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Trends in Membrane Distillation for Wastewater Treatment

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Abstract

Membrane distillation (MD) is a promising technology that enables the treatment of high-salinity wastewater. To monitor the state and trends of MD technology for wastewater treatment, the patent filings from the last nine years were analyzed. A total of 72 documents with a special focus either on the membrane itself or on the equipment and process were found. China, United States and Japan play a leading role in the development of these technologies. Most of the inventions concentrating on the membrane apply polymers as the material. Inventions describing the equipment and process are mainly related to system and module design, but also cover the combination of MD with other technologies, the treatment customization to a specific type of wastewater, fouling control and cleaning, and energy recovery. Finally, enhancements in water flux and energy efficiency are found to be key factors to broaden the application of MD technology in wastewater treatment.

Keywords

Membrane Distillation, Patents, Trends, Wastewater

1. Introduction

Water is an essential component for life on earth and a precious resource for human civilization. Access to safe and affordable drinking water is considered one of the basic human necessities and remains one of the main challenges of the 21st century. The current global water supply presents many challenges, as 785 million people lack even a basic drinking-water service [1]. It is of fundamental importance to implement a clean water supply in the affected areas, especially in developing countries, where water and wastewater infrastructure are often non-existent.

In general, water availability is limited. Water stress, resulting from water resources exploration for irrigation, domestic and industrial use, tends to aggravate in the next decades [2]. Climate change and global demand for food and energy, pushed by population growth and industrial development, are the main ingredients responsible for the deepening of the water crisis [3].

Recently, membrane distillation (MD) has gained meaningful attention as a promising technology for the production of fresh water via the treatment of high-salinity wastewater [4]. MD is a membrane-based thermally driven process, in contrast to the pressure driven membrane-based processes generally used for wastewater treatment [5]. In MD, a vapor pressure gradient is produced by a temperature differential across a hydrophobic porous membrane [6]. Vapor evaporates from the wastewater feed and diffuses through the membrane, driven by the partial pressure difference, and is then condensed in the permeate side [7]. Due to the hydrophobicity of the membrane, liquid water molecules are prevented from moving through the pores [8]. MD has many advantages in comparison to most conventional processes, such as distillation and reverse osmosis. For instance, operating temperatures are relatively low (30˚C - 90˚C) [6]. Moreover, operating pressure is lower than that used in pressure-driven membrane processes like reverse osmosis [9]. Another advantage of MD is the high purity of the treated wastewater, with up to 100% retention of solid or nonvolatile contaminants on the retentate side [10]. Furthermore, the performance and the energy consumption of MD are not significantly affected by the salinity of the feed wastewater [11].

The major barriers for industry adoption of MD technology include: membrane and module design, membrane pore wetting, low permeate flux and high thermal energy demand [6] [7] [12]. Nevertheless, during the past few years, significant research has been carried out for the development of MD applied to wastewater treatment [13]-[18]. Due to this recent and expanding research, significant advances in membrane design and performance have been made and the process has become much more attractive [19].

In view of MD's potential use for removing contaminants from wastewater and for producing fresh water, it is of great interest to uncover the main challenges to the development of this technology and its future trends.

Technology foresight is a systematic process for investigating future technological developments and their interaction with the economy, society and environment. In this research, a foresight study of MD for wastewater treatment was conducted by investigating patent activity on the subject. Effectively, patent applications are important technology indicators that provide detailed information with extensive coverage worldwide. Through the collection of data from patents, this study aims to identify the evolution in the number of patent applications over time, the main applicant countries, the profile of the applicants, as well as to present an overview of the major technological developments. The trends in MD for wastewater treatment can represent strategic alternatives to solve global water scarcity in the future.

2. Methodology

The identification of the trends in MD applied to wastewater treatment involved two steps:

- Search of patent applications related to the subject; and
- Analysis of the patent applications retrieved.

The details of each step are explained as follows.

