (amaia.ortiz@imdea.org, www.water.imdea.org)

² Chemical Engineering Department, University of Alcalá, Ctra. Madrid-Barcelona Km 33.600, 28871. Alcalá de Henares, Madrid, Spain

³ Civil and Mechanical Engineering Department, University of Cassino and Southern Lazio, Viale dell'Università, 03043, Cassino, Italy

Abstract: Due to the increasing number of yearly discarded Reverse Osmosis (RO) modules, intensive research is being conducted in developing suitable membrane recycling techniques. Among other alternatives, the use discarded RO membranes as mechanical support for anion exchange membrane (AEM) preparation by coating method has been recently proposed for the first time. The recycled AEMs have a good permselectivity but a high electrical resistance. In an effort to reduce the electrical resistance of the recycled AEMs, this work proposes an activation treatment consisted on the subsequent immersion of the membranes in diluted acid and alkali solutions.

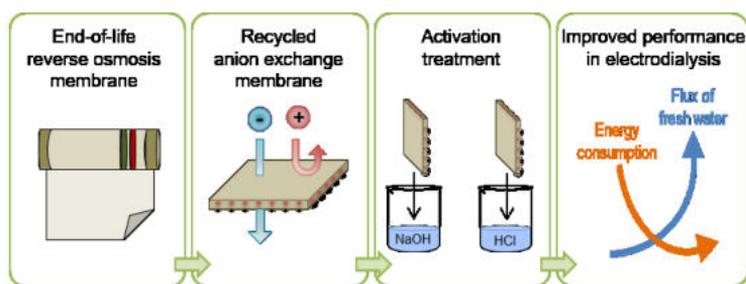


Figure 1. Graphical abstract.

The effects of acid and alkali concentrations and exposition times on the electrochemical properties were studied and the best combination was selected. In such a way, a decrease of 37 % in membrane electrical resistance was achieved. The performance of activated and non-activated membranes in desalination by electro dialysis was compared. The results showed that the proposed activation treatment increased the flux of fresh water (from 1.2 to 4.9 L·h⁻¹·m⁻²), reduced the energy consumption (from 5.2 to 3.0 kWh·m⁻³) and improved the current efficiency (from 38 % to 71 %). In conclusion, this work shows a simple and low cost methodology for the improvement of the electrochemical properties of recycled electromembranes and thus, their performance in electro dialysis.

PREPARATION OF ION-EXCHANGE MEMBRANES FOR ELECTROCHEMICAL SEPARATION PROCESSES

K. Smolińska-Kempisty¹, A. M. Siekierka¹, M. Bryjak¹, J. Wolska¹

¹ *Depart. of Process Engineering and Technology of Polymeric and Carbon Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland*

Abstract: During the last years the popularity of the renewable energy sources has gained constantly rising, because that the total energy demand is growing at an alarming rate [1]. The „traditional“ sources of energy are getting exhausted hence a search for other energy origins has been launched. It seems that Salinity Difference Energy called as *Blue Energy* can be such new and dynamically developing approach [2]. It is a method of energy generation by mixture two solutions with different salt concentrations. Today, harvesting energy from the salt gradient can be done by three methods: Pressure Retarded Osmosis (PRO), Reversed Electrodialysis (RED) including Capacitive Reversed Electrodialysis (CRED) and Capacitive Mixing (CapMix) [2]. The key point of all this processes for the production energy is availability of suitable membranes. The presented studies were focused on preparation of ion-exchange membranes by chemical modification, introducing cation- and anion-exchange groups onto membranes. For the preparation of cation-exchange membranes poly(acrylic acid), poly(methacrylic acid) or copolymer of these two monomers were set. In the case of anion-exchange membranes ethylenediamine was used to introduce amine functionality. The obtained membranes were characterized by determining their weight increase, water content and ion exchange capacity. Additionally the change of surface character was investigated by measuring contact angle. All materials were successfully modified, regardless of the type of compound grafted on the surface. This fact was confirmed e.g. by measuring the surface energy of the modified films. Depending on the nature of the compound used, changes of acidic or basic components of surface tension were noted.

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IMPROVING COUNTERION PERMSELECTIVITY OF AN ANION-EXCHANGE MEMBRANE

M.V. Porozhnyy, V.V. Sarapulova, N.D. Pismenskaya,
V.V. Nikonenko

*Membrane Institute, Kuban State University, 149 Stavropolskaya st., Krasnodar, Russia
 (v_nikonenko@mail.ru, www.kubsu.ru)*

Abstract: One of the factors affecting the low permselectivity of commercial ion-exchange membranes is the presence of gaps (cracks and splits) between the membrane polymer material and the fibers of the reinforcing cloth. In order to block these gaps and narrow the spaces available for diffusion, it is suggested to cover the membrane surface with a thin film of a conducting sulfonated perfluorinated polymer containing carbon nanotubes (CNTs) as a reinforcing agent.

Samples of modified membranes were prepared via casting a 7.2% MF-4SK (Plastpolymer, Russia) solution containing different mass fractions of CNTs (up to 3% of polymer) onto the surface of an anion-exchange MA-41P membrane (Shehekinoazot, Russia). The conductivity of the samples was measured using a clip cell method. The diffusion permeability coefficient was determined using a two-compartment cell. The experiments were carried out in the 1M NaCl solution.

The experimental results presented in Table show that CNTs introduced into the modifying layer allow decreasing the membrane permeability with the maximum effect at 0.5% of mass fraction. Increasing the fraction of CNTs up to 3% results in the decreasing effect. This is explained by the fact that CNTs tend to agglomerate at higher concentrations, which results in the decreasing degree of crosslinking of the polymer. The effect of CNTs on the electrical conductivity is less pronounced.

Table. Transport characteristics of the samples

Membrane	Diffusion permeability, $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	Conductivity, mS cm^{-1}	Coion transport number
MA-41P	13.9	10.9	0.023
MA-41P _{0%}	12.5	10.2	0.023
MA-41P _{0.1%}	11.5	10.5	0.021
MA-41P _{0.25%}	10.9	10.7	0.019
MA-41P _{0.5%}	9.6	9.2	0.020
MA-41P _{2%}	10.4	9.6	0.021
MA-41P _{3%}	12.8	9.4	0.026

The coion transport number is the parameter characterizing the membrane permselectivity and can be derived from the electrical conductivity and diffusion permeability. The sample MA-41P_{0.25%} has the lowest counterion transport number, which indicates its highest permselectivity.

We are grateful to Russian Foundation for Basic Research (project #20-08-00933) for financial support.

I-V CURVES OF MK-40 HETEROGENEOUS MEMBRANE COATED WITH POLYELECTROLYTE LAYERS

V. Titorova, V. Sarapulova, K. Kirichenko, N. Pismenskaya

Kuban State University, Stavropolskaya st. 149, 350040 Krasnodar, Russia

Abstract: Heterogeneous membranes may be used as durable and selective supports in creation of monovalent selective membranes through layer-by-layer modification. However, we have previously shown that when modified with a single layer of polyelectrolyte carrying the fixed groups oppositely charged to the groups of the membrane bulk, the heterogeneous membrane has lower limiting current and stronger generation of H^+ and OH^- ions than the homogeneous membrane¹. Since it is known that application of homogenizing layer may reduce the concentration polarization and increase the limiting current², in our recent study we compared the MK-40 commercial heterogeneous membrane and MK-40+2 sample modified with MF-4SC (homogenizing layer) and polyethyleneimine (oppositely charged layer) and shown that by this approach the limiting current value is preserved and pH change due to generation of H^+ and OH^- ions is only 0.2³. Here we add MK-40+1 membrane (modified only with homogenizing layer) to comparison and it can be seen that the apparent constancy of the limiting current between MK-40 and MK-40+1 in reality is the increase between MK-40 and MK-40+1 followed by decrease between MK-40+1 and MK-40+2.

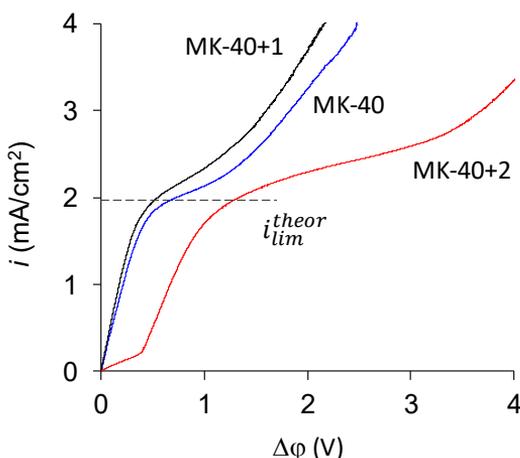


Figure. I-V curves of MK-40 commercial heterogeneous membrane and of its modifications registered in 0.02 M NaCl solution

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ELECTRODIALYSIS WITH BIPOLAR MEMBRANE: DESIGN OF EXPERIMENTS AND STATISTICAL MULTIFACTORIAL ANALYSIS OF EXPERIMENTAL DATA

J. Kroupa¹, J. Cakl², P. Doleček²

¹ *Mega a.s., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic*

² *University of Pardubice, Faculty of Chemical Technology, Institute of Chemical Engineering, Studentská 95, 532 10 Pardubice, Czech Republic, (email: jiri.cakl@upce.cz, www.upce.cz)*

Abstract: Electrodialysis with bipolar membrane (EDBM) is the process that allows the recovery of acid and base from corresponding salt. Produced acid and base can be reused as the source of waste salt technology; thus, it is possible to decrease the OPEX and also the environmental impact of many industrial technologies.

