



On behalf of the NYM organising committee, I would like to welcome you all to the online version of the 17th Network Young Membrains Meeting. In a more normal year, we would have been hosting the event in Manchester, just before ICOM 2020 in London. I would like to thank, in advance, all speakers for agreeing to take part in the online meeting and the European Membrane Society for their generous sponsorship of the prizes for the three best presentations. In addition, we also have plenaries from three eminent early career researchers in membrane science to look forward to.

Hope you enjoy the meeting!

Andrew

Dr. Andrew Foster (Chair, University of Manchester)
Dr. Greg Mutch (Vice Chair, University of Newcastle)

NYM committee:

Dr Zamidi Ahmad (University of Manchester)
Dr. Edidiong Asuquo (University of Manchester)
Dr. Bibiana Comesana Gandara (University of Edinburgh)
Dr. Richard Kirk (University of Manchester)
Dr. Saeed Mazinani (University of Bath)



Zoom meeting details and guidelines

- On-line access to the conference will be provided via the **Zoom platform**. You can use your computer (PC or Mac), tablet, or phone. If you use a tablet or phone, please download the Zoom app in the App Store or Google Play. If you use your computer, you can either [download the app](#) (we recommend doing so) or open Zoom via any of the commonly used web browser clients. **There are two open Zoom sessions available for presenters wanting to check their setup before the meeting.**

Pre-Meeting Zooms (GMT)	Zoom Meeting No	Password
30 th Nov, 12.00-12.30 pm	982 9763 4544	311071
30 th Nov, 7.00-7.30 pm	938 6730 4606	280530

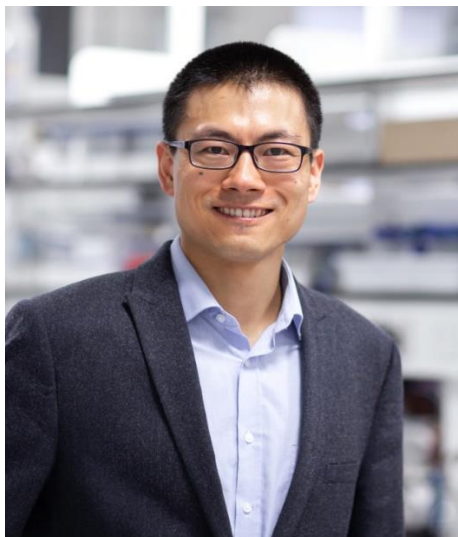
Notes for presenters and attendees:

- The sessions are arranged in themes, with the expectation that presenters will remain engaged for their full session to aid discussion.
- Presenters are asked to connect into their session **10 min before** the listed start time to check in with the moderators. The sessions will also run **10 min after** the end time to allow for supplementary questions to the presenters.
- Presenter is expected to connect camera at both introduction by moderator and end of talk to answer questions.
- Questions submitted via the chat function will be relayed by the moderator at the end of each presentation.
- Attendees must both mute their microphone and turn off their video, prior to connection to the sessions.
- Zoom meeting details for the NYM 2020 meeting (3-4 Dec) are listed below.**

Sessions (GMT)	Zoom Meeting No	Password
1&2 (Thurs 8.50-1.10 pm) THURS MORNING	955 3280 4667	220222
3&4 (Thurs 1.50-5.10 pm) THURS AFTERNOON	955 5209 5395	974856
5&6 (Fri 8.50-1.10 pm) FRIDAY MORNING	953 6768 9042	343132
7&8 (Fri 1.50-5.10 pm) FRIDAY AFTERNOON	914 3784 3396	058819



Plenary Speaker



Qilei Song

Barrer Centre, Department of Chemical Engineering, Imperial College
London

Speaker Bio:

Qilei Song is a Senior Lecturer in the Department of Chemical Engineering at Imperial College London and one of the principal investigators at the Barrer Centre. He is leading an interdisciplinary research group at Imperial developing membrane materials for separation and emerging energy applications including fuel cells, electrolyzers, redox flow batteries, and next-generation battery separators. He has published over 40 peer-reviewed articles with 3000+ citations. His recent research was awarded the IChemE Nicklin Medal and the prestigious ERC Starting Grant in 2019, which provides 1.5 Million Euro to develop new membrane materials for energy conversion and storage. He works closely with industry including Shell, Toyota, Schlumberger, and BP-ICAM.



Plenary Speaker



Zachary P. Smith

MIT Department of Chemical Engineering

Speaker Bio:

Zachary P. Smith joined the Department of Chemical Engineering at the Massachusetts Institute of Technology as an Assistant Professor in January 2017. His research focuses on the molecular-level design, synthesis, and characterization of polymers and inorganic materials for applications in membrane and adsorption-based separations. Prof. Smith has been recognized with several awards, including the U.S. Department of Energy (DOE) Early Career Award, the American Institute of Chemical Engineers 35 Under 35 Award, the American Chemical Society PRF Doctoral New Investigator Award, and the DOE Office of Science Graduate Fellowship. He was also selected as a U.S. delegate to the Lindau Nobel Laureate meeting on chemistry in 2013. He has published over forty peer-reviewed articles, holds four patents, and is a co-founder of Flux Technology. Prof. Smith earned his bachelor's degree in Chemical Engineering from the Pennsylvania State University Schreyer Honors College and his Ph.D. in Chemical Engineering from the University of Texas at Austin. While at the University of Texas, he developed structure–property relationships for gas diffusion and sorption in polymeric membranes. His postdoctoral training at the University of California, Berkeley examined the design of metal–organic frameworks for selective adsorption-based separations.



Plenary Speaker



Rahul R. Nair

National Graphene Institute & Department of Chemical Engineering and Analytical Science, The University of Manchester, UK

Speaker Bio:

Rahul R. Nair is a Professor of Materials Physics at the National Graphene Institute (NGI), Henry Royce Institute, and Department of Chemical Engineering and Analytical Science at the University of Manchester and holds a prestigious Royal Society Fellowship and ERC starting grant. He has published over 60 highly cited peer-refereed research articles, including five *Science*, four *Nature*, and more than a dozen *Nature* series publications during the last eleven years. His awards include a Leverhulme Early Career Fellowship from the Leverhulme Trust, IUPAP Young Scientist Award (2014) from the International Union of Pure and Applied Physics, the Moseley Medal and Prize (2015) from the Institute of Physics, Lee Hsun Lecture Award on Materials Science (2018) from the Institute of Metal Research, Chinese Academy of Sciences, the Creativity prize (2018) from the Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW), and the Philip Leverhulme Prize (2018) from the Leverhulme Trust. He has also been selected as a Highly Cited Researcher from 2016 by Thomson Reuters.

The main scope of his research is the novel synthesis and construction of application-oriented devices based on two-dimensional (2D) crystals to explore new physical phenomena. His group is actively engaged in the design and development of 2D materials based membranes and nanofluidic devices for probing fundamental molecular transport at the nanoscale and their potential applications in our daily life.



Thurs 3rd Dec morning

Session 1: Membranes for gas separation and pervaporation

Chair: Andrew Foster

Vice Chair: Bibiana Comesana Gandara

Zoom Meeting: 955 3280 4667 Password: 220222

Session 1 (GMT)	Speaker	Institution	Title
9.00-9.30 am (plenary)	Dr. Qilei Song	Imperial College, London, UK	Membrane Technology for COVID-19 and Climate Change: Challenges and Opportunities
9.30-9.45	Noelia Esteban	University of Valladolid, Spain	New Microporous Polymer Materials for Advanced Applications
9.45-10.00	Eleonora Ricci	University of Bologna, Italy	Multicomponent effects in CO ₂ /CH ₄ separation with glassy membranes
10.00-10.15	Cenit Soto	University of Valladolid, Spain	Enhancement of CO ₂ /CH ₄ selectivity for biogas upgrading via Thermal Rearrangement of Mixed Matrix Membranes
10.15-10.30	Jiangtao Liu	King Abdullah University of Science and Technology (KAUST), Saudi Arabia	Smart Membrane with Light- switchable Valves
10.30-10.45 am	Monica Alberto	The University of Manchester, UK	PIM-1/graphene thin Film Nanocomposite membranes (TFNs) for pervaporation

Break / discussion (30 min)



Thurs 3rd Dec morning

Session 2: Membranes for pollution removal and other studies

Chair: Saeed Mazinani

Vice Chair: Zamidi Ahmad

Zoom Meeting: 955 3280 4667 Password: 220222

Session 2 (GMT)	Speaker	Institution	Title
11.15-11.30 am	Berta Alcalde	University of Girona, Spain	A polymer inclusion membrane (PIM) for the removal of fluoride from natural waters
11.30-11.45	Sebastian Leaper	The University of Manchester, UK	Effective arsenic removal using electrospun PVDF membranes enhanced by POSS-functionalised graphene oxide in membrane distillation
11.45-12.00	Luis Felipe Dos Santos Esteves	University of Duisburg-Essen, Germany	Fluid Flow in porous membrane based on momentum sink added to governing momentum equations
12.15-12.30	Sajjad Mohsenpour	The University of Manchester, UK	Morphological changes in polymeric membranes by addition of graphene oxide: Experimental and thermodynamic study
12.30-12.45	Ahmed Ameen	The University of Manchester, UK	Opportunity and evaluation of Polymer of intrinsic microporosity PIM-1 to treat sour natural gas by Hybrid membrane-amine process: Economic study
12.45-1.00 pm	Ngai Yin Yip	Columbia University, New York, USA	New Insights into Solute-Selectivity Relationship of Thin-Film Composite Polyamide Membranes

Lunch / discussion (60 min)



Thurs 3rd Dec afternoon

Session 3: Membranes for gas separation

Chair: Bibiana Comesana Gandara

Vice Chair: Andrew Foster

Zoom Meeting: 955 5209 5395 Password: 974856

Session 3 (GMT)	Speaker	Institution	Title
2.00-2.15 pm	Laura Matesanz Niño	University of Valladolid, Spain	Gas Separation Membranes obtained by Partial Pyrolysis of Polyimides having Polyethylene oxide moieties
2.15-2.30	Anand Jain	Magdeburg University, Germany	High performing 6FDA-DAM:DABA mixed matrix membranes with ZIF-8 and GO mixtures for effective CO ₂ /CH ₄ separation
2.30-2.45	Jose Miguel Luque-Alled	The University of Manchester, UK	Physical aging prevention of PIM-1 based mixed matrix membranes (MMMs) in CO ₂ /CH ₄ gas separations
2.45-3.00	Sharon Lin	Massachusetts Institute of Technology, USA	Thermal free volume modification effects on gas transport properties for a 6FDA-HAB polyimide with BOC functionality
3.00-3.15 pm	Albert Xiuyuan Wu	Massachusetts Institute of Technology, USA	Elucidating the role of fluorine content on the gas sorption properties for fluorinated polyimides

Break / discussion (30 min)



Thurs 3rd Dec afternoon

Session 4: Electrochemical membrane applications

Chair: Zamidi Ahmad

Vice Chair: Greg Mutch

Zoom Meeting: 955 5209 5395 Password: 974856

Session 4	Speaker	Institution	Title
3.45-4.15 pm (plenary)	Prof. Zachary P. Smith	Massachusetts Institute of Technology, USA	Processable Porous Materials for Membrane-Based Gas Separations
4.15-4.30	Aitor Marcos-Madrazo	Universidad de Cantabria, Spain	Development of Membrane Coated Electrodes for CO ₂ electroreduction
4.30-4.45	Phumlani Msomi	University of Johannesburg, South Africa	Enhancing polymer electrolyte membrane properties for fuel cell application using nanostructured materials
4.45-5.00 pm	Chunchun Ye	The University of Edinburgh, UK	Membranes from sulfonated polymers of intrinsic microporosity for aqueous redox flow batteries

End of day



Friday 4th Dec morning

Session 5: Membranes for desalination

Chair: Edidiong Asuquo

Vice Chair: Zamidi Ahmad

Zoom Meeting: 953 6768 9042 Password: 343132

Session 5 (GMT)	Speaker	Institution	Title
9.00-9.30 am (plenary)	Prof. Rahul R. Nair	The University of Manchester, UK	Science and technology of 2D materials based membranes
9.30-9.45	Oneeb Ul Haq	Chonbuk National University, Republic of Korea	Facile synthesis of ultrathin IEM for brackish water desalination via MCDI
9.45-10.00	Jehad Abbaas Abed Alhaleem Kharraz	University of Hong Kong, Hong Kong	Macro-corrugated and nano-patterned hierarchically structured superomniphobic membrane for treatment of low surface tension oily wastewater by membrane distillation
10.00-10.15	Swatantra Pratap Singh	Indian Institute of Technology Bombay, India	Doped Laser-Induced Graphene Catalytic Filters and Membranes for Wastewater Treatment
10.15-10.30	Ulrich Hellriegel	Karlsruhe University of Applied Sciences, Germany	Energy efficient desalination with membrane capacitive deionization (MCDI): Findings of theoretical and pilot studies
10.30-10.45 am	Clara Skuse	The University of Manchester	Graphene oxide membranes for desalination via membrane distillation

Break / discussion (30 min)



Friday 4th Dec morning

Session 6: Ceramic membranes

Chair: Greg Mutch

Vice Chair: Andrew Foster

Zoom meeting: 953 6768 9042 Password: 343132

Session 6 (GMT)	Speaker	Institution	Title
11.15-11.30 am	Amanmyrat Abdullayev	Technische Universität Berlin, Germany	Effect of Particle Shape on Properties of Freeze Cast Mullite Ceramic Membranes
11.30-11.45	Fabrício Eduardo Bortot Coelho	University of Torino, Italy	Photocatalytic Ultrafiltration ZrO ₂ /TiO ₂ Membrane
11.45-12.00	Mogolodi Dimpe	University of Johannesburg, South Africa	Fe ₃ O ₄ -SiO ₂ coated tyre-based activated carbon nanofibers as a nanoadsorbent for ultrasound assisted dispersive solid phase extraction of arsenic, cadmium and thallium in environmental samples
12.15-12.30	Esra Eray	Aalborg University, Denmark	Enhanced Fabrication of Silicon Carbide Membranes for Water Treatment
12.30-12.45	Natalia Cristina Fontão	University of Bremen, Germany	Asymmetric porous SiOC membranes for microfiltration produced by phase-inversion tape casting technique
12.45-1.00 pm	Hassan Alali Alhweij	University of Bath, UK	Comparative study of novel antifouling sulfonated polyaniline nanofiltration membranes and conventional treatment for water and seawater (pre)treatment

Lunch / discussion (60 min)



Friday 4th Dec afternoon

Session 7: Membranes for filtration

Chair: Saeed Mazinani

Vice Chair: Edidiong Asuquo

Zoom Meeting: 914 3784 3396 Password: 058819

Session 7 (GMT)	Speaker	Institution	Title
2.00-2.15 pm	Sucipta Laksono	University of Duisburg-Essen, Germany	Relating Fouling Mechanisms of Ultrafiltration Capillary Membranes in Mini-plant Operation to Characteristics of Algae-contaminated Water
2.15-2.30	Ali Sayegh	Karlsruhe Institute of Technology, Germany	Treatment of hydrothermal liquefaction liquid waste with pressure driven membrane technologies
2.30-2.45	Pablo López-Porfiri	The University of Manchester, UK	Supported Liquid Membranes (SLM) using green solvents for bio-based organic acids extraction.
2.45-3.00 pm	Ana Carolina Santana	Federal University of ABC, Brazil	Cotreatment of landfill leachate and synthetic wastewater: effect on mixed liquor filterability and membrane fouling
3.00-3.15 pm	Giorgio Pratofiorito	Karlsruhe Institute of Technology, Germany	Biofilm online monitoring in a nanofiltration system

Break / discussion (30 min)



Friday 4th Dec afternoon

Session 8: Membranes for healthcare applications

Chair: Edidiong Asuquo

Vice Chair: Saeed Mazinani

Zoom Meeting: 914 3784 3396 Password: 058819

Session 8	Speaker	Institution	Title
3.45-4.00 pm	Francesca Liva	University of Pisa, Italy	Fabrication and characterization of a biotechnological Bruch's membrane for an in vitro model of the outer blood-retinal barrier
4.00-4.15	Serena Regina	Institute on Membrane Technology (CNR-ITM), Italy	Development of membranes with antibacterial and antiradical activity
4.15-4.30	Prantik Samanta	Karlsruhe Institute of Technology, Germany	DOC and antibiotic removal from pig manure by nanofiltration (NF) to produce ammonium enriched liquid
4.30-4.45 pm	Kseniya Papchenko	University of Bologna, Italy	Evaluating sustainable materials for membrane separations through molecular simulations: the case of Polyhydroxyalkanoates (PHA)
4.45-5.00 pm	Andrew Foster	Closing remarks	
To follow	NYM committee meeting	Best presentation awards (sponsored by EMS) Prize Announcements	1 st prize (500 Euros) 2 nd prize (300 Euros) 3 rd prize (200 Euros) Certificates from EMS Video mailed to all attendees



New Microporous Polymer Materials for Advanced Applications

N Esteban^{1*}, *ML Ferrer*², *C Ania*^{3,4}, *JG de la Campa*⁵, *C Álvarez*^{5,6}, *ÁE Lozano*^{1,5,6}, *JA Miguel*¹

1 IU CINQUIMA, Univ. de Valladolid, Paseo Belén 5, 47011 Valladolid (Spain)

2 Materials Science Factory, Instituto de Ciencia de Materiales de Madrid-ICMM-CSIC, Campus de Cantoblanco, 28049 Madrid, (Spain).

