History of Membrane Technology in Spain

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This significant amount of research publications in membrane technology in Spain covers almost all the fields of membranes, both fundamental and applied.shows in fact that the major subject categories involved are Chemistry and Chemical Engineering, with transversal contributions from other categories as Materials and Environmental Science, which aim at the appointed potential of membrane technology as an alternative solution to existing processes in industry as will be discussed later. Furthermore, there is an important contribution of Biochemistry, Genetics and Molecular Biology that gives an idea of the close relation between membranes and Biological Sciences, although in this analysis, out of about 2700 documents, some could be surely more related with biological than synthetic membranes.

membrane technology membrane processes

1. Early Historic Background

The filtration process can indeed be considered the oldest existing separation technique. It was already known and exploited by civilizations as ancient as the Egyptians and the Chinese. However, limiting ourselves to Europe, we can consider the work of Lucretius (95–55 BC), “De Rerum Natura”, as the beginning of the science of separation in our continent [1].

However, this beginning was quite slow, since more than 15 centuries had to pass in order to find new works related to the subject. Among these works, that of the French Abbé Nollet is often considered a pioneer in membranology. In 1748, Nollet made the first experiment with semi-permeable membranes (porcine bladders, in fact) [2]. The separation studies carried out throughout the nineteenth century, already more numerous and systematic, led to a better understanding of the separation processes and the laws that govern them. Very important in these aspects are the works of Fick on diffusion [3], Traube [4], Pfeffer [5], and Van’t Hoff [6][7] with pressure osmotic, and many other interesting works from Raoult, Graham, etc.

From Traube’s pioneering work, Zsigmondy was the first to develop a cellulose nitrate membrane suitable for the sterilization of small amounts of fluid, [8], later marketed by Sartorius [9].

A really entertaining and interesting insight into these early years of membranology can be found in [10]. Figures such as Abbé Nollet, Dutrochet, Doebereiner, Graham, and many other pioneers of membrane science parade through this pleasant historical “review”. A work more related to membrane technology, although already classic is that of Lonsdale, the first Editor in Chief of the *Journal of Membrane Science* [11].

However, from a practical point of view, the true starting point of what we can without fear call the membrane technology revolution can be found in the asymmetric cellulose acetate membrane developed by Loeb and Sourirajan in 1960 [12], which allowed solving some of the necessary challenges to obtain a material (the membrane) with the selectivity and stability features necessary to be applied on a large scale in desalination of seawater by reverse osmosis.

Before the 1980s different processes with membranes are used industrially and proposed scientifically as promising alternatives for other applications. In the late 70s and 80s, membrane technology was starting to be presented as a strategic science and technology with definitions, history, and agenda [13].

In all these pioneering studies, the contribution of Spanish researchers in membrane technology is practically absent [14][15].

By the end of the 1970s, when membrane technology began to be mature, research in Spain was also ready to make its input. As it occurred in the rest of the world, the problems addressed by membrane processes in southern countries focused on the poor quality of drinking water and water supply [16], as well as on wastewater management from dairy and paper industries [17], and membrane researchers started to formulate this in terms of membrane technology for example by using reverse osmosis. The first Spanish contributions to membrane processes were thus found in general chemical engineering journals [18][19][20] or more specific journals dealing with actual industrial or environmental challenges in food, paper, and metallurgical industries. Thus, it is not surprising to find that the first Spanish contributions to membrane research will be related to the then recently discovered cellulose acetate membranes [21][22][23][24] as well as others dealing with reverse osmosis water desalination plants [25][26]. Two previous articles on ion-exchange membranes could be remarked [27][28] although, apparently without subsequent continuity. Regarding the work of Muro et al. [26] on seawater desalination plants, this is mostly a national desalination policies review and does not present actual research. Likewise, Guzmán's article (followed by a later one in 1984, [29], are descriptive works on the underlying engineering in two water desalination plants in the Canary Islands. Thus, we can consider the group born at the Complutense University of Madrid, by the hand of Juan Ignacio Mengual, as the first active research group on synthetic membranes in Spain. On his part, Cristóbal Fernández Pineda, upon obtaining his teaching position at the University of Malaga, would create his own group at that university, also very active in these early years of membranology in Spain.