The effects of current density and product concentration (acid and hydroxide) on the purity and quantity of both acid and base produced were studied in the three-compartment configuration of the EDBM stack. To reduce the number of experiments, the methodology of the central composite design was used together with the response surface methodology for modeling and analysis of the most important process effects.

Experiments were carried out using laboratory unit P EDR-Z/4x (MemBrain, Czech Republic) operated in the feed and bleed mode. Membranes included cation-exchange heterogeneous membrane Ralex CM(H)-PP, anion-exchange heterogeneous membrane Ralex AM(H)-PP (both Mega, Czech Republic), and heterogeneous bipolar membrane Ralex BM 3.1 (MemBrain, Czech Republic). Aqueous sodium sulfate solutions were used as model feeds.

The experimental results were modeled by the second-order polynomial equations using response surface methodology. The level of the confidence was set at 95% for all responses and the probability was expressed as p-value at the significance level of 0.05. The regression coefficients were calculated using the least square method. Still, due to certain variations in both the predicted response and the coefficients estimates, the ANOVA tests of analysis of variance were made to show that the hypothesis was valid. The final model was taken as satisfactory when the regression was significant and the lack of fit was insignificant for the confidence interval tested.

It can be concluded that the concentration of both products, i.e., acid and hydroxide, plays an important role for purity as well as the time necessary to reach the steady-state in the systems investigated. The obtained regression model can be used to predict the significance level of individual studied parameters.

PRODUCTION OF TETRAALKYLAMMONIUM HYDROXIDE BY IMPROVED ELECTRO-ELECTRODIALYSIS PROCESS

L. Čopák

MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic

Abstract: Electro-electrodialysis (EED) is an electro-membrane separation technique which can be employed for production of hydroxides from organic cations¹. These compounds are typically used as catalysts of various reactions in organic chemistry. Our experimental work deals with production of hydroxides from the aqueous and non-aqueous solutions of tetraethylammonium bromide (TEABr) or tetrapropylammonium bromide (TPABr). For this purpose, we used a stack designed and developed in MemBrain consisting of one cation exchange membrane (CEM PP Ralex®), one anion exchange membrane (AEM PP Ralex®) and three spacers. In order to enhance the module performance, the middle spacer was modified to enable filling with an ion-exchange resin. Mixedbed was prepared from cation exchange resin (Purolite® C160 Na) and anion exchange resin (Amberjet® 4200 Cl) in ratio 40:60 wt. %. We tested the effect of resin presence on the desalination rate, product purity, etc. For example, this modification led to shorter time of desalination (by 23 %), higher feed processing capacity (by 21 %) or higher overall salt flux (higher by 18 %).

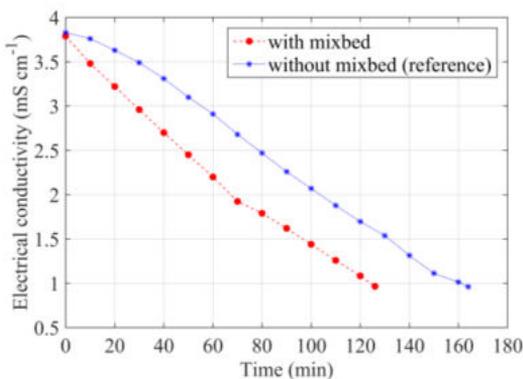


Fig. 1 Desalination curves of methanol solution of TPABr with and without usage of ion exchange resin in the salt solution chamber.

Acknowledgement: The research was funded using institutional support for the Long-term Conceptual Development of a Research Organization provided by the Ministry of Industry and Trade of the Czech Republic.

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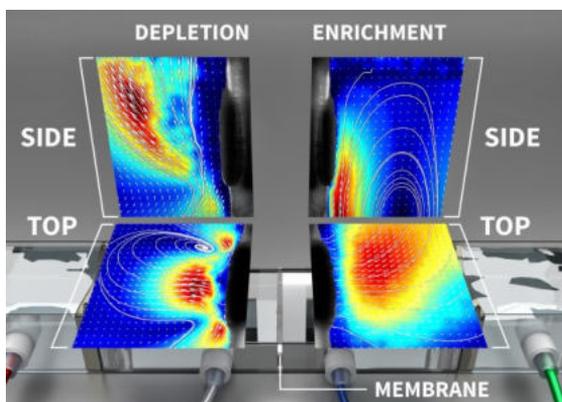
COMPUTER RECONSTRUCTION OF THE LIQUID FLOW IN THE VICINITY OF THE MEMBRANE USING MULTI-VIEW OBSERVATION

T. Bellon¹, Z. Slouka^{1,2}

¹ University of Chemistry and Technology, Prague, Chemical Engineering Dep.,
Technická 5, 166 28 Praha 6, Czech Republic

² University of West Bohemia, New Technologies Research Centre, Univerzitní 8,
306 14, Pilsen, Czech Republic

Abstract: Electroconvection has been recognized as one of the major mechanisms driving overlimiting currents in ion-exchange systems. Here we use particle image velocimetry for visualization of the electroconvection on a small piece of commercially available heterogeneous cation-exchange membrane. We performed chronoamperometric measurement under the various experimental condition and evaluate the intensity of electroconvection as a flow rate in a pseudo-2D plane which is in focus during measurement. The electroconvection takes the form of two countercurrent vortices that suck in the liquid from sides and discharge the liquid from the center of the membrane. The intensity of these countercurrent vortices increases with increasing driving voltage and decreasing with electrolyte concentration. Further analysis of the stagnant points of vortices shows that their mutual distance and the distance from the membrane correlate with the vortex intensity. Using multi-view observation from the top and from the side of the membrane we discovered the differences between the direction of the vortices in the vertical plane which is highly influenced by a dilute solution of lower concentration on the depleted side of the membrane and enriched solution on the other side with higher ionic concentration. The opposite direction of the liquid flow when the external electric field connected is most probably a result of natural convection due to different electrolyte concentrations. By a combination of PIV analysis of multi-view observation, we performed a reconstruction of a pseudo-3D profile of the liquid flow in the vicinity of the membrane.



Overview of multi-view observation of the IE system using observing the system from the top and from the side of the chip.

EXPERIMENTAL OBSERVATION OF PHENOMENA DEVELOPING ON ANION-EXCHANGE MEMBRANE DURING CURRENT-VOLTAGE MEASUREMENT

T. Bellon¹, Petr Polezhaev¹, Z. Slouka^{1,2}

¹ University of Chemistry and Technology, Prague, Chemical Engineering Dep., Technická 5, 166 28 Praha 6, Czech Republic

² University of West Bohemia, New Technologies Research Centre, Univerzitní 8, 306 14, Pilsen, Czech Republic

Abstract: Ion-exchange systems represented, for example, by ion-exchange membranes on ion-exchange resin particles exhibit nonlinear current-voltage curves, on which one finds three distinct regions. These regions are referred to as underlimiting, limiting and overlimiting ones. Each of these regions reflects proceeding phenomena responsible for the ion transport. It is known that all important transport processes take place on the depletion side of the ion-exchange systems. We capture the situation at the interface between a cation-exchange system and an electrolyte on the depletion side as it develops during the measurement of a current-voltage curve by using fluorescent and optical observations. Our observations allow to describe qualitatively transport phenomena occurring in ion-exchange systems and to assign their onset to the particular points on the current-voltage curve. We show that current voltage-curve for the studied systems, namely a single cation-exchange particle and a heterogeneous cation-exchange membrane, have a shape typical for ion-exchange systems, i.e. we can clearly recognize underlimiting, limiting and overlimiting region. Interestingly, the overlimiting region of both systems can be divided into two parts based on the slope of the current-voltage curve in this region. We show that there is a qualitative and quantitative change in the developed electroconvection as the major mechanism governing the overlimiting current when the system transitions from the first part of the overlimiting region to the second one. This transition of electroconvection causes its mixing effect to change from local to global. Figure 1 shows measured CVC curve and corresponding images displayed at given points on CVC curve.

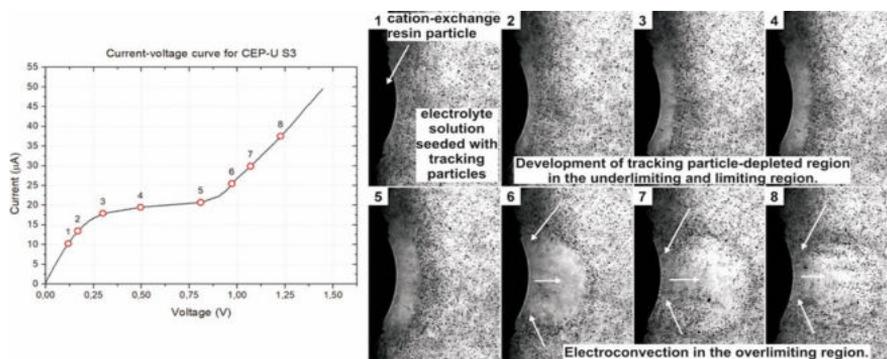


Fig. 1. Measured current-voltage curve with corresponding images from optical microscope displayed at given point marked on CVC curve.

