Chapter 10

Research Trend of Membranes for Water Treatment by Analysis of Patents and Papers' Publications

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Additional information is available at the end of the chapter

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Abstract

Since the beginning of water shortage by disasters such as global warming, environmental pollution, and drought, development of original technology and studies have been undertaken to increase the availability of water resources. Among the technologies, water treatment technology using membranes has a better water quality improvement than existing physicochemical and biological processes. Moreover, it is environmental-friendly technology that does not use chemicals. Water treatment membranes are applied to various fields such as wastewater treatment, water purification, seawater desalination, ion exchange process, ultra-pure water production, and separation of organic solvents. Furthermore, water treatment technologies using membranes will increasingly expand. The core technology of the water treatment membrane is to control the size of pores for membrane performance and is being researched to improve performance. In this chapter, the frequencies of presentation are filed by country, institution, and company through technology competitiveness and evaluation of patents and papers. In addition, evaluation of technologies for wastewater treatment, water purification, seawater desalination, and ion exchange process was carried out in the same way as before. Finally, future research directions were suggested by using evaluation results.

Keywords: patents, water treatment, desalination, ion exchange, membrane

1. Introduction

The world is now expected to become water scarce as a result of global warming, and by 2025, it is estimated that water-scarce countries will increase by more than 30% compared to 1995 [1]. The twentieth century was the era of black gold, represented by oil, but the age of water, or blue gold, is expected to emerge in the twenty-first century. Due to the global problems faced by the world, such as population growth, industrialization, and climate change, a steady increase in water demand and a disparity in regional water supply are urgently needed to be resolved. Population Action International (PAI) currently has 550 million people living in water-pressure or water-starved countries, and from 2.4 billion to 3.4 billion people will live in water-starved or water-deprived countries by 2025. According to the World Meteorological Organization (WMO) report, 653 million people in 2025 and 2.43 billion in 2050 will suffer direct water shortages.

Various water treatment techniques have been studied to secure water resources in order to solve the water shortage phenomenon. In the water treatment field, there are water treatment processes such as wastewater and wastewater treatment to remove pollutants, water treatment for drinking water, and seawater desalination for seawater reuse (**Figure 1**).

There are also a number of related technologies, among which water treatment technologies using membranes have shown very high growth rates of 10–20% per year [2, 3]. Frost and Sullivan estimate that the world's membrane-based water treatment market will grow from $ 5.54 billion in 2012 to $ 1.27 billion by 2020 (CAGR of 10.2%). Major growth factors include increased demand for drinking water, reuse of sewage, increased desalination facilities based on membranes, and strengthening of environmental standards. In particular, it is expected that there will be a significant increase in the market in the Asia-Pacific region based on rapid industrialization, population growth, and demand for advanced technologies [4].