2.1. Search of Patent Applications

The Derwent Innovations Index was used to search for patents. It is a commercial database that covers over 39 million patent documents from 40 worldwide patent-issuing authorities in the field of chemistry, electrics, electronics, and engineering. An advanced search using keywords and the International Patent Classification (IPC)[1] was performed on the Derwent Innovation Index website. The search in the database was made using the following keywords in the title/abstract field:

- (*membrane AND distillation*) *AND* (*wastewater OR wastewater OR sewage OR effluent*)

The documents were also filtered by the IPC as belonging to at least one of the following groups:

- B01D-061/36: Pervaporation; Membrane distillation; Liquid permeation;
- B01D-063/00: Apparatus in general for separation processes using semi-permeable membranes;
- B01D-069/00: Semi-permeable membranes for separation processes or apparatus characterized by their form, structure or properties; Manufacturing processes specially adapted therefor;
- B01D-071/00: Semi-permeable membranes for separation processes or apparatus characterized by the material; Manufacturing processes specially adapted therefor.

The objective of this search strategy was to restrict the research only to documents that involved MD applied to wastewater treatment with a special focus on the membrane, apparatus, or process. As already mentioned, the documents were retrieved by considering the main keywords and the main IPC classification groups related to MD applied to wastewater treatment, in order to select the most suitable documents for the study. The limitations of the search are mostly

[1]The IPC is the international classification system created by the Strasbourg Agreement (1971) which divides technological areas in classes from A to H. Within each class, there are subclasses, main groups and groups in a hierarchical system, with classification for the technological contents of the patents.

related to documents that were either not comprised in the Derwent Innovations Index or did not receive any of the chosen IPC classifications. The patent search included documents indexed in the database in the 2011-2019 period. A total of 95 patent applications were found and were imported into an Excel spreadsheet. As patent applications are often filed in more than one country, constituting a patent family that shares the same priority application, it is important to mention that, in this work, patents with the same priority were counted only once.

2.2. Analysis of the Patent Applications

The 95 patent applications retrieved from the search were read and checked. After removing nonrelevant documents, a total of 72 that concerned MD applied to wastewater treatment remained. This number of patent applications is expressive and representative for this study, considering that MD is a new technology and is not yet applied in industrial scale.

The trends presented in this study are based on the contents of the 72 relevant patent documents that resulted from the search. The analysis led to the identification of the evolution in the number of patent applications over time, the main applicant countries and the profile of the applicants. Furthermore, the documents were manually and carefully reviewed, being divided into two categories: "Membrane" and "Equipment and process". For those pertaining to the "Membrane" category, information about membrane material, structure and properties was evaluated. For the ones pertaining to the "Equipment and process" category, the type of wastewater and the industry sector were identified, when mentioned, as well as the focus of the invention.

3. Results and Discussion

As noted in Chapter 2, the following categories were used to classify the 72 analyzed patent documents:

- "Membrane": includes technologies related to the membrane material, structure, and properties.
- "Equipment and process": covers technical information on MD apparatus and process design.

Figure 1 shows the distribution of the documents into these categories. A total of 32 documents (44%) are related to the "Membrane" category, while the remaining 40 documents (56%) belong to the "Equipment and process" category.

Figure 2 shows the evolution of patent documents published on the subject in the 2011-2019 period. The number of patent applications published each year varied from a minimum of 5 (in 2012) to a maximum of 11 (in 2018), with an average of 8 documents being published per year. The consistent number of patent documents published in recent years suggests that research on MD has been constantly carried out and shows its relevance for wastewater treatment.

According to the country or organization of priority, China (CN), United

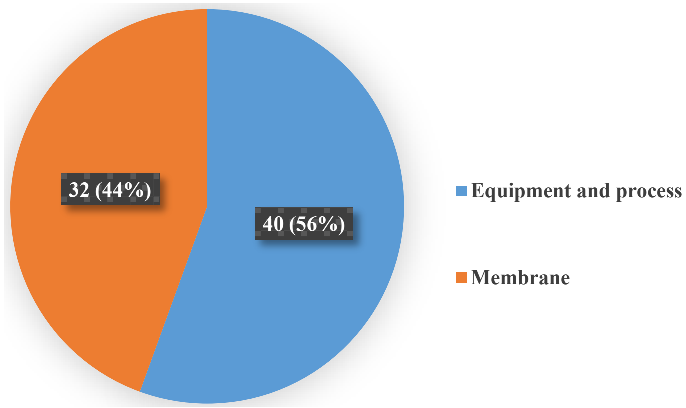

Figure 1. Number (percentage) of patent documents related to MD applied to wastewater treatment distributed between the "Membrane" and "Equipment and process" categories, retrieved from the Derwent Innovations Index database, indexed between 2011 and 2019 (own research).