STRUCTURE OF HETEROGENOUS ION EXCHANGE MEMBRANES STUDIED BY MICRO-COMPUTED TOMOGRAPHY

L. Vobecká¹, M. Svoboda^{1,2}, J. Beneš², Z. Slouka^{1,2}

¹ *University of Chemistry and Technology Prague, Dept. of Chemical Engineering, Technická 3, Prague 6, 16628, Czech Republic*

² *University of West Bohemia, New Technologies – Research Centre, Univerzitní 8, Pilsen, 30614, Czech Republic (sloukaz@vscht.cz)*

Abstract: Heterogeneous ion exchange membranes are inherent and functional part of electromembrane separation units such as electrodialysis or electrodeionization. They usually contain finely ground ion exchange resin, polyethylene or polypropylene as a binder and a polymeric mesh. The resin is dispersed (randomly distributed) within the binder. On one side, the nonconductive parts (binder, mesh) of the membrane provide for the mechanical strength of the membrane, on the other side they mostly worsen its electrochemical properties (such as resistance). The optimal composition and distribution of individual components within the heterogeneous membranes are thus required.

We developed a technique based on computed tomography that allows one to reconstruct the 3D structure of these membranes (both the surface and the bulk) not only in their dry state but also upon swelling. This feature enables to study (i) structural changes of the membrane incurred by the exposure of the membrane to water environment or by changes in the composition or concentration of the water solutions in which the membranes are soaked [1], and (ii) the effect of the structure on the electrochemical behavior [2]. The technique has been used to describe the effect of swelling/shrinkage on the structure of the heterogeneous membranes, to quantify volumetric changes in the resin when changing the ionic strength or composition of the external water solution and to evaluate the ion-exchange surface areas of these membranes. The major conclusions of our studies are: (i) the shrinkage and swelling are caused by the action of the dispersed ion-exchange resin, (ii) the extent of swelling is indirectly proportional to the ionic strength of the solution, (iii) the extent of swelling increases with decreasing size of the major counterion (with the same charge number).

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SORPTION AND PERTRACTION OF IBUPROFEN BY COMMERCIAL POLYMERIC MEMBRANES

M. Bourassi^{1,3}, J. Herciková², J. Gaálová³, M. Kárászová³

¹ Faculty of Science, Charles University, Institute for Environmental Studies, Benátská 2, 128 01 Prague 2, Czech Rep., mahdi.bourassi@icpf.cas.cz

² University of Chemistry and Technology Prague, Department of Organic Chemistry, Technická 5, 166 28 Prague, Czech Rep. jana.hercikova@vscht.cz

³ Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova 135, 165 02 Prague 6, Czech Republic (gaalova@icpf.cas.cz, www.icpf.cas.cz)

Abstract: Ibuprofen is one of the most consumed non-steroidal anti-inflammatory drug. That is why the concentration of residual Ibuprofen and its metabolites in waters is increasing and is a matter of interest of many research groups[1]. The common separation processes using porous membranes like ultrafiltration, nanofiltration and reverse osmosis are tested also for removal of pharmaceuticals from water and are quite effective the rejection of different emerging contaminants by nanofiltration and reverse osmosis often reaches 80-100% [2-6], depending on used membrane, experimental conditions etc.. Present research focuses on separation of the Ibuprofen from aqueous solutions using the commercial polymeric membranes, namely PERVAP™ 4060 by DeltaMem AG and polystyrene and polypropylene film from GoodFellow Cambridge Ltd. The sorption from aqueous solution of Ibuprofen of different initial concentrations were tested. Pertraction with aqueous solution of Ibuprofen as donor phase and pure water as receiving phase were performed. During the sorption measurements, the sample of the membrane cut into pieces was immersed in the aqueous solution of Ibuprofen. Samples of the solution were taken in defined intervals and the decrease of the amount of Ibuprofen in the solution was evaluated. During the pertraction measurement, the circular sample of the membrane was put into the diffusion cell and the samples were taken from both the donor and the acceptor phase to see if the Ibuprofen passed through the membrane.

It was approved that the Ibuprofen has a good affinity to the membranes because there was a significant decrease of the concentration during the sorption measurement. It was also found that the pertraction could be used for separation of Ibuprofen from water because the concentration of Ibuprofen in the donor phase decreased. The pertraction separation process thus could be considered as an alternative to the membrane processes using porous membranes.

Acknowledgement: This research was supported by the Czech Republic Foundation for grant No. 19-08153Y

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MICROFILTRATION MEMBRANES BASED ON NONWOVENS MATERIALS FOR PARTICLE SEPERATION

E. Boyraz¹, F. Yalcinkaya¹, J. Maryska¹

¹ Faculty of Mechatronics, Informatics and Interdisciplinary Studies, Technical University of Liberec, Studentska 1402/2, 46117 Liberec, Czech Republic (evren.boyraz@tul.cz)

Abstract: The existing water resources in the world are decreasing nowadays due to domestic, agricultural, industrial and similar wastes. Therefore, the treatment of wastewater is important for our present and future. The membrane process (microfiltration and ultrafiltration), chemical destabilization (conventional coagulation) and electrochemical destabilization (electrocoagulation) are the most common processes for the wastewater filtration. Non-woven materials are commonly used in the decontamination process for the particle separation removal larger than 1 μm [1]. Non-woven materials have randomly oriented fibers creating pores that the fluid can flow through. They have many advantages that can be controllable such as pore size, the density of fibers and design. They are also cheap material for the water filtration. In this work, the non-woven membranes were prepared and they have been used for the particle separation. The performance of non-woven membranes such as flux, and the relationship between pore size, air permeability, and lamination process were investigated.

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USE OF FUNCTIONALIZED ZNO NANOPARTICLES FOR MEMBRANE WITH ANTIBIOFOULING PROPERTIES

Z. Gončuková¹, A. Galizia², H. Monclús², J. Comas², L. Dvořák¹

¹ *Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec, Studentská 2, 461 17 Liberec, Czech Republic*

² *Laboratory of Chemical and Environmental Engineering (LEQUiA), Institute of the Environment, University of Girona, c/ Maria Aurèlia Capmany, 69. Girona E17003, Spain*

Abstract: Membrane (bio)fouling is limiting factor, which affects application of membrane bioreactors (MBR) for wastewater treatment¹. Lots of studies have been devoted to mitigate this negative phenomenon to date. However, there is no unique solution yet². Modification of membranes using zinc oxide nanoparticles (ZnO NPs) appears to be a promising option for biofouling mitigation³. Therefore, the main objective of this study was to prepare membranes with antibiofouling properties, and evaluate them while filtrating real activated sludge.

Firstly, membranes matrix based on polyethersulfone (PES) and sulfonated polyethersulfone (SPES) polymers were doped with surface-functionalized ZnO NPs, which gave them antibacterial properties. The surface-functionalization of ZnO NPs was achieved by silane coupling agent ((3-Aminopropyl)triethoxysilane; APTES) resulting in bonding of -NH₂ groups of APTES with -SO₂Cl groups of chlorosulfonated polyethersulfone (SPES-Cl).

All membranes, i.e. reference membrane (PES/SPES), PES/SPES/ZnO membrane (without chemical anchoring of ZnO NPs) and PES/SPES/ZnO-APTES membrane were evaluated in short-term and middle-term test with activated sludge in order to determine their fouling rates and permeability values. During the short-term test, the critical flux was estimated for each membrane. In the case of reference membrane, the critical flux was 5 LMH, while for membrane with ZnO-APTES nanoparticles was 8 LMH. Due to the very low permeability even at high transmembrane pressure, it was not possible to estimate the critical flux for membrane with ZnO (unmodified) NPs. The middle-term filtration test (5 days) showed slower decrease in permeability for PES/SPES/ZnO-APTES membrane than for reference (PES/SPES) membrane as well as membrane with unmodified ZnO NPs.

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APPLICATION OF BIOBASED ANODE MATERIAL IN MICROBIAL NUTRIENT RECOVERY CELL FOR SIMULTANEOUS RECOVERY OF NUTRIENTS AND GREEN ENERGY FROM WASTEWATER

K. Shahid¹, D. L. Ramasamy¹, A. Pihlajamäki¹

¹ *Department of Separation Science, School of Engineering Science, Lappeenranta-Lahti University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland
(Kanwal.Shahid@lut.fi, <https://www.lut.fi/web/en/school-of-engineering-science/research/membrane-technology>)*

Abstract: The principal goal of this work is to explore the potential of newly synthesized chitosan beads as bio-anode in microbial fuel cell (MFC) and investigated for its applicability to recover nutrients from the wastewater. This was accomplished by converting MFC into microbial nutrient recovery cell (MNRC) as show in Figure 1 and the MNRC system performance was assessed in terms of nutrient recovery and energy production. Bio-electrochemical systems (BES) is a promising technology capable of oxidizing organic matter present in wastewater while producing green energy or producing beneficial compounds using bio-electrically active bacteria as catalysts [1-4]. In this line, the MFC technology has been widely recognized as an emerging bio-electrochemical process that uses respiring microbes for the extraction of energy from the wastewater containing loads of organic matter [5]. The aim of the current investigation was to utilize the developed chitosan-based bio anode material for proliferation of microbial species in order to recover the nutrients from the wastewater.

