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Membrane News Twente

News magazine of the Membrane Science and Technology Group

Membrane Science & Technology

MNT, p/a University of Twente - TNW/MTO
PO Box 217 , NL-7500 AE Enschede, Netherlands
membrane@utwente.nl - www.utwente.nl/tnw/mtg
Telephone: +31 (0) 53 489 2950 - Fax: +31 (0) 53 489 4611

Membrane Science and Technology

Vision

The research group Membrane Science and Technology of the University of Twente, headed by Prof. Kitty Nijmeijer, focuses on the multidisciplinary topic of polymer membrane science and technology to control mass transfer through interfaces.

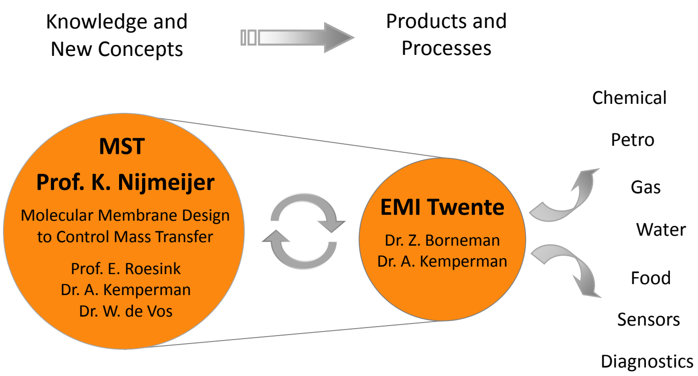

Figure 1 - Organizational structure research group.

The group consists of two separate entities (Figure 1): the academic research group Membrane Science and Technology (MST) and the European Membrane Institute Twente (EMI), which performs confidential research directly with the industry.

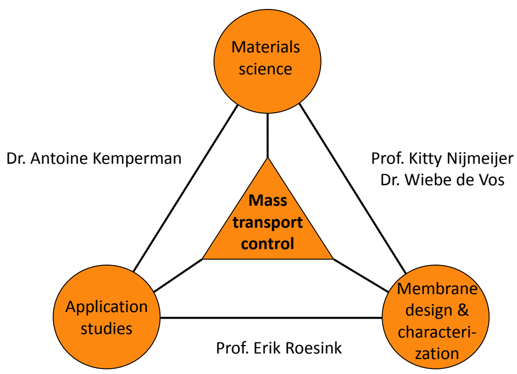

Figure 2 - Membrane Science & Technology.

Research within the group is dedicated to the design, development, characterization and application of polymer membranes for Energy, Water and Life Sciences. We aim at tailoring membrane design, morphology and characteristics on a molecular level to control mass transport in applications (Figure 2). More specifically, our research focuses on the separation of molecular mixtures and achieving selective mass transport. We consider our expertise as a multidisciplinary knowledge chain ranging from molecular design to process applications.

Most of our research is dedicated towards specific applications. We distinguish three main application clusters, i.e. Energy, Water and Life Sciences (Figure 3).

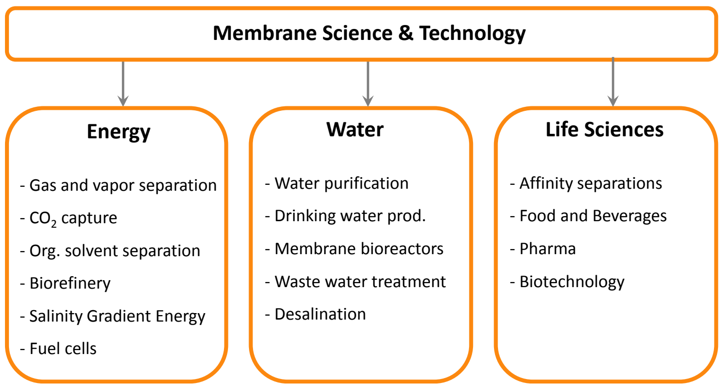

Figure 3 - Major application clusters Membrane Science & Technology.

Energy

The research cluster Energy is dedicated to the molecular design and synthesis of polymer membranes for e.g. gas and vapor separations (CO_2 capture, olefin/paraffin separation,

water vapor removal), biorefinery applications, fuel cells and the generation of energy from the mixing of salt and fresh water ('salinity gradient energy' or Blue Energy). Relevant research aspects are control of structure-properties relationships, ultimate selectivity, molecular recognition, and separation of complex, multi-component mixtures.

Water

Within the application cluster Water, research addresses the development of membranes and the application of membrane technology for water treatment, e.g. water purification, desalination, membrane bioreactors and waste water treatment. In particular it investigates the relation between membrane design and morphology and membrane properties in relation to performance, selectivity and causes, consequences and control of fouling.

Life sciences

The cluster Life Sciences focuses on the design of porous membranes to separate complex multicomponent mixtures in pharmaceutical, food, beverage and biotech applications. Important subjects are the tuning of the material properties and structure (e.g. pore morphology and porosity), the development of functional materials (e.g. affinity separations of biomolecules) and the creation of new and/or improved processes (e.g. faster processes, higher yields, less fouling). In addition, aspects related to process design and industrial implementation, such as scale-up of novel membrane fabrication methods, are investigated.

The research group consists of 30-35 people among which approximately 15-20 Ph.D. students, three permanent researchers, five B.Sc. and M.Sc. students and five academic staff members. Next to the head of the group, Prof. Kitty Nijmeijer, the staff consists of Prof. Erik Roesink and Dr. Wiebe de Vos, who recently joined the group, Dr. Antoine Kemperman and Dr. Zandrie Borneman, who is responsible for the EMI Twente. Next to extensive, general knowledge on polymer membrane science and technology, each of the staff members has his/her own specific field of dedicated expertise (Table 1).

Table 1 - Specific expertise of the staff members of MST.

Name	Specific expertise
Prof. Kitty Nijmeijer	Membrane design and characterization, molecular selectivity, molecular recognition, dense membranes, Energy and Water
Prof. Erik Roesink	Membrane formation, porous systems, phase inversion, solvent-free membranes, biomimetic membranes, Water and Life Sciences
Dr. Antoine Kemperman	Causes, consequences, cleaning and control of membrane fouling, interactions at the interface, Water European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry
Dr. Wiebe de Vos	Membrane surface science, surface modification, multilayers, polymer brushes, Water and Energy.
Dr. Zandrie Borneman	European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry

Knowledge valorization

Our group has decided to establish a significant effort in the valorization of its knowledge. The European Membrane Institute Twente (EMI Twente) was established in 1995 and performs confidential contract research directly with the industry and public organizations. Research is governed by questions from stakeholders. To guarantee confidentially, we work with highly skilled researchers with longstanding experience in membrane technology in our group. Students are not involved. EMI Twente creates, transfers and translates (fundamental) scientific knowledge into products, processes and applications. Projects can last from only a few days up to three years and can involve membrane development and synthesis, membrane characterization, and/or membrane application studies. The EMI Twente acts as the interface between the academic research and the industrial needs.

Services

The EMI Twente provides the following services:

- Membrane development
- Membrane characterization
- Membrane application studies
- Desktop studies
- Consultancy
- Selling of equipment (e.g. test cells for gas separation, UF and MF, casting knives, cloud point meters, hollow fiber spinning lines and spinnerets

For more information, please contact: Prof. Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl, www.utwente.nl/tnw/mtg) and Dr. Zandrie Borneman (z.borneman@utwente.nl, www.utwente.nl/tnw/emi).

Tenure tracker on "thin polymer films for functional membranes"

On the first of October, the MST group was joined by a new staff member and assistant professor, Dr. Wiebe M. de Vos. He will work on existing lines of investigation within the group but will also aim to expand the groups research in the use of thin layers of polymer (< 100 nm) to modify existing membranes or to act as membranes. Furthermore he will take over as the main lecturer for the Membrane Technology course.

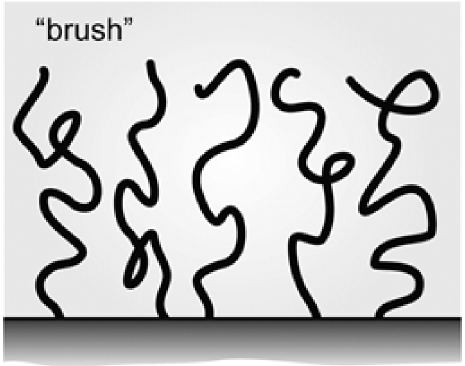

Figure 1 - Schematic depiction of a brush, a system where polymers are grafted so densely to an interface that they overlap and stretch away from the surface.