These first names already allow us to note a curious characteristic of membrane research in Spain. Surprisingly most of the research groups on the subject come from departments of Applied Physics of Spanish Universities. So are Mengual and Fernández Pineda, but also Fernando Tejerina and Javier Garrido and Julio Pellicer in the University of Valencia. José Antonio Ibáñez and Antonio Hernández were disciples of Fernando Tejerina in The Autonomous University of Barcelona and afterwards in Murcia and Valladolid, respectively. All of these published works are related to the application of the Thermodynamics of Irreversible Processes on the explanation of the different electrokinetic phenomena observed in charged membranes.

Thus, these first works dealt with salt diffusion [30], transport models [31], membrane current, membrane potential, charge densities, or ionic permeabilities. In parallel, the study of the properties of permeability [32] and solute separation [33] in membranes would continue its course. In the next years, Fernández-Pineda, very active in publishing, would produce several papers on hydrodynamics and separation properties of cellophane membranes.

A colleague of Fernández-Pineda at the same University (Málaga) as—with whom she also publishes several articles—professor Juana Benavente specialized in electrokinetic properties, firstly using cellophane membranes [34], but later with many other membrane materials [35].

Meanwhile, Antonio Hernández from the University of Valladolid published works on the permeation of ionic salts species through various polymeric membranes [36][37]. Another group of papers, such as Garrido et al., 1989, Díaz et al., 1989, or Alegret et al., 1989 [38][39][40], focused on membranes not in industrial separation but as an important part of electrodes and sensors.

2. Development

In 1987, new names (not linked to Applied Physics) began to appear dedicated to membrane research (apart from new articles associated with desalination companies [41]) especially chemical engineers [42], which would give rise to a thriving group of researchers at the Polytechnic University of Valencia, for example.

The end of the 80s registers the appearance of one of the largest membrane groups in Spain, that led by Inmaculada Ortiz, initially at the University of the Basque Country, and since the early 90s, at the University of Cantabria. Being part of a purely Chemical Engineering department, Prof. Ortiz published her first paper on liquid membranes in 1988 in *Industrial and Engineering Chemistry Research* [43]. This group of chemical engineers introduced a strong focus on the design and development of membrane processes using process simulation tools and explored the scale-up of membrane processes with numerous pilot plant case studies in collaboration with the chemical industry.

The young but increasing membrane technology field attracts many researchers due to the big range of applications where synthetic membranes can offer a solution for separation problems in the industry. A paper in 1988, by researchers of the Instituto de la Grasa from the Spanish Superior Research Council, CSIC [44], presented the application of Ultrafiltration to the regeneration of olive brines.

Alonso et al. used membrane filters to control the population of *Pseudomonas aeruginosa* in water [45].

At the University of Granada, there was from the beginning a group active in electrokinetic studies on porous plugs [46][47], which later evolved into a group using network thermodynamics to model membrane transport [48]. More studies continue to evaluate the performance of RO in water desalination [49][50].

The group of Organic Chemistry from the Instituto de Ciencia y Tecnología de Polímeros (CSIC) started to publish on the properties of UF membranes cast from polyamide, being one of the first groups in Spain researching on membrane preparation [51][52].

In 1992, the group of Jose Coca, from the University of Oviedo, started to publish regarding the application of reverse osmosis membrane processes to dairy whey treatment [53], a research line which later has been revealed as very productive [54][55].

The mid-90s saw other research groups with different backgrounds starting to contribute to membrane science as an emerging technology. One of those was the group of University of Zaragoza, led by Jesús Santamaría, who published in 1994 their first paper on ceramic membrane reactors [56] and soon became an internationally recognized group on zeolite and other ceramic membranes [57].

Step by step, the 80s and early 90s would see a progressive increase in the applications of membrane processes, and with them, of the publications of Spanish researchers, increasingly associated with groups of chemical engineers or chemists, mostly interested in the different processes in which membranes were finding increasing potential but also in the way to develop new membranes with selected features.