3 Instituto Nacional del Carbón, INCAR-CSIC, 33080 Oviedo, (Spain).

4 CEMHTI CNRS (UPR 3079), University of Orléans, 45071 Orléans, (France).

5 Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Juan de la Cierva 3, 28006 Madrid, (Spain).

6 SMAP, UA-UVA_CSIC, Associated Research Unit to CSIC. Universidad de Valladolid, Facultad de Ciencias, Paseo Belén 7,47011 Valladolid, (Spain).

Keywords: Porous polymer; microporosity, thermal stability; catalysis; gas separation.

The search for new advanced materials having enhanced properties is essential to apply in high added-value applications. In this context, the search and development of new porous polymer materials is widely required by the industry to develop absorbent materials for gas purifications, for CO₂ capture applications and for the synthesis of confined catalysts with enhanced properties.¹

In this way, our group has developed a new generation of porous polymer materials formed by SEAr condensation of ketones having electron-withdrawing groups and rigid polyaromatic moieties, which have a D_{3h} symmetry. These materials have two moieties (lactam and 2,2-bipyridine) able to be straightforwardly modified, which has permitted to obtain tailor-made materials with high control of the structure, and consequently of the final properties.

These new microporous copolymer networks were obtained in quantitative yields by reacting stoichiometrically a rigid trifunctional aromatic nucleophilic monomer (1,3,5-triphenylbenzene, 135TPB) with mixtures of two ketones, namely 4,5-diazofluoren-9-ona (DAFO) and Isatin, in different molar ratios (1/1 and 1/3). The reaction proceeded in a superacidic media (triflic acid) employing chloroform as cosolvent.² Additionally, for comparison sake, the homopolymers 135TPB-DAFO and 135TPB-Isatin, were also obtained and characterized.

The resulting polymer networks were essentially amorphous showing high thermal stabilities (above 500 °C) and large specific surface areas (over 700 m²/g).³ The derived materials showed promising results for metal catalysis, CO₂ adsorption and as fillers for gas separation mixed matrix membranes.

References

1. D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, "Design and Preparation of Porous Polymers", *Chem. Rev.* 2012, **112**, 3959–4015.
2. B. Lopez-Iglesias, F. Suárez-García, C. Aguilar-Lugo, A. González Ortega, C. Bartolomé, J.M. Martínez-Ilarduya, J.G. De La Campa, Á.E. Lozano, C. Álvarez, "Microporous Polymer Networks for Carbon Capture Applications", *ACS Appl. Mater. Interfaces.* 2018, **10**, 26195–26205.
3. N. Esteban, "New high porosity polymer networks for advanced applications" *MS Thesis*, University of Valladolid, 2019.



Multicomponent effects in CO₂/CH₄ separation with glassy membranes

E. Ricci, F.M. Benedetti*, V.E. Burla*, M.G. De Angelis**

*Department of Civil, Chemical, Environmental and Materials Engineering
University of Bologna, Italy

Keywords: competitive sorption; swelling; glassy polymers; NELF model.

The permeability of gases in dense membranes is the product of their solubility and diffusivity. Competitive sorption and swelling effects, which are still scarcely characterized, are responsible for significant deviations of the separation performance of glassy polymers between pure- and mixed-gas conditions.

It was observed for several different materials that competitive sorption between CO₂ and CH₄ lowers the solubility of CH₄ to a higher extent compared to CO₂, enhancing the solubility-selectivity (α_S). On the other hand, swelling induced by CO₂ increases the diffusivity of CH₄, thus lowering the diffusivity-selectivity (α_D) (**Figure 1**).¹

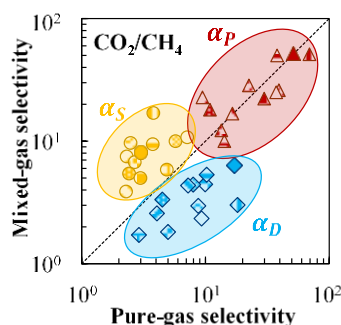


Figure 1. Comparison of pure-gas and mixed-gas CO₂/CH₄ α_S , α_D , and α_P of several glassy polymers.

The strength of multicomponent effects in CO₂/CH₄ gas transport in glassy membranes was quantified for a large polymers set, analysing mixed-gas sorption and permeation data. Mixed-gas sorption measurements are only available for a small number of materials, therefore the Nonequilibrium Lattice Fluid (NELF)² model was used to expand the database investigated.

Relationship were drawn between competitive sorption and swelling effects with materials properties, such as free volume, cohesive energy, and functional groups. Establishing structure-property relations allows to identify guidelines for the design of membrane materials capable of leveraging competitive sorption while reducing the detrimental effects of swelling, to retain a better gas separation performance at mixed-gas conditions.

References

1. E. Ricci, F.M. Benedetti, M.E. Dose, M.G. De Angelis, B.D. Freeman, D.R. Paul, “Competitive sorption in CO₂/CH₄ separations: the case of HAB-6FDA polyimide and its TR derivative and a general analysis of its impact on the selectivity of glassy polymers at multicomponent conditions”, *J. Membr. Sci.*, In press, <https://doi.org/10.1016/j.memsci.2020.11837>.
2. F. Doghieri, G.C. Sarti, “Nonequilibrium Lattice Fluids: A Predictive Model for the Solubility in Glassy Polymers”, *Macromolecules* 1996, **29**, 7885-7896.



Enhancement of CO₂/CH₄ selectivity for biogas upgrading via Thermal Rearrangement of Mixed Matrix Membranes

C. Soto^{1,2}, C. Aguilar³, A. González⁴, L. Palacio^{1,2}, P. Prádanos^{1,2}, A. Hernández^{1,2}, Á. E. Lozano^{1,3,4}

1. Surfaces and Porous Materials (SMAP), Associated Research Unit to CSIC. University of Valladolid, Spain.
2. Institute of Sustainable Processes (ISP), Valladolid, Spain.
3. Materials Research Institute, National Autonomous University of Mexico, CDMX, Mexico.
4. Department of Organic Chemistry, School of Sciences, University of Valladolid, Spain.
3. Institute for Polymer Science and Technology (ICTP-CSIC), Madrid, Spain
4. IU CINQUIMA, University of Valladolid, Spain.

Keywords: biogas upgrading, thermal rearrangement; mixed matrix membranes.

Production of biogas via anaerobic digestion or by other sources has been shown to significantly contribute to the mitigation of greenhouse gas emissions. Biogas primarily consists of CH₄ (50–70%) and CO₂ (30–50%) and is subject to the most rigorous quality specifications when intended to be used as a natural gas substitute or as vehicle fuel. Overall, CO₂ concentrations in the gas mixture must be lowered to 2.5–4 % prior injection into natural gas grids¹. In this context Membrane-based CO₂ separation has gained a significant market share from 2012 to 2016 based on the recent advances on polymer science².

Well-designed Mixed Matrix Membranes (MMMs) have shown a promising performance for CO₂ separation from biogas. In this work, the gas permeation properties of MMMs made in our lab were determined for the CO₂/CH₄ gas pair mixtures. These MMMs, were made by combining a poly(o-hydroxypolyamide, HPA, (obtained by the reaction of 2,2-bis[4-chlorocarbonylphenyl]hexafluoropropane, 6FCl, and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, APAF) and a porous polymer network (PPN) filler having high thermal resistance and excellent capability to capture CO₂.

These mixed matrix membranes were subjected to a heat treatment to remove the solvent (at 180°C) and thermally rearranged at 375°C under nitrogen atmosphere, in order to convert the HPA-PPN membrane to a β-TR-PBO-PPN one (TR-MMM). The chemical structure and thermal stability of the precursor membranes and the TR-MMM ones were characterized by FTIR, DSC and TGA. Gas permeability was determined in a constant-volume variable pressure permeation system at 3 bar and 35°C. The values of permeability coefficients and the ideal selectivity for CO₂/CH₄ gas pair are plotted at the corresponding Robeson's plot in Figure 1. It was clearly observed that the permeability of the MMMs to CO₂ and CH₄ increased with the PPN content. The improvement in permeability was significantly higher for the TR-MMMs, with an optimal permeability for the membrane loaded with a 30% of PPN, in such a way that this TR-MMM showed a permeability-selectivity value exceeding the Robeson's 1991 limit and getting close to the Robeson's 2008 one. This study has confirmed the outstanding performance of these β-TR-MMMs for gas purification of mixtures having CO₂ as a component.

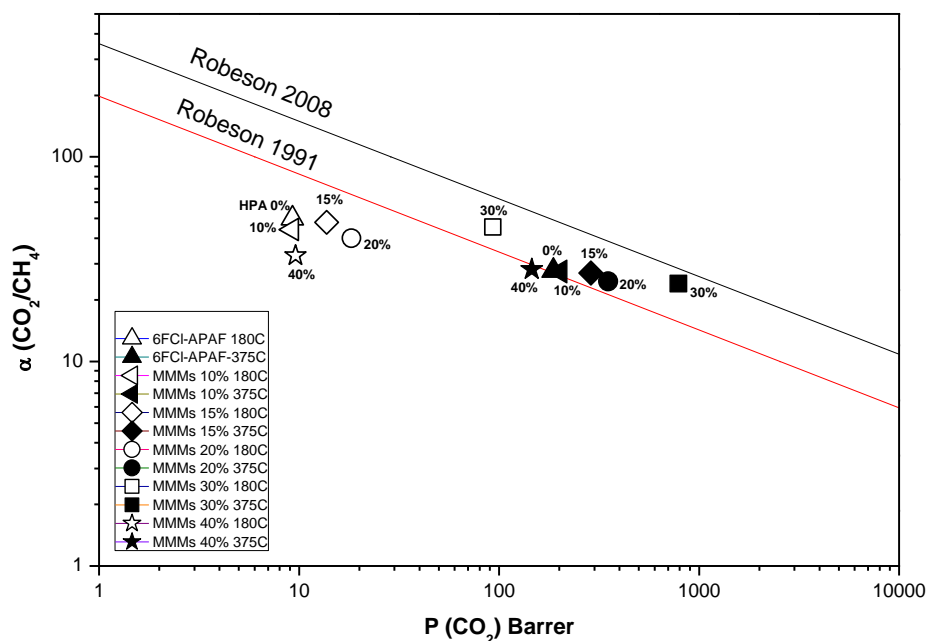


Figure 1. Robeson⁴⁻⁵ for the HPA-PPN MMMs and their corresponding β -TR-PBO MMMs for the CO₂/CH₄ gas pair.

Acknowledgements

This work was supported by the Spanish Government through project MAT2016-76413-C2-1-R, MAT2016-76413-C2-2-R and the Regional Government of Castilla y León and the EU-FEDER (CLU2017-09, UIC082 and VA088G19)

References

1. R. Muñoz, L. Meier, I. Diaz, D. Jeison, "A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading". *Rev. Environ. Sci. Bio/Technology*, 2015, **14**, 727–759,
2. S.H. Han, Y.M. Lee, *et al.*, "Tuning microcavities in thermally rearranged polymer membranes for CO₂ capture", *Phys. Chem. Chem. Phys.*, 2012 **14**, 4365–4373.
3. Lopez-Iglesias, *et al.*, "Microporous Polymer Networks for Carbon Capture Applications", *ACS Appl. Mater. Interfaces*, 2018, **10**, 26195–26205.
4. L.M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes", *J. Membr. Sci.*, 1991, **62**, 165-185.

L. M. Robeson, "The upper bound revisited", *J. Membr. Sci.*, 2008, **320**, 390-400



Smart Membrane with Light-switchable Valves

Jiangtao Liu¹, Shaofei Wang^{1,2}, Tiefan Huang¹, Priyanka Manchanda¹, Edy Abou-Hamad³, Suzana P. Nunes^{1*}

¹Biological and Environmental Science and Engineering Division (BESE), Advanced Membranes and Porous Materials Center (AMPM), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.

²Current address: Massachusetts Institute of Technology (MIT), Department of Chemical Engineering, Cambridge MA 02139, USA

³Core Labs, King Abdullah University of Science and Technology, Thuwal, 23955, Saudi Arabia

Keywords: Covalent organic framework (COFs), trans-/cis-azobenzene, light responsive membrane

Smart materials, which can change their structures in response to external stimuli, such as pH, chemicals, electric field, heat, and light, have attracted tremendous attention from researchers. Among the external stimuli, light is highly efficient, non-invasive, and environmentally friendly.

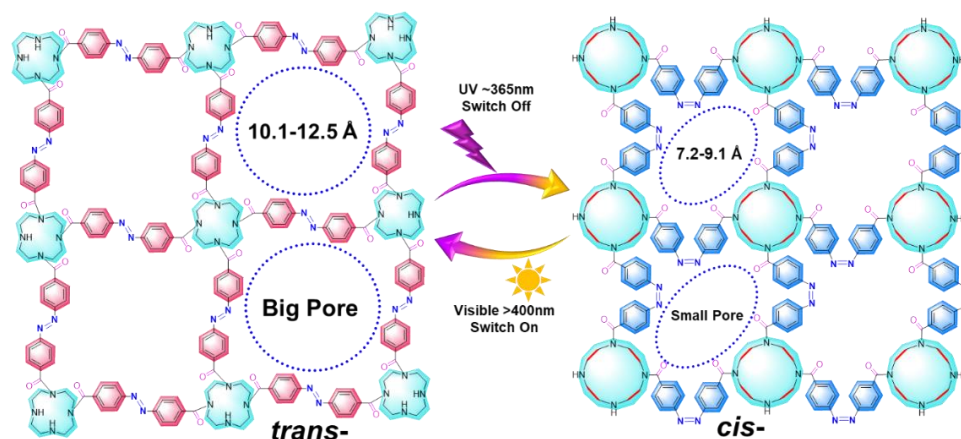


Fig. 1. Photoisomerization of the light-responsive membranes.

Different from the traditional membranes with fixed pore dimensions, in this work, we designed a novel covalent organic network (CON) membrane, whose pore size can be dynamically controlled by the light-switchable azobenzene ligands under UV and visible light. The azobenzenes were implanted as light switches to bridge the flexible cyclen building blocks. The resultant CON membranes fold and unfold as an origami with nanopores that can be photoswitched between On- (open pores) and Off-state (smaller pores) channels for molecular separation. We propose a new covalent organic network (CON) with excellent light response. The resultant smart CON membranes have nanopores that can be photoswitched between On- (open pores) and Off-state (smaller pores) valves for molecular separation. The CON membranes were tested in different organic solvents and exhibit permeances as high as $56.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, in the following order: acetonitrile > acetone > methanol > ethanol > isopropanol > DMF. Interestingly, the smart *cis*-CON membranes with Off-state valves under UV show higher rejection for dye molecules than the *trans*-CON analogue with On-state valves. Clearly, the membranes with “On-Off-On” light-switchable pores have unique merits, such as *in situ* size tunability, precise molecular sieving, high solvent permeance, good mechanical flexibility, and fabrication simplicity, which may pave the way to remote control of molecules separation, reactant supply and valuable drug purification from the pharmaceutical industry.