The developed bioanode was systematically investigated for its potential in terms of nutrient removal and recovery, chemical oxygen demand (COD) removal (Figure 3) and energy production from municipal wastewater (Figure 2a). The comparative evaluation of bioanode with the most used commercial activated carbon AC (a popular choice for anode) was made in terms of stable voltage production and nutrient recovery. Significant removal of nutrients in the form of phosphorus and ammonium ions was demonstrated by using chitosan beads, even in the presence of interfering ions such as sulfate. Besides, the maximum power density estimated for the chitosan beads ($\sim 600 \text{ mW/m}^2$) was found as efficient as the commercial AC system (650 mW/m^2) (Figure 2b).

Overall, the present study demonstrates a facile/ schematic self-driven route for recovery and enrichment of nutrients from wastewater into a recovery solution along with stable voltage production during the whole procedure. These findings revealed that the MNRC system not only can treat the wastewater but can also be used to recover the valuable substances such as nutrients and other valuable components from wastewater with simultaneous production of green energy.

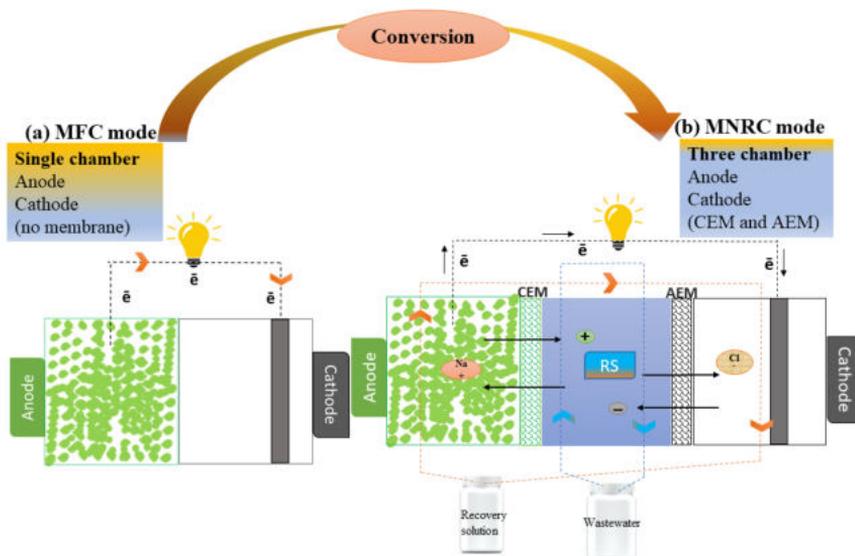


Figure 1. Schematic illustration of (a) MFC and (b) MNRC configurations.

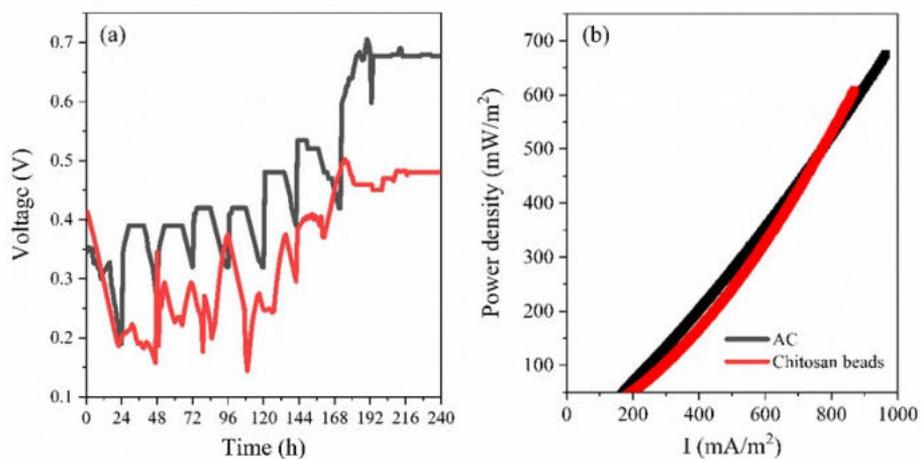


Figure 2. The OCV profile vs time (during the inoculation period of 10 days) and (b) power density vs current density for AC and chitosan beads.

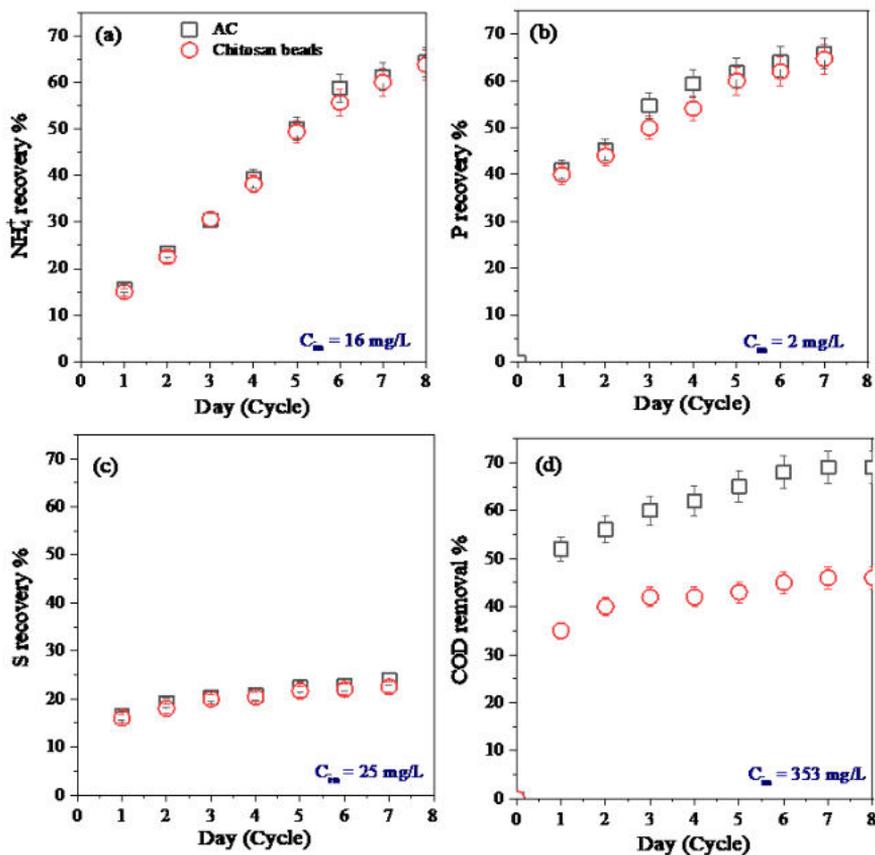


Figure 3. (a) NH_4^+ recovery % (b) Phosphorus (P) recovery % (c) Sulphur (S) recovery % and (d) COD removal % for AC and chitosan containing MNRC System for 8 cycles (i.e. 8 days of operation).

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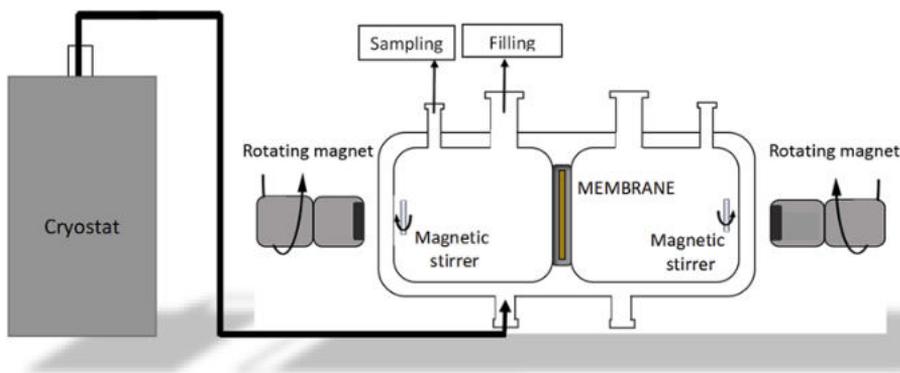
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SEPARATION OF ANTIBIOTICS FROM WATER BY MEMBRANE PROCESSES

J. Gaálová¹, M. Bourassi¹, P. Cuřínová¹

¹ Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova 135, 165 02 Prague 6, Czech Republic
(gaalova@icpf.cas.cz, www.icpf.cas.cz)

Abstract: Highly efficient membrane materials were tested in selective separation of several antibiotics from water: Tetracycline, Trimethoprim, Sulfamethoxazole, as well as their mixture. Numerous sorption and pertraction experiments have been done, confirming that an accumulation of the antibiotic in the membrane is clearly higher during the sorption than during the pertraction, which is caused by the transport of the substance through the membrane. Plus, during the sorption, the membrane is saturated in the whole volume. In addition, the substances influence the transport of each other as there is a possibility of coupling effect in case of pertraction of mixture of antibiotics. Prepared and used membranes were characterized by IR spectroscopy.



Schema of the diffusion cell.

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WATER TREATMENT AND REUSE WITH ULTRAFILTRATION AND NANOFILTRATION

L. Hoferková¹, J. Lev¹, M. Holba¹, D. Polášek², J. Polášek², M. Vlček²

¹ ASIO TECH, spol. s r.o., Kšírova 552/45, 619 00 Brno

² AQUA PROCON s.r.o., Palackého tř. 12, 612 00 Brno

Abstract: This article introduces membrane application study in the industry as a part of a research project Application of membrane filtration with in-line coagulation. The aim of the research is water reuse in the industry with the application of nanofiltration membranes.