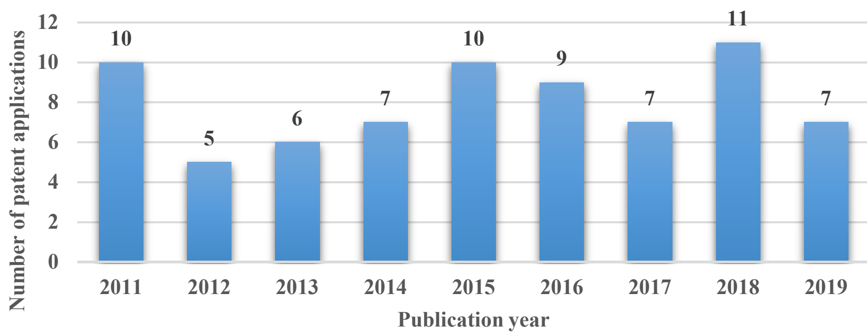

Figure 2. Evolution over time of patent applications published on MD applied to wastewater treatment, retrieved from the Derwent Innovations Index database, indexed between 2011 and 2019 (own research).

States (US) and Japan (JP) are the top three countries, making up 75% of the patent documents retrieved (**Figure 3**). China has 24 patent documents alone, while the United States and Japan have 20 and 10, respectively. The country of priority is usually where the technology was developed, indicating that these three countries play a leading role in the field.

Companies are the most important type of applicant in the period of search, accounting for 39 documents which represent 54% of the total. It is worth noting that10 companies have filed more than one patent application during the analyzed period.The profile of the patent applicants is presented in **Figure 4**. The name of these companies, the country of origin and the number of patent applications are specified in **Table 1**. The Japanese company Sumitomo Electric Ind Ltd stands out with 5 patent applications, followed by the Chinese company China Petroleum & Chem Corp (also known as Sinopec) and by the Saudi Arabian company Sabic Global Technologies B. V., with 4 patent applications each. **Table 1** also shows that Japan, United States and China are the country's most frequently chosen by main companies for filing the patent's priority applications.

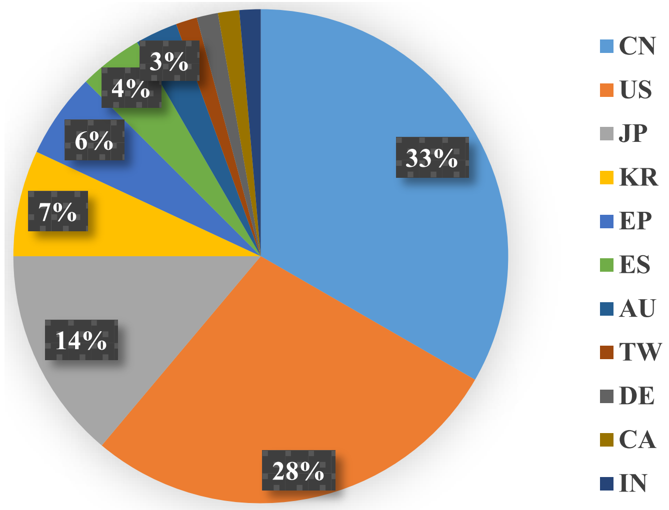

Figure 3. Distribution of patent applications about MD applied to wastewater treatment per country of origin, retrieved from the Derwent Innovations Index database, indexed between 2011 and 2019 (own research). Country codes: AU (Australia); CA (Canada); CN (China); DE (Germany); EP (European Patent Office); ES (Spain); IN (India); JP (Japan); KR (Korea); TW (Chinese Taipei); US (United States).