In fact, from 1990 onwards, there is a clear increase in the number of publications from Spanish researchers related to membrane technology as can be seen in **Figure 1**. This trend has been maintained and even increased in the following decades, also linked to an important general rise of scientific research in Spain. Several factors contributed to this increase:

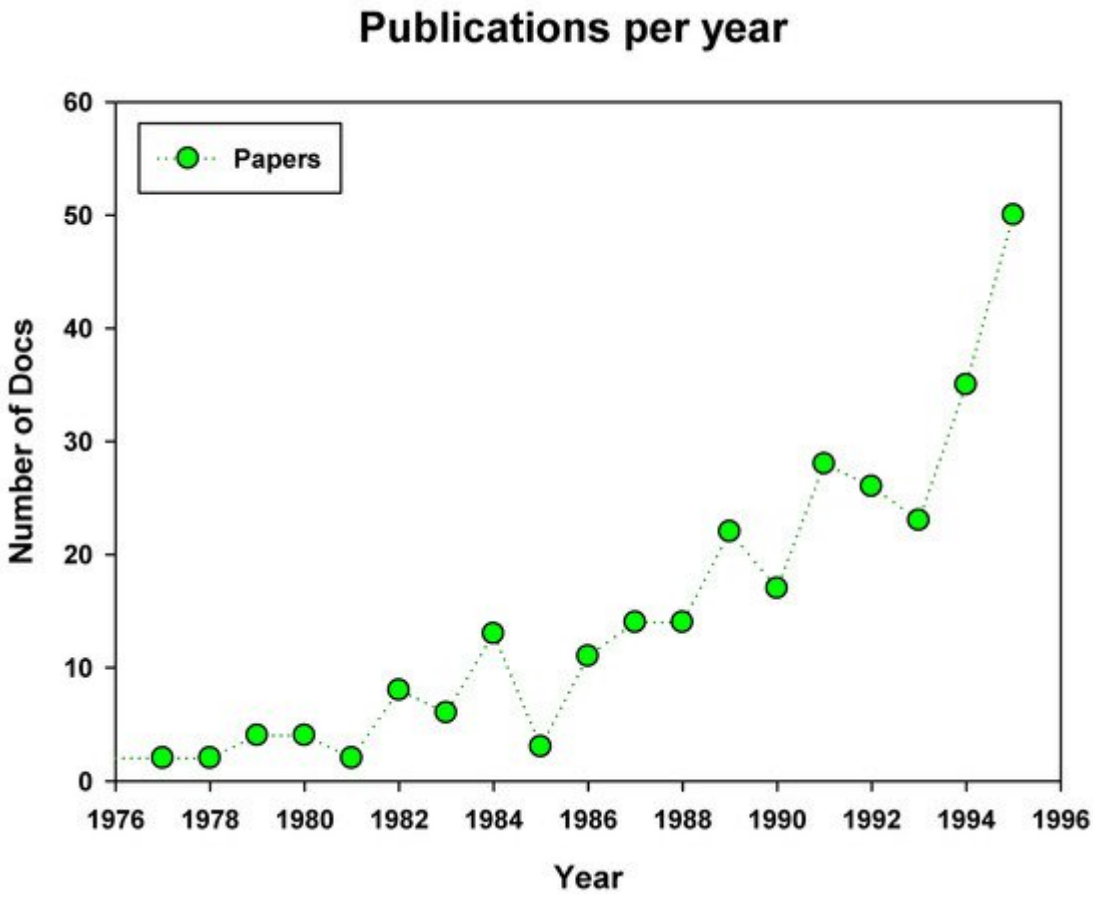

Figure 1. Spanish based membrane publications in international journals from 1970 to 1995.

(1) University Reform Law, issued in 1983, was the first law in democracy that sought to modernize the obsolete and undemocratic structure of the Spanish university. On the other hand, the opening and democratization of the access to the university in these years led to an almost exponential increase in the number of students, rising from 170,000 in the 1959–60 academic year to more than 1,440,000 in the year 1994–95 [58].