During most of his career, Wiebe has investigated thin layers of polymers adsorbed or otherwise attached to surfaces. In this way it is possible to functionalize surfaces to give for example anti-fouling properties, change the wetting properties, enable storage of enzymes and reduce frictional forces. For his PhD project, under the supervision of Prof. Martien Cohen Stuart (Wageningen University), the focus was very strongly on one system: the polymer brush. Polymer brushes are dense layers of polymer chains end-attached to an interface that stretch out into the surrounding solution (figure 1). Topics of investigation ranged from the very fundamental: "How does the structure of a polymer brush change as a function of polydispersity" to the more applied: "Can the anti-fouling properties of a brush be combined with the cleaning properties of a detergent". In addition he worked on different methods to prepare polymer brushes, including one method named the

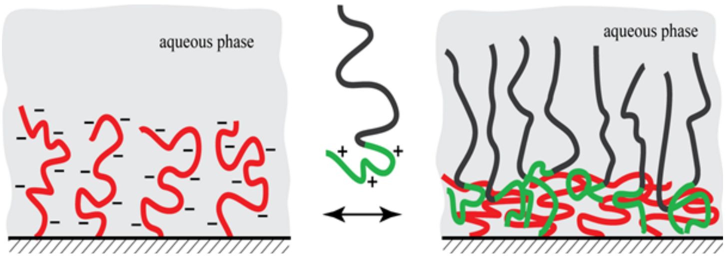

Figure 2 - Schematic depiction of the formation of a neutral zipper brush: a system where the adsorption of a diblock-copolymer to the high surface area of a polyelectrolyte brush layer leads to a new and very dense neutral brush layer. Desorption of the diblock-copolymer restores the original brush layer.

"zipper brush" approach that allowed the creation of very dense polymer brushes by simple adsorption from solution. The problem when preparing ordinary brushes by adsorption of diblock-copolymers is the lack of surface area at the interface. In the zipper brush approach this is solved by using a sparse polyelectrolyte brush to create a much larger amounts of surface area. Adsorption of a diblock-copolymer containing an oppositely charged polyelectrolyte block and a neutral polymer block then allows the formation of a very dense neutral polymer brush (see figure 2).

After finishing his PhD in 2009, Wiebe joined the University of Bristol (UK) to work with Prof. Terry Cosgrove and Prof. Rob Richardson as a Postdoctoral Fellow. During this project he developed a unique new setup that combines a surface force

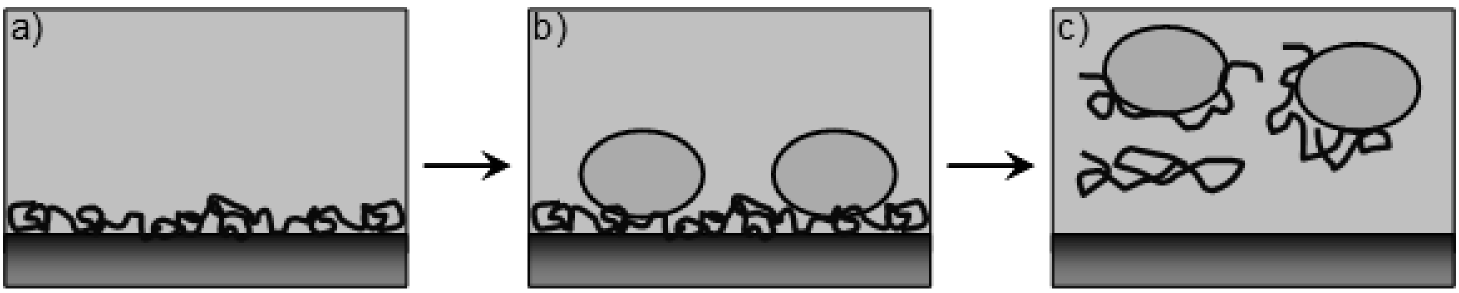

Figure 3 - Schematic depiction of the sacrificial layer approach. The interface is pre-coated with a thin polymer layer (a), when the interface gets dirty (b) the layer is simply removed (sacrificed) (c). The clean interface is then pre-coated again (back to a).

type apparatus with neutron reflection. With this setup it is, for the first time, possible to study the effect of compression on the structure of polymer layers, allowing a clear relation of the measured polymer structures to the forces needed for compression.

The key challenge of his tenure track will be to apply his knowledge on thin polymer layers to create novel and functional membranes. This could relate to the use of polymer brushes for anti-fouling membranes, but also to membranes where the permeability is controlled by a pH or temperature responsive polymer. Another aspect of this is that for a true membrane application, simple methods are needed to apply the polymer layer to the membrane. Furthermore, it would be much desirable to be able to replace the thin polymer layer in case of damage or fouling. A simple example of this would be the use of a sacrificial polymer layer (figure 3) to make membrane cleaning easier. A thin polymer layer is adsorbed onto a membrane surface, and when the membrane becomes dirty, a trigger such as pH, temperature or addition of surfactants is used to remove the polymer layer, and with it all attached fouling agents. The sacrificial layer is then reapplied.

For more information please contact Dr. Wiebe M. de Vos (w.m.devos@utwente.nl, phone: +31 53 489 4495).

Vacancies

Nanofiltration for Extreme Conditions

Next to their well-known use to decrease hardness of potable water, nanofiltration membranes have large potential for applications involving more extreme conditions, such as very high or low pH. High performance nanofiltration membranes are generally prepared via an interfacial polymerization reaction, yielding a thin polyamide layer. The inherent limited pH stability of polyamides restricts the application window of such membranes. In this project, alternative chemistry for the interfacial polymerization reaction will be investigated that should result in a new class of nanofiltration membranes with superior chemical stability.

We are looking for a highly motivated and enthusiastic researcher with a Ph.D. degree in Polymer Chemistry or Materials Science, with adequate experimental and theoretical skills. Knowledge of membrane technology is a pre.

We prefer candidates with a good team spirit, who like to work in an internationally oriented environment. Fluency in English is a requirement. An interview and a scientific presentation will be part of the selection procedure.

Interested candidates can send their motivation letter and CV (including references) to Dr. Antoine Kemperman (a.j.b.kemperman@utwente.nl, phone: +31 53 489 2956).

Responsive Polymer Brushes as an on-off switch for Protein Molecules

Polymer brushes, dense arrays of polymers end-attached to an interface, are generally considered as one of the most powerful and versatile methods to modify surface properties. Recently there has been much interest in brushes consisting of two chemically different polymers (mixed polymer brushes), as these systems have been shown to have an enormous potential as responsive surface layers. The focus in this project will be on combining such responsive layers with the specific interactions of biological molecules such as enzymes and receptor molecules. This can lead to a polymer brush that with a certain trigger switches between a protective state, in which the biological component is hidden deep inside a protective brush layer, and an active state in which the biological component is exposed to the solution (see figure). This would allow one to prepare surfaces with very specific functionalities that can be switched on and off. Applications would include catalytic membranes, antibacterial coatings and biosensors.

We are looking for highly motivated and enthusiastic researchers with a Ph.D. degree in Surface Chemistry, Physical Chemistry, Materials Science, Biochemistry or a related topic, with adequate experimental and theoretical skills.

We prefer candidates with a good team spirit, who like to work in an internationally oriented environment. Fluency in English is a requirement. An interview and a scientific presentation will be part of the selection procedure.

Interested candidates can send their motivation letter and CV (including references) to Dr. Wiebe M. de Vos (w.m.devos@utwente.nl, phone: +31 53 489 4495).

Membranes in the biobased economy: Electrodialysis of amino acids for the production of biochemicals

The depletion of fossil fuels, the increasing oil prices and the emission of CO_2 rise the need for green alternatives for the production of energy, fuels and chemicals. Emerging sustainable technologies based on renewable resources promote the shift of conventional refineries toward biorefinery concepts. It is well known that a significant amount of biomass feedstocks can be used for the production of such bioenergy, biofuels and biobased chemicals (chemicals produced from biobased feeds). An interesting feedstock for the production of biobased chemicals are amino acids that can be obtained from cheap protein sources (e.g. side streams from the production of biotransportation fuels from rapeseed oil), as amino acids already have the functionalities (i. e. –N and –O) required for the production of chemicals. In such feeds, the amino acids are usually present as a mixture and need to be isolated for further processing. Since amino acids are zwitterionic molecules whose charge is determined by the surrounding pH, electrodialysis (ED) is an attractive technology to isolate and separate amino acids for further processing into bulk or specialty chemicals. Figure 1 shows the conventional route and this proposed novel route based on ED for the production of chemicals. ED is an electro-membrane process that uses an electrical potential difference over the membrane as driving force for the selective extraction of ions from solutions. It can also be used in biorefinery applications to separate e.g. amino acids, as long as there is a difference in charge behavior with respect to pH. A schematic representation of the separation of the different amino acids depending on their charge is shown in Figure 2.