PIM-1/graphene thin Film Nanocomposite membranes (TFNs) for pervaporation

Monica Alberto^a, Rupesh Bhavsar^b, Jose Miguel Luque-Allad^a, Eric Prestat^{c,d}, Lei Gao^b, Peter M. Budd^b, Aravind Vijayaraghavan^c, Gyorgy Szekely^a, Stuart M. Holmes^a, Patricia Gorgojo^a

^a School of Chemical Engineering and Analytical Science, The University of Manchester, UK

^b School of Chemistry, The University of Manchester, UK

^c School of Materials, The University of Manchester, UK

^d SuperSTEM Laboratory, SciTech Daresbury Campus, UK

Keywords: Alkyl functionalization, Graphene oxide, Polymer of intrinsic microporosity PIM-1, Thin film nanocomposite membranes, Pervaporation

The development of membranes able to provide high fluxes, high selectivities and long-term stability has seen significant progress in recent years, but there are still limitations to overcome. It has been shown that the addition of graphene-based materials into the polymer of intrinsic microporosity PIM-1 improves the membrane separation performance¹. Regarding the flux of the membrane, thin membranes are desirable as the flux is directly proportional to the reciprocal of membrane thickness². Herein, thin film nanocomposite (TFN) membrane of PIM-1 incorporating micrometer and nanometer-sized alkyl-functionalized graphene-based materials were studied for the recovery of *n*-butanol from binary aqueous solutions. The thickness of these membranes is in the range of 1-1.5 μm (Figure 1a-f). As an evidence by the superior overall membrane performance, the interfacial interaction between the filler and the polymer matrix is enhanced when the lateral flake size is in the nanometer range. TFN membranes showed an improvement of ca. a third of the value achieved for pristine PIM-1 membranes when nanometer-sized reduced octyl-functionalized graphene-based flakes were used as fillers. Moreover, the addition of such fillers also led to an enhancement of approximately 40% of the permeate flux (Figure 2g). Additionally, an enhancement in the separation factor and productivity of such membranes was observed for higher operating temperatures and higher *n*-butanol content in the feed solution.

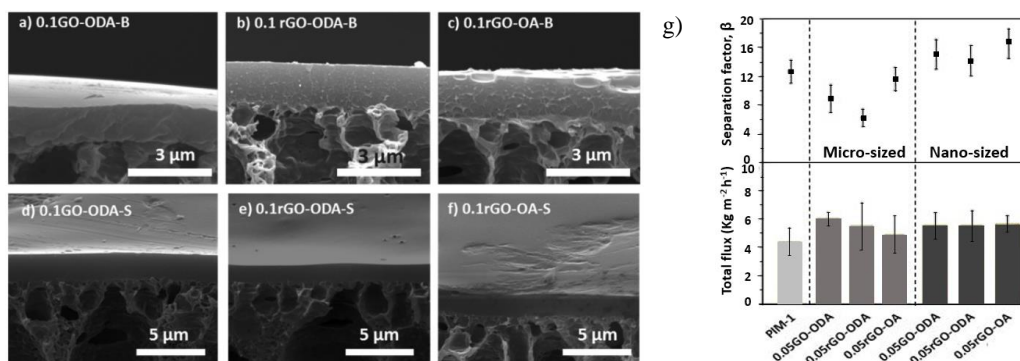


Figure 1. (a-f) Scanning electron microscope (SEM) images and (g) PV performance of TFN membranes.

References

¹ M. Alberto, *et al.*, Enhanced organophilic separations with mixed matrix membranes of polymers of intrinsic microporosity and graphene-like fillers, *J. Membr. Sci.* **526** (2017) 437–449.

² L. Gao, M. Alberto, P. Gorgojo, G. Szekely, P.M. Budd, High-flux PIM-1/PVDF thin film composite membranes for 1-butanol/water pervaporation, *J. Membr. Sci.* **529** (2017) 207–214.



A polymer inclusion membrane (PIM) for the removal of fluoride from natural waters

B. Alcalde, C. Fontàs, E. Anticó

University of Girona, Chemistry Department, C/ Maria Aurèlia Capmany, 69, 17003 Girona, Spain

Keywords: Polymer inclusion membranes; Fluoride; Removal; Natural water

Many people are exposed to excessive amounts of fluoride through contaminated drinking water coming from natural geological sources. Fluoride intake in low concentration has beneficial effects for both bones and teeth making them denser and harder. Nonetheless, in prolonged exposure at high concentration, fluoride can cause dental and skeletal fluorosis¹. The World Health Organization (WHO 2011) has prescribed the maximum permissible limit of fluoride in drinking water in 1.5 mg·L⁻¹. However, the concentration of fluoride in natural waters can exceed this value and, therefore, there is a need for simple and efficient techniques to remove this anion. In this study, we present the use of a polymer inclusion membrane (PIM) to remove fluoride from natural waters. In PIMs³, a suitable extractant is immobilized within the chains of a polymer, such as polyvinyl chloride (PVC) or cellulose triacetate (CTA). The polymer provides the membrane with mechanical strength whereas the carrier is the responsible for the extraction. In general, PIMs are easy to prepare, possess good mechanical properties (e.g. strength and flexibility), and are versatile in terms of the target chemical species they can extract.

The commercial ionic liquid Aliquat 336 (trioctylmethylammonium chloride) has been used as the carrier for PIM and CTA as the polymer. The effect of the addition of other components to the membrane such as plasticizers or the solvating agent tributyl phosphate (TBP) have been investigated. For that, both synthetic solutions of F⁻ (from 10 to 200 mg L⁻¹) and spiked natural waters were used as a feed phase, whereas a 1 M NaCl solution was used as stripping phase. It was found that the best PIM composition was CTA (30%, wt), Aliquat 336 (50%, wt), and TBP (20%, wt), which allowed the quantitative removal of fluoride for the different water types tested. It was observed that the presence of other ions present in water samples affects the kinetics of the fluoride transport, but the PIM was able to remove the anion from fluoride naturally occurring waters. Moreover, the reuse of the PIM was also investigated, and it was found that after 5 cycles of 24 h each, the fluoride removal only decreased a 11%.

In conclusion, it has been demonstrated that a PIM system can be envisaged as an efficient and economical solution to remove fluoride from natural waters.

References

1. V. Kimambo, P. Bhattacharya, F. Mtalo, J. Mtamba, A. Ahmad, "Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art", *Groundwater Sustain. Dev.* 2019, **9**, 100223.
2. World Health Organization (WHO), "Guidelines for Drinking-water Quality", fourth ed. World Health organization, pp. 370-373.
3. M.I.G.S. Almeida, R.W. Cattrall, S.D. Kolev, "Polymer inclusion membranes (PIMs) in chemical analysis", *Anal. Chim. Acta*, 2017, **987**, 1-14.

Acknowledgements

The financial support of the Spanish government through research project CTM2016-78798-C2-2-P (AEI/FEDER/UE) is acknowledged.



Effective arsenic removal using electrospun PVDF membranes enhanced by POSS-functionalised graphene oxide in membrane distillation

S. Leaper*, E. O. Avendaño Cáceres**, J. M. Luque-Allad*, P. Gorgojo*

* School of Chemical Engineering and Analytical Science, University of Manchester, M13 9PL, UK

** Faculty of Engineering, Universidad Nacional Jorge Grohmann, Avenida Miraflores S/N, Miraflores 23000, Peru

Keywords: arsenic removal, membrane distillation, graphene oxide, POSS, electrospun

Arsenic contamination in groundwater is a growing problem which threatens drinking water supplies in the Tacna region of Peru and many other parts of the world.¹ Existing technologies like coagulation/adsorption require large quantities of chemicals and alternatives like ion exchange or reverse osmosis can be expensive, can struggle to ensure complete arsenic removal and produce toxic effluents.² Membrane distillation (MD) is a simple and robust technology for achieving very high removal rates of dissolved inorganic substances and can achieve high concentration ratios in cases where zero liquid discharge is required. For the technology to become competitive however, highly permeable and fouling resistant membranes are required.

This work demonstrates complete removal (below the detection limit of 0.045 ppb) of inorganic arsenic from water using electrospun polyvinylidene difluoride (PVDF) membranes enhanced by functionalised graphene oxide in membrane distillation. These membranes became more hydrophobic and mechanically stronger with the addition of reduced graphene oxide functionalised with polyhedral oligomeric silsesquioxane molecules (POSS-rGO) which was incorporated into the spinning solutions. The flux of the best performing rGO-enhanced membrane (containing 2 wt.% of POSS-rGO) was 21.5% higher than the pure PVDF membrane and almost double that of a commercial polytetrafluoroethylene (PTFE) membrane after 24 hours of testing, with rejection values exceeding 99.9%. Furthermore, the flux of this membrane was stable over 5 days ($\sim 28 \text{ Lm}^{-2}\text{h}^{-1}$) of continuous testing and was more stable than the others when treating a concentrated fouling solution of calcium carbonate and iron (III) sulphate heptahydrate. It also achieved higher permeate quality ($50.5 \mu\text{Scm}^{-1}$) in these conditions compared to control membranes. The Young's modulus and ultimate tensile strength of the best performing membrane increased by 38 and 271%, respectively, compared to the pure polymer membrane while both had similar porosities of $\sim 91\%$.

References

1. Chakraborti, D. *et al.* Groundwater arsenic contamination in the Ganga River Basin: a future health danger. *Int J Environ Res Public Health*, 2018, **15** (2), 180.
2. Sanjrani, M. *et al.* ARSENIC CONTAMINATED GROUNDWATER IN CHINA AND ITS TREATMENT OPTIONS, A REVIEW. *AEER*, 2019, **17** (2), 1655-1683.



Fluid Flow in porous membrane based on momentum sink added to governing momentum equations

L.F. Esteves, I. Elsherbiny, S. Panglich

Chair of Mechanical Process Engineering and Water Technology, University of Duisburg-Essen, Germany

Keywords: Porous Membrane, Fluid Flow, Governing Momentum Equations.

Modeling fluids filtration through membrane pores requires dealing with different membrane structures when the goal is to understand the pore size distribution on fluid flow characteristics and cake layer formation. Nevertheless, this task requires reliable mathematical model of a porous body, whose geometric features are as close as possible to polymeric membrane structures. This work, which focuses only on the fluid-dynamics aspects of the water flow, aims at investigating the possible modeling approaches for the physical description of the system, and it represents a preliminary step towards a more complex model taking into account the relationship between fluid properties and pore size distribution. Although of the specific application, most of the considerations associated with both modeling and numerical simulation are valid in more general framework of flow over porous media. Two subregions of the computational domain have been considered, since the equations must be coupled through physically significant continuity conditions at the interface separating the two subdomains.

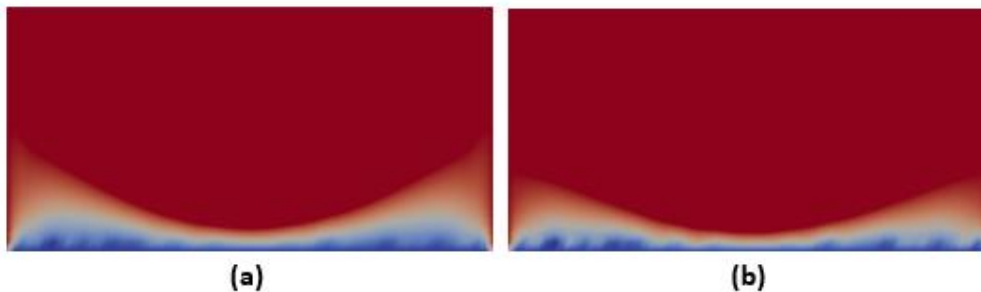


Figure 1. Pressure drop at the porous region in two different simulation times: (a) $t = 10$ seconds and (b) $t = 100$ seconds.

Navier-Stokes in the whole domain was considered to avoid difficulties of this heterogeneous approach and at the bottom of domain was introduced suitable terms that mimic the presence of the porous media. Compared to existing methods for porous membrane modeling, this approach is more flexible in terms of pore size and pore size distribution. This approach is believed to contribute significantly in modeling of several membrane processes, since its flexibility allows developing of different codes capable of solving micro and nanoscale phenomena.

References

1. F. Cimolin, M. Discacciati, “Navier-Stokes/Forchheimer models for filtration through porous media”, *Applied Numerical Mathematics*, 2013, **72**, 205-224.
2. B. Haddadi, C. Jordan, M. Miltner, M. Harasek, “Membrane modeling using CFD: Combined evaluation of mass transfer and geometrical influences in 1D and 3D”, *Journal of Membrane Science*, 2018, **563**, 199-209.

Morphological changes in polymeric membranes by addition of graphene oxide: Experimental and thermodynamic study

Sajjad Mohsenpour, Patricia Gorgojo

School of Chemical Engineering and Analytical Science, University of Manchester, M13 9PL, UK

Keywords: Flory Huggins theory; Graphene Oxide; Membrane Morphology

In a phase inversion process, membrane morphology can be tailored by precise control of the thermodynamic properties of the casting solution.^[1] In this investigation, Flory Huggins theory,^[2] was used to study the impact of adding graphene oxide (GO) on the morphology of polyethersulfone (PES) and Polyvinylidene fluoride (PVDF) mixed matrix membranes (MMMs). Theoretical binodal lines were constructed and validated by conducting a cloud titration experiment. It was observed that by adding GO, the binodal line moved towards the solvent-nonsolvent line in the phase diagram and the thermodynamic instability increased. PES/GO and PVDF/GO hybrid membranes were fabricated by a phase inversion method. Furthermore, the membranes were characterized using various techniques including scanning electron microscopy (SEM), contact angle, porosity, pore size determination and pure water flux (PWF) measurements. Both the thermodynamic instability and the viscosity of the casting solution increased by the addition of GO. Higher thermodynamic instability induced thinner selective top layers and higher porosities. The highest porosity and PWF occurred at 0.1 wt.% GO and 0.3 wt.% GO for PES/GO and PVDF/GO systems, respectively. However, by further increasing the GO loading, high viscosity hindered solvent-nonsolvent demixing, which decreased the porosity and PWF of the fabricated membranes. Hence, a high demixing rate between solvent-nonsolvent induced finger-like morphology, however low miscibility between solvent and nonsolvent caused spongy-like morphology and smaller pore size in the substrate of the membrane (Figure 1).

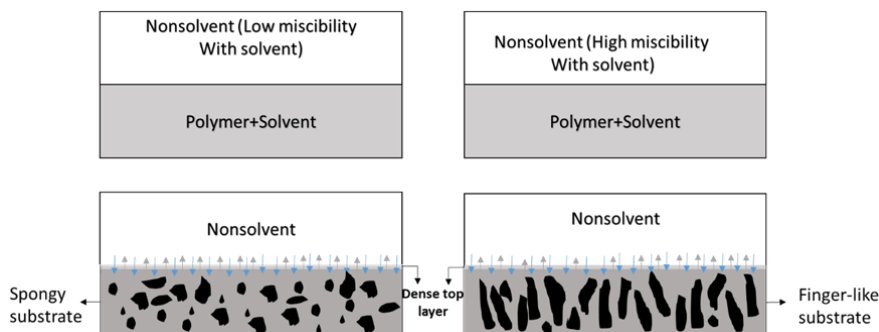


Figure 1 Effect of solvent-nonsolvent exchanging rate on morphology of membrane

References

- [1] S. Mazinani, S. Darvishmanesh, A. Ehsanzadeh, and B. Van der Bruggen, "Phase separation analysis of Extent/solvent/non-solvent systems and relation with membrane morphology," *Journal of Membrane Science*, vol. 526, pp. 301-314, 2017.
- [2] S. Mohsenpour, F. Esmailzadeh, A. Safekordi, M. Tavakolmoghadam, F. Rekabdar, and M. Hemmati, "The role of thermodynamic parameter on membrane morphology based on phase diagram," *Journal of Molecular Liquids*, vol. 224, pp. 776-785, 2016.



Opportunity and evaluation of Polymer of intrinsic microporosity PIM-1 to treat sour natural gas by Hybrid membrane-amine process: Economic study

Ahmed W Ameen, Peter M. Budd, Patricia Gorgojo***

Keywords: PIM-1; CO₂; hybrid membrane-amine; economic study; natural gas

Natural gas contains high amount of impurities that require to be removed prior to storing or transporting. Acid gases CO₂ and H₂S are the most crucial among those impurities, which are traditionally removed by absorption using amines. Hybridizing the amine-based process by installing membranes upstream has been found to be economically attractive,¹.

Recently, polymer of intrinsic microporosity PIM-1 has been reported for CO₂ removal with performances exceeding those of commercial membrane materials,². Yet, the main drawback of PIM-1 is the drop in the performance over time due to physical aging,³.

In this work, a hybrid membrane-amine process with PIM-1 membranes was compared to the standalone amine process. Three different PIM-1 performances have been studied: i) fresh PIM-1 (ideal case), ii) aged PIM-1 (worst case), and iii) enhanced aged PIM-1 (enhanced case). The enhanced case was acquired by improving the membrane aged performance until the hybrid membrane-amine process became more feasible than the standalone amine process. Net Present Value (NPV) of the processes were obtained and compared. In addition, the sensitivity of different factors such as membrane replacement cost and sale gas price were studied.