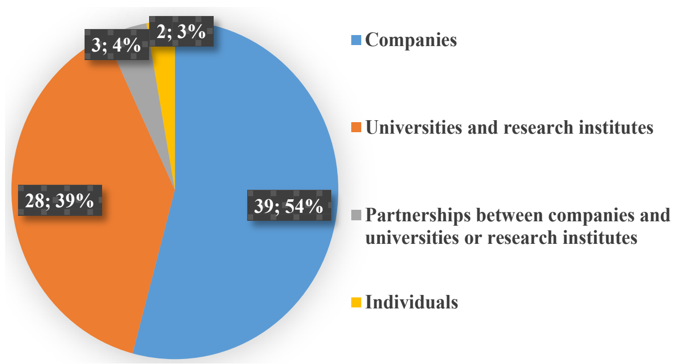

Figure 4. Profile of the patent applicants in the field of MD applied to wastewater treatment, retrieved from the Derwent Innovations Index database, indexed between 2011 and 2019 (own research).

Universities and research institutes are the second most important type of applicant, having filed 28 applications (39% of the total). The two most important contributors for these 28 documents are China (13) and United States (7). Three institutions have filed 2 patents each during the analyzed period: Zhejiang Sci-Tech University (China), King Abdullah University of Science and Technology (Saudi Arabia) and Netherlands Organization for Applied Scientific Research (Netherlands). Furthermore, partnerships between companies and universities or research institutes have originated only 3 patent applications, corresponding to 4% of the retrieved documents. Therefore, a significant cooperation between companies and universities in the research field of MD applied wastewater treatment has not been observed.

Table 1. Main company applicants, country of origin and number of patent applications.

Company Name	Country of origin of the patent applications	Number of patent applications
Sumitomo Electric Ind Ltd	Japan	5
China Petroleum & Chem Corp	China	4
Sabic Global Technologies B. V.	United States	4
Asahi Kasei Corp	Japan	3
Abengoa Water Sl	Spain	2
Beijing Zhongkeruisheng Resources Enviro	China	2
General Electric Co[a]	China and United States	2
Membrane Distillation Desalination Co Ltd[a]	China and Canada	2
Milton Roy Co	United States	2
Toray Chem Korea Inc	Korea	2

[a]These companies have filed one priority application in each of the listed countries.

3.1. Analysis of Patent Filings on "Membrane"

Hydrophobicity is an essential requirement for MD membranes, because it prevents the feed liquid from entering membrane pores due to the surface tension. Therefore, this feature has to be considered when choosing the membrane material and designing its production process. The membranes must be made from intrinsic or modified hydrophobic materials. Hydrophobic polymers are the most common choice for the MD membrane material due to their characteristics of easy fabrication, modification, and scale-up, as well as low costs.

The reduction of fouling and scaling is also of significant importance in the field of wastewater treatment, due to the variety of contaminants that might be present, depending on the nature of the wastewater to be treated. To address this problem, composite polymeric membranes, membranes combining polymeric and inorganic materials, and purely inorganic membranes have been proposed as an alternative to the traditional hydrophobic polymeric membranes.

This study identified that polymeric materials are more frequently used than inorganic materials in MD applied to wastewater treatment. The examination of the 32 documents on "Membrane" showed that 22 patent documents use polymeric materials, 6 documents employ a membrane containing both polymeric and inorganic materials, and 4 documents apply purely inorganic membranes. More details on the documents are presented below.

3.1.1. Polymeric Membranes

Hydrophobic microporous polymeric membranes appear often in the analyzed patent documents, the most commonly cited polymers being: polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF). Membrane geometry is usually hollow fiber or flat sheet. Some examples of membrane material and geometry are presented in Table 2.

Table 2. Examples of patent documents related to hydrophobic microporous polymeric mem-branes, their material and geometry.

Polymer	Geometry	Patent numbers – References
PTFE	Hollow fiber	CN102941025 [20] CN103386261 [21]
PP	Hollow fiber	CN103785303 [22] CN104511247 [23]
PVDF	Hollow fiber Flat sheet	CN108993173 [24] WO2011117443 [25]

Most of the documents shown in **Table 2** are related to hollow fiber membranes, which have been prepared by spinning, while the flat sheet membrane has been produced by means of electrospinning. According to the inventors, this process generates a nanostructured membrane which has high permeate flow and allows a considerable reduction in heat loss due to conduction.