We have chosen textile wastewater and lab tests were performed during the first year of the project. Textile industry has generally significant water demand along with the heat energy. Nanofiltration membrane technology was chosen as suitable choice for wastewater reuse in textile industry, since it has relatively high fluxes and excellent removal of dyes, COD and divalent ions. [1]

There are two sources of wastewater – dye bath production and steam production from boilers. The composition of dye-facility wastewater varies significantly in the high COD concentrations, colour and turbidity. To reduce fouling and obtain better final permeate quality from the filtration, pre-treatment methods have been investigated in lab-scale unit with nanofiltration membrane as well.

We also discovered the opportunity of water and energy savings from boiler condensate. It is partially reused based on the conductivity lower than 60 $\mu\text{S}/\text{cm}$. Otherwise it is discharged wastewater with high temperature regardless of higher temperature (up to 80 °C). We have used a lab-scale nanofiltration membrane system for boiler condensate treatment in order to obtain water that can be reused in the boilers.

The results demonstrated that using nanofiltration has an acceptable efficiency in simultaneous reduction COD, turbidity and conductivity. Our results are going to be introduced at our conference presentation.

Acknowledgment: Project TH04030332 is conducted with the financial support from the Technology Agency of the Czech Republic TA CR.

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COUPLED PRODUCTION OF AROMA COMPOUNDS BY TWO STRAINS OF MICROORGANISMS USING MEMBRANE HYBRID SYSTEM

M. Mihaľ, I. Červeňanský, J. Markoš

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 81237 Bratislava, Slovakia (mario.mihal@stuba.sk)

Abstract: Some of the natural substances are impossible to produce directly using one strain of microorganism and they must be produced via one or more intermediates requiring the use of different production strain for each one. Good example is bioproduction of phenylacetaldehyde and phenylacetic acid from 2-phenylethanol by the bacteria *Gluconobacter oxydans*. 2-Phenylethanol can be produced by the biotransformation of L-phenylalanine using yeasts *Saccharomyces cerevisiae*. Both, phenylacetaldehyde and 2-phenylethanol are strong inhibitors and its in situ removal from the fermentation medium is necessary to apply to increase the effectivity of the bioproduction. The way how to do it is by using of membrane hybrid system with immersed and external capillary membrane modules for extractive biotransformation that are the promising solution for that case.

In this work three types of aromas: 2-phenylethanol, phenylacetaldehyde and phenylacetic acid were produced in a special type of hybrid systems consisted of two interconnected membrane bioreactors containing two different production strains. In the first bioreactor (3 L stirred tank bioreactor) 2-phenylethanol from substrate L-phenylalanine was produced by *Saccharomyces cerevisiae*. Produced 2-phenylethanol was continually extracted via immersed capillary silicone rubber membrane module from the first bioreactor to the fermentation medium of the second bioreactor (15 L airlift reactor), which contained production bacteria *Gluconobacter oxydans* transforming 2-phenylethanol to phenylacetic acid or phenylacetaldehyde depending on the type of the bacteria strain. During the production of phenylacetic acid product was accumulated in the second bioreactor, while in case of production of phenylacetaldehyde product was continually extracted via external extraction unit to the regeneration unit for the extractant, where it was accumulated.

Acknowledgement: This work was supported by the Slovak Research and Development Agency under the contract No. APVV-16-0111 and No. APVV-18-0134.

PREMIX MEMBRANE EMULSIFICATION FOR PRODUCING EMULSIONS AT LARGE SCALE

O. Alliod¹, C. Charcosset¹

¹ *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEPP, UMR 5007, 43 boulevard du 11 novembre 1918, F-69100, VILLEURBANNE, France*

Abstract: Membrane emulsification has been increasingly reported these last years for the preparation of emulsions, double emulsions and a large range of colloids such as microspheres and microcapsules. Membrane processes are divided into two types: direct membrane emulsification and premix membrane emulsification. In this last technique, large droplets of coarse premix are disrupted into fine droplets by utilizing a microporous membrane. Premix membrane emulsification holds several advantages over direct membrane emulsification : (1) the flux can be much higher than in direct membrane emulsification, (2) the mean droplet sizes are smaller than in direct membrane emulsification with a droplets/ pore ratio equals to 1 or less, (3) the experimental set-up is simpler than in direct ME, e.g. no pump or stirrer are needed, except for the preparation of pre-emulsion, (4) less membrane fouling is obtained and membrane cleaning is easier. In our previous work, we developed an original set-up using a high-pressure syringe pump, longer membranes of 10 cm instead of 1 cm and applied pressure up to 60 bar instead of 6 bar, which allows flowrate 100 times higher than usually obtained¹.

The aim of the present study was to produce emulsions with droplets between 1 and 5 microns using this set-up at high flowrates (up to 200 ml/min). The influence of both composition (interfacial tension, ratio between the hydrophilic and hydrophobic phases, viscosity...) and process (flowrate, pressure, membrane length...) have been investigated to a better prediction of the final droplet size of the emulsion and energy

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CO₂ SEPARATION FROM FLUE GAS USING HYBRID MEMBRANE-X SEPARATION PROCESSES: A TECHNICAL REVIEW

J. R. Ronzon Tirado, L. Kratky

Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Process Engineering, Technická 4, Prague 6, Czech Republic, phone +420-723-646-467, email: JoseRenato.RonzonTirado@fs.cvut.cz

Abstract: Membrane-X separation processes utilization for flue gases represent an opportunity to modernize and optimize current infrastructure to fulfil the increasingly strict environmental regulations. On one hand the membrane process equipment is relatively simpler, smaller, and cheaper to operate than traditional gas separation methods but on the other, high purity products from the membrane process are difficult or acquire. Thus, combining membrane with conventional methods could result in a process with the benefits of both. Depending on the configuration of the equipment the incorporation could be done from adding steps to the process to fully integrating both separation technologies in a single reactor or compact group of apparatuses.

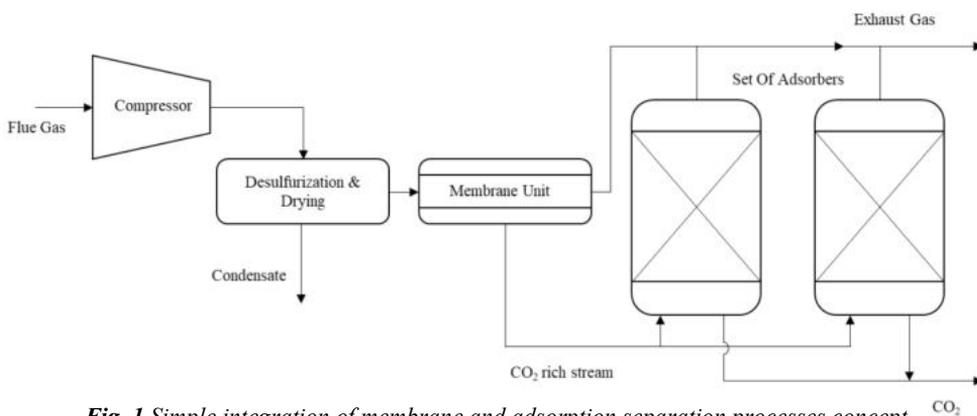


Fig. 1 Simple integration of membrane and adsorption separation processes concept.

The paper, therefore, scopes to overview a technical state of art being in CO₂ separation techniques using hybrid processes based on membrane-X separation. Based on patent, industrial and literature searches, technological set-up, process parameters, advantages, disadvantages, and cost of CO₂ separation from flue gas are finally overviewed and compared with conventional ones. SWOT analysis of hybrid membrane-X hybrid separation processes is done, research needs, and challenges are presented.

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ANALYTICAL EQUATION FOR THE CONCENTRATION DISTRIBUTION OF HYDROXYL RADICALS NEAR THE SURFACE OF REACTIVE ELECTROCHEMICAL MEMBRANE DURING THE ANODIC OXIDATION OF ORGANIC POLLUTANTS

E.D. Skolotneva ¹, S.A. Mareev ¹, V.V. Nikonenko ¹,
N.D. Pismenskaya ¹, M. Cretin ²

¹ Membrane Institute, Kuban State University, 149 Stavropolskaya st., Krasnodar, Russia
(mareev-seymon@bk.ru, www.kubsu.ru)

² Institut Européen des Membranes - UMR5635, Montpellier, France

Abstract: Anodic oxidation is a promising next-generation technology for the treatment of water contaminated with organic pollutants. Although a large number of experiments were performed using reactive electrochemical membranes (REM) up to the date, the theory of the process and the mathematical modeling, in particular, are developed poorly. We present an analytical equation for the dependence of hydroxyl radical (OH[•]) concentration on the distance from the REM surface during the electrooxidation of organic compounds.