The performance for fresh PIM-1 was obtained from the composite hollow fibre reported by Liang,⁴. By inputting this performance, the hybrid membrane-amine process shows a very clear advantage economically compared to the standalone amine process. On the other hand, when the aged performance of PIM-1 is used the hybrid process is no longer attractive. Somewhere in between, the enhanced aged PIM-1 performance leads to higher NPV for the hybrid membrane-amine process over the standalone amine process. Thus, the PIM-1 performance in the enhanced aging case can be the target for researchers to make this polymer a commercial material for the sweetening of natural gas.

References

1. Hamad, F. *et al.* Treatment of highly sour natural gas stream by hybrid membrane-amine process: Techno-economic study. *Sep. Purif. Technol.* **237**, 116348 (2020).
2. Budd, P. M. *et al.* Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: Polybenzodioxane PIM-1. *J. Memb. Sci.* **325**, 851–860 (2008).
3. Low, Z. X., Budd, P. M., McKeown, N. B. & Patterson, D. A. Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers. *Chem. Rev.* **118**, 5871–5911 (2018).
4. Liang, C. Z., Liu, J. T., Lai, J. Y. & Chung, T. S. High-performance multiple-layer PIM composites hollow fiber membranes for gas separation. *J. Memb. Sci.* **563**, 93–106 (2018).



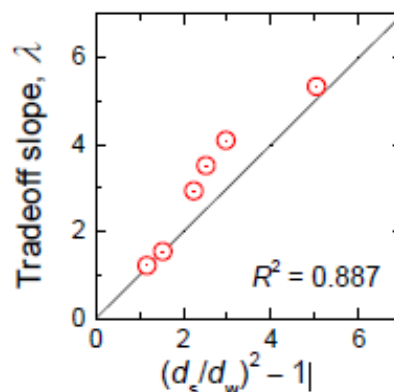
New Insights into Solute-Selectivity Relationship of Thin-Film Composite Polyamide Membranes

Xi Chen, Chanhee Boo, and Ngai Yin Yip

Department of Earth and Environmental Engineering, Columbia University, New York, New York, 10027, United States

Keywords: transport theory; solution-diffusion; permeability-selectivity tradeoff; reverse osmosis; nanofiltration;

Thin-film composite polyamide (TFC-PA) membranes are widely used in nanofiltration (NF) and reverse osmosis (RO) for aqueous separations. The solution-diffusion (S-D) mechanism is the most broadly accepted theory for transport in osmotic membranes. The S-D model predicts a tradeoff between permeability and selectivity, but fundamental understanding of the first principles governing this relationship is incomplete. Therefore, there are no rigorous theoretical frameworks to describe the transport phenomena in TFC-PA membranes by permeant properties. Here, we present a study to better understand the permeability-selectivity tradeoff relationship in TFC-PA membranes. Water and solute permeabilities of TFC-PA membranes with different selectivities are carefully characterized using neutral organic solutes of various sizes and dimensions. Analysis of the experimental results indicates that solute size is the principal factor governing the tradeoff trend in S-D transport. We showed that the tradeoff slope between permeability and selectivity, λ , is predicted by $(r_s/r_w)^2 - 1$, where r is permeant radius and subscripts S and W denote solute and water, respectively. This relationship for NF and RO aqueous membranes is analogous to the relationship established for gas separation membranes, $\lambda = (r_B/r_A)^2 - 1$, by Robeson, Freeman, et al. Additionally, a second transport regime that cannot be fully described by the conventional S-D framework is identified for the first time. To describe the transport trends in the two regimes and the transition between, a set of characteristic elements is proposed. The characteristic elements are evaluated against solute and solvent properties to shed light on the underlying transport mechanism. This study reconciles experimental evidence with theoretical principles as a first step towards a fundamentals-based approach for a priori predicting transport behavior in TFC-PA membranes using only intrinsic properties of the permeant and polymer. Findings of this study provide new insights for understanding transport mechanisms in osmotic membranes and can inform the rational design of next-generation aqueous separation membranes.





Gas Separation Membranes obtained by Partial Pyrolysis of Polyimides having Polyethylene oxide moieties

Laura Matesanz Niño^{1,2}, Pedro Prádanos¹, Antonio Hernandez¹, Jesús Ángel de Miguel³, José G. de la Campa⁴, Cristina Alvarez^{1,4}, Laura Palacio¹, Michele Galizia⁵, Ángel E. Lozano^{1,3,4}, Alfonso González-Ortega²

1 SMAP, UA-UVA_CSIC, Associated Research Unit to CSIC. University of Valladolid, Science Faculty, Paseo Belén 7, E-47011 Valladolid, Spain.

2. Department of Organic Chemistry, Facultad de Ciencias, Universidad de Valladolid, Science Faculty, Paseo Belén 7, E-47011 Valladolid, Spain.

3. IU CINQUIMA, University of Valladolid, Paseo Belén 5, E-47011 Valladolid, Spain.

4. Institute of Polymer Science and Technology, ICTP-CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain.

5. CBME, Sarkeys Energy Center, University of Oklahoma, Norman, OK 73019, USA.

Keywords: Gas separation membranes, partial pyrolysis, heat treatment, PI-PEO.

In the last years, aliphatic-aromatic copolyimides having polyethylene oxide chains (PEO) have been used for gas separation applications because they show an excellent balance of permeability and permselectivity when gas mixtures containing CO₂ are employed¹. In a previous work, a new generation of gas separation membranes were obtained by blending a whole aromatic copolyimide, PI, with an aliphatic-aromatic copolyimide having PEO in the aliphatic part, PI-PEO. After the thermal removal of the PEO moieties, at medium temperature, the thermally treated gas separation membranes showed good gas separation properties, lower than those observed for the aromatic polyimide but having high plasticization resistance. However, it was observed a serious shrinkage of the membranes, which could take account of the permeability decrease².

With the target of improving the gas separation properties, by decreasing the shrinkage, the blends of PI and PI-PEO were made by adding as a comonomer, for both components, 3,5-diaminobenzoic acid (DABA), which is able to form physical and chemical crosslinkings during the thermal removal of the PEO groups. These polymer membranes were characterized before and after the thermal treatment². The thermal treatment, at 375 °C under nitrogen, produced highly-crosslinked materials with good mechanical properties and low shrinkage. Gas separation properties were very good, due to the crosslinking process, in such way that the gas separation properties were alike to those observed for the pristine PI. Plasticization and physical aging were enhanced, which permits the use of these membranes in high performance gas separations.

Finally, in order to increase the productivity of this generation of membranes, the use of membranes derived of the monomer, 2,4,6-trimethyl-1,3-diaminobenzene, TMPD, was considered. This approach produced gas separation membranes with much better permeability.

1. H. B. Park, J. Kamcev, L. M. Robeson, M. Elimelech, B. D. Freeman, "Maximizing the right stuff: The trade-off between membrane permeability and selectivity", *Science*, 2017, **356**, 1138–1148.

2. L. Escorial, *et al.* "Partially pyrolyzed gas-separation membranes made from blends of copolyetherimides and polyimides", *Eur. Polym. J.* 2018, **103**, 390–399.

3. D. M. Muñoz, E. M. Maya, J. de Abajo, J. G. de la Campa, A. E. Lozano. "Thermal treatment of poly(ethylene oxide)-segmented copolyimide based membranes: An effective way to improve the gas separation properties", *J. Memb. Sci.* 2008, **323**, 53–59.



High performing 6FDA-DAM:DABA mixed matrix membranes with ZIF-8 and GO mixtures for effective CO₂/CH₄ separation.

Anand Jain^{1,2}, W. Hintz¹, V. Fila²

¹ Faculty of Process and Systems Engineering, Otto-von-Guericke-University, Magdeburg Universitätsplatz 2, Magdeburg-39106, Germany.

² Department of Inorganic Technology, University of Chemistry and Technology Prague, Technicka 5, Dejvice-Praha 6, 16628 Czech Republic

Keywords: 6FDA-polyimide; ZIF-8; GO; mixed matrix membrane; CO₂ separation

The increase of energy consumption by human activities (such as burning of fossil fuel and biogas) has largely contributed to huge amount of CO₂ emission.¹ Now more than ever, the need of highly efficient membrane materials is required to ensure membrane technology outperforms the other conventional separation processes.²⁻⁴ This work presents the gas separation properties of 6FDA-DAM:DABA and its enhanced mixed matrix membranes (MMMs) performances with ZIF-8 nanoparticles, NPs (particle size of <40 nm) and GO nanosheets. The 6FDA-polyimide was obtained through two-stage poly-condensation polymerization method, while the ZIF-8 NPs were synthesized using dry and wet method. The MMMs were prepared using 5-15 wt.% ZIF-8 filler loading independently or as a mixture with 1 wt.% of GO nanosheets. All the materials were characterised accordingly, including DSC, TGA, FTIR, XRD and SEM. The gas separation was measured with CO₂:CH₄ 50/50 vol.% binary mixture at 2-8 bar feed pressure, at 25 °C. The pristine 6FDA-DAM:DABA shows CO₂ permeability of 152 Barrer and CO₂/CH₄ selectivity of 54.2. The optimum loading ZIF-8 MMMs, 10 wt.% and 15 wt.% improved the CO₂ permeability to 1083 and 1104 Barrer, respectively. Accordingly, the MMMs lost their selectivity by 50.0 - 51.8%, due to the increased of polymer chain packing after filler addition. However, the performances are still resided above the 2008 upper bound. The feed pressure variation study shows that the MMMs retained the high separation properties, despite the significant observation of dual-sorption effect. This indicates the MMM stability and its potential for the CO₂/CH₄ separation purposes.

References

1. J.K. Adewole, *et al.*, "Current challenges in membrane separation of CO₂ from natural gas: A review", *International Journal of Greenhouse Gas Control*, 2013,**17**, 46-65.
2. J.C. Abanades *et al.*, "Emerging CO₂ capture systems", *International Journal of Greenhouse Gas Control*, 2015,**40**, 126-166.
3. N. MacDowell *et al.*, "An overview of CO₂ capture technologies", *Energy & Environmental Science*, 2010,**3(11)**, 1645.
4. G. Huang *et al.*, "Pebax/ionic liquid modified graphene oxide mixed matrix membranes for enhanced CO₂ capture", *Journal of Membrane Science* 2018,**565**, 310-379.



Physical aging prevention of PIM-1 based mixed matrix membranes (MMMs) in CO₂/CH₄ gas separations

Jose Miguel Luque-Alled ^{1, a}, Ahmed Ameen ^a, Monica Alberto ^a, Marzieh Tamaddondar ^b, Andrew B. Foster ^b, Peter Budd ^b, Aravind Vijayaraghavan ^c, Patricia Gorgojo ^{*a}

^a School of Chemical Engineering and Analytical Science, University of Manchester, M13 9PL, UK

^b School of Chemistry, University of Manchester, M13 9PL, UK

^c School of Materials, University of Manchester, M13 9PL, UK

Keywords: Gas separation, physical aging, PIM-1, functionalised graphene oxide, mixed matrix membranes

Physical aging in high free volume polymers such as PIM-1 is the main matter of concern for gas separation applications¹. Several strategies have been successfully developed to inhibit this process. However, they are based on lab-scale studies which are unsuitable for the formation of thin and large-scale membranes needed in industrial applications^{2, 3}. This prevents the incorporation of PIM-1 membranes into the market for gas separation applications. Here, a strategy to prevent physical aging to a high extent in PIM-1 using graphene nanofillers, is reported. Although thick films (~50 μm) are used in this study for simplicity, this strategy has great potential to be scaled-up to thin (~100 nm) and large-scale (several m²) membranes using membrane fabrication techniques widely employed in the preparation of conventional polymeric membranes. In this study, covalent chemical functionalisation of graphene oxide (GO) with PIM-1 leads to adequate dispersion of these PIM-functionalised GO nanofillers into PIM-1 polymer matrices and therefore homogeneous preparation of MMMs. The higher the amount of PIM-functionalised GO in the MMM, the higher the aging prevention as demonstrated by the smaller decrease of gas permeability over time. Other chemically modified GO materials such as (3-Aminopropyl)triethoxysilane-GO (APTS-GO) were also functionalised with PIM-1 and tested. The best performance in terms of aging control was achieved by a membrane containing 5 wt.% of PIM-functionalised APTS-GO nanofiller, which showed a CO₂ permeability drop of only 777 Barrer (relative CO₂ permeability of 0.76) after 150 days. This represents ~ 4-fold less CO₂ permeability drop than pure PIM-1 (CO₂ permeability drop of 2908 Barrer, relative CO₂ permeability of 0.53).

References

1. Low, Z. X.; Budd, P. M.; McKeown, N. B.; Patterson, D. A., Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers. *Chemical Reviews* 2018, **118** (12), 5871-5911.
2. Nguyen, T. B.; Rodrigue, D.; Kaliaguine, S., In-situ cross interface linking of PIM-1 polymer and UiO-66-NH₂ for outstanding gas separation and physical aging control. *Journal of Membrane Science* 2018, **548**, 429-438.
3. Lau, C. H.; Nguyen, P. T.; Hill, M. R.; Thornton, A. W.; Konstas, K.; Doherty, C. M.; Mulder, R. J.; Bourgeois, L.; Liu, A. C. Y.; Sprouster, D. J.; Sullivan, J. P.; Bastow, T. J.; Hill, A. J.; Gin, D. L.; Noble, R. D., Ending Aging in Super Glassy Polymer Membranes. *Angewandte Chemie-International Edition* 2014, **53** (21), 5322-5326.



Thermal free volume modification effects on gas transport properties for a 6FDA-HAB polyimide with BOC functionality

*S. Lin**, *T. Joo**, *F. M. Benedetti**, *L. C. Chen**, *A. X. Wu**, *K. Mizrahi Rodriguez**, *Q. Qian**, *C. M. Doherty***, *Z. P. Smith**

* Massachusetts Institute of Technology, United States

** CSIRO Manufacturing, Australia

Keywords: Thermal modification, gas transport, polyimide films, free volume modification

Gas transport in polymers is mainly governed by free volume and free volume distribution, but there are limited opportunities to rationally and selectively manipulate free volume without changing polymer chemistry. In this study, we report a free volume modification method through the use of solid-state deprotection chemistries. Tert-butoxycarbonyl (t-BOC), a common chemical protecting group, was appended onto a polyimide consisting of 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB). This polymer (6FDA-HAB-t-BOC) was subsequently formed into a self-standing film, after which different thermal treatments were performed to selectively remove t-BOC at temperatures well below the glass transition temperature. The effects of these thermal treatments on the packing structure (using fractional free volume calculations and positron annihilation lifetime spectroscopy) and corresponding gas transport properties were studied. In particular, higher temperature treatments resulted in a structural densification of the polymer. Pure-gas permeability experiments revealed that different thermal treatments can effectively change gas transport properties. The mechanism of transport for each treatment is decoupled in terms of diffusion and sorption. These findings suggest that thermal deprotection of functional groups in glassy polymer films can be used to selectively manipulate free volume to alter gas transport properties.



Elucidating the role of fluorine content on the gas sorption properties for fluorinated polyimides

A. X. Wu*, J. A. Drayton*, K. Mizrahi Rodriguez**, Z. P. Smith*

* Department of Chemical Engineering, Massachusetts Institute of Technology, USA

** Department of Materials Science and Engineering, Massachusetts Institute of Technology, USA

Keywords: transport modelling; dual-mode model; infinite dilution sorption; enthalpy-entropy compensation; isosteric enthalpy

Perfluoropolymers have garnered significant interest in applications for membrane-based gas separations, such as helium recovery, due to their exceptional separation performance.^{1,2} Unlike all other classes of polymers, perfluoropolymers have unique sorption selectivities for certain gas pairs, which can result in unprecedented performance.³ It has been previously shown that hydrocarbon and perfluorinated polymers display distinct thermodynamic partitioning characteristics, but the mechanism in which fluorine affects gas sorption and sorption selectivity in polymers is not well-understood.⁴ Therefore, this study aims to investigate partially fluorinated polyimides to help bridge the gap between the distinct sorption behaviour of hydrocarbon and perfluorinated polymers. To this end, we present an in-depth experimental analysis of sorption isotherms, spanning a range of temperatures and gases, for four polyimides containing varying fluorine content. With respect to the dual mode model, we have developed a new method involving linear free energy relationships for the fitting of dual mode parameters, resulting in a single set of universal best-fit parameters for each gas-polymer pair. Observed improvement in sorption selectivity for the highly fluorinated materials was found to be primarily a result of increased Henry sorption selectivity with respect to fluorine content, while changes in Langmuir sorption selectivity were negligible with respect to fluorine content. By evaluating multiple temperatures, the energetics of Henry and Langmuir sorption were deconvoluted with respect to fluorine content and penetrant size, which reveals that there is a larger enthalpic penalty for penetrant-polymer mixing associated with the Henry sorption mode in the highly fluorinated materials. Findings from this experimental study are compared to the newly developed perfluoropolymer upper bound to provide guidance on how fluorinated polyimides compare to other fluorinated polymers.⁵

References

1. C.A. Scholes, U.K. Ghosh, "Review of Membranes for Helium Separation and Purification", *Membranes*, 2017, **7**, 1–13.
2. L.M. Robeson, "The Upper Bound Revisited", *J. Membr. Sci.*, 2008, **320**, 390–400.
3. Z.P. Smith, *et al.*, "Influence of Diffusivity and Sorption on Helium and Hydrogen Separations in Hydrocarbon, Silicon, and Fluorocarbon-Based Polymers", *Macromolecules*, 2014, **47**, 3170–3184.
4. T.C. Merkel, "Gas and Vapor Transport Properties of Perfluoropolymers", In *Materials Science of Membranes for Gas and Vapor Separation*, 2006, pp 251–270.
5. A.X. Wu, J.A. Drayton, Z.P. Smith, "The Perfluoropolymer Upper Bound", *AIChE J.*, 2019, **65**, 1–12.