In theory, ED could be used to isolate every single amino acid from a protein hydrolysate as long as there exists a difference in the iso-electric points. In practice however, only fractionation of the amino acids into three main groups (basic, acidic and neutral) can be obtained. To obtain further separation within these three groups, modification of the amino acids is required. The latter can be achieved by enzymatic reactions, for instance by using an amino acid specific decarboxylase,

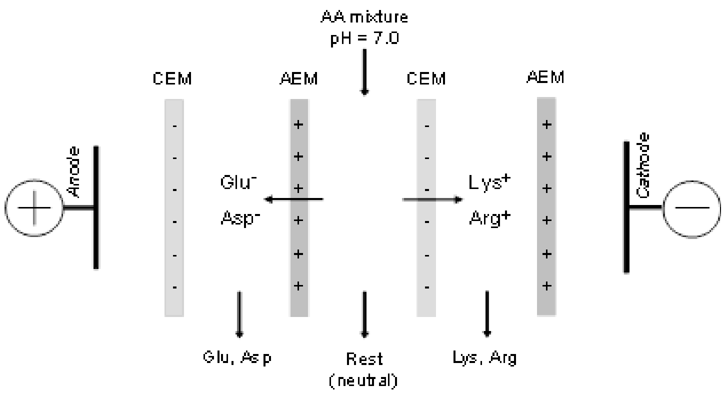

Figure 2 - Schematic representation of electrodialysis for the separation of amino acids.

which removes the acidic group of the corresponding amino acid and changes the charge behavior of that amino acid. At the same time these reaction products form intermediate building blocks for the production of chemicals. In a next ED step, separation within a group could be achieved.

Objectives and scope of the project

The aim of the present work was to develop an energy efficient separation method for the isolation of different

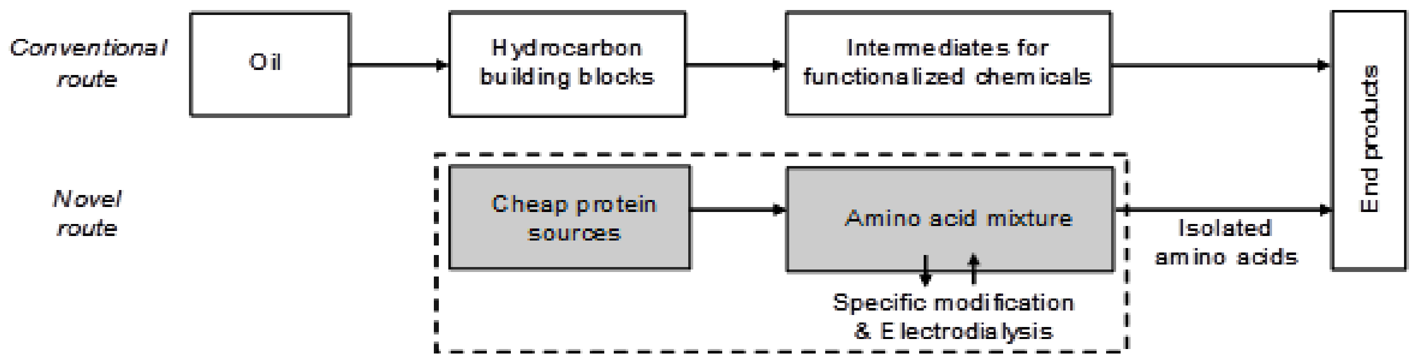

Figure 1 - Conventional and novel route for the production of functionalized chemical intermediates.

amino acids combining enzymatic modification and electrodialysis to obtain pure product streams of single amino acids or modification products thereof. The concept was applied for the separation of both simple and complex mixtures of acidic, neutral and basic amino acids.

Enzymatic modification and electrodialysis: Acidic, basic and neutral amino acids

ED with commercially available ion exchange membranes was applied for the isolation of the acidic amino acids L-glutamic acid (Glu) and L-aspartic acid (Asp) from a mixture of amino acids. Based on the differences in their isoelectric points, Glu and Asp, both negatively charged at neutral pH, could be separated from neutral and basic amino acids (Figure 3). The subsequent enzymatic decarboxylation of Glu into the intermediate building block γ-aminobutyric acid (GABA, a building block for the production of e.g. PVP) with the enzyme glutamic acid α-decarboxylase (GAD) [1] allowed the further separation of GABA and the negatively charged Asp (Figure 4) at a current efficiency of 70% and a recovery of 90% [2].

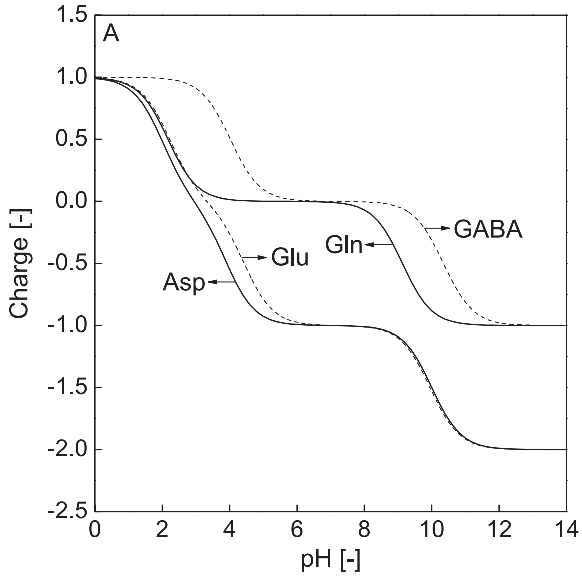

Figure 3 - Charge behavior of Glu and Asp, Gln and GABA with respect to pH.

The same approach could be applied to isolate Lys and Arg, where Lys was enzymatically converted into 1,5 – pentanediamine (PDA) [3] for its further separation from Arg with ED [4]. Also serine (Ser) could be converted into ethanolamine (Etn) with the enzyme serine decarboxylase (SDC) and isolated with electrodialysis. These separations are extremely sensitive to small changes in the pH as these result in immediate changes in the charge behavior of the respective amino acids. To control the pH a novel membrane concept was presented for internal pH. The performance

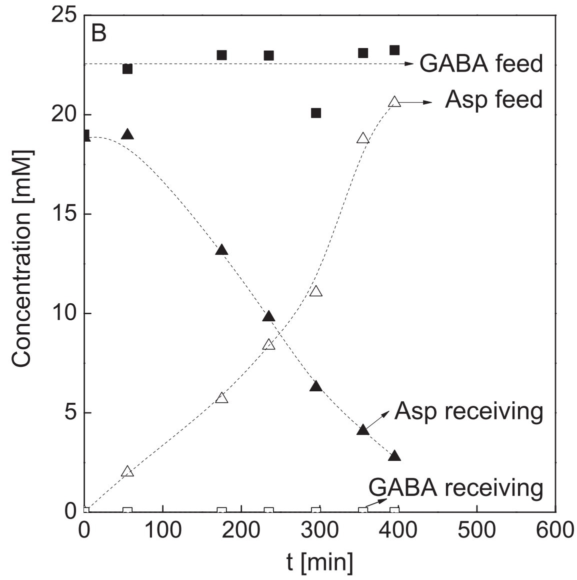

Figure 4 - Concentration behavior during the separation of Asp from GABA.

of electrodialysis with standard CEM and with a structured bipolar membrane (sBPM, Figure 5) was compared for the separation of Etn from Ala. Electrodialysis with a sBPM resulted in similar recoveries but increasing the product purity.

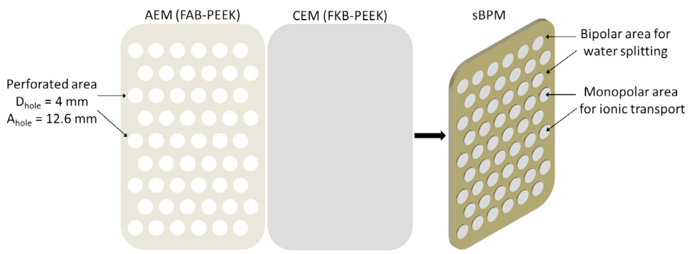

Figure 5 - Preparation of the structured bipolar membrane (sBPM).