(2) The increase in the number of students led to the creation of new universities and the proportional increase in the number of professors who, in addition, were now required to have a research curriculum to stabilize their positions.

(3) Considering that in Spain, the research work was always closely linked to the University, with little contribution until this century from the industrial sector, such a notable increase in university size and quality, led to a consequent expansion of research in general and research in applied fields such as membrane technology in particular.

(4) In parallel, the 90s would see an important effort from the various democratic governments to provide Spanish researchers with funding. Thus, the consolidated groups and new groups created to cover new emerging topics found more financing possibilities that allowed them to acquire increasingly complex instrumental equipment, take part regularly in internationally recognized congresses and send their best young researchers to foreign research centers establishing collaborations that enriched the research background of the national groups.

This clearly somewhat superficial analysis of the first decades of membrane research in Spain can be completed with a view to the main source of publication of Spanish research reports dealing with membranes. Between 1970

and1995, 38 out of the 286 articles reported were published in the *Journal of Non-equilibrium Thermodynamics*, a journal clearly focused on the thermodynamic analysis of irreversible processes, including electrokinetic processes. The outcome of this journal is closely followed (36 documents) by the main reference on membrane science, the *Journal of Membrane Science*, founded in 1976 “to draw together a new field, tentatively called ‘membranology’, which turned to ‘membrane technology’", and has included contributions from Spanish researchers from almost the very beginning [23]. The relative importance of these journals can be seen in **Figure 2**, where the number of papers in the main international journals during these pioneering years is depicted.