Development of Membrane Coated Electrodes for CO₂ electroreduction

A. Marcos-Madrado*, C. Casado-Coterillo, Á. Irabien

* Department of Chemical and Biomolecular Engineering, Universidad de Cantabria, Av. Los Castros s/n, Santander 39005, Cantabria, Spain

Keywords: CO₂ electroreduction, membrane role, MCEs, mixed matrix membranes, copper

Electrochemical reduction of CO₂ (CO₂RR) is a promising technology for coupling CO₂ conversion into value added products and energy storage from renewable sources¹. Catalyst design has been the main research subject, where mass transport limitations in electrochemical cell reactors are noticed as one of the mayor challenges². In this regard, the study of the type of ion exchange membrane in polyelectrolyte membrane reactors (PEMER) has gained relevance. Anion Exchange Membranes (AEMs) are emerging as an alternative to Nafion, especially in alkaline media³. The AEM provides a protective layer that prevents catalyst degradation and allows the decoupling of the gas, ions and electrons transport, which has been reported to provide excellent results for ethylene production². Sustainable membrane materials and membrane coated electrode configurations need exploring a more active role of the membrane in the CO₂RR.

In this work, we studied the performance of new Membrane Coated Electrodes (MCE) by performing the casting of a chitosan(CS):polyvinyl alcohol (PVA)-based membrane layer over a Gas Diffusion Electrode (GDE), with Cu nanoparticles as catalyst⁴ in a continuous filter-press electrochemical reactor. We have studied the influence of membrane orientation, which led to explore different cell configurations where the membrane is not only a barrier between the compartments but also provides stability and selectivity providing transport of CO₂ to the catalyst, and reactants and products between the anode and cathode.

The influence of membrane composition was studied using three MCEs, one with a pure polymeric overlayer, and two with Mixed Matrix Membranes (MMMs) as overlayer, where the CS:PVA matrix was filled Cu-exchanged stannosilicate UZAR-S3 and zeolite Y, respectively. The performance of these MCEs was studied at three fixed current densities (10, 50 and 90 mA/cm²) and the production of formate, ethanol and propanol was observed, with H₂ as undesired product of the HER taking place at the cathode. Overall, significant formate production was observed at the lowest current: the Faraday Efficiencies were 28 %, 33 % and 41 % for the polymeric, Cu-UZAR-S3 and Cu-Y MCEs respectively, and a great production of ethanol was obtained with the Cu-Y MCE at 90 mA/cm², with a FE of 51 %.

References

1. Yang W, Dastafkan K, Jia C, Zhao C. Design of Electrocatalysts and Electrochemical Cells for Carbon Dioxide Reduction Reactions. *Adv Mater Technol.* 2018;3(9):1-20.
2. García de Arquer FP, Dinh CT, Ozden A, et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science (80-)*. 2020;367(6478):661-666.
3. Liu Z, Yang H, Kutz R, Masel RI. CO₂ Electrolysis to CO and O₂ at High Selectivity, Stability and Efficiency Using Sustainion Membranes. *J Electrochem Soc.* 2018;165(15):J3371-J3377.
4. Marcos-Madrado A, Casado-Coterillo C, Irabien Á. Sustainable Membrane-Coated Electrodes for CO₂ Electroreduction to Methanol in Alkaline Media. *ChemElectroChem.* 2019;6(20):5273-5282.



Enhancing polymer electrolyte membrane properties for fuel cell application using nanostructured materials

P, F Msomi

University of Johannesburg, Department of Chemical sciences, Johannesburg, South Africa

Email: pmsomi@uj.ac.za

Keywords: Fuel cell; Nanomaterials; Polymer electrolyte, Functionalization of polymers

A series of polymer electrolyte membranes were prepared then blended with different nanomaterials to study the influence of nanomaterials on the membrane properties for direct methanol fuel cell application. The membranes for alkaline anion exchange fuel cells were synthesized by anchoring trimethylamine on poly (2, 6-dimethyl-1, 4-phenylene) (PPO) and polysulfone (PSF) then blended with titanium dioxide (TiO₂), zinc oxide (ZnO) and graphene oxide. The membranes for proton exchange fuel cells were devolved by blending Nafion membrane with graphene oxide, nanofibers and ZrO₂ to enhance the Nafion basic properties. The polymer electrolyte membranes basic properties such as ion exchange capacity, ion conductivity, and water uptake, and fuel permeability were improved by the presence of nanomaterials. When the composite membranes were evaluated in a methanol fuel cell, the membranes with nanomaterials were found to have higher peak power density compared to pristine membranes. This indicated that nanomaterials can positively influence the properties of the polymer electrolyte membranes and give improved performance in direct methanol fuel cell applications.



Membranes from sulfonated polymers of intrinsic microporosity for aqueous redox flow batteries

*C.C. Ye**, *A.Q. Wang***, *R. Tan***, *C.G. Bezzu**, *Q.L. Song***, *N.B. McKeown**

* The University of Edinburgh, UK

** Imperial College London, UK

Keywords: Sulfonated polymers of intrinsic microporosity; flow batteries; hydrophilic microporous membranes, crossover-free

Membrane separators are key components in flow battery systems to provide the transport for charge carriers while preventing the crossover against redox active molecules.¹ However, fast ion-selective membranes with desired properties remain unavailable, which limits the development of flow battery technology.² Here we show hydrophilic microporous membranes based on sulfonated polymers of intrinsic microporosity that simultaneously possess high ionic conductivity, transport selectivity, chemical stability and mechanical robustness. Rigid and hydrophilic backbones act as exquisite molecular-sized barriers that enable membranes with fast transport of small salt ions and free crossover towards redox active molecules. The aqueous organic flow batteries assembled with these membranes show both excellent energy efficiency and capacity retention, outperforming equivalent batteries based on benchmark Nafion[®] membranes. The high ionic conductivity and transport selectivity of these membranes further suggest promising opportunities for a number of electrochemical energy conversion and storage devices.³

References

1. M. Park, J. Ryu, W. Wang, J. Cho, “Material design and engineering of next-generation flow-battery technologies”, *Nat. Rev. Mater.*, 2017, **2**, 16080.
2. R. Tan, *et al.* “Hydrophilic microporous membranes for selective ion separation and flow-battery energy storage”, *Nat. Mater.*, 2020, **19**, 195-202.
3. M.J. Baran, *et al.* “Design rules for membranes from polymers of intrinsic microporosity for crossover-free aqueous electrochemical devices”, *Joule*, 2019, **3**, 2968-2985.



Facile synthesis of ultrathin IEM for brackish water desalination via MCDI

Oneeb ul Haq*, **Ye Chan Lee***, **Jae-Hwan Choi****, **Youn-Sik Lee***

* Division of Chemical engineering, Chonbuk National University, Republic of Korea.

** Department of Chemical Engineering, Kongju National University, Republic of Korea.

Keywords: Ion exchange, membrane, deionization.

Introduction Water had become a scarce source on the planet. Two-thirds of the world population are expected to be under stress conditions within 10 years. Desalinated water has been a major share of potable water, and a critical component of sustaining life and economic growth. Capacitive deionization (CDI), one of most efficient desalination methods, which has proved to be a cost effective, clean and green technology. One of the most essential developments in CDI is to introduce ion-exchange membranes (IEMs) between electrodes¹. The resulting configuration is called a membrane capacitive deionization (MCDI) cell.

Methods

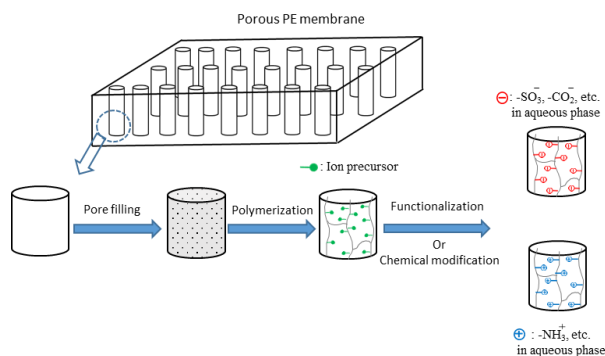


Fig.1 Schematic routes of anion & cation membrane and MCDI cell.

Results The anion- and cation-exchange polymeric membrane has been synthesized by pore filling technique. Which exhibit higher ion exchange capacity (IEC) due to the presence of charged functional groups on the surface which generates hydrophilic -hydrophobic micro phases in the membrane, which can offer continuous pathways for ion transport and durability.

Table: Membrane properties

Sample code	IEC (mmol/g)	DL (%)	Water uptake (%)	Thickness (um)	Resistance (Ω.cm ²)
CMX	1.5 ^a	22	28	170	3.2
AMX	1.4 ^a	20	25	140	3.4
PE-CSPS-5	1.0 ^b	11	36	30	0.35
PCMS-PE-I	3.0	2	5	29	0.28
PS-PE-S	2.8	5.2	6	28	0.7

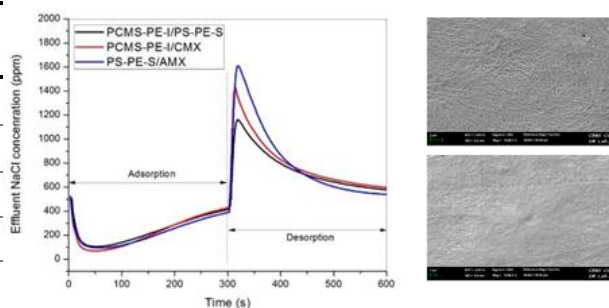


Fig: MCDI graph & SEM images of membrane



Conclusion In this study, both anion - and cation-exchange membranes were successfully synthesized to show much higher IEC than corresponding reported membranes¹⁻². Even though the membranes IEC values are very high, their dimensional stabilities are still very high, due to the presence of the supporting membrane (PE). The synthesized membranes have much lower electrical resistances than the corresponding reported membranes, due to their higher IEC and lower thickness. The performance of MCDI cells assembled using the synthesized membranes was comparable to the commercial membranes-based ones

References

- [1] N. Kang et al. / Reactive and Functional Polymers 99 (2016)
- [2] Q. Qiu et al. /Desalination 417 (2017) 87–93



Macro-corrugated and nano-patterned hierarchically structured superomniphobic membrane for treatment of low surface tension oily wastewater by membrane distillation

*J. Kharraz**, *H. Arafat***, *A. An**

* School of Energy and Environment, City University of Hong Kong, Hong Kong SAR

** Center for Membrane and Advanced Water Technology, Khalifa University, UAE

Keywords: Re-entrant structure; Water repellent; Self-cleaning; Oily wastewater; Micro patterns

The full implementation of membrane distillation (MD) for treatment of low surface tension industrial oily wastewaters is still hindered mainly due to major membrane issues such as wetting and fouling. In this study, a hierarchically assembled superomniphobic membrane with three levels of re-entrant structure was designed and fabricated to enable effective treatment of low surface tension, hypersaline oily wastewaters using direct contact MD. The overall structure is a combination of macro corrugations obtained by surface imprinting, micro spherulites morphology achieved through the applied modified phase inversion method and nano patterns obtained by fluorinated Silica nanoparticles (SiNPs) coating (Fig. 1). This resulted in a superomniphobic membrane (SOM) surface with remarkable anti-wetting properties repelling both high and low surface tension liquids.

Measurements of contact angle (CA) with DI water, an anionic surfactant, oil, and ethanol demonstrated a robust wetting resistance against low surface tension liquids showing both superhydrophobicity and superoleophobicity. CA values of $160.8 \pm 2.3^\circ$ and $154.3 \pm 1.9^\circ$ for water and oil were obtained, respectively. Calculations revealed a high liquid-vapor interface for the fabricated membrane with more than 89% of the water droplet contact area being with air pockets entrapped between adjacent SiNPs and only 11% in contact with the solid membrane surface. The high liquid-vapor interface endowed the membrane with high liquid repellency, self-cleaning and slippery effects, characterized by a minimum droplet-membrane interaction and complete water droplet bouncing on the surface within only 18 milliseconds. When tested in DCMD with synthetic hypersaline oily wastewaters, the fabricated SOM showed stable, non-wetting MD operation over 24 h, even at high concentrations of low surface tension 1.0 mM Sodium dodecyl sulfate and 400 ppm oil, potentially offering a sustainable option for treatment of low surface tension oily industrial wastewater.

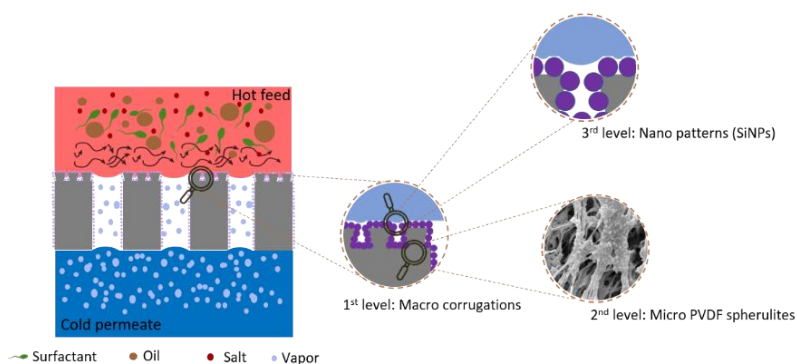


Figure 1. Hierarchically structured superomniphobic MD membrane.



Doped Laser-Induced Graphene Catalytic Filters and Membranes for Wastewater Treatment

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

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

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

Keywords: Laser Induced Graphene; Wastewater treatment; Biofouling; Catalytic membranes

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} 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.

References

1. Singh, S. P.; Li, Y.; Zhang, J.; Tour, J. M.*; Arnusch, C. J.* Sulfur-doped laser-induced porous graphene derived from polysulfone-class polymers and membranes *ACS Nano* **2018**, *12* (1), 289–297.
2. Gupta, A., Holoidovsky, L., Thamaraiselvan, C., Thakur, A. K., Singh, S. P., Meijer, M. M., and Arnusch, C.J. Silver-Doped Laser-Induced Graphene for Potent Surface Antibacterial Activity and Anti-biofilm Action. *Chem. Commun.* **2019**,55, 6890—6893.



Energy efficient desalination with membrane capacitive deionization (MCDI): Findings of theoretical and pilot studies

U. Hellriegel^{1,3,4}, E. Cañas Kurz^{1,3,4}, A. Caravella², B. Gabriele¹, A. Figoli³ and J. Hoinkis⁴

¹Laboratory of Industrial and Synthetic Organic Chemistry (LISOC), Department of Chemistry and Chemical Technologies, University of Calabria, Via Pietro Bucci 12/C, 87036 Arcavacata di Rende (CS), Italy

²Department of Computer Engineering, Modeling, Electronics and System Engineering, University of Calabria, Via Pietro Bucci 45/A, 87036 Arcavacata di Rende (CS), Italy

³Institute on Membrane Technology, National Research Council (ITM-CNR), Via Pietro Bucci 17/C, 87036 Arcavacata di Rende (CS), Italy

⁴Center of Applied Research (CAR), Karlsruhe University of Applied Sciences, Moltkestrasse 30, 76133 Karlsruhe, Germany

Keywords: Capacitive Deionisation (CDI), Desalination, Energy Efficiency, Pilot Scale, Modelling

To make membrane capacitive deionization (MCDI)¹ deployable for sustainable drinking water production, modular pilot scaled concepts and modelling strategies have been developed. Lab scale experiments demonstrate that an energy efficient desalination of brackish water is visible with commercial MCDI modules and can be a viable option compared to other desalination technologies. Salt solutions can be desalinated from 1000 mg L⁻¹ below 450 mg L⁻¹ with a specific energy consumption of SEC = 0.6 kWh m⁻³ (Figure 1). After upscaling the module and the treated volume, the SEC value can be halved. The mobility of different ions as well as the composition of the model water largely affects the removal efficiency.