Electrodialysis of complex amino acid mixtures

ED, even though successful for the separation of specific amino acids, is not applicable for the separation of mixtures containing the positively charged amino acid arginine (Arg), one of the major components in biobased feeds and an important precursor for the production of chemicals due to its poisonous effect on commercially available cation exchange membranes (CEMs). Our work confirmed that the inhibiting effect of Arg is related to the water content of the cation exchange membrane during the ED experiments: lower water content results in a strong decrease of amino acid recovery in the presence of Arg. To overcome this limitation, ED with self-prepared cation exchange membranes with a high swelling degree (SPEEK) and ED with ultrafiltration membranes (EDUF) was applied. The results clearly proof the superior behavior of these SPEEK membranes for the isolation of amino acids in the presence of Arg (Figure 6).

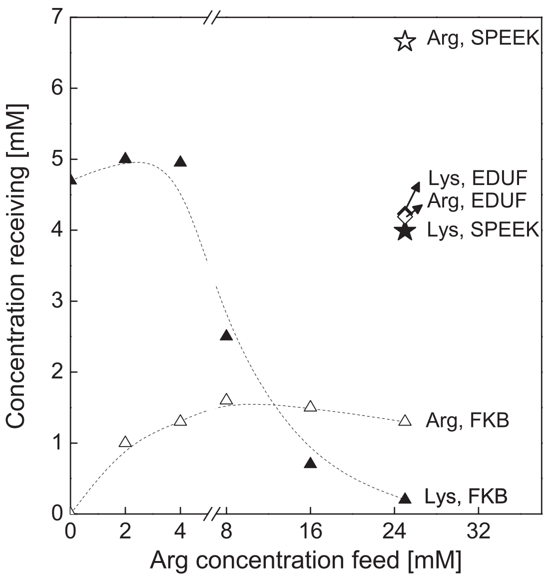

Figure 6 - Concentration of Arg and Lys in receiving stream during the separation of Lys (25 mM) and Arg as a function of the Arg concentration with ED - FKB, ED - SPEEK and with EDUF.

Separation of more complex biobased amino acid mixtures containing Arg proofed the successful separation of the acidic amino acids, glutamic acid (Glu) and aspartic acid (Asp), and the basic amino acids, Lys and Arg, from neutral alanine (Ala). As such, the work shows the strong potential of electromembrane processes for biorefinery applications.

Mixed matrix membranes (MMMs) for process intensification

Finally, an integrated system combining enzymatic conversion and separation in only a single system was evaluated for the targeted modification and separation of amino acids. To accommodate this, mixed matrix membranes as support for enzyme immobilization were prepared successfully (Figure 7). As a model system the conversion of Glu to GABA using the enzyme GAD was chosen. Relizyme EP403 was selected as enzyme carrier.

The membranes were tested for enzyme (GAD) immobilization and activity tests were performed based on the conversion of L-glutamic acid to GABA. Even though there is a decrease in activity when using mixed matrix membranes compared to the free particles, the prepared membranes are suitable for enzyme immobilization and further glutamic acid conversion and have enough mechanical strength. As a final test, electrodialysis experiments with integrated MMM were carried out for simultaneous conversion and separation of the acidic amino acids (Figure 8). After 8 h experiment 2.5 mmol of GABA was produced and retained in the middle compartment (Receiving 1) while Glu and Asp were further separated towards Receiving 2.

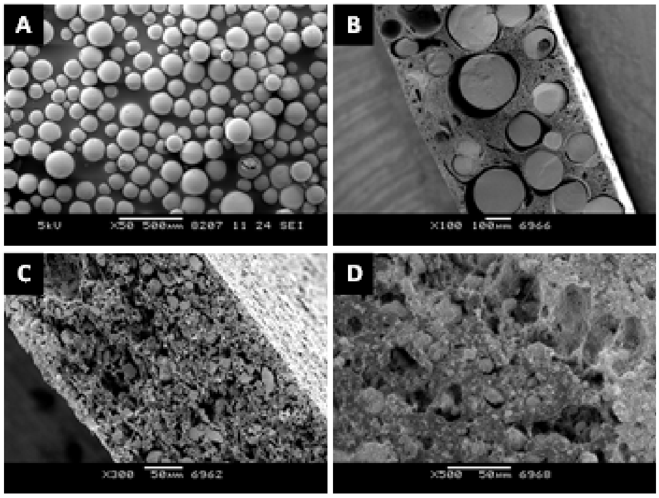

Figure 7 - Relizyme EP403 and MMMs characterization with SEM: A) Relizyme EP403. B) Cross section of the MMM containing unmilled dried Relizyme EP403. C) Cross section of the MMM with milled dried Relizyme EP403, particle size: <20 μm. D) Surface of the MMM with milled dried Relizyme EP403, particle size: <20 μm.

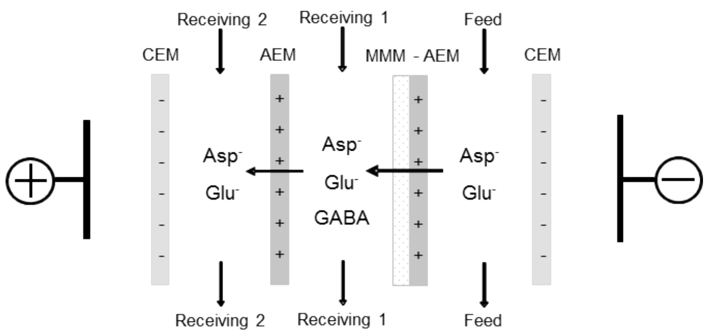

Figure 8- Schematic representation of the electrodialysis with an integrated MMM for simultaneous enzymatic conversion and separation

The results obtained in this study open the route for process intensification, combining enzymatic conversion and separation with electrodialysis in one integrated process for the successful isolation of amino acids for biorefinery applications. Altogether gives this work a high value as a contribution to promote the shift of conventional refinery toward a biobased economy.

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[3] Y. Teng, E.L. Scott, A.N.T. van Zeeland, J.P.M. Sanders, The use of l-lysine decarboxylase as a means to separate amino acids by electrodialysis, Green Chemistry, 13 (2011) 624-630.

[4] O.M.K. Readi, M. Gironès, W. Wiratha, K. Nijmeijer, On the Isolation of Single Basic Amino Acids with Electrodialysis for the Production of Biobased Chemicals, Industrial & Engineering Chemistry Research, (2012).

Permporometry

Background

Permporometry is a rather unknown characterization technique based on capillary condensation and gas diffusion to measure the active pores in ultrafiltration membranes. Eyraud[1] introduces the technique in the eighties of the 20th century and it is the only method, known so far, suitable to determine active transport pores with diameters ranging from 1.5 till 50 nm. Permporometry differs from the routine structure related characterization methods like microscopic techniques and mercury intrusion since these are not able to discriminate between active and inactive transport pores. Compared with permeation related characterization methods such as capillary flow porometry and molecular weight cut-off measurements, permporometry measures at low pressures and describes the complete pore size distribution.

Capillary flow porometry is very suitable and fast method for macroporous systems. Darcy's law describes the pressure needed to extrude the pore filling liquid. E.g. using water as wetting medium capillary flow porometry requests 145 bars to open a pore with a diameter of 20 nm. Even with commonly used low surface tension wetting liquids, like the often-used perfluor compounds such as Porofil® or porewick®, a pressure of about 32 bars is still requested for 20 nm pore opening. Especially, for hollow fiber membranes this value often exceeds the burst and collapse pressure. Since permporometry measures pressure less it is especially suited to measures mesopores (2 – 50nm) in polymeric membranes.

As described before, permporometry is based on controlled pore blocking by capillary condensation of a vapor, present as a component in gas streams with a different composition e.g. air and nitrogen that each flow along one side of the membrane surface, simultaneously measuring the vapor activity in the gas streams and the diffusional oxygen-transport through the membrane. In permporometry it is important that the condensable vapor is inert and does not interfere with the membrane matrix. The closing and opening of the pores by capillary condensation is related to the vapor activity as described in the Kelvin equation (1) where as the amount of oxygen that diffuses is related to the number of open pores.

$$\ln P_r = -\frac{2\gamma V}{r_k RT}\cos\theta \qquad \text{Eq. 1}$$

Where P_r is the relative pressure (-); γ is the interfacial tension (N/m); V is the molar volume (m^3/mol); R is the gas constant (J/mol•K); T is the temperature in (K); r_k is the Kelvin radii describing the curvature of the interface (m). The contact angle θ is assumed to be zero ($\cos\theta$ = 1).

For a cylindrical pore model, the relation between the pore radius r_p(m) and the Kelvin radius r_k (m) as given by the Kelvin equation is the pore radius minus the thickness of the vapor adsorption layer t (m). Therefore r_p may be calculated from:

$$r_p = r_k + t$$

Cuperus[2] determined for some solvent/membranes combinations the thickness of the t-layer (Table 1).

