Historical Perspective on Membrane Science and Technology

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Over the last few decades, considerable effort has been devoted to developing better membranes and extending their range of applications to different areas. Membrane processes already have an established role in gas separation and water treatment, and their applications in the food, pharmaceutical, and health areas have been continuously increasing. In the last few years, membrane processes proved to have a key role in biorefinery and bioenergy production processes, namely for process intensification and the recovery and purification of valuable products. Membranes are also a crucial component of electrochemical energy conversion devices, including fuel cells and electrolysers. Moreover, the growing environmental concerns have drawn attention to the use of fossil-based polymers and toxic solvents for membrane fabrication. Therefore, the development of new membranes, using polymers from renewable sources and more sustainable fabrication methods, is being pursued.

membrane processes | membrane synthesis and characterisation | integrated (hybrid) solutions | sustainable approaches | circular economy | water–energy–material–food nexus | Portuguese membrane research

1. Instituto Superior Técnico—Universidade de Lisboa (IST)

In early times, synthetic membranes were often associated with filtration and separation unit operations and, on a smaller scale, with a myriad of applications, such as battery separators, biosensors, controlled release systems, medical devices, etc. The huge developments in the 1960s and 1970s at the level of polymeric membranes and membrane modules allowed them to be implemented on an industrial scale of a vast number of membrane processes that required the mechanisms underlying the performance of this enormous diversity of membrane materials, structures and processes to be approached systematically. This was the driving force that moved Peter Bungay (National Institutes of Health), Harry Lonsdale (Founder of Journal of Membrane Science) and Maria Norberta de Pinho (IST) to organise (June 26–July 8) a NATO Advanced Study Institute (ASI) on “Synthetic Membranes: Science, Engineering and Applications” in Portugal in 1983. The book edited by the Institute organisers [1], in addition to numerous citations in Google Scholar, earned the following comment in Polymer News: “an outstanding contribution to the educational aspects of membrane science. In fact, if there are senior-level courses on membrane science, this is, the ‘textbook’ to use”. This NATO–ASI congregated and interconnected the major membrane groups of Europe and the U.S.A. and was the precursor of the “European Society for Membrane Science and Technology”.

By that time, the Membrane group of the Chemical Engineering Department of Instituto Superior Técnico (IST), under the guidance of Maria Norberta de Pinho, progressed into two main lines of research: (1) Synthesis and Characterisation of Polymeric Membranes; (2) Design and Optimisation of Membrane Processes in Water, Food, Pulp and Paper, Cork, and Chemical Industries.

From the first line of research, it is of particular interest to mention the synthesis of (1.1) Bi-Soft Segment Polyurethane Membranes for Pervaporation [2], which were further investigated (a project sponsored by the Portuguese Foundation for Science and Technology (FCT), 2003–2006) in terms of different soft segments towards the development of hemocompatible membranes for extracorporeal blood oxygenation [3], being the object of European (WO 2008/041126), U.S.A. (US2010/0111761) and Singapore (GST registration No: 200004489C) patents; (1.2) Integral Asymmetric Cellulose Acetate/Silica Hybrid Membranes for the selective removal of blood toxins in the Artificial Kidney [4]; and (1.3) Nanocomposite Membranes of Cellulose Acetate/Silver Nanoparticles and Cellulose Acetate/Silver Ion Exchanged Zeolites with bactericide activity for biofouling control [5].

In the second line of research, the design of membrane hybrid processes was carried out in the framework of European and national projects with industrial partners such as those coordinated by IST (scientific coordination of Maria Norberta de Pinho): “Treatment and Fractionation of Bleach Plant Effluents by Membrane Based Processes” (BRITE-EURAM(DGXII-EU)(1991–1994)) [6][7]; ”Integrated Process for Purification/Recovery of Ammonium Containing Water in Coke Plants” (EC(DG XVII)/ESSC Coal Research(1997–2000)) [8][9]; ”Valorization & Treatment of the Cork Industry Wastewaters” (JNICT/DGA(1996–1999)) [10]; ”Wine Must Concentration and Rectification by Nanofiltration and Electrodialysis“ (FCT/POCTI(2005–2008)) [11].