A developed FEM simulation model for CDI is being compared with the modified Donnan model², which can describe experimental data sufficiently, also when applied voltages at the module are low. For calculating specific energy consumption, RC models will be implemented.

For desalinating brackish water with higher concentrations of salt, a combination process of low-pressure RO membranes and MCDI is tested at pilot scale in coastal area of Vietnam. Hereby, the MCDI module acts as polisher, compensating fluctuations of salt concentration which can occur in tropical coastal regions according to raining and dry seasons. The low-pressure concept allows a low-cost and easy to implement setup.

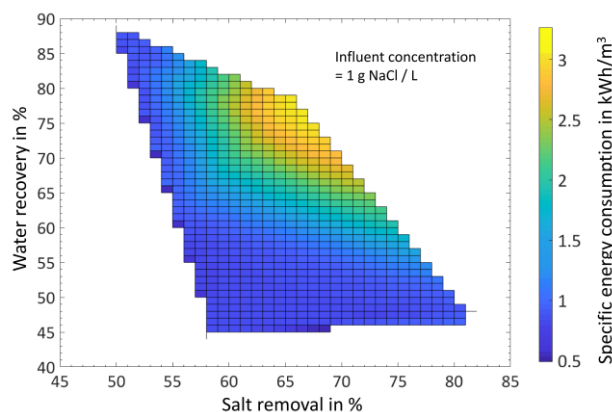


Figure 1. Specific energy consumption of a laboratory MCDI module, depending on water recovery and salt removal

References

1. M.E. Suss et al., "Water desalination via capacitive deionization: what is it and what can we expect from it?", *Energy Environ. Sci.*, 2015, **8**, 2296.
2. P. M. Biesheuvel, S. Porada, M. Levi, M.Z. Bazant, "Attractive forces in microporous carbon electrodes for capacitive deionization", *J. Solid State Electrochem.*, 2014, **18**, 1365-1376.



Graphene oxide membranes for desalination via membrane distillation

*C M Skuse**, *M Alberto**, *S Leaper**, *P Gorgojo**, *A Gallego-Schmid***, *A Azapagic****

* School of Chemical Engineering and Analytical Science, The University of Manchester

**Tyndall Centre for Climate Change Research, School of Mechanical, Aerospace and Civil Engineering, The University of Manchester

***Sustainable Industrial Systems, Department of Chemical Engineering and Analytical Science, The University of Manchester

Keywords: Desalination; Graphene; Membrane Distillation

The sustainable production of water is one of the greatest challenges facing modern day civilisation. Reverse osmosis is currently the most widespread desalination technique, however concerns over its associated greenhouse gas emissions and production of brine have ignited research into alternative methods. One such technology is membrane distillation, (MD) which is able to produce drinking water from seawater at atmospheric pressure and using low grade or waste heat.

Graphene oxide is a promising membrane additive in MD, having demonstrated improvements in membrane flux, anti-fouling and mechanical properties^{1,2}. This study explores various chemical functionalisations of graphene materials, including iron nanoparticles and porous graphene, as coatings and as nanofillers to produce robust, scalable polymeric membranes that make clean water more accessible.

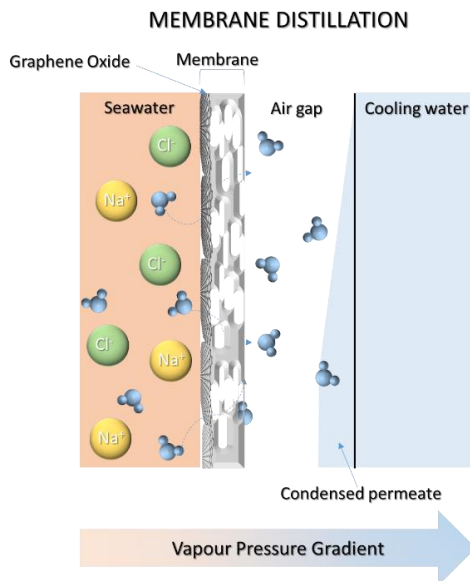


Figure 1. Diagram of an air gap membrane distillation system with a laminate graphene oxide layer

References

1. Leaper, S. *et al.* Flux-enhanced PVDF mixed matrix membranes incorporating APTS-functionalized graphene oxide for membrane distillation. *J. Memb. Sci.* **554**, 309–323 (2018).
2. Intrchom, W. *et al.* Immobilization of Graphene Oxide on the Permeate Side of a Membrane Distillation Membrane to Enhance Flux. *Membranes (Basel)*. **8**, 63 (2018).



Effect of Particle Shape on Properties of Freeze Cast Mullite Ceramic Membranes

Amanmyrat Abdullayev,* Maged F. Bekheet and Aleksander Gurlo

Fachgebiet Keramische Werkstoffe / Chair of Advanced Ceramic Materials, Institut für Werkstoffwissenschaften und -technologien, Fakultät III, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin, Germany

* presenting author: Amanmyrat.abdullayev@ceramics.tu-berlin.de

Keywords: mullite; membrane; particle shape; needle-like;

Ceramic membranes have superior chemical and thermal stability compared to polymeric membranes, which is due to the stability of their ceramic materials such as alumina, zirconia etc. The morphology of ceramic powders (i.e. particle shape), used for membrane fabrication, has a great influence on their packing density and consequently, it will affect the porosity and mechanical property of the obtained ceramic membrane.¹ Despite ceramic powders with spherical or irregular shapes are generally used for membrane fabrication, there are few studies reported the influence of particle shape on the property of porous ceramic membranes. Recently, Miyake et al. investigated the behaviour of alumina porous bodies fabricated from spherical, rod-shaped and disc-shaped particles.² Rod-shaped particles led to higher porosity while having lower compressive strength. That lower compressive strength might be due to the low aspect ratio of rod-like shaped particles used, which were around 2-4.

In this work, we chose mullite as model material, because it can be synthesized easily in a needle-like shape with higher aspect ratio, i.e. around 30, see **Figure 1**. Porous ceramic membrane supports fabricated from needle-like and irregularly shaped mullite have been studied. Freeze casting technique with various solid content and tert-butanol as a freezing media is used to get highly porous structures. Shrinkage, compressive strength and porosity of mullite bodies investigated using XRD, porosimetry and SEM.

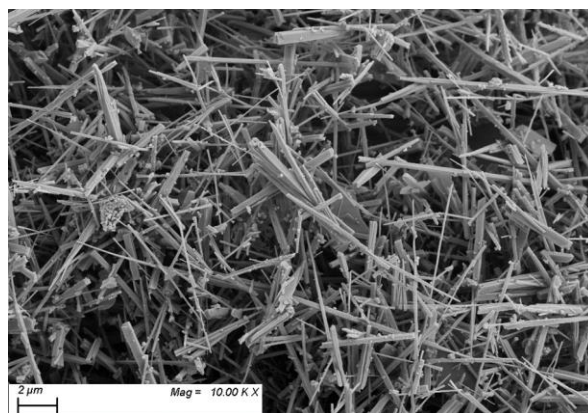


Figure 1. Mullite whiskers with an aspect ratio around 30 used for membrane preparation

References

1. Wouterse, A., Williams, S. R., & Philipse, A. P. "Effect of particle shape on the density and microstructure of random packings". *Journal of Physics: Condensed Matter*, (2007), **19(40)**, 406215.
2. Miyake, K., Hirata, Y., Shimonosono, T., & Sameshima, S. "The Effect of Particle Shape on Sintering Behavior and Compressive Strength of Porous Alumina". *Materials*, (2018), **11(7)**, 1137.



Photocatalytic Ultrafiltration ZrO₂/TiO₂ Membrane

*F.E. Bortot Coelho**, *V. M. Candelario***, *G. Magnacca**

* Department of Chemistry, University of Torino, Via P.Giuria 7, 10125 Torino, Italy.

** LiqTech Ceramics A/S, Industriparken 22 C, 2750 Ballerup, Denmark

Keywords: Ultrafiltration, Membrane Fabrication, Zirconia; Silicon Carbide, Photocatalysis

The increasing demand for water requires sustainable processes for wastewater treatment, clean water production, and water reuse in an optic of circular management of water sources. In this context, filtration is an efficient technology but it has some drawbacks such as membrane fouling and the accumulation of pollutants in the retentate flow. In parallel, the degradation of pollutants can be achieved by Advanced Oxidation Processes (AOPs), such as photocatalysis. Therefore, this work combined membrane filtration and AOPs to develop an ultrafiltration membrane with photocatalytic properties, in which solar light can be used to maintain clean the membrane surface from fouling and at the same time to degrade recalcitrant pollutants such as Contaminants of Emerging Concern (CECs). The photocatalytic ultrafiltration layer, based on Ce-ZrO₂/TiO₂, was prepared by a modified sol-gel process. For that, a microporous SiC support with a ZrO₂ interlayer (provided by LiqTech Ceramics A/S) was dip coated with the prepared gel. The support and interlayer have pore sizes around 15 μm and 70 nm. After firing at 600°C, the top layer presented a pore size around 10 nm, an average thickness of 2 μm (Figure 1), and no cracks nor major defects. X-Ray Diffraction analysis indicated the presence of tetragonal zirconia, due to the yttria addition (8 %mol Y₂O₃) during the synthesis. The photocatalytic properties of the membrane were successfully demonstrated towards the degradation of humic substances and the reduction of Cr(VI) using visible light. Filtration tests are being performed in order to fully characterize the membranes. However, preliminary results indicate that the developed membranes possess high water flux and good retention of large organic molecules, which combined with the anti-fouling and photocatalytic properties may allow innovative and sustainable water treatment processes.

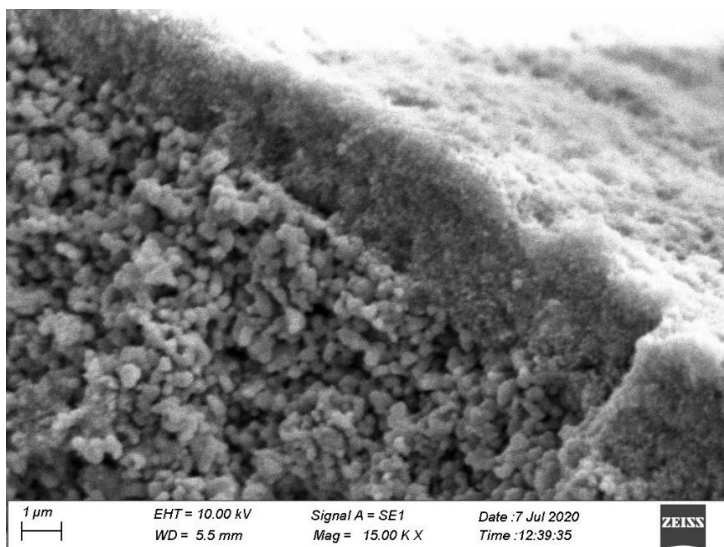


Figure 1. Cross-section of the photocatalytic membrane. The darker layer is the ZrO₂/TiO₂ top active layer and the lighter is the ZrO₂ interlayer.



Fe₃O₄-SiO₂ coated tyre-based activated carbon nanofibers as a nanoadsorbent for ultrasound assisted dispersive solid phase extraction of arsenic, cadmium and thallium in environmental samples

M, Dimpe^{1*}, P, Nomngongo

*Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa
mdimpe@uj.ac.za*

Keywords: Metal oxides, Activated carbon, Tyres, Nanofibers, Wastewater

The toxicity of trace metals such as arsenic, cadmium and thallium have been well documented and their adverse effects includes sleeping disabilities, speech disorder, high blood pressure, poor concentration, memory loss, mood swings, fatigue, allergic reactions and depression¹. In addition, arsenic, cadmium and thallium have the potential to disrupt the human cellular enzymes². Therefore, in order to solve the problem that is associated with toxic elements, green and effective sample preparation techniques need to be developed. Therefore, in this study, magnetic iron oxide-silica nanoparticles coated tyre based activated carbon nanofiber (Fe₃O₄-SiO₂@ACNF) nanocomposite was prepared and reported for the first time as a nanoadsorbent for the ultrasound assisted dispersive solid phase extraction (UA-DSPE) of arsenic, cadmium and thallium from complex matrices. The concentrations of As, Cd and Tl were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The synthesized nanocomposite was characterized by Fourier transform infrared spectroscopy, x-ray diffraction, scanning electron microscopy, transmission electron microscope and Brunauer, Emmett and Teller surface area. Various parameters such as pH, eluent concentration, extraction time and mass of adsorbent were optimized using the response surface methodology based Box-Behnken design. Under optimum conditions, limit of detection (LOD) and quantification (LOQ) of UA-DSPE were 10, 80, 90 ng L⁻¹ and 33, 266, 300 ng L⁻¹ for As, Cd and Tl, respectively. In terms of precision, the relative standard deviation (%RSD) ranged from 0.6-0.8%. Furthermore, the accuracy of the proposed method was verified by spike recovery test and satisfactory recoveries (95-99%) were obtained. Finally, the UA-DSPE method was successfully applied to wastewater (influent and effluent) and river water samples for the extraction and preconcentration of As, Cd and Tl.

References

1. V. K. Gupta, *et al.*, Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review. *Crit Rev. Environ. Sci. Technol.*, 2016, **46**, 93-118.
2. A. Abbas, *et al.*, Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. *Sep. Purif. Technol.*, 2016, **157**, 141-161.



Enhanced Fabrication of Silicon Carbide Membranes for Water Treatment

*Esra Eray***, *Vittorio Boffa***, *Mads K. Jørgensen***, *Victor Candelario**

* Liqtech International A/S, Industriparken 22C, DK-2750 Ballerup, Denmark

** Department of Chemistry and Bioscience, Center of Membrane Technology, Aalborg University, Fredrik Bajers Vej 7H, DK-9220 Aalborg Øst, Denmark

Keywords: Silicon carbide membrane; ceramic processing; membrane fabrication; filtration; water treatment

Purification and reuse of water are becoming an attractive solution for the ever-increasing water scarcity and water quality deterioration issues. Membrane-based filtration and separation processes offer several benefits over the conventional treatment technologies. First, they are effective processes offering high pollutant removal efficiency. Second, there is no need for chemical additives except those required for membrane cleaning. Moreover, filtration units work with lower energy cost, smaller area requirement, are compact in design and operate easier than other traditional methods. In this perspective, porous ceramic membranes have attracted great attention, due to their advantages in terms of higher flux, better separation properties, and fouling resistance, longer working life and smaller footprints compared to the most commonly used polymeric membranes^{1,2}. Silicon carbide (SiC) membranes possess all the above-mentioned features, together with high mechanical strength, good thermal and chemical resistance, superior hydrothermal stability, therefore, they emerged as excellent porous material among the other ceramic membranes³.

In this study, a detailed study on the fabrication of homogenous and defect-free pure silicon carbide membranes on silicon carbide support by controlling crucial parameters such as effect of powder mixing ratio, solid loading, use of SiC powders with different particle size were studied. The structural morphology of the membrane layers was investigated. The optimized protocol was up-scaled on industrial SiC supports. Moreover, the intrinsic properties of the new SiC membranes were checked in filtration tests. The prepared novel pure SiC membranes exhibit attractive water permeability and effective removal of particles. These membranes have a potential to be applied in the water treatment since they showed the proper robustness to change the water quality.

References

1. P.S. Goh, A.F. Ismail, "A review on inorganic membranes for desalination and wastewater treatment", *Desalination*, 2018, **434**, 60-80.
2. Z. He, Z. Lyu, Q. Gu, L. Zhang, J. Wang, "Ceramic-based membranes for water and wastewater treatment", *Colloids Surfaces A*, 2019, **578**, 123513.
3. B. Hofs, J. Ogier, D. Vries, E.F. Beerendonk, E.R. Cornelissen "Comparison of ceramic and polymeric membrane permeability and fouling using surface water", *Sep. Purif. Technol.*, 2011, **79**, 365-374.

Acknowledgements

This project is a part of project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 765860 (AQUALity).



Asymmetric porous SiOC membranes for microfiltration produced by phase-inversion tape casting technique

N. C. Fontão¹, M. Wilhelm¹, K. Rezwan^{1,2}

¹ University of Bremen, Advanced Ceramics, Am Biologischen Garten 2, IW3, Germany

² MAPEX—Centre for Materials and Processes, University of Bremen, Am Fallturm 1, Bremen,

Keywords: Polymer-derived ceramic; polysiloxane; membrane performance.