Table 1 - t-layer thicknesses as determined by Cuperus[2] of different solvent-membrane material combinations.

solvent	γ-alumina	PC	PPO	PSF
cyclohexane	0.5 nm	--	--	--
ethanol	0.4 nm	0.5 nm	0.5 nm	0.5 nm
methanol	0.7 nm	0.25 nm	0.25 nm	0.25nm
carbon tetrachloride	0.4 nm	--	--	--

From the diffusional flux the amount of pores can be calculated using the Knudsen flow, equation (2).

$$J_{k,i} = \frac{n\pi r^2 D_{k,i}\Delta p_i}{RT\tau l} \qquad \text{Eq. 2a}$$

$$D_{k,i} = 0.66r\left\{\frac{8RT}{\pi M_i}\right\}^{0.5} \qquad \text{Eq. 2b}$$

with the Knudsen diffusion coefficient

$J_{k,i}$ diffusional flux (mol/s m^2)

n number of pores (1/m^2)

r pore radius (m)

τ ortuosity (-)

ΔPi partial pressure gradient (pa)

l thickness of skin layer

M_i molecular mass of the gas (g/mol)

The principle of the method is shown schematically in figure 1. At a relative pressure equal to unity, all membranes pores are filled with liquid and no diffusional gas transport occurs. On reducing the relative pressure, the condensed vapor is evaporated first from the largest pores, in accordance with the Kelvin equation (Eq.1), and the diffusive gas flow through these open pores is quantified. On reducing the relative pressure further, also smaller pores open and become available for gas diffusion. When the relative pressure is reduced to zero, all the membrane pores are open and gas flow proceeds through them all.

Since a specific pore radius, , is related to a specific vapor pressure (Eq.2), and the magnitude of the oxygen gas flow provides information about the number of these specific pores. Stepwise reducing the vapor pressure and simultaneously measuring the oxygen transport can calculate the pore size distribution.

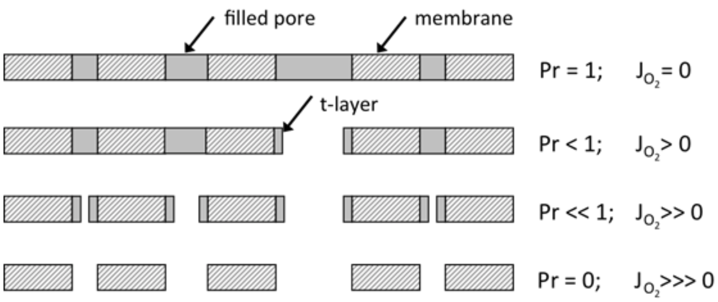

Figure 1 - The principle of permporometry. Pores open by lowering the vapor activity.

Experimental

A schematic drawing of the experimental set-up employed is given in figure 2. The wetting liquid vapor activity is adjusted by mixing a saturated vapor stream with an air and nitrogen stream. The oxygen increase in the nitrogen stream is

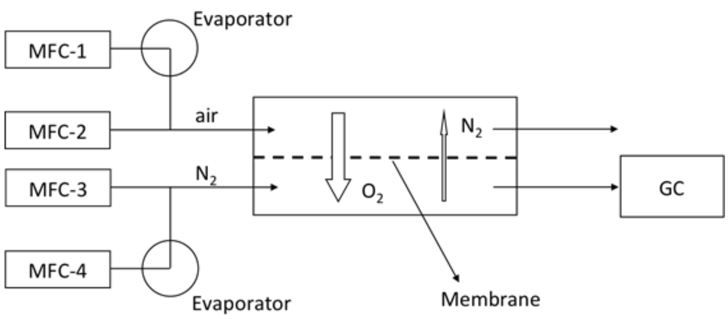

Figure 2 - Experimental set-up employed in permporometry. MFCs are mass flow controlers to adjust the vapour activity. The GC measure the oxygen content in the nitrogen gas.

measured using a gas chromatograph, attached with a mole sieve 13X column.

Before starting a measurement the fibers are glued in a module, or in case of flat sheet membranes clamped in a flow cell and consequently rinsed by to remove possible pore stabilizing agents and preservatives. After that the fibers are rinsed with the condensable wetting liquid. Then the still wetted membrane is mounted in the permporometry set-up. This implies that the measurement starts at a relative pressure equal to one. After equilibrium in the oxygen transport is reached the vapor activity is lowered stepwise. By using the equations 1 and 2 the pore size distribution was calculated.

Summarizing

Permporometry is a pressure less characterization techniques that quantifies pores in the 1.5 till 50 nm scale. Contrary to other characterization techniques, like thermoporometry, mercury porosimetry and electron microscopy, it only measures the pores that actively contribute to the separation. When compared with the often-used molecular weight cut-off method it not provide one pore size (MWCO-value) but provides you a complete pore size distribution. The knowledge of having a monodispersed or bimodal pore size distribution is very useful when optimizing the membrane performances.

References

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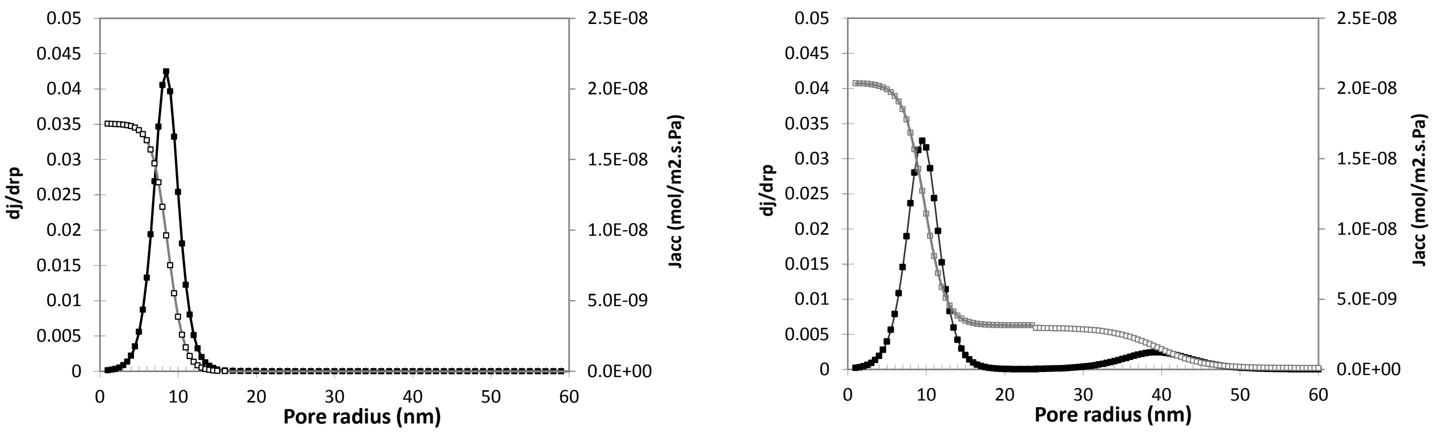

Figure 3 - Pore size distribution measurements by permporometry shows, in contrary to other characterization techniques, the presence of a bimodal pore size distribution.

Erasmus Mundus joint Master and Doctorate in membrane engineering

Erasmus Mundus is a cooperation and mobility programme in the field of higher education that aims to enhance the quality of european higher education and to promote dialogue and understanding between people through cooperation with Third World Countries. Within this framework, the Erasmus Mundus Joint Master (EM3E) and Doctorate (EUDIME) in Membrane Engineering was granted as one of the nine submitted proposals among 151 applications submitted in 2010.

EM3E and EUDIME offer an advanced Master and Doctorate educational programme at international level with excellence, innovation, mobility and multidisciplinarity in investigating approaches on membrane science and technology and its applications to different engineering areas. The programme is designed to provide its participants with necessary competences and knowledge to understand and relate the concepts of material science, technology and engineering and apply these in solving real-world membrane challenges.

EUDIME doctorate program

The EUDIME doctorate program combines the expertise of eight leading European institutions: University of Twente (The Netherlands), Institute of Chemical Technology Prague (Czech Republic), University of Montpellier 2 and University Paul Sabatier-Toulouse (France), University of Leuven (Belgium), and University of Calabria (Italy), University of Lisboa (Portugal), University of Zaragoza (Spain). Each EUDIME research project is a collaboration between three of the involved institutes. Doctoral students perform their research activities, mostly laboratory-based, at their home institute. Next to that, the program includes two mandatory mobility periods of 6 months each in two different host universities of the consortium. In addition, depending on the research needs, the participants can collaborate with any partner institute. Successful candidates are awarded a fully recognized multiple and/or a joint degree issued by three consortium institutions (the home university, where the doctoral candidate spends the majority of the training/research time, and the two host universities visited during the mobility periods), completed by a diploma supplement.