A significant number of patent documents employing polymers are about composite membranes (7 out of 22 documents). For instance, WO2012100318 [26] and US2011031100 [27] describe a composite membrane containing hydrophilic and hydrophobic polymer layers comprising a fluorinated surface-modifying macromolecule (SMM). These kinds of composite membranes have been proposed for use in MD as a possible solution to obtain higher mass transfer and lower heat transfer through the membrane. In addition, omniphobic membranes have been developed to deal with high salinity produced water which usually contains surfactants. These surface-modified membranes have significantly increased organic fouling resistance. In particular, one patent document discloses a composite membrane for distillation of a contaminated brine solution [28]. This membrane comprises an omniphobic substrate having a re-entrant structure, as well as a surface coating with a dual functional layer which is hydrophilic in air and oleophobic in water, allowing it to be antiwetting and antifouling in the presence of hydrophobic and amphiphilic contaminants.

3.1.2. Membranes Combining Polymeric and Inorganic Materials

The patent documents related to membranes combining polymeric/inorganic materials involved composite and/or mixed matrix membranes. The incorporation of additives is an effective and widely used method to design a MD membrane with desirable morphology, permeation performance, hydrophobicity or anti-fouling properties. CN103372378 [29] and CN109985536 [30] use hydrophilic/hydrophobic composite membranes comprising PVDF and an inorganic material, respectively: graphitic carbon nitride; and titanium dioxide and lithium chloride. WO2012100326 [31] describes a flat-sheet composite mixed matrix hydrophilic/hydrophobic membrane: the hydrophilic layer containing a hydrophilic polymer and inorganic nanoparticles of high thermal conductivity, and the hydrophobic layer containing a fluorinated surface-modifying macromolecule (SMM). The membrane is manufactured by a phase inversion method and is useful for direct contact MD. WO2014111889 [32] reveals the manufacture of a multi-layered polymeric and mixed matrix membrane that involves providing a support layer, casting a hydrophilic layer on a surface of the support layer and finally casting a hydrophobic layer on the hydrophilic layer. The membrane is used in a plate-and-frame membrane module for direct contact MD. CN110152504 [33] reports the method for preparing a blended modified PVDF film: obtaining a casting solution by adding titanium dioxide, graphene and a porogen to a polar solvent, adding PVDF, and uniformly mixing; and then obtaining the blended matrix film by scraping the casting solution, solidifying in a coagulation bath, soaking and air-drying. The film is useful for vacuum MD in the field of high salinity organic wastewater.

3.1.3. Inorganic Membranes

When it comes to purely inorganic membranes, the applied materials are carbon nanotubes [34] [35] [36] and graphene [37]. In order to be suitable for the use in MD, inorganic materials must be modified for improved hydrophobicity. CN107096393 [34] presents the preparation of a thermal stable and super-hydrophobic ceramic-carbon nanotube composite membrane via chemical vapor deposition, using a ceramic hollow fiber membrane as a carrier. By changing preparation conditions, such as the amount of catalyst and the reaction temperature, membranes with varied structures and properties are obtained by the inventors.

3.2. Analysis of Patent Filings on "Equipment and Process"

The analysis of patent filings on "Equipment and process" indicate the great potential of MD technology for wastewater treatment. The careful reading of the documents enabled the identification of the type of wastewater and industry sectors that are likely to benefit from this technology. Furthermore, the inventions described in the patent applications are of significant value to identify the main challenges and future opportunities for implementation of MD.

3.2.1. Types of Wastewater

Out of 40 documents on "Equipment and process", 27 specify the target type of wastewater to be treated. From these, 22 documents are directed to industrial wastewater; 3 documents mention that the wastewater might be domestic or industrial; and 2 documents refer solely to domestic wastewater. These results imply that MD is prone to be applied for industrial wastewater treatment, rather than for domestic wastewater treatment.