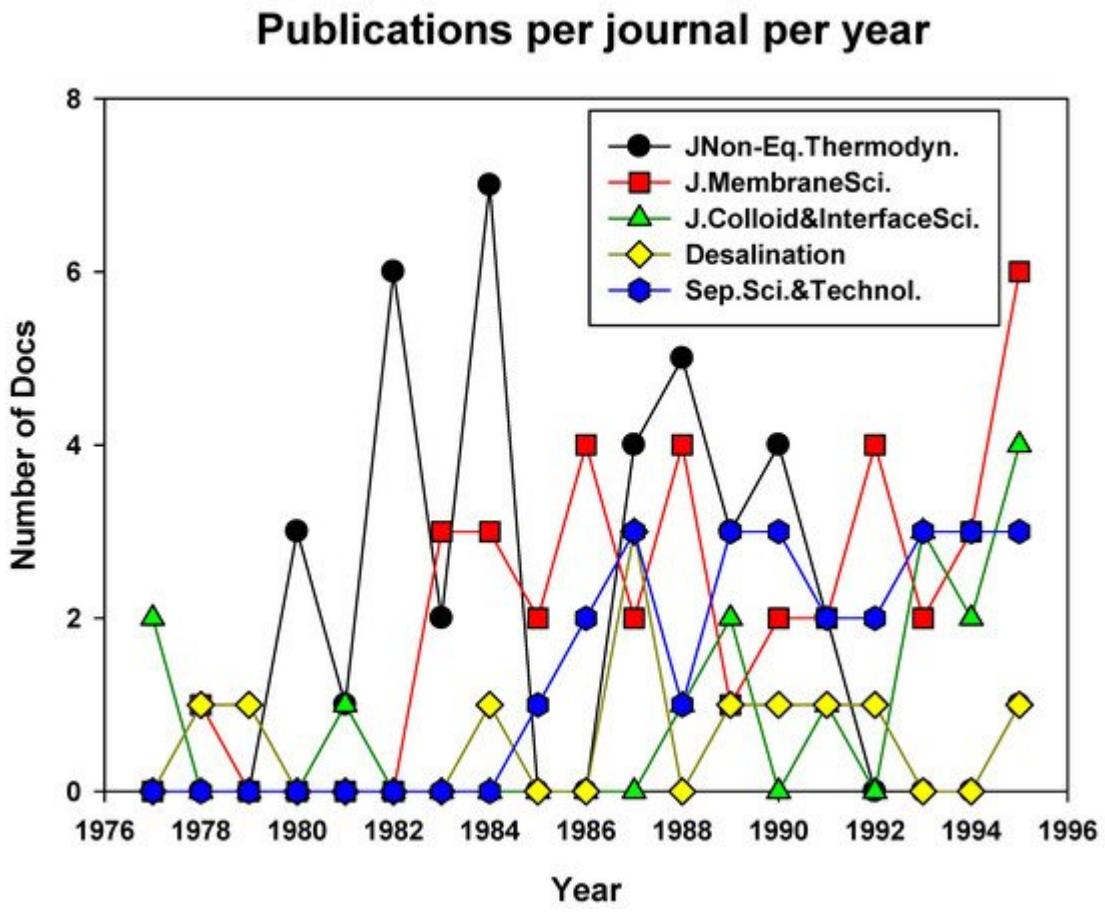

Figure 2. Spanish based membrane-related publications in selected international journals from 1970 to 1995.

Journals mostly devoted to physical properties of separation of charged species as *Journal of Non-Equilibrium Thermodynamics* or *Journal Colloid and Interface Science*, will be preferred in the initial part of the period while, as more and more researchers move to study the process itself and its applications, the journals mainly devoted to separation as *Desalination*, *Separation Science and Technology* or, the most important one, *Journal of Membrane Science* would start to attract maximum attention to the Spanish membrane researchers. From 1988 onwards, Spanish researchers started contributing to the development of membrane processes in journals focused on chemical engineering and chemical technology, that already included sections devoted to separation such as *Industrial & Engineering Chemistry Research* (7), *AIChE Journal* (4), and *Chemical Engineering Science* (4). However, these latter are not included in **Figure 2** for clarification.

The fact that a broader list of journals was available for authors to publish their contributions shows us the rise of applications and approaches related to membranes that Spanish researchers were beginning to explore. Thus, in 1977 or 1978, while the total number of publications in the journals selected in **Figure 2** almost equaled 100% of the existing ones, in 1995, only 30% of the total articles were published in those 5 journals in **Figure 2**, the rest being published elsewhere. They were thus distributed among 27 different journals and magazines, covering a wide variety of fields, from catalysis, materials science to chemical or food engineering.

Another important milestone was the creation of a Spanish Membrane Group (Grupo Español de Membranas, GEM), a consequence of the interest of Spanish researchers who had begun to meet in several reputed international congresses on the topic (Euromembrane or the International Congress on Membranes and Membrane Processes, ICOM, as flag representation, and their specific sub-sections on Inorganic Membranes, ICIM, or Membrane Reactors, ICCMR, among others) and wanted to be aware of mutual research efforts and synergies. Certainly, the birth of the GEM was influenced by the European Society of Membrane Science and Technology (now European Membrane Society, EMS) founded in 1982, and in some way imitated it. The group, founded in the beginning of the 90s, was initially chaired by Juan Ignacio Mengual, with Antonio Hernández as secretary, but the unfortunate loss of its president and the growing drive of chemical engineers would result in the slow languishment of GEM until its effective disappearance. The spirit of association could be then maintained for the duration of the thematic network on selective membranes promoted by Ane Urtiaga and funded by the Spanish Ministry of Science and Innovation in 2002–2004, which fostered the exchange of ideas and the transfer of knowledge on membrane science and technology from the academy to the industry and society.

An important impulse pushed by the research groups actively involved in national associations would translate into the necessity of the creation of some type of international scientific congress that allows Iberian researchers to meet and discuss their common work. This resulted in the series of Ibero-American Congresses on Membrane Science and Technology (CITEM) of which X editions have been held to date. The first one was organized by the Universidad de Murcia in Murcia in 1992. Further editions were held at: Rio de Janeiro, 1994; Aveiro, 2001; Florianópolis, 2003; Valencia, 2005; Campina Grande, 2007; Sintra, 2010; Salta, 2012; Santander 2014 and Mexico DF, 2016. In all cases the CITEM congresses have proved a genuine ability to promote the mutual collaboration between Ibero-American research groups, obviously with more Iberian researchers was major in those celebrated in Spain or Portugal while Ibero-American researchers were the majority in the meetings held at the other side of the Atlantic Sea.

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