EM3E master

EM3E is an educational program launched by the European Commission to promote the cooperation and mobility in higher education. It is a unique opportunity to offer attractive scholarships to non-European and European students. The Erasmus Mundus Master in Membrane Engineering EM3E offers an advanced education program related to membrane science and engineering at the interface between material science and chemical engineering and focused on specific fields of application, i.e. 1) Energy, Environment and Water, 2) Nanoscience and Nanotechnology and 3) Biotechnologies, Food and Health. The involved partner universities are: University of Twente (Netherlands), University of Lisboa (Portugal), University of Zaragoza (Spain), Institute of Chemical Technology Prague (Czech Republic), University Paul Sabatier (Toulouse, France) and University Montpellier 2 (France, coordinating organisation), University of Calabria (Italy) and the Catholic University of Leuven (Belgium).

Second EUDIME meeting 2012 (University of Calabria, Italy).

EUDIME project -Molecular Organic Framework (MOF) polymer architectures for gas separation

Home university: Membrane Science and Technology

Host universities: University of Montpellier 2 (France), Catholic University of Leuven (Belgium)

The control of anthropogenic carbon dioxide emission is one of the most important environmental concerns of the current era and is becoming more challenging with the rapid increase in global population, industrialization and energy demands. There is significant need of technologies that will reduce the level of carbon dioxide emission. The performance of polymeric membranes, is limited by a trade-off between membrane permeability and selectivity [1]. Over the last two decades, research focused on increasing the polymeric membranes performance above this trade-off curve to make it more cost competitive with conventional processes.

Mixed-matrix membranes, comprising of inorganic particles e.g. zeolites, carbon molecular sieves (CMS), metal peroxides (MOs), carbon nanotubes (CNTs), Metal organic frameworks (MOFs), dispersed in a continuous polymeric matrix provide an interesting approach for improving the gas separation properties of polymeric membranes [2]. Recent developments showed some promising features of MOFs as a gas storage media and adsorbent for gas separation. MOFs represent a class of porous materials that consist of an inorganic cluster connected by organic bridges and tuned into three-dimensional arrangements (Figure 1). The high surface area, controlled porosity, adjustable chemical functionality, high affinity for certain gases and affinity with polymer chains, make them a potential candidate to make high performance mixed-matrix membranes. Virtually all designs and variations in both metal and organic linker in the MOFs are possible using appropriate chemistry [3]. MMMs frequently suffer from insufficient adhesion between the polymer matrix and the particles. However, the flexibility on MOFs design also allows us to tune the properties of the MOFs such that it integrates extensively with the polymer matrix and thus enhances the interaction between matrix polymer and particles to circumvent possible defects. In addition to aforementioned properties of MOFs, several of these MOFs have the striking feature of being selectively flexible during adsorption processes. Different MOFs based mixed-matrix membranes have been investigated in the past but at low feed pressures with improved performance for gas separation [4-6].

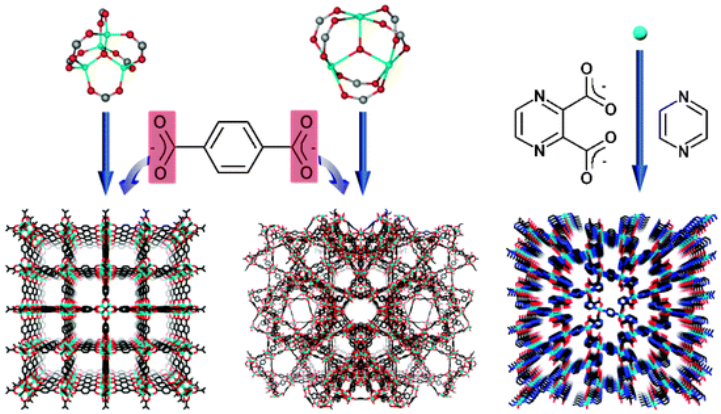

Figure 1 - Schematic representation of the construction of MOFs [3].

This project focuses on the development of new MOFs and mixed-matrix membrane architectures for gas separation (e.g. CO_2-CH_4, N_2-O_2 etc.) with high permeability and selectivity. We study the incorporation of different MOFs in mixed-matrix membranes of different composition and effect of filler at low and elevated pressures. Next to material design and membrane fabrication in flat and hollow fiber geometries, the project focuses on the fundamental understanding of gas transport in dense gas separation membranes. It intends to identify structure-property relationships using material related characterization techniques (Thermal, SEM and spectroscopy) combined with sorption measurements.

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Membrane runners participate in Batavierenrace

It is already a long-term tradition that the research group Membrane Science and Technology participates in the so-called Batavieren race, the annual world's longest relay race from Nijmegen to Enschede. The 40th Batavierenrace started at midnight on the 28th of April 2012 at the University Sports Centre in Nijmegen. As usual the route went through Germany, the quiet Dutch region De Achterhoek, the Old Market in Enschede and finally finished on the campus of the University of Twente.

This year our team again participated under the well-known name "Membrane runners", however combined forces came from many research groups including "Membrane Science and Technology", ''Inorganic Membranes'', ''Soft Matter, Fluidics and Interfaces'', ''Physics of Complex Fluids'' and ''Catalytic Processes and Materials'' from the University of Twente. From Aachen University in Germany we hosted our colleagues from the Chemical Engineering Department.

The first Batavierenrace was organized in 1972 by a group of students from the University of Nijmegen. The name of the race refers to the journey of the Batavians in 50 BC, who sailed down the Rhine from Nijmegen to Rotterdam. Due to infrastructural reasons, the route had to be changed and finishes nowadays in Twente.The race with a total distance of 175 km is divided into 3 sessions (night, morning and afternoon) containing together 25 stages ranging this year from 2.9 to 10 km. While one person runs his stage, accompanied by a fellow teammate on a bike, the rest of the team is transported by a small van from waypoint to waypoint.

All Membrane Runners gave their best to contribute to the success of the team. Our fastest runners were Olga Kattan Readi and Erik Vriezekolk from the research group Membrane Science and Technology. Unfortunately because of 3 stages that could not be occupied and 1 disqualification we eventually were ranked at the 325th position. However this result does not change the fact that we wish to keep on participating in Batavierenraces in coming years and we are always looking forward to this wonderful, sporting, competitive and social event. At the end of the day the efforts of the runners were rewarded with a Barbeque Party that was given at John Heeks´ place on the campus of the University of Twente.

This event would not have been possible without the financial support of our sponsors. The Membrane Runners would like to express their gratitude to Bernd Krause from Gambro Dialysatoren GmbH, Sybrand Metz from Wetsus (Research Institute for Sustainable Water Technology), Zandrie Borneman and Antoine Kemperman from the European Membrane Institute, Rob Lammertink from Soft Matter, Fluidics and Interfaces and Arian Nijmeijer from Inorganic Membranes.

GAMBRO

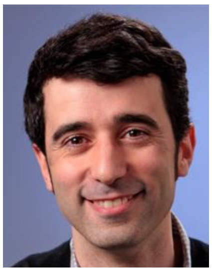
Sfi.

EMI Twente

wetsus

New people

Occurence and removal of nanoparticles



Name
Roberto Flores

Origin
Italian

Contact
+31 (0) 30 6069 651
roberto.floris@kwrwater.nl

Roberto Flores is a civil hydraulic engineer graduated from the University of Cagliari (Italy). He performed his Master Dissertation in the field of water resources management applying the MODSIM-DSS (Colorado State University) at the Agri-Sinni water system (Southern Italy) to model the complex water supply system under drought conditions and analyze the water shortage risk.