In the system under study, the oxidation of organic pollutants by hydroxyl radicals occurs close to the surface of REM due to the short life of OH[•]. Assuming that a) oxidation of organic compounds proceeds only via the assistance of hydroxyl radicals near the electrode surface; b) concentration of organic compound is high enough to be considered as a constant; c) oxygen evolution, via H₂O₂ oxidation, is negligible. The boundary conditions for the problem are as follows: at infinite distance from the REM surface, the concentration of OH[•] is zero; at the surface, it is constant, c_{OH}^s , and can be calculated from the equation $-D_{OH} \left[\frac{dc_{OH}^{\bullet}}{dx} \right]_{x=0} = \frac{j}{F}$. The analytical solution of the problem gives the hydroxyl radicals concentration profile:

$$c_{OH^{\bullet}} = \frac{4zk_Rc_Rc_{OH^{\bullet}}^s}{\left[\sqrt{\frac{8}{3}k_{OH^{\bullet}}c_{OH^{\bullet}}^s + zk_Rc_R} \left(1 - \exp\left(-x\sqrt{\frac{zk_Rc_R}{D_{OH^{\bullet}}}}\right) \right) + \sqrt{zk_Rc_R} \left(1 + \exp\left(-x\sqrt{\frac{zk_Rc_R}{D_{OH^{\bullet}}}}\right) \right) \right]^2} \exp\left(-x\sqrt{\frac{zk_Rc_R}{D_{OH^{\bullet}}}}\right)$$

where D_{OH} and c_{OH} are the diffusion coefficient and concentration of hydroxyl radicals, respectively; k_{OH} is the rate constant of the recombination reaction of OH[•]; c_R is the concentration of organic compound; k_R is the rate constant of the organic compound oxidation by hydroxyl radicals; z is the number of hydroxyl radicals involved in oxidation reaction of organic compound; x is the distance from the REM surface.

We are grateful to Russian Science Foundation (project #19-79-00268) for financial support.

COMPUTATIONAL STUDY OF FLUORINATED POLYMER OF INTRINSIC MICROPOROSITY PIM-2 WITH EXPERIMENTAL DATA COMPARISON

C. Muzzi¹, A. Fuoco¹, S. Bekir^{2,3}, T. Uyard⁴, M. Monteleone¹, E. Esposito¹, M. Longo¹, M. P. De Santo⁵, M. Lanč⁶, K. Friess⁶, O. Vopička⁶, P. Izák^{6,7,8}, J. C. Jansen¹, E. Tocci¹

¹ Institute on Membrane Technology (CNR-ITM), Via P. Bucci, 17/C, 87036, Rende, CS, Italy (e.tocci@itm.cnr.it, www.itm.cnr.it)

² Institute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

³ Department of Medical Services and Techniques, Vocational School of Health Services, Kirsehir Ahi Evran University, Kirsehir, 40100, Turkey

⁴ Department of Fiber Science and Apparel Design, College of Human Ecology, Cornell University, Ithaca, NY, 14853, USA

⁵ Department of Physics and CNR-Nanotec, University of Calabria, Rende, CS, Italy

⁶ Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, Prague 6, 166 28, Czech Republic

⁷ Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojova 135, 165 02, Prague 6 – Suchbátka, Czech Republic

⁸ Institute of Environmental Technology VSB-TUO, 17. listopadu 15/2172, 708 33, Ostrava-Poruba, Czech Republic

Abstract: A new synthesis technique¹ has led to the formation of self-standing films of the linear polymer synthesized from commercially available 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethylspirobisindane (TTSEBI) and decafluorobiphenyl (DFBP) monomers, PIM-2, bringing new interest in this material. A computational study was performed in order to understand the gas transport properties of this polymer, belonging to the promising class of polymer of intrinsic microporosity (PIM) and results were compared with the experimental analysis². It was found a high fractional free volume (FFV) of about 34% and a Brumauer-Emmett-Teller (BET) surface area of 642 m²g⁻¹, in agreement with experimental value of 636 m²g⁻¹. The low BET surface area and the high FFV, thus the low interconnectivity, is responsible for the about average permeability performance, that sees CO₂ being the most permeable gas and N₂ the least permeable gas. Sorption isotherms show dual-mode behaviour for all gasses, except for H₂ that follows Henry's law. Solubility coefficients decrease as a function of gas critical temperature. Polymer chains appear not to have particular interaction with gas molecules, but to form inter- and intra-chains halogen and hydrogen bonds.

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TRANSPORT ASYMMETRY OF BILAYER ION-EXCHANGE MEMBRANES

A. N. Filippov, N. A. Kononenko, S. A. Shkirskaya

Department of Higher Mathematics, Gubkin University, Leninskii prospect 65-1, Moscow, 119991, Russia (a.filippov@mtu-net.ru, <http://kvm.gubkin.ru/filippov.html>)

Abstract: Bilayer polymer membranes with different layer densities of fixed charges have the property of asymmetry of diffusion permeability¹, current-voltage characteristics^{2,3}, membrane potential and ion separation coefficient⁴ when changing the direction of action of the external driving force (gradients of electrolyte concentration, electric potential or pressure). This makes it possible to use such membranes as sensors, switches, diodes, and fuel cell components. This work shows how the degree of asymmetry of transport properties of bilayer membranes can be controlled by varying the ratio of layer thicknesses, the difference in their exchange capacities, the coefficients of the equilibrium distribution of ions, and other physical and chemical parameters.

We show the possibility of theoretical calculation of the degrees of asymmetry of diffusion permeability, limit current, streaming potential and rejection coefficient from a single point of view on the basis of the fine-porous membrane model using the same set of system parameters and illustrate this with our own experimental results. It is concluded that the maximum degree of asymmetry is achieved due to a greater difference in the values of the exchange capacities of the layers. Other parameters (under presence of the charge capacity difference) may increase or decrease the asymmetry of transport properties to a lesser extent.

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MODELLING ION TRANSFER THROUGH ION EXCHANGE MEMBRANES IN ELECTRODIALYSIS FOR MULTI-IONIC SOLUTIONS

S. Ozkul¹, J. van Daal¹, R. Bisselink², N. Kuipers², H. Bruning¹,
J. Dykstra¹, H.H.M. Rijnaarts¹

¹ *Environmental Technology Department, Wageningen University & Research, 6708 WG Wageningen, the Netherlands*

² *Food and Biobased Research, Wageningen University & Research, 6708 WG Wageningen, the Netherlands*

Abstract: Water reuse is one of the solutions to prevent depletion of freshwater resources. However, continuous use of water in closed cycle systems can result in accumulation of specific ions in the water cycle, which limits the possibilities for re-use applications. Especially in agriculture, accumulation of sodium ion (Na⁺) in the irrigation water negatively affects the soil permeability and limits the crop growth. Developing ion selective desalination technologies that remove specific ions could in many cases increase the potential for water reuse. Electrodialysis (ED) is a desalination technology that has been mainly used for brackish water desalination and reuse. ED has a potential to selectively remove or recover specific ions. It is an electrically driven membrane process in which ion transport takes place as a result of electro-migration and diffusion across the membranes. Understanding these mechanisms behind ion transport mechanisms in ED is important to enhance the ion selectivity of the process. In this research we aim to explain these mechanisms based on theoretical and experimental studies considering multi-ionic solutions. For that purpose, a two-dimensional theoretical model was developed in order to describe the transport of ions and water through membranes in an ED cell. The computational domain of this model is a repeating unit of an ED cell, which includes one diluate channel, one cation exchange membrane (CEM), one concentrate channel and one anion exchange membrane (AEM). The two-dimensional process model describes transport of ions across the membranes with the extended Nernst-Planck equation. Furthermore, chemical (acid-base) equilibria were included. Different material characteristics of the membranes (AEM and CEM) used in the ED cell, such as thickness, membrane charge and porosity were also considered in the model. Furthermore, ion specific properties, including the chemical affinity of the membrane materials for specific ions, and the diffusion coefficients were analysed and included in the model. In order to validate the model desalination experiments were performed using a laboratory scale batch-mode ED setup. The effect of various operational parameters on selectivity was studied, such as the current density and the water flowrate. During the experiments the pH, electrical conductivity, temperature and water level of the three solutions (diluate, concentrate and electrolyte) were recorded continuously.

A PROCESS MODEL OF ELECTRODIALYSIS INCLUDING MEMBRANE DEFORMATION EFFECTS

G. Battaglia, L. Gurreri, A. Cipollina, A. Tamburini, M. Ciofalo, A. Pirrotta, G. Micale

Dipartimento di Ingegneria, Università degli Studi di Palermo (UNIPA) - viale delle Scienze Ed.6, 90128 Palermo, Italy (luigi.gurreri@unipa.it)

Abstract: Electrodialysis (ED) is an electro-driven process that makes use of ion exchange membranes (IEMs) under an applied electric field. The main application of ED is the desalination for drinking water production. A transmembrane pressure (TMP) distribution may arise in ED stacks due to an uneven pressure distribution in the two fluid channels, thus causing membrane/channel deformation and flow redistribution. This can occur in large-scale non-parallel configurations, e.g. cross-flow arrangements. Detrimental effects of membrane deformation have widely been studied with reference to several membrane processes. However, this aspect has been neglected in ED applications.

In this work, a novel process model of ED units including the effects of membrane deformation is presented¹. The model was developed with a multi-scale architecture. The model simulates the fluid-structure interaction (i.e. membrane deformation and flow redistribution) in a cell pair² based on correlations from small-scale numerical simulations (structural mechanics and computational fluid dynamics)^{3,4}. Then, transport and electrochemical phenomena occurring in ED systems are simulated. Cross-flow ED units were simulated in two-dimensions (length and width). Results showed that mild deformations have a negligible impact on the ED process performance. However, configurations prone to larger deformations (e.g., thin membranes) exhibited more significant effects, with an increase in the specific energy consumption. The same approach can be used for other configurations (e.g. counter-flow and asymmetrical channels in parallel flow) and for reverse electrodialysis.