The assessment of tannic-ultrafiltration (UF) membranes’ interactions and membrane fouling characteristics have led to the development of integrated processes of flocculation/flotation/UF and ozonation/UF for tannins recovery from cork processing wastewaters [10][12][13]. Furthermore, nanofiltration (NF) concentrates were used as vegetal tanning agents in the leather industry [14]. UF and NF have also been investigated for the tertiary treatment of leather industry effluents [15][16][17]. In the pulp and paper industry, pioneering work was carried out on water recovery by the NF of bleach plant effluents and the development of hybrid processes of NF/ED and flotation/UF [6][7][18][19][20][21][22].

The prediction of the membrane processes performance through the modelling of the selective mass transfer was carried out in the membranes (surface forces/pore flow model) and at the membrane/fluid interfaces (quantification of concentration polarisation through mass transfer coefficients) for pressure-driven and pervaporation processes [23][24][25]. Flow management and mass transfer in spiral-wound modules with recourse to computational fluid dynamics (CFD) were given special attention by the team of Viriato Semião, Vitor Geraldes and Maria Norberta de Pinho [26]. The membrane characterisation by spectroscopic (attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS)) and microscopic (scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM)) techniques provided data that were correlated to the membrane selective permeation properties [27][28].

From 2004 to 2009, the membrane groups of IST and Nova School of Science and Technology—*Universidade NOVA de Lisboa* (FCT NOVA) were members of the European Network of Excellence (Sixth Framework Programme): “Expanding Membrane Macroscale Applications by Exploring Nanoscale Material Properties”, coordinated by Gilbert Rios at Institut Européen des Membranes. Divulgation activities were carried out, such as the “Membranes in Medicine“ workshop.

The present research at IST addresses: (1) The role of water dynamics in the membrane pores (investigated through deuterium and proton nuclear magnetic resonance (NMR)) on the selective permeation properties; (2) UF/NF membranes with bactericide activity and biofouling control in drinking water production; (3) Water recovery and sub-products valorisation in cork and food industries, namely polyphenols and polysaccharides in the wine industry; (4) Case-specific mass transfer correlations; (5) Minimisation of concentration polarisation and fouling prevention; (6) Microfluidics and membrane microdevices for the artificial kidney and artificial lung.

2. NOVA School of Science and Technology—Universidade Nova de Lisboa (FCT NOVA)

Membrane research at FCT NOVA started with the PhD work of João Crespo, which was focused on the study of different bioreactors for the simultaneous production of organic acids and vitamin B12 [29]. The first contact with membranes was related to the development of membrane bioreactors during a period (1980s) when this technology was in its initial stages.

The membrane group at FCT NOVA grew significantly over the years, hopefully with a few relevant contributions for the community, namely on the understanding of transport mechanisms in membrane contactors (including a pioneer work on the use of ionic liquids in membrane contactors, which started with the PhD project of Isabel Coelhoso [39][40][41] and later with Raquel Fortunato [42][43] and Luísa Neves [44][45]) and, more recently, new approaches to membrane contactors for protein crystallisation [46] and production of nanoemulsions [47].

The membrane group of NOVA is now hosted in two different locations: at the research centre, Associated Laboratory for Green Chemistry (LAQV-REQUIMTE, the largest research centre in the country, which is focused on research and education in Sustainable Chemistry and Processes) at the faculty campus in Caparica; and at the private not-for-profit research centre iBET, in Oeiras, where the lab directly coordinated by Vanessa Pereira works on the integration of (photocatalytic)membranes (with a relevant contribution on membranes development by Rosa Huertas) with advanced oxidation processes, aiming the elimination of resilient organic micropollutants from water/wastewater streams [60][61].