The documents cover a wide range of industry sectors. The petroleum and petrochemical industry are mentioned in a considerable number of documents [38] [39] [40]. Some are directed to sources of oily wastewater, including petroleum refining, metals manufacturing, and food processing [41]. WO2017140927 [42] mentions the pharmaceutical and textile industries as possible sectors. JP2018083189 [43] and JP2019048257 [44] name wastewater from food, chemical, electronic, pharmaceutical and cleaning industries. As expected, many of the documents have a special focus on saline wastewater, with 11 documents on "Equipment and process" citing it explicitly.

3.2.2. Focus of the Inventions

The information extracted from the patent documents enabled the identification of the most important topics related to "Equipment and process". Table 3 shows the documents found for each focus, as well as brief examples of their contents.

A great number of patent documents concern constructive features of the equipment, usually proposing new membrane modules and system designs with the aim of improving process efficiency. EP2283988 [50] claims a method for preparing a planar membrane module. US2011284444 [55] discloses a condensing tube applied in an air-gap MD module to not only support the membrane but also provide the selection of different air gap thicknesses, in order to increase the permeate flux by adjusting variable parameters. WO2016006670 [59] and JP2018083189 [43] describe compact MD apparatus with high water treatment capacity. CN108622983 [38] and US2011180383 [53] propose assemblies that improve heat efficiency in a MD process. CN108067100 [46] develops a spiral-wound membrane distilling device obtained by coupling a hydrophobic and a condensing membrane. US2016310900 [57] reveals membrane modules submerged in a feed solution tank. WO2017140927 [42] and JP2019048257 [44] apply for new hollow-fiber membrane module designs.

Another important aim of the inventions is to propose a combination of technologies. US2012132588 [41] describes a method and system for treating oily wastewater. The oily wastewater is pretreated using at least one of electrocoagulation, flotation or absorption; and then treated using MD. JP2014188468 [63] combines MD, reverse osmosis and catalyst oxidation to provide a water treatment system for space applications. WO2015162314 [66] performs a pretreatment before MD, in order to eliminate calcium hardness in waste brine from desalination plants. Calcium hardness is eliminated by a chemical treatment followed by decantation or filtration. WO2016135701 [67] discloses an integrated forward osmosis-membrane distillation module for water treatment applications. The module utilizes an isolation barrier which leads to higher efficiency of the forward osmosis and membrane distillation processes by enhancing their respective driving forces. CN106495382 [61] proposes a solution for the treatment of sweet industrial wastewater that combines filtration, incineration, nanofiltration and MD to obtain crude glycerol and water as final products.

Some documents are directed to the treatment of a specific type of wastewater, so that customized equipment and processes involving MD were presented. KR2013101279 [68] separates and recovers dimethylformamide from industrial wastewater. JP2015100775 [39] provides a solution to purify oil and salt-containing wastewater generated in a petroleum production process. KR2016149699 [69] reveals a device and method for the treatment of wastewater containing ammonia. US2017057854 [71] describes a method for treating the effluent waste from a

Table 3. Focus of the inventions about MD applied to wastewater treatment on "Equipment and Process".

Focus	Examples	Patent numbers-References
Constructive features of the equipment (20 documents)	• improvements in system design • compact MD apparatus • multistage process • improvements in module design	CN105692739 [45] CN108067100 [46] CN108619913 [38] CN204261564 [47] CN209065483 [48] DE102012017860 [49] EP2283988 [50] EP2606953 [51] JP2014004497 [52] JP2018083189 [43] JP2019048257 [44], US2011180383 [53] US2011180479 [54] US2011284444 [55] US2014263061 [56] US2016310900 [57] US2019144309 [58] WO2016006670 [59] WO2016172539 [60] WO2017140927 [42]
Combination of technologies (8 documents)	• electrocoagulation, flotation or absorption • reverse osmosis and catalyst oxidation • filtration, incineration, nanofiltration • forward osmosis	CN106495382 [61] EP2671845 [62] JP2014188468 [63] KR2016123822 [64] US2012048803 [65] US2012132588 [41] WO2015162314 [66] WO2016135701 [67]
Customized equip./process for specific wastewater types (6 documents)	• fluorine-containing wastewater • wastewater from cation-exchange column regeneration • oil and salt-containing wastewater • ammonia-containing wastewater	KR2013101279 [68] KR2016149699 [69] JP2015100775 [39] JP2015100776 [40] JP2018065101 [70] US2017057854 [71]
Fouling control and cleaning (3 documents)	• cation-sequestering method • X-ray excitation of luminescent materials	CN108704486 [72] US2014263055 [73] US2016107126 [74]
Energy recovery (3 documents)	• heat recovery system • usage of solar heat energy	CN106219855 [75] CN108622983 [76] JP2011167597 [77]