After a brief experience at the AATO Sardegna (Sardinian Local Water Authority) on May 2010, he went to The Netherlands to follow a one-year post graduation internship founded by the European Social Found (EEUU). After that he started to work at KWR – Watercycle Research Institute, were he investigated how the various turbulent transport mechanisms affect the hydraulic behavior of sediment in drinking water networks. In September 2011, Roberto started his PhD study within the NanoNextNL consortium on "Occurrence and removal of nanoparticles in influent and effluent of drinking and wastewater treatment plants". The motivations of this research arise from the increasing use of eNPs (engineered nanoparticles) in consumer products, pharmaceutical products, etc. which could lead to an increased release in the environment making eNPs an emerging source of pollutants in air, soil and water systems. Some aspects related to eNPs are largely unknown or not well understood, for instance their toxicity, their fate and behavior in the environment. In addiotion, their removal effectiveness in the drinking (waste) water treatment plant is unknown and insufficient analytical techniques to measure those eNPs are available. This lack of knowledge makes eNPs removal from water a technological and societal priority with respect to water safety. WTPs (Water Treatment Plants) are key nodes within the eNP lifecycle because they represent the first barrier against the release of eNPs in the environment and for human safety via water. WTPs, however, are not specially designed to remove them. Technical issues surrounding eNPs in water treatment plants are: (i) Do eNPs occur in water sources? (ii) How do they affect the performances of present WTPs? (iii) Will they be removed during water treatment processes? In order to address the research questions mentioned above first an overview and inventory will be made mostly by reviewing available literature and investigating databases on produced and (commercially) available nanomaterials on the market. Second, because in the last decades membrane separation techniques have emerged as the most viable solution to problems such as virus and micro pollutants rejection, ion rejection and separation, investigation of the removal efficiency of eNPs by membrane separation techniques will be performed (i.e. by characterization the nanoparticle rejection and membrane permeability) using a lab-scale set-up designed to evaluate membrane performance under different operating conditions. Last the influence of other processes (i.e. coagulation, sand filtration, etc...) on eNPs removal is difficult to predict but thus could be investigated as coupled pre-treatment for membrane filtration. This research is carried out in collaboration with the Membrane Science and Technology Group of the University of Twente and the Water Technology Group of KWR under the coordination and supervision of Kitty Nijmeijer, Emile Cornelissen and Jan Hoffman.

Prize

Euromembrane 2012 Best Oral Presentation Award for Wojciech Ogieglo, September 2012. London

Wojciech Ogieglo was awarded with the best oral presentation prize during the European membrane conference, Euromembrane 2012, in London. The Euromembrane conference has been organized since 1992, roughly every 2-3 years, in various cities of Europe where membrane research groups are active. The conference is aiming at bringing together academic and industrial scientists from the field of membrane technology to stimulate contacts and to exchange new ideas related to their work.

The presentation of Wojciech dealt with his fundamental research on ultra-thin polymeric films (<100 nm), which are becoming more and more important in the state of the art industrially applied membranes. Somewhat unexpectedly, films of such small thickness may behave different to the bulk of the polymer, which impacts membrane characteristics. In particular, the penetrant sorption dynamics and equilibrium properties of thin films are investigated with a use of a very precise and accurate optical technique, spectroscopic ellipsometry applied in-situ.

Developing an ideal platform for adsorption

Name
Vic van Dijk

Origin
Dutch

Contact
+31 (0) 53 489 5266
v.h.a.vandijk@utwente.nl

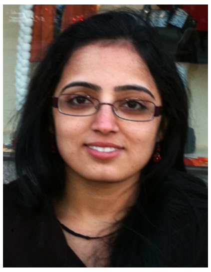
Vic van Dijk completed the master Chemical Engineering, track Process Technology at the University of Twente in September 2011. He has experience in different fields. DSM invited Vic on an internship about energy reduction in both the Netherlands and China. Living in China for two months was a pleasant and impressive experience. Vics bachelor assignment was on the absorption of carbon dioxide using aqueous amino acid salt solutions, and his master assignment dealt with the influence of water vapour on photocatalytic oxidation. Since Vic enjoyed conducting research projects a lot, he decided to go for a PhD in the groups Soft Matter, Fluidics and Interfaces (prof. dr. ir. Rob Lammertink), and Membrane Science and Technology. The coming four years will be spent on developing an ideal platform for adsorption using a polymeric membrane structure. This membrane is coated with an inorganic material, for example silica. The silica can be modified such that only specific compounds from an aqueous mixture adsorb onto it. Such a hybrid membrane structure is expected to be mechanically flexible due to the organic polymeric core skeleton. The fluid that flows through the membrane pores "sees" only inorganic material. This inorganic crust opens up possibilities for modification using inorganic chemistry, in order to adsorb certain compounds selectively. By applying a thin layer of inorganic material onto the accessible pore walls, we hope to minimise diffusion limitations and to maximise the surface/volume ratio.

Point of Use (PoU) drinking water treatment systems

Name
Charu Chawla

Origin
Indian

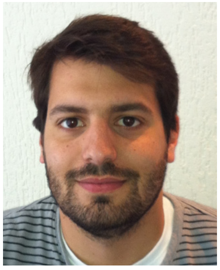
Contact
+31 (0) 582 843103
charu.chawla@wetsus.nl



Charu Chawla obtained her Bachelors degree in Chemical Engineering from D.C.R. University of Science and Technology, India. She did her summer internships at two different manufacturing companies namely National Fertilizers Limited (Panipat) and Coral Chemicals Pvt. Ltd, India. After her graduation, she worked as a Business Analyst at Deloitte Touché Tohmatsu India. During her services at Deloitte, she worked on a project funded by UNICEF, titled "Identification of potential reduction of carbon footprint by utilizing openly dumped cow dung and kitchen waste to generate methane as a clean fuel to be used as cooking gas in a poor community". The project dealt with the reduction of carbon footprints via effective utilization of kitchen waste so as to generate methane, as an alternative fuel source to serve the increasing energy demands. Due to her strong inclination towards studying environment and its related issues, she resigned from the job to join academics as a research assistant at The University of Western Ontario (London, Canada) under the supervision of Dr Madhumita Ray and Dr George Nakhla. She completed her Master of Engineering Sciences at The University of Western Ontario. During her masters, she studied the effect of advanced oxidation processes such as ultrasonication treatment on the anaerobic biodegradability of natural estrogens (estrone). Upon completion of her masters in Canada, she joined as a PhD candidate at Universiteit Twente under the supervision of Dr Kitty Nijmeijer and Dr Antoinne Kempermann. She is located at Wetsus research facility in Leeuwarden. Her project aims at studying intermittent operation of Point of Use (PoU) drinking water treatment systems in developing countries. It deals with looking into the effect of non-continuous operation of an ultrafiltration membrane system on fouling layer characteristics, identifying key foulants and understanding their corresponding fouling behaviors under different operating conditions.

Picture showing membrane with wave-shaped structures (Enver Guler).

Produced water treatment with membranes



Name
Jordi Moreno

Origin
Spanish

Contact
+31 (0) 582 843181
jordi.moreno@wetsus.nl

Jordi Moreno received his B.Sc. Environmental Science degree of the University of Girona, Catalonia in 2010. The final project of the degree was titled "Diagnosis & evaluation of the tertiary treatment from WWTP of Tossa de Mar". After that, he finished the Water Science and Technology Master Degree at the University of Girona. His master thesis was made in collaboration with the Laboratory of Chemical and Environmental Engineering (LEQUIA) and entitled "The evaluation and performance of membrane bioreactor coupled with reverse osmosis system (MBR-RO) focusing on reverse osmosis (RO) and MBR (microfiltration flat sheet modules) fouling control". In May 2012, Jordi started his PhD study in the Membrane Science and technology Group of the University of Twente in close collaboration with Wetsus, Centre of Excellence for Sustainable Water Technology in Leeuwarden, The Netherlands (www.wetsus.nl) where he performs the main part of his research. His project, "Produced Water treatment with Membranes" basically uses membrane technology for oil – water separation.

Recent developments in oil production technologies emphasize the application of Improved Oil Recovery (IOR) and Enhanced Oil Recovery (EOR) technologies. These processes rely on the injection of aqueous liquids into an oil reservoir. Current practice for offshore applications is that seawater is used as source water. Often, seawater shall be desalinated to meet the injection specifications. As an alternative, produced water can be treated for reinjection. In order to allow the reinjection of produced water, pretreatment and purification of the water is necessary. This project investigates both pre-treatment requirements, membrane fouling and development of new membranes for produced water treatment. The effect of residual oils, production chemicals (scale and corrosion controlling chemicals) and biocides on membrane performance will be evaluated. The purpose of this project is to identify, develop and demonstrate methods to pretreat and purify the produced water for reinjection. Next to artificial feed waters, produced water from oil production locations will be used in laboratory experiments.