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A VALIDATED MULTI-SCALE MODEL OF A NOVEL ELECTRODIALYTIC ACID-BASE FLOW BATTERY

A. Culcasi, A. Zaffora, A. Cosenza, M. Di Liberto, L. Gurreri,
A. Tamburini, A. Cipollina, G. Micale

Dipartimento di Ingegneria, Università degli Studi di Palermo (UNIPA) - viale delle Scienze Ed.6, 90128 Palermo, Italy (luigi.gurreri@unipa.it)

Abstract: Electrical energy storage is crucial for a deeper penetration of intermittent renewable energies, e.g. solar and wind. The Acid/Base Flow Battery (AB-FB) is a novel, sustainable, environmental-friendly storage technology with high energy density¹. The process is based on reversible electro dialytic techniques that convert the electrical energy in the chemical energy associated to pH gradients and *vice versa*. The bipolar membrane electro dialysis process operates in the charge phase, while the bipolar membrane reverse electro dialysis in the discharge phase. The stack consists of repetitive units, called triplets, made up of an anion-exchange membrane, a bipolar membrane, and a cation-exchange membrane, separated by spacers forming the channels where the acid, base and salt solutions flow.

This work presents for the first time an experimentally validated AB-FB process model along with a sensitivity analysis. The model is based on a multi-scale simulation strategy, where four different dimensional scales are integrated within a comprehensive simulation tool with distributed parameters. The lowest hierarchical level concerns the channels. It includes CFD simulations for the estimation of polarization phenomena and pressure losses, and the correlations for the physical properties of the solutions. The middle-low hierarchical level simulates the triplets, by computing mass balances, membrane fluxes, electrical resistance and electromotive force. The middle-high scale simulates the stack by an electrical sub-model intended to compute the shunt currents, and by a hydraulic sub-model to calculate pressure losses. Finally, the highest hierarchical level simulates the external hydraulic circuit including dynamic mass balances in the tanks.

The model was validated against an original experimental campaign, showing a good agreement. A broad sensitivity analysis was performed in order to explore the behavior of the battery under several scenarios. The model outcome illustrates how stack geometry, operating parameters and battery layouts (e.g. open-loop vs closed-loop operations) can affect the process performance. By adopting some measures to tackle the shunt currents and taking thermodynamic advantages from open-loop operations, the round trip efficiency reached values up to 70%. This original model will orient the identification of optimized and competitive AB-FB systems.

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REMOVAL OF MEMBRANE FOULING AFTER POLYMER FLOODING PRODUCED WATER TREATMENT

K. Janegova¹, R. S. B. Soares^{1,2}

¹ MemBrain s.r.o., Pod Vinici 87, Straz pod Ralskem, 471 27, Czech Republic
(kristyna.janegova@membrain.cz, www.membrain.cz)

² Institute of Chemistry, University of São Paulo, Av. Professor Lineu Prestes 748,
São Paulo, SP 05508-000, Brasil

Abstract: Polymer flooding has been successfully applied as an oil exploitation method in oil and gas industry. Partially hydrolyzed polyacrylamide (HPAM) is one of the most common polymers used in polymer flooding¹. Along with polymer flooding, there is also an increasing amount of produced water per year, which consists of a complex mixture of chemical additives, HPAM, crude oil, suspended solids and salts. Polymer flooding produced water can be reused to decrease water demand if appropriately handled. Electrodialysis (ED) has been successfully used to reduce the salinity of the polymer flooding produced water^{1,2}. However, recent articles report that HPAM causes fouling – especially on anion exchange membranes³. Ion exchange membranes (IEMs) received after pilot desalination of polymer flooding produced water were subjected to *ex-situ* chemical cleaning at 60 °C. The cleaning was realized consequently with acid (0.1M HCl) and base (0.1M NaOH) solution, or acid, base and sodium dodecylbenzenesulfonate (0.4 wt%) solution. IEMs were characterized to determine the efficiency of the cleaning procedures using optical and scanning electron microscopy, FTIR, evaluation of swelling degree, ion exchange capacity, resistance, and permselectivity. The results demonstrated that the electrochemical properties of IEMs can be improved after the cleaning, however individual results are also strongly dependent on the position of an IEM in the ED stack.

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THE SENSITIVITY OF POLYELECTROLYTE MULTILAYER NF MEMBRANES TO VARIOUS SURFACTANTS

Á. Bóna^{1,2}, N. Nemestóthy¹, I. Galambos²

¹ *Research Institute on Bioengineering, Membrane Technology and Energetics, University of Pannonia, H-8200 Veszprém, Egyetem u. 10.*

² *Soós Ernő Water Technology Research and Development Center, University of Pannonia, H-8800 Nagykanizsa, Zrínyi M. u. 18. (bona.aron@sooswrc.hu, www.soooswrc.hu)*

Abstract: An increasingly noteworthy NF membrane technology, the layer-by-layer (LbL) method involves building alternating polycation and polyanion layers on a substrate (usually a UF membrane) to produce a thin dense polyelectrolyte multilayer (PEM) film which acts as an active separation layer. These membranes offer a powerful self-healing ability and high chemical stability: resistance to chlorine, a wide pH range and solvent resistance (if the supporting substrate allows this). This technology has matured to commercial products, providing fouling resistant hollow fiber NF membranes which can be applied for difficult feeds, such as surface water without any pretreatment.

Conversely, a known downside of these membranes is that PEM can be destabilized by very high salinity (above 2-3 mol/dm³) or by surfactants above their critical micellar concentration (CMC). However, effects at concentrations below CMC are unknown, although the usefulness of this information points beyond theoretical knowledge: the fouling-resistant LbL membranes could be applied for various challenging separation tasks (e.g. industrial wastewater treatment, food industrial separations, etc.) where surfactants can be present in varying amounts.

By measuring the changes of the membrane properties (flux, rejection of various compounds) through progressively elevating the concentrations of different surfactants (cationic and anionic) on these membranes, we propose a hypothesis for the mechanism of the degradation process.

MEMBRANE PROCESSES USING FOR THE PREPARATION POLYMERIC SORBENTS

J. Wolska¹, M. Bryjak¹, N. Jalilnejad², N. Kabay²

¹ *Depart. of Process Engineering and Technology of Polymeric and Carbon Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland*

² *Chemical Engineering Department, Faculty of Engineering, Ege University, 35100 Izmir, Turkey*

Abstract: During the last years the different chemical substances, pharmaceutical and cosmetic goods that are toxic to human endocrine system, so called “endocrine disruptors” (EDs), have been identified in natural waters. The most of vital functions of the human body can be altered by EDs, which interfere with the natural production, release, or elimination of hormones. Therefore, that chemicals disturb the performance of the endocrine system and can cause adverse health effects in humans and other mammals [1]. Due to refractory content of endocrine disruptors in water bodies it is hardly to control a content of such pollutants as well as to develop the efficient methods for their detection in the waters and foods. The presented studies are focused on preparation of thermosensitive and molecularly imprinted polymer sorbents for selective recognizing of endocrine disruptors, such as bisphenol A (BPA) were studied. A method for syntheses of uniform microspheres containing template removing substances with high specific surface areas was designed by combining membrane emulsification (ME) technique and suspension polymerization. In the first step the oil in water emulsion by ME was prepared. After emulsification the suspension polymerization was carried out. During studies such parameters as e.g. amount of template, initiator or organic phase and composition of water phase were altered to investigate their effect on geometry of obtained microspheres. The research was focused on selection of such process parameters that guaranteed preparation of thermosensitive, monodisperse microspheres with template foot-prints and high surface areas. It was shown that membrane emulsification is the useful method for formation of monodispersed particles with foot-prints of separated species. The obtained imprinted microspheres could be used as thermosensitive sensors used to detect BPA in water or food. It has additionally been shown that by changing the temperature, it is possible to regenerate sorbents without the use of hazardous chemicals, but only hot water.

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STUDY OF ION TRANSPORT IN NANOCANNELS MADE IN SILICON CHIPS BY OPTICAL AND FOCUSED ION BEAM LITHOGRAPHY

D.V. Lebedev^{1,2}, A.M. Mozharov^{3,4}, I.S. Mukhin^{3,4}, A.S. Bukatin^{2,3},
A.O. Golubok^{2,4}, A.A. Evstrapov², A.D. Smirnov⁵

¹ Saint Petersburg State University, 13B Universitetskaya Emb., St Petersburg 199034, Russia (denis.v.lebedev@gmail.com)

² Institute for Analytical Instrumentation RAS, 26 Rizhskii pr., St. Petersburg 190103, Russia

³ St. Petersburg Academic University, 8/3 Khlopina Street, St. Petersburg 194021, Russia

⁴ ITMO University, 9 Kronverksky pr., St. Petersburg 197101, Russia

⁵ CJSC "Svetlana-EP", 27 Engels Ave., St. Petersburg 194156 Russia

Abstract: Today, the study of ion transport in nanochannels is important not only in the field of fundamental science, but also in various practical applications such as biomedicine [1], genetic engineering [2], sensor development etc. The use of lithography methods opens up wide possibilities for the creation of micro- and nanochannels, nanoscale pores, as well as the implantation of functional active nanostructures into them. In this study, we developed and tested a technique for fabrication of microfluidic chips with two flow cells (cameras) with 0.05 cm³ volume, interconnected with a system of nanochannels (width 90 nm, depth 20 nm). For nanochannels fabrication and study of the FIB etching, CrossBeam Neon40 (Carl Zeiss) system of crossed electron and ion beams was used. This technique allows to create arrays of channels with various widths and depths. To study the transport properties of the obtained nanochannels, an experimental setup was developed and assembled, the main element of which is a microfluidic chip, consisting of two half-volumes separated by nanochannels. Ag / AgCl wires were used as measuring electrodes. A series of experiments was carried out to record the current-voltage (I-V) characteristics of the nanochannel at various electrolyte concentrations. An aqueous KCl solution was chosen as the base electrolyte. The I – V characteristic was measured in the voltage range of -0.2 ... + 0.2V. With an increase in concentration from 0.01 to 1 M, the channel conductivity increased from 7.3 to 11.8 pS. The authors attributed such a low increase in conductivity to the presence of a significant uncompensated electric charge within the channels. The synthesized systems with micro- and nanoscale and nanopores can be used in studies of the transport properties of various ions and molecules. In addition, such structures can be successfully used in the development of highly sensitive biosensor systems and in lab-on-a-chip systems.