Asymmetric porous SiOC membranes with different pore characteristic and membrane morphology for microfiltration were produced for the first time by adapting the phase-inversion¹ tape casting technique to the polymer-derived ceramic (PDC) route.² Polymethylsiloxane (MK) was used as a ceramic precursor. The produced tapes were pyrolyzed under N₂ atmosphere. The structure and surface characteristics were tailored by changing the pyrolysis temperatures (600 and 1000 °C) and the additives contents, such as and polyvinylpyrrolidone (PVP) and solid loading (particles of cross-linked MK pyrolyzed at 600 °C, MK600). Scanning electron microscopy analysis revealed the asymmetric morphology composed by a thin skin-layer (average pore size < 2 μm) and a sponge-like support. The differences in membranes porosity (33-47%) and overall pore size distribution (1 - 10 μm) can be controlled according to the slurry composition. The addition of PVP increased the slurry viscosity, altering the rate of demixing in the phase inversion process, and led to bigger pore sizes in the membrane structure. On the other hand, the incorporation of particles improved the slurry processability, enhanced the mechanical flexural resistance of the membrane (20 – 48 MPa), and reduced the average pore size. Higher mechanical strengths, as well as enhanced hydrophilic character, are associated with the higher pyrolysis temperature (ceramization process). The water permeation performances of membranes pyrolyzed at 1000 °C were assessed in a dead-end configuration device under different pressures (1 – 3 bar). The obtained water permeation fluxes (5 – 55 m³/m².h, at 3 bar) indicates the advantages of the asymmetric structure - a porous skin-layer followed by a porous support-layer which minimizes mass transport limitations. It turned out that the phase-inversion tape casting technique is a flexible and promising alternative to produce tailorable PDC membranes suitable for microfiltration applications.

References

1. A. K. Hołda, I. F.J. Vankelecom. “Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes”, *J. Appl. Polym. Sci.*, **132**, 42130.
2. C. Vakifahmetoglu, D. Zeydanli, P. Colombo. “Porous polymer derived ceramics”, *Mat. Sci. Eng. R.*, **106**, 1-30.



Comparative study of novel antifouling sulfonated polyaniline nanofiltration membranes and conventional treatment for water and seawater (pre)treatment

H Alhweij^{a,b}, J Wenk^a, E Emanuelsson^a, S Shahid^a

^aDepartment of Chemical Engineering and Water Innovation and Research Centre (WIRC@Bath),
University of Bath, UK

^bStantec UK Limited, UK

Keywords: Nanofiltration; sulfonated polyaniline; NOM removal; antifouling; conventional treatment

Natural organic matter (NOM) in surface water and seawater is a heterogeneous mix of compounds occurring at varying concentrations that can affect water quality achieved by water treatment processes. For example, commercial pressure-driven membranes are prone to fouling due to strong hydrophobic interactions between NOM-foulants and the membrane surface. The aim of this work was to explore the potential application of the in-situ tailored nanofiltration sulfonated polyaniline (S-PANI) membranes (molecular weight cut off \approx 900 Da) for NOM removal and assess its antifouling propensity. Benchmarking of S-PANI membrane performance was conducted against a set-up of conventional treatment processes including coagulation, adsorption, flocculation, sedimentation, and filtration at optimised operating conditions for each process. The S-PANI membranes retained up to 92% and 94% of the NOM compared to 72% and 59% removal by the conventional treatment in both artificial freshwater and seawater, respectively. Analysis of the apparent molecular weight distribution (AMWD) of the NOM revealed that the conventional processes had mainly remove high molecular weight NOM with marginal removal of low molecular weight (LMW) species (<3 kDa), which are considered to be more problematic in water treatment. In contrast, the S-PANI membrane rejection which was dominated by the size exclusion retained all NOM species above 1 kDa and 11 to 13% of the NOM below 1 kDa. The S-PANI membrane exhibited antifouling properties including total flux recovery ratio of 93 to 96% and low irreversible fouling of 2.7 to 4.6% in artificial seawater and freshwater sample, respectively. Pure water flushing cycles almost re-established membrane performance over prolonged filtration periods. Recovered NOM from the S-PANI membrane showed lower affinity between the membrane and the NOM compared to commercial membranes. Fourier transform infrared (FT-IR) spectroscopy helped to determine the functional groups of foulants. However, the broad overlapping bands of the membrane-foulant constrained the ability to define the affinity of certain foulants to the membrane surface. The results highlight that the developed S-PANI membrane exhibited a high and consistent NOM removal with intrinsic antifouling behaviour compared to conventional treatment. Therefore, the S-PANI membrane could be considered as an alternative solution to tackle more stringent quality requirements for surface water and seawater (pre)treatment.



Relating Fouling Mechanisms of Ultrafiltration Capillary Membranes in Mini-plant Operation to Characteristics of Algae-contaminated Water

S. Laksono, I.M.A. ElSherbiny, S. Panglisch

Chair for Mechanical Process Engineering and Water Technology, University of Duisburg-Essen, Germany

Keywords: Algae fouling, ultrafiltration, pore blocking models,

Algae-contaminated surface waters may serve as potential source for drinking water; however, they should be properly treated using ultrafiltration membranes. Studies regarding fouling potential by individual algal organic matters (AOMs) that may influence membrane performance at full-scale operation is lacking. In this study, performance and fouling mechanisms inside polyethersulfone capillary membranes during mini-plant tests using were attempted to be correlated to chemical and physical characteristics of algae-contaminated feeds. Freshwater and seawater algae were employed in intact and lysed conditions. Lysed feeds were characterized by higher organic contents and essentially low particle size distribution than intact feeds, which were responsible for drastic membranes' performance decay (Fig. 1). High-molecular weight AOMs were more retained, whilst low-molecular weight AOMs and cell debris were less retained and resulted in a rather mechanical irreversible fouling. Fouling rates by individual blocking and cake filtration fouling mechanisms per every filtration cycle were estimated (Fig. 2) and combined with fouling reversibility calculations to elaborate fouling mechanism scenarios occurred during multiple filtration cycles.

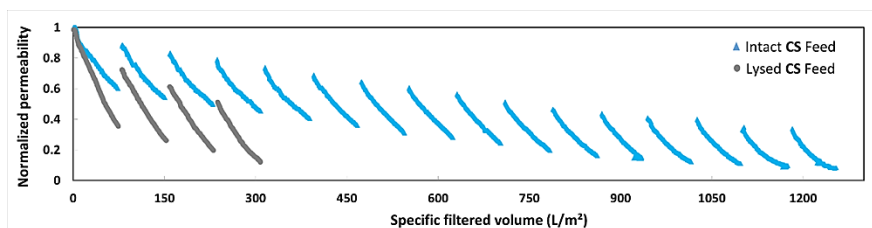


Figure 1. Exemplary performance for mini-plant filtration using *Chlorella Sorokiniana* freshwater algae in different cell conditions

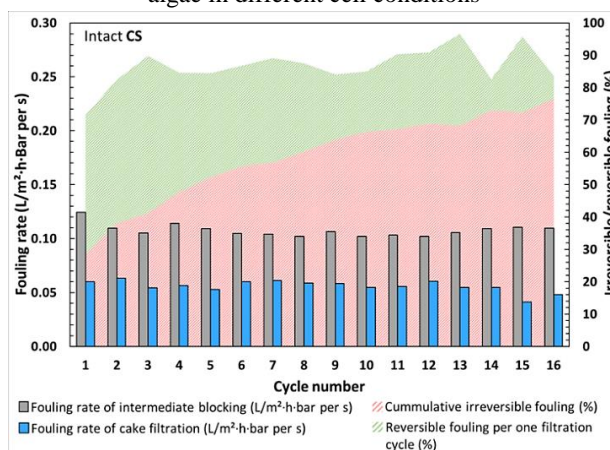


Figure 2. Analysis of membrane fouling occurred in capillary ultrafiltration membrane during mini-plant filtrations of *Chlorella Sorokiniana* in intact condition



Treatment of hydrothermal liquefaction liquid waste with pressure driven membrane technologies

*Ali Sayegh**, *Malek Youssef**, *Florencia Saravia***, *Harald Horn****

* Karlsruhe Institute of Technology, Engler-Bunte-Institut, Water Chemistry and Water Technology, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

** DVGW-Research Center at the Engler-Bunte-Institut, Water Chemistry and Water Technology, Karlsruhe Institute of Technology, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

Keywords: Hydrothermal Liquefaction; liquid phase by-product; filtration; polymeric membranes

The production of the bio-crude by hydrothermal liquefaction (HTL) of sewage sludge leads to additional liquid, gaseous and solid phases by-products.¹ Especially, the liquid phase contains high concentration of organic compounds, which recovery is essential for an efficient HTL process. Recently, membrane technologies such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are used to treat process water.² In this study, several membranes in the range from ultrafiltration to reverse osmoses are tested in dead-end pressure driven filtration of the liquid phase.

Experiments were carried out using the following polymeric membranes: NF-270, NF-245, NF-90, BW-30 (DuPont Water Solutions) and HYDRACoRe 10 and HYDRACoRe 50 (Hydranautics). Electrical conductivity, pH value, concentrations of dissolved organic carbon (DOC), total nitrogen, volatile fatty acids (VFA) and selected inorganic ions' concentrations were measured for both the feed and the permeate.

Results showed, that the permeability of all membranes during the filtration decreased rapidly. Small organic compounds, e.g. VFA, phenols, organic compounds of nitrogen represent the main constituents of the DOC. Interactions between membrane material and these compounds play a key role, influencing membrane performance. Additionally, the permeability decline was linked to the fouling layer on the membrane surface, which is enhanced by the high DOC concentration (30 g/l). The feed solution has a high electrical conductivity (62 mS/cm), consequence of the high concentration of the monovalent ions potassium, sodium and ammonium. Thus, filtration experiments with dense membranes (NF 90 and BW 30) were carried out at 40 bar, due to high osmotic pressures produced by the ion-rejection. Filtration with the other membranes having low retention of monovalent ions induced low "effective" osmotic pressures and a pressure of 20 bar was applied. NF 90 and BW 30 showed high retention of DOC (70-80 %) but extremely low permeability in comparison to the other membranes.

For practical applications, only NF 270 and NF 245 can offer an acceptable permeability with low DOC rejection (30 %). It can be speculated that a combination of membrane processes (pressure driven membranes and membrane distillation) and the use of alternative membrane materials (e.g. ceramic) is a better option to treat this industrial wastewater.

References

1. R.B. Madsen, *et al.*, "Predicting the Chemical Composition of Aqueous Phase from Hydrothermal Liquefaction of Model Compounds and Biomasses", *Energy Fuels*, 2016, **30**, 10470-10483.
2. F. Zhou, C. Wang, J. Wei, "Separation of acetic acid from monosaccharides by NF and RO membranes: Performance comparison", *J. Membr. Sci.*, 2013, **429**, 243-251.



Supported Liquid Membranes (SLM) using green solvents for bio-based organic acids extraction.

*P. López-Porfiri**, *P. Gorgojo**, *M. Gonzalez-Miquel***

* School of Chemical Engineering and Analytical Sciences, Faculty of Science and Engineering, The University of Manchester, Manchester M13 9PL, UK.

** Departamento de Ingeniería Química Industrial y del Medioambiente, ETS Ingenieros Industriales, Universidad Politécnica de Madrid, C/ José Gutiérrez Abascal 2, Madrid, Spain.

Keywords: Supported liquid membrane; bio-refinery; organic acid recovery; green solvent.

Bio-based organic acids constitute an important group of building block chemicals that can be produced from renewable resources as a sustainable alternative to conventional petrochemical-derived commodities. However, their efficient separation from fermentation broths has become a major challenge for the production process.¹ Currently, organic acids recovery is carried out by liquid-liquid extraction using hazardous volatile organic solvents, opposing to initial green efforts.

Supported Liquid Membranes (SLM) have been proposed as a selective separation process of diluted solutions.² Moreover, the minimal solvent amount requirement in their fabrication will enhance the development of environmentally friendly processes, such as using green solvents as extraction media.

The main goal of this study is to determine green solvent-based SLM feasibility in organic acid extraction from aqueous media. Process performance, i.e., solute permeability, selectivity from fermentation by-products, and membrane stability, will be assessed through experimental measurements illustrating in Figure 1. The present study is contributing to evolving further novel downstream technologies for the bio-refinery industry.

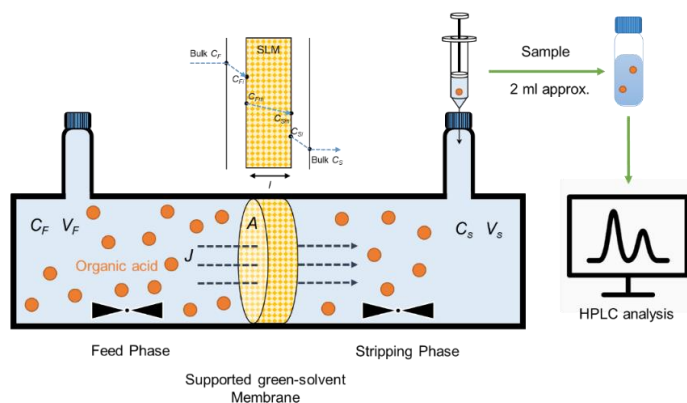


Figure 1. Bio-organic acid extraction with SLM experiment.

References

1. J. M. Pinazo, M. E. Domine, V. Parvulescu, and F. Petru, "Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes," *Catal. Today*, vol. 239, pp. 17–24, 2015
2. L. J. Lozano, C. Godínez, A. P. de los Ríos, F. J. Hernández-Fernández, S. Sánchez-Segado, and F. J. Alguacil, "Recent advances in supported ionic liquid membrane technology," *J. Memb. Sci.*, vol. 376, no. 1–2, pp. 1–14, 2011.



Cotreatment of landfill leachate and synthetic wastewater: effect on mixed liquor filterability and membrane fouling

A. C. Santana***, E. L. Subtil*, F. P. Manéo**

* Federal University of ABC (UFABC/Brazil)

** Technological Research Institute (IPT/Brazil)

Keywords: mixed liquor filtration; flux; fouling resistance; reversible fouling.

The objective of this research was to evaluate the effect of the cotreatment of landfill leachate (LL) with synthetic wastewater (sWW) on mixed liquor (ML) filterability and membrane fouling. The ML used were obtained from two different phases of a stable pilot scale MBR: first, the reactor was fed only with sWW, then with sWW and 20% (v/v) of real LL. For each ML, filterability tests were conducted on an Amicon 8400 stirred filtration cell with a commercial ultrafiltration membrane. The tests were performed at room temperature ($22.8 \pm 0.3^\circ\text{C}$), 580 rpm agitation and until a recuperation of 33% of the initial volume on permeate form. Flux Loss (FL) and Flux Recovery Rate (FRR) were calculated for each case, and Resistance-in-series model was applied. The results showed that FL was between 67 – 70% for both ML, which is in accordance with current literature^{2,3}. It was also observed a similar reversible FL (32% and 31% for sWW and sWW+LL, respectively) but an increase on irreversible FL for cotreatment (from 34% for 39%). An expressive reduction on FRR by chemical cleaning (from 31% to 18%) and on total FRR (from 97% to 79%), and the increase on not recoverable and inorganic irreversible resistance (from 1% to 11%) were observed on cotreatment. Cake resistance was the main fouling resistance fraction for both ML (74% and 73% of total fouling resistance), as previous studies had reported^{1,3,4}. In conclusion, it was observed that the cotreatment at 20% had little affect on filtration flux at the analysed hydrodynamic conditions but promoted a partial replacement of the reversible fraction by not recoverable and inorganic irreversible fouling fraction.

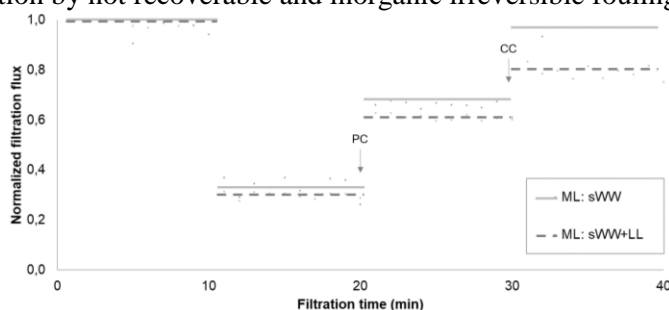


Figure 1. Normalized flux for both ML filtration
PC: physical cleaning; CC: chemical cleaning (basic).