The research group’s involvement in education programmes should be emphasised, namely the European Master programme EM3E, later EM3E-4SW, coordinated by Andre Ayral, and the Doctoral programme, Eudime, coordinated by Enrico Drioli.

3. Faculdade de Engenharia—Universidade do Porto (FEUP)

Since the end of the 1990s, Adélio Mendes' group at the University of Porto has been developing research on several topics of membrane separation technology. Since then, this group's contributions to the membrane-related field have been based on four pillars: development of materials for the fabrication of membranes, such as carbon molecular sieve membranes [62][63][64][65][66][67], palladium and ceramic membranes [68]; study of membrane processes, such as membrane reactors for propyne hydrogenation [69] and methanol steam reforming [70][71][72], direct methanol fuel cells (DMFCs) [73][74] and proton exchange membrane (PEM) fuel cells [75]; fundamental studies, namely the development of phenomenological models and simulators for membrane separation processes [76][77], membrane reactors [78][79][80], PEM fuel cells [81][82], redox flow batteries [83][84]; and technological projects, namely the development of membrane processes for recovering cutting oil and extraction of beer flavours for introducing in de-alcoholised beer for partially recovering the original flavour [85][86][87][88].

The first membrane-related article of the group at the University of Porto was published in 2002 [89] and concerned the removal of volatile organic compounds, such as acetone, ethyl acetate and ethanol from the air, using GKSS (Geesthacht, Germany) polyetherimide (PEI) membranes coated with polydimethylsiloxane (PDMS). Regarding the preparation and characterisation of carbon molecular sieve membranes, the first work was published in 2004 by Lagorsse et al. [62]. Brandão et al. [90] studied the mass transport in composite PDMS membranes loaded with palladium nanoparticles. Several studies on the use of hollow fibre membranes in membrane contactors with amino acid salt solutions were also published for CO_2 removal in anaesthetic circuits [91][92][93]. In 2004, Janknecht et al. [85] studied the use of micro and ultrafiltration membranes for the removal of industrial cutting oil from oil emulsions.

The first Portuguese contribution to the field of direct methanol fuel cells membranes was reported by Silva et al. in 2005 [74]. Further work was developed in collaboration with Suzana Nunes from GKSS, who prepared sulfonated poly (ether ether ketone) (sPEEK) composite membranes with zirconium oxide for DMFC. Composite sPEEK membranes for DMFC with different additives were studied and compared with commercial Nafion® membranes (DuPont, Wilmington, DE, USA) [94][95]. Brandão et al. [96] modified these Nafion® membranes with Pd composite nanoclusters to reduce methanol crossover in DMFC. Concerning the development of PEMs for fuel cells, Boaventura et al. [75] prepared and characterised proton-conducting sulfonated polytriazole membranes. Studies on the utilisation, modification, activation and ageing of PEM fuel cells have also been developed [97][98][99][100][101][102].

Mendes' research group's future perspectives of CMS membranes separation technology are focused on developing a strategy to deliver this technology as quickly as possible for widespread use. A strategy to control the pore size for the different separations with industrial relief, such as the enrichment of oxygen or nitrogen from the atmospheric air, the separation of hydrogen from different streams, the separation of carbon dioxide from natural gas or biogas, among others, is currently being developed. Moreover, the use of supported hollow fibre CMS membranes is being investigated. In the future, pervaporation will also be a very relevant research topic in this technology.

Driven by the will of curbing down the notorious impact of burning fossil fuels on the global climate, currently, in Portugal, there are two spin-off companies from the University of Porto addressing membrane processes:

SEA+TECH, an environmental, energy and engineering consulting company, which aims to develop energy-efficient and sustainable systems for the production, treatment, and recycling of water, for commercial or industrial applications; and CarboPora—a company targeting the development, production and commercialisation of membrane gas separation processes, namely oxygen-enriched air, CO_2 removal from flue gas streams, methane separation/purification from biogas and hydrogen separation/purification from natural gas mixtures.

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