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AN ENANTIOSPECIFIC SORPTION OF α -PINENE IN ALD FUNCTIONALIZED POLYCARBONATE MEMBRANES

L. Brožová¹, M. Otmar¹, J. Žitka¹, P. Izák², R. Zazpe^{3,4}, J. M. Macák^{3,4}

¹ Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovsky Sq.2, 162 06 Prague 6, Czech Republic (brozova@imc.cas.cz)

² Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 135, 165 02 Prague 6, Czech Republic (www.imc.cas.cz)

³ Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 53002 Pardubice, Czech Republic

⁴ Central European Institute of Technology, Brno University of Technology, Purkynova 123, 612 00 Brno, Czech Republic

Abstract: Many molecules in living organisms are chiral. The individual enantiomers of chiral compounds often differ with their biological properties; e.g., in the case of some terpenoids, the enantiomers can be distinguished by a specific flavor or smell. If one of the enantiomers has a therapeutic effect, the other can be inactive or even toxic. To the contrary of other separation techniques, the uniqueness of chiral separation lays in the fact, that individual enantiomers exhibit quite identical chemical and physical properties, and therefore some asymmetric surroundings must be created to achieve their distinction. Among of various enantioseparation methods (preferential crystallization, preparative HPLC, simulated moving bed, etc.), a chiral separation through polymer membranes has recently emerged. This technology seems to be advantageous for its low financial cost, continuousness and easy scalability of the process.

In this work, we studied an enantiospecific sorption of α -pinene in polycarbonate membranes with a high aspect ratio, which were functionalized by an atomic layer deposition (ALD) of (–)- α -pinene. The first membrane was blank, second one was treated by ALD of (–)- α -pinene alone and the third one was treated by ALD of aluminum oxide followed by a ALD layer of (–)- α -pinene.

In a series of experiments using sorption balance, we found that the blank polycarbonate membrane and the membrane treated by ALD with (–)- α -pinene absorbed a higher amount of (–)- α -pinene than (+)- α -pinene. On images from a scanning electron microscopy (SEM) a significant swelling of the second membrane and decrease pore diameter is apparent. Probably, there could be some difference in retention of the individual enantiomers during diffusion through the membrane pores induced by ALD. The second membrane with the additional aluminum oxide showed a double specific sorption of (–)- α -pinene compared to the sorption of (+)- α -pinene and even to the racemic mixture.

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THE EFFECT OF THE NATURE OF ION-EXCHANGE MATERIALS ON FOULING WITH POLYPHENOLS DURING THE ED PROCESSING OF JUICES AND WINES

N.D. Pismenskaya¹, V.V. Sarapulova¹, K.A. Tsygurina¹, V. Perreault², S. Mikhaylin², L. Bazinet²

¹ Membrane Institute, Kuban State University, 149th Street, Krasnodar, Russia

² Institute of Nutrition and Functional Foods (INAF), Laboratory of Food Processing and Electro-Membrane Processes (LTAPEM), Food Science Department, Université Laval, Québec, QC, Canada (author@email.address, n_pismen@mail.ru)

Abstract: The process of the anthocyanins adsorption by the ion-exchange resins and membranes from the model aqueous solutions, wine and juices having the pH of 3, 6 and 9 is studied. It is shown that the pH of the internal solution of the cation-exchange resin KU-2-8 and membranes CMX, MK-40 is 2-3 units lower, and the pH of the internal solution of the anion-exchange resins (AV-17-8, AV-17- 2P, EDE-10P) or membranes (AMX, MA-41, MA-41P, MA-40) is 2-4 units higher than the pH of the external fluid (model solution, wine or juice). This effect is caused by the Donnan exclusion of hydroxyl ions or protons as co-ions, which are the products of protolysis reactions. Due to the pH shift, the electric charge of anthocyanins inside the ion-exchange materials (IEM) differs from their charges in the external fluid. For example, the model solution at a pH of 6 contains anthocyanins as molecules having no electric charge. In the resins AV-17-8 (MA-41) and AV-17-2P (MA-41P), anthocyanins are in the form of singly charged anions, and, in the resin EDE-10P (MA-40), they are transformed into doubly charged anions. Due to the electrostatic interactions of these anions with the positively charged fixed groups of the anion-exchange materials, their adsorption capacity is higher than it could be expected based on the pH of the anthocyanins containing fluid. The contribution of the electrostatic interactions of anthocyanin ions with the polar fixed groups increases with the increase in ion-exchange capacity of the IEMs and the decrease in anthocyanin concentration of the external fluid. The adsorption caused by the π - π (stacking) interactions with aromatic matrix (AV-17-8, AV-17-2P, KU-2-8, AMX, MA-41, MA-41P, CMX, MK-40) or the hydrogen bonds with the secondary and ternary amino groups (EDE-10P, MA-40) enhances anthocyanin and other polyphenol adsorption on IEMs during wine and juices processing using electrodialysis or ion exchange techniques.

This new knowledge provides an understanding of the fouling mechanisms of ion-exchange materials by polyphenols and will help to develop cleaning strategies as well as strategies for extracting anthocyanins from juices and wine using IEMs.

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LIST OF THE PARTICIPANTS

A

Adamová S. Czech Republic	
Ahmad M. Z. United Kingdom	56, 112
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ČEZ Energetické produkty, s.r.o. is a subsidiary of ČEZ, a. s., which is the 100 % owner of the company. Since 2009 the company has been providing comprehensive services not only in the management of combustion products of the conventional power plants of CEZ Group's. The company is also active in processing of CCPs (sale of fly ash, gypsum, slag and stabilized fly ash above all), operation and maintenance of equipment and technology of fuel and combustion products management. The company currently has nearly 1000 employees.

Our company is one of the founding members of the Association for the use of coal combustion products (ASVEP), which deals with the use of coal combustion products in the construction industry. ASVEP is also participating on the preparation of the relevant legislation (technical requirements for application, a national strategy for CCPs, etc.).

The company closely cooperates with universities in order to enhance research and development in all fields, where the company is active. In recent years, the company has implemented several projects dealing with the new possibilities of CCPs application.

The company also provides services in order to comply with requirements following from Regulation No. 1907/2006/EC (REACH Regulation) on registration, evaluation, authorization and restriction of chemical substances.

Since 2009 the company closely cooperates with the Association ECOBA, in 2013 the company became a full member. As part of the association's activities ECOBA participate in the preparation of legislation and regulations regarding the use of CCPs in the EU, preparation of rules and standards in the application of CCPs as construction products. These products are essentially important in existing industrial technologies above all by reducing greenhouse gases emissions associated with the extraction and processing of natural mineral raw materials.

ČEZ Energetické produkty, s.r.o. owns certificates on management systems of quality ISO EN 9001, environment ISO EN 14001 and safety ISO 45000.



Company ČEZ Energetické produkty, s.r.o., as a promoter of CCPs as a green strategy, deals with the optimization of the existing water management in conventional power plants technologies in order to implement environmentally friendly technologies and to improve quality of produced CCPs. That is the reason why our company carries out studies and subsequently is going to invest in projects focused on water savings, where the proposed technologies mainly use membrane technologies (reverse osmosis, ultrafiltration, etc.)

It is worth mentioning the currently ongoing investment projects within the solution of overbalanced waters at conventional power plant EPR II, see photo.



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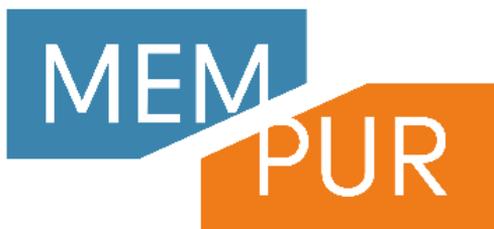
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Membránové procesy

Čištění odpadních vod



The **Czech Membrane Platform (CZEMP)** associates prominent experts and institutions centred on research, development, implementation and application of membrane operations in technological processes of broad spectrum of industry. Hence, the development of the founded Platform is a prerequisite for the interconnection of research and educational subjects with production sphere and other institutions, which are engaged in technologies aiming at a constantly sustainable growth of society.

Basic Mission

- CZEMP interconnects activities of professional community, academic sphere, industrial producers or users of products and technologies in the membrane area
- CZEMP ensures the transfer and stabilization of infobases concerning membrane topics and supports the education in the field
- CZEMP promotes the coordination of activities of subjects acting in the area of research and development of membrane processes, pursuing programmes and both domestic and foreign financial resources
- CZEMP supports and defends common interests of its members with the aim to popularize membrane topics and create a proper atmosphere for their development and stabilization

The conference MELPRO 2020 si financially supported by
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