References

1. A. Cosenza, G. Di Bella, G. Mannina, M. Torregrossa, G. Viviani, "Biological Nutrient Removal and Fouling Phenomena in a University of Cape Town Membrane Bioreactor Treating High Nitrogen Loads", *Journ. of Environm. Engineer.*, 2013, **139**, 773-780.
2. L.-C. Juang, D.-H. Tseng, Y.-M. Chen, G. U. Semblante, S.-J. You, "The effect soluble microbial products (SMP) on the quality and fouling potential of MBR effluent", *Desalin.*, 2013, **326**, 96-102.
3. N. C. M. Silva, W. G. Moravia, M. C. S. Amaral, K. C. de S. Figueiredo, "Evaluation of fouling mechanisms in nanofiltration as a polishing step of yeast MBR-treated landfill leachate", *Environm. Techn.*, 2018, **40**(4), 1-32.
4. N.O. Yigit, G. Civelekoglu, I. Harman, H. Koseoglu, M. Kitis, "Effects of various backwash scenarios on membrane fouling in a membrane bioreactor", *Desalin.*, 2009, **237**, 346-356.



Biofilm online monitoring in a nanofiltration system

G., Prato Fiorito, F., Saravia*, H., Horn***

* DVGW-Research Center at the Engler-Bunte-Institut, Chair of Water Chemistry and Water Technology, Karlsruhe Institute of Technology, Engler-Bunte Ring 9, 76131 Karlsruhe, Germany

** Karlsruhe Institute of Technology, Engler-Bunte-Institut, Chair of Water Chemistry and Water Technology, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

Keywords: Nanofiltration; Biofouling; Optical Coherence Tomography; Biofilm sensors

Biofouling in nanofiltration (NF) and reverse osmosis (RO) separation processes leads to a severe permeability decline due to membrane blocking and a pressure drop increase in the membrane module. Thus, monitoring of biofilm formation can be considered as an important tool to optimise membrane filtration. Optical Coherence Tomography (OCT) has been proved as a valid technique to observe and quantify biofouling. The main drawbacks of this technique are its high cost, the data handling and the difficulty to apply it in the industry. The present study investigates the approach of biofilm sensors as a cheaper alternative to OCT imaging, providing a reliable and consistent signal during process operation. Experiments were carried out with a membrane set-up equipped with four flat sheet cross-flow membrane units (FSMU) and biofilm sensors. A volatile fatty acid solution was used as feed. For comparison, FSMU were operated and biofilm growth were monitored at the same time via OCT directly on the membrane and by the biofilm sensors in the pipes. The conditions inside the sensor (temperature, pressure and flow velocity) were maintained as close as possible to the conditions in typical spiral wound modules. The received signals were analysed to find a possible correlation between biofilm sensor signal and biofilm growth detected via OCT-imaging. Additionally, filtration parameter, such as pressures, temperature and permeability were collected.

Results showed so far, that the OCT-imaging delivers high quality and precise information (location, amount, structure) about biofilm growth, meanwhile the pipeline biofilm sensor just delivers a signal when the membrane is already covered by biofilm.



Fabrication and characterization of a biotechnological Bruch's membrane for an *in vitro* model of the outer blood-retinal barrier

F. Liva*, A. De Acutis**, F. Montemurro***, C. De Maria****, E. Orlandini*, D. Cuffaro*, E. Nuti*, A. Rossello*, G. Vozzi*****

* Department of Pharmacy, University of Pisa, Via Bonanno 6, 56126 Pisa, Italy;

** Department of Ingegneria dell'Informazione, University of Pisa, Via Caruso 16, 56122 Pisa, Italy;

*** Research Center "E. Piaggio", University of Pisa, Largo Lucio Lazzarino 1, 56122, Italy.

Keywords: AMD, RPE cells, biopolymer, electrospinning, Bruch's membrane.

Advanced age-related macular degeneration (AMD) is the leading cause of blindness in the elderly worldwide, without effective therapeutic options. Although the exact pathogenic mechanisms of AMD are not elucidated yet, its main leading events are structural and morphological changes occurring with age in the outer blood-retinal-barrier (oBRB), especially in the Bruch's membrane (BrM), an acellular layer acting as a semi-permeable filter between the retinal pigment epithelium (RPE) cells and the choroidal vascular network (CVN)¹. Engineered platforms, such as *in vitro* models, may be beneficial in understanding AMD aetiology and providing more reliable devices for new drugs testing. Therefore, the aim of the presented work is to fabricate a biotechnological BrM resembling the native interface between RPE and CVN for the implementation of an oBRB *in vitro* model to test the permeability and safety of novel drug candidates and to study their impact on retinal cells in physiological and pathological (AMD) conditions. For the development of the engineered BrM, nanofiber-based gelatin membrane crosslinked with (3-Glycidioxypropyl) trimethoxysilane with a well-defined micro and nano porosity were fabricated by electrospinning process. Several combinations of electrospinning parameters were tested in order to get electrospun mats with mechanical, chemical and physical cues approaching those of the native BrM. Their mechanical properties, permeability and diffusion have been thoroughly analysed and compared with values referring to the BrM under physiological and pathological conditions². The elastic modulus, the ultimate stress, the strain and the toughness of the membrane were evaluated by tensile test. The static diffusion coefficient of membranes was assessed by applying a biomolecule (Methylene Blue), a drug (Levodopa) and 2 inhibitors with high affinity for the catalytic domain of metalloproteinases, as indicators. In order to mimic the cellular environment of oBRB, RPE cells will be cultivated over the engineered BrM. The fabricated electrospun mats are a reliable and valuable model of BrM, considering that the values of the different studied physical parameters are close to those of BrM under physiological conditions. Cell cultivation tests are currently being carried out and will be presented at the conference. Taken together, our findings are encouraging, showing that the electrospun membranes are capable to reproduce the *in vivo* properties of BrM, indicating that gelatin-GPTMS membranes can be used as a substrate for RPE cells cultivation in *in vitro* model of the oBRB.

References

1. Liva F, Cuffaro D, Nuti E, et al. Age-related Macular Degeneration: Current Knowledge of Zinc Metalloproteinases Involvement. *Curr Drug Targets*. 2019.
2. Curcio CA, Johnson M. Structure, Function, and Pathology of Bruch's Membrane. In: *Retina Fifth Edition*. ; 2012.



Development of membranes with antibacterial and antiradical activity

S, Regina*, R, Mazzei*, T, Poerio*, C, Sabia**, R, Iseppi**, 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

**Department of Life Sciences, University of Modena and Reggio Emilia, Via G. Campi 287, 41125 Modena, Italy

Keywords: PVA membranes; pectin; antibacterial; antiradical; green crosslinker

Over the last few years, the development of membranes with antibacterial and antiradical activity is increasingly emerging as a suitable strategy in the biomedical field, food packaging and in water filtration processes to mitigate the biofilm formation. Embedded in membranes, many inorganic compounds (e.g., silver nanoparticles, iron oxide, titanium dioxide, graphene oxide, and others) and biopolymers (e.g., cellulose and chitosan) are used to promote these properties.

In this study, pectin (PEC), a heteropolysaccharide, was employed as functional additive and simultaneously as crosslinking agent in order to obtain antibacterial and antiradical polyvinyl alcohol (PVA)-based membranes with improved physico-chemical stability. The membranes were prepared by Evaporation-Induced Phase Separation (EIPS) with different PVA/PEC ratio.

Fourier Transform Infrared (FTIR) spectroscopy analysis confirmed the successful crosslinking reaction pointing out the presence of absorption bands of ester groups, not present in PVA membrane spectra. 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%) measured by acid-basic titration was a further confirmation of the formation of covalent ester bonds between PVA-hydroxyl and PEC-carboxyl groups.

The antibacterial and antiradical activity of the PVA/PEC membranes was evaluated testing the inhibitory effects against *E. coli*, *S. aureus*, *P. aeruginosa*, *E. faecalis* and *B. subtilis* in solid and liquid culture and the scavenging activity against 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical, respectively.

It has been observed that PVA/PEC membranes showed microbial inhibitory zones (on solid culture), bacteria concentration decrease (from 10^7 to 10 Unit Forming Colonies, in liquid culture) and complete bleaching of DPPH solution (0.06 mM) in 15 minutes, unlike non-reacting PVA membranes.

The resulting data proved that the presence of pectin has a profound influence on membrane properties and suggested that this could be used i) as functional additive in membrane preparation to prevent bacteria adhesion to membrane surface and ii) as non-toxic and eco-friendly crosslinking agent to improve the resistance of biopolymers.



DOC and antibiotic removal from pig manure by nanofiltration (NF) to produce ammonium enriched liquid

P. Samanta **, M. D. Illiyyin*, F. Saravia**, H. Horn* ***

* Karlsruhe Institute of Technology, Engler-Bunte-Institut, Water Chemistry and Water Technology, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

** DVGW-Research Center at the Engler-Bunte-Institut, Water Chemistry and Water Technology, Karlsruhe Institute of Technology, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany

Keywords: Pig manure, DOC, antibiotics, nanofiltration, LC-OCD

Usage of large amount of antibiotics (AB) in pig farming leads to excrete substantial amount of ABs as manure and spread in soil and water body¹. The sorption of ABs in pig manure depend on manure properties such as organic matter (OM) content, pH etc². Therefore, the objectives of this research study are to eliminate dissolve organic carbon (DOC) and ABs from pig manure to produce ammonium enriched stream.

Detail characteristics analysis of different pig manure samples from southern part of Germany is done. Accordingly, a model manure feed solution with 1.5 g/L DOC, 1 g/L ammonium and 50 µg/L of ABs is prepared to be filtered by NF270, HC50 and NTR7450 membranes in dead end filtration system to probe the AB and DOC removal.

Initially, liquid chromatographic organic carbon detector (LC-OCD) showed a narrow size distribution (400 to 500 Dal) of OM present in pig manure. The DOC and AB retention of NF270 is found 90 and 99% respectively. Whereas for HC50 the DOC and AB retention is noticed around 80 and 90% and for NTR7450 it is found around 50 and 90% respectively. Subsequently, the ammonium retention remained roughly around 40, 30 and 20% for the NF270, HC50 and NTR7450 membranes respectively.

It shows that loose NF can be used to eliminate 80 to 90% of DOC and ABs from pig manure slurry respectively for producing concentrated ammonium enriched stream.

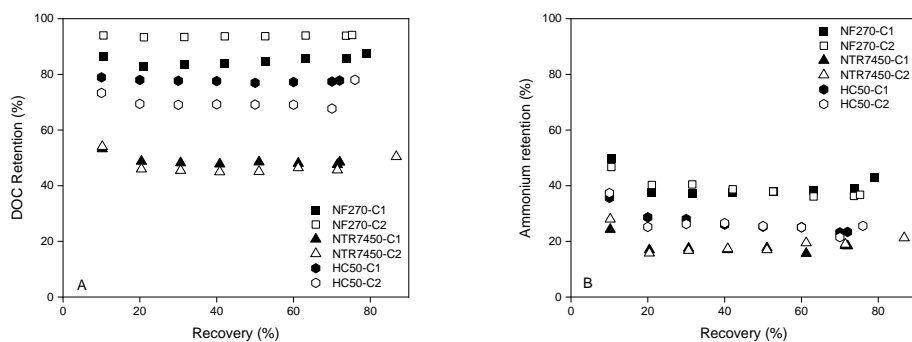


Figure 1. (A) DOC and (B) ammonium retention of model pig manure samples by NF270, HC50 and NTR7450 membranes are presented

References

1. L. Feng *et al*, "Removal of antibiotics during the anaerobic digestion of pig manure", *Sci. of the Tot. Env.*, 2017, **604**, 219-225.
2. S. Thiele-Bruhn, M. O. Aust "Effects of pig slurry on the sorption of sulfonamide antibiotics in soil", *Arch. of Env. Cont. and Toxic.*, 2004, **47**, 34-39.



Evaluating sustainable materials for membrane separations through molecular simulations: the case of Polyhydroxyalkanoates (PHA)

*K. Papchenko**, *E. Ricci**, *M.G. De Angelis**

* Department of Civil, Chemical, Environmental, and Materials Engineering – DICAM, University of Bologna, Italy

Keywords: polyhydroxyalkanoates; molecular dynamics; transport properties; gas separation.

Polyhydroxyalkanoates (PHA) are a family of linear optically active semi-crystalline polyesters produced by bacterial fermentation, known for their overall sustainability, including biodegradability and biocompatibility. PHA are also characterized by thermoplasticity and good mechanical properties, comparable to those of commercially relevant standard polymers.¹

The gas transport properties of these materials are still scarcely characterized experimentally, and their determination is complicated by a number of uncertainty sources, such as a time-dependent degree of crystallinity. In this study we aim at evaluating the physicochemical and transport properties of such materials with molecular simulations, to gain information about their applicability in the membrane gas separation field. In order to draw correlation between the molecular structure and the performance of these materials, three homopolymers and two copolymers of the PHA family were considered:

- poly(3-hydroxybutyrate) (P3HB);
- poly(3-hydroxyvalerate) (P3HV);
- poly(4-hydroxybutyrate) (P4HB);
- poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV);
- poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHBB).

Molecular models of each material were simulated using Molecular Dynamics (MD), obtaining amorphous density and solubility parameter values, that were successfully validated with experimental data found in literature^{2,3}. The simulated values of radius of gyration, accessible free volume, density, cohesive energy and elastic modulus in the different copolymers were correlated to their chemical composition.

Sorption and diffusion in the polymers were then analysed for three gases, O₂, CH₄ and CO₂, by means of Grand Canonical Monte Carlo (GCMC) and MD simulations. The results were compared with experimental values, obtained through permeation tests at different temperatures, performed on PHBV with 8% of 3-hydroxyvalerate monomers purchased from Merck-Sigma.

References

1. K. Sudesh, H. Abe, Y. Doi, "Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters", *Prog. Polym. Sci.*, 2000, **25**, 1503-1555.
2. H. Mitomo, N. Morishita, Y. Doi, "Structural changes of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) fractionated with acetone-water solution", *Polymer*, 1995, **36**, 2573-2578.
3. H. Mitomo, W.-C. Hsieh, K. Nishiwaki, K. Kasuya, Y. Doi, "Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) produced by *Comamonas acidovorans*", *Polymer*, 2001, **42**, 3455-3461.



Participant Index (A-Z)

Name	Institution	Abstract page
Amanmyrat Abdullayev	Technische Universität Berlin, Germany	40
Monica Alberto	The University of Manchester, UK	19
Berta Alcalde	University of Girona, Spain	20
Hassan Alali Alhweij	University of Bath, UK	45
Ahmed Ameen	The University of Manchester, UK	24
Fabício Eduardo Bortot Coelho	University of Torino, Italy	41
Mogolodi Dimpe	University of Johannesburg, South Africa	42
Esra Eray	Aalborg University, Denmark	43
Noelia Esteban	University of Valladolid, Spain	14
Luis Felipe Dos Santos Esteves	University of Duisburg-Essen, Germany	22
Natalia Cristina Fontão	University of Bremen, Germany	44
Oneeb Ul Haq	Chonbuk National University, Republic of Korea	34-35
Ulrich Hellriegel	Karlsruhe University of Applied Sciences, Germany	38
Anand Jain	Magdeburg University, Germany	27
Jehad Abbaas Abed Alhaleem Kharraz	University of Hong Kong, Hong Kong	36
Sucipta Laksono	University of Duisburg-Essen, Germany	46
Sebastian Leaper	The University of Manchester, UK	21



Participant Index

Name	Institution	Abstract page
Sharon Lin	Massachusetts Institute of Technology, United States	29
Jiangtao Liu	King Abdullah University of Science and Technology (KAUST), Saudi Arabia	18
Francesca Liva	University of Pisa, Italy	51
Pablo López-Porfiri	The University of Manchester, UK	48
Jose Miguel Luque-Allied	The University of Manchester, UK	28
Aitor Marcos-Madrado	Universidad de Cantabria, Spain	31
Laura Matesanz Niño	University of Valladolid, Spain	26
Sajjad Mohsenpour	The University of Manchester, UK	23
Phumlani Msomi	University of Johannesburg, South Africa	32
Kseniya Papchenko	University of Bologna, Italy	54
Giorgio Pratofiorito	Karlsruhe Institute of Technology, Germany	50
Serena Regina	Institute on Membrane Technology (CNR-ITM), Italy	52
Eleonora Ricci	University of Bologna, Italy	15
Prantik Samanta	Karlsruhe Institute of Technology, Germany	53
Ana Carolina Santana	Federal University of ABC, Brazil	49
Ali Sayegh	Karlsruhe Institute of Technology, Germany	47



Participant Index

Name	Institution	Abstract page
Swatantra Pratap Singh	Indian Institute of Technology Bombay, India	37
Clara Skuse	The University of Manchester, UK	39
Cenit Soto	University of Valladolid, Spain	16-17
Albert Xiuyuan Wu	Massachusetts Institute of Technology, United States	30
Chunchun Ye	The University of Edinburgh, UK	33
Ngai Yin Yip	Columbia University, New York, USA	25