Novel Polyimide Architectures: Towards Membranes with Tunable Transport Properties

Name
Zeljka Madzarevic

Origin
Serbian

Contact
+31 (0) 1527 84703
z.madzarevic@tudelft.nl

Born and raised in Serbia, Zeljka started her academic studies in 2006 at the Faculty of Technology and Metallurgy, University of Belgrade, Serbia at the department of Organic Chemical Technology and Polymer Engineering. After four years she graduated with honors and obtained the title of Bachelor of Science. She continued with her Master studies in Polymer Engineering within the same research group, working on "Synthesis of PMAA hydrogels and their composites with zeolites for removal of harmful dyes by adsorption". During the time of her studies at the University of Belgrade, Zeljka received the Scholarship of Ministry of Science and Sport. In June 2011 she completed her MSc and wanted to pursue her academic career further in the field of novel polymer materials. In October 2011 she joined the Novel Aerospace Materials group at TU Delft and started her PhD under the supervision of prof. dr. Theo Dingemans and in close collaboration with the Membrane Science and Technology group of the University of Twente. In her current Ph.D. project, Zeljka works on high-performance polymer architectures based on polyetherimide chemistries as potential materials for high-pressure gas separation applications. Polyimides are very attractive for high-performance applications due to their excellent combination of physical, chemical and mechanical properties. At the same time, there is an increasing need for new energy-saving alternative methods for CO2 capture. In this project she will design and synthesize new monomers and polymers, investigate their thermo-mechanical properties and study their usefulness as films for a variety of gas separation applications (e.g. separation of high pressure CO_2/CH_4). Series of PEI films with slight structural differences will be synthesized and investigated, and by comparing results, systematic and significant insight into the effects of molecular structure on their gas separation properties will be obtained. Zeljka will focus on structural alterations that simultaneously inhibit chain packing and rotational motion on the polymer backbone, since they lead to an increase in permeability while maintaining or increasing selectivity of the membrane. Tailoring the intersegmental packing and intersegmental resistance to motion allows achieving very attractive productivities without sacrificing selectivity.

ASPASIA Grant for Kitty Nijmeijer

Dr. Kitty Nijmeijer of the MESA+ research group Membrane Science & Technology received an ASPASIA grant of the Dutch Science Foundation NWO. The ASPASIA grant aims to facilitate the promotion of female scientist to associate professor or professor. Kitty Nijmeijer will use the grant of 200.000 euro to further expand her research on polymer-molecular organic framework (MOF) architectures for gas separation. The idea is to develop so called mixed matrix membranes using a polymer as a matrix and different types of MOFs as selective additive to increase the membrane permeability and selectivity. A MOF consists of a metal ligand with organic linkers. Especially this structure reflects the strength of the use of MOFs for membrane applications compared to conventional nano-particles like zeolites etc. Due to the organic linkers, MOFs have the intrinsic ability to integrate with the matrix polymer. The organic linker of the MOF can be tuned such that its structure and physical properties fit to those of the matrix polymer. This overcomes the major disadvantage of existing mixed matrix membranes i.e. the occurrence of defects due to incompatibility issues between the polymer and the additive. At the same time, the metal ligand in the MOF can be chosen such that it has an increased affinity for the target molecule and as such significantly enhances the selectivity and the permeability of the membrane for a specific component. Initially, Kitty Nijmeijer will mainly focus on the separation of CO2 from CH4, an important high-pressure separation in the chemical industry. However, because the concept is very flexible and numerous combinations of metallic ligand and organic linkers can be envisaged, once explored, the concept can be easily extended to other applications.

Visit of His Royal Highness The Prince of Orange

On May 23, 2012, his Royal Highness The Prince of Orange visited Wetsus. Dr. Kitty Nijmeijer of the research group Membrane Science and Technology of the University of Twente was invited to join this meeting as a representative of the University of Twente/MESA+. His Royal Highness was accompanied by Prof. Robbert Dijkgraaf, President of the Royal Netherlands Academy of Arts and Sciences and Erik Oostwegel, CEO of Royal Haskoning.

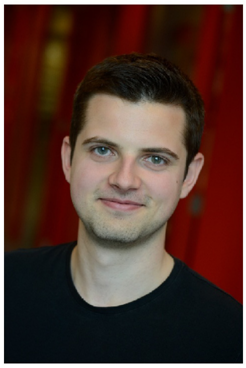
Wetsus is a Center of Excellence for Sustainable Water Technology, located in Leeuwarden in the Northern part of The Netherlands. It offers a platform for extensive research in the field of water, e.g. water purification, salinity gradient energy, tailored membrane design for e.g. selective ion transport or anti fouling membranes. The University of Twente and more specifically the research group Membrane Science and Technology (MST) is one of the key members and founding fathers of Wetsus. MST has an intensive collaboration with Wetsus and supervises 7 Ph.D. students that perform their research within this Wetsus/UTwente collaboration.

After an introduction about Wetsus, the visit was continued with an extensive lab tour at the Wetsus facilities. Six research topics were highlighted and the Prince and the other visitors were informed about the newest developments in water science and technology. One of the research topics addressed during the tour was the generation of power from the mixing of sea and river water, i.e. Blue Energy or Salinity Gradient Energy. The visit was concluded with a lunch in the adjacent Johannes de Doper Science center with a limited number of representatives of Wetsus' industrial participants and universities, among which Dr. Kitty Nijmeijer (see enclosed picture). During this lunch, the Wetsus innovation system and the ambitions of the Dutch water sector in terms of research and innovation were discussed.

For more information about Wetsus, please visit www.wetsus.nl or contact Dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl)

Follow us on Twitter: The Membrane Science and Technology group has his own Twitter account!
Follow @MST_UTwente for the latest news of the MST group in a nutshell!

Paul Drude Medal Awarded to Wojciech Ogieglo at the 7th Workshop Ellipsometry, March 2012 in Leipzig



The Paul Drude Medal is a prize awarded to young scientists for exceptional contributions to the field of ellipsometric metrology or spectroscopy presented as an oral presentation during cyclic Ellipsometry Workshops which are organized by the German Association on Ellipsometry.
The presentation of Wojciech Ogieglo was entitled: "Superimposed effects of nano-scale confinement and penetrant on behavior of ultra-thin glassy polymer membranes". The talk presented a part of fundamental studies on transport in ultra thin (h<100 nm) polymer films with the use of in-situ Spectroscopic Ellipsometry. Films with thickness in this range are becoming increasingly important in such relevant application areas as membranes, coatings and micromachinery. However, it turns out that their behavior may not simply be extrapolated from bulk or thick film behavior due to so called nano-confinement effects. These effects manifest themselves, for instance, in the specific nature of polymer chain dynamics in nano-scale, which can be further influenced by the presence of various fluid penetrants. To study and understand the superimposed effects of nano-scale confinement and penetrants with Spectroscopic Ellipsometry an appropriate approach to the optical modeling of the system is needed that takes into account changes of polymer matrix related to penetrant diffusion.

Marcel Mulder Award for David Vermaas

David Vermaas, Ph.D. Student of the Membrane Science & Technology Group of the University of Twente and Wetsus, Centre of Excellence for Sustainable Water Technology in Leeuwarden, has won the Marcel Mulder Award of 2012. The award of 5000 euro is a remembrance to Prof. Marcel Mulder, who was, next to professor in Membrane Process Technology at the University of Twente, the originator of Wetsus. The prize is awarded annually to a Wetsus researcher that combines scientific excellence with technological innovation and practical relevance.

The work of David Vermaas was related to Reverse Electrodialysis (RED), which is a process to generate sustainable energy from the mixing of sea and river water. This process can be applied everywhere where river water flows into the sea. It is a sustainable, environmentally friendly, renewable source of energy.
David's work was dedicated to improve the obtained power output per membrane area in RED, by changing the distance between the membranes and membranes with an embedded profile to replace the traditional flat membranes with plastic spacers. The result of his work led to a double power output per membrane area and a reduction of the required pumping power with an order of magnitude. The outcome of this work can be used directly in the pilot power plant at the Afsluitdijk, which is currently built by the spin-off company Redstack.
The work resulted in 3 publications: one in the Journal of Membrane Science, one in Environmental Science & Technology and one in Energy Procedia. One other publication is recently submitted. In addition, David is inventor of a patent on a novel electrode system for Reverse Electrodialysis, using capacitive electrodes for cleaner and safer electrode reactions.
For more information please contact prof. dr. ir. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: + 31 (0)53 489 4185).

MNT- Information

Membrane News Twente is published two times per year and aims to inform the membrane community about the activities of the Membrane Technology Group of the University of Twente (membrane@utwente.nl www.utwente.nl/tnw/mtg).

Editors
Kitty Nijmeijer
Enver Güler

PhD defense

March 22, 2013, 16.45 h, University of Twente

Olga Kattan, Membranes in the biobased economy: Electrodialysis of amino acids for the production of biochemicals

Publications

- Olga Kattan Readi, Miriam Girones, Wika Wiratha, Kitty Nijmeijer, On the isolation of single basic amino acids with electrodialysis for the production of biochemical, accepted for publication in Industrial and Engineering Chemistry Research (2012).
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- Enver Guler, Yali Zhang, Michel Saakes, Kitty Nijmeijer, Tailor-made anion exchange membranes for salinity gradient power generation using reverse electrodialysis, Accepted for publication in ChemSusChem (2012).
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