cation-exchange column regeneration cycle. JP2018065101 [70] propose a method of treating a fluorine-containing water using a hydrophobic porous membrane.

Fouling control and cleaning of membranes is also a problem of concern to some of the documents analyzed. US2014263055 [73] presents a cation-sequestering method to prevent membranefouling. According to the method, ethylenediaminetetraacetate ions are added to the wastewater, where they bond with the cations to form a non-scaling ionic complex. The wastewater with the ionic complex is then treated by a process like MD to produce pure water. The pH of the wastewater is subsequently reduced to release the cation from the ethylenediaminetetraacetate ions, which are afterwards reused in a closed loop. US2016107126 [74] describes a method to prevent biofouling by X-ray excitation of luminescent materials placed within the membrane modules and which are capable of emitting in the violet to ultraviolet range. CN108704486 [72] discloses a method and system for cleaning and drying the membrane in a vacuum MD process. The method improves process efficiency by directly cleaning and drying the membrane after the vacuum MD of wastewater, thus avoiding the complex assembly and disassembly of membrane components.

Energy recovery is another aspect considered by the patent applications. JP2011167597 [77] describes a MD system with a raw water tank and a heat exchange apparatus using solar energy. The system is supposedly low cost and capable of being placed even in an area with inadequate infrastructure where energy acquisition and large capital investment are difficult. CN106219855 [75] discloses a device and method for water treatment with a direct air-cooling and heat recovery unit. The main advantages claimed by the inventors are the reduction of power consumption in the air-cooling system by recycling the steam waste heat and the production of high-quality fresh water through the MD system. CN108622983 [76] presents a MD device that is coupled to a heat recovery system. The latent heat of water vapor is recovered in order to heat and maintain the temperature of the raw water.

4. Conclusions

MD is a promising technology for wastewater treatment. It is a thermally driven separation process, in which only vapor molecules are able to pass through a porous hydrophobic membrane. Despite its many attractive features, like low operating pressure and high retention of contaminants, its large-scale commercialization still faces some technical challenges, such as low water flux and energy efficiency.

This patent analysis presented an overview of patent activity in MD applied to wastewater treatment. Although MD is a new technology and is not yet applied in industrial scale, the number of patent documents found was expressive and enabled the assessment of trends in the field. Some of the main findings are highlighted below:

- A consistent number of patents on "Membrane" and "Equipment and process" have been published each year over recent years.
- China, United States and Japan play a leading role in the development of the technologies, as 75% of the patent documents analyzed were originally filed

in one of these countries.

- More than half of the patent applications were filed by companies, demonstrating that there is commercial interest and research investment on MD applied to wastewater treatment by big corporations such as Sumitomo, Sinopec, Sabic, Asahi Kasei, General Electric and Toray.
- Most of the patent documents on "Membrane" apply polymers as the membrane material, especially hydrophobic polymers like PTFE, PP and PVDF.
- Composite membranes with special wettability have also been an important focus of research for the treatment of challenging wastewaters, such as high salinity brine and wastewater containing oils or low surface tension components.
- Patent documents on "Equipment and process" are applicable to wastewater from a variety of industry sectors like petroleum and petrochemical, pharmaceutical, textile, chemical, electronic, metals manufacturing and food processing.
- Patent documents on "Equipment and process" are mainly related to constructive features of the equipment, combination of technologies, customized equipment and process for specific wastewater types, fouling control or cleaning of membranes, and energy recovery. It is evident from the contents of the patent documents that improved process efficiency and energy consumption are very relevant concerns that need to be considered when designing membrane modules and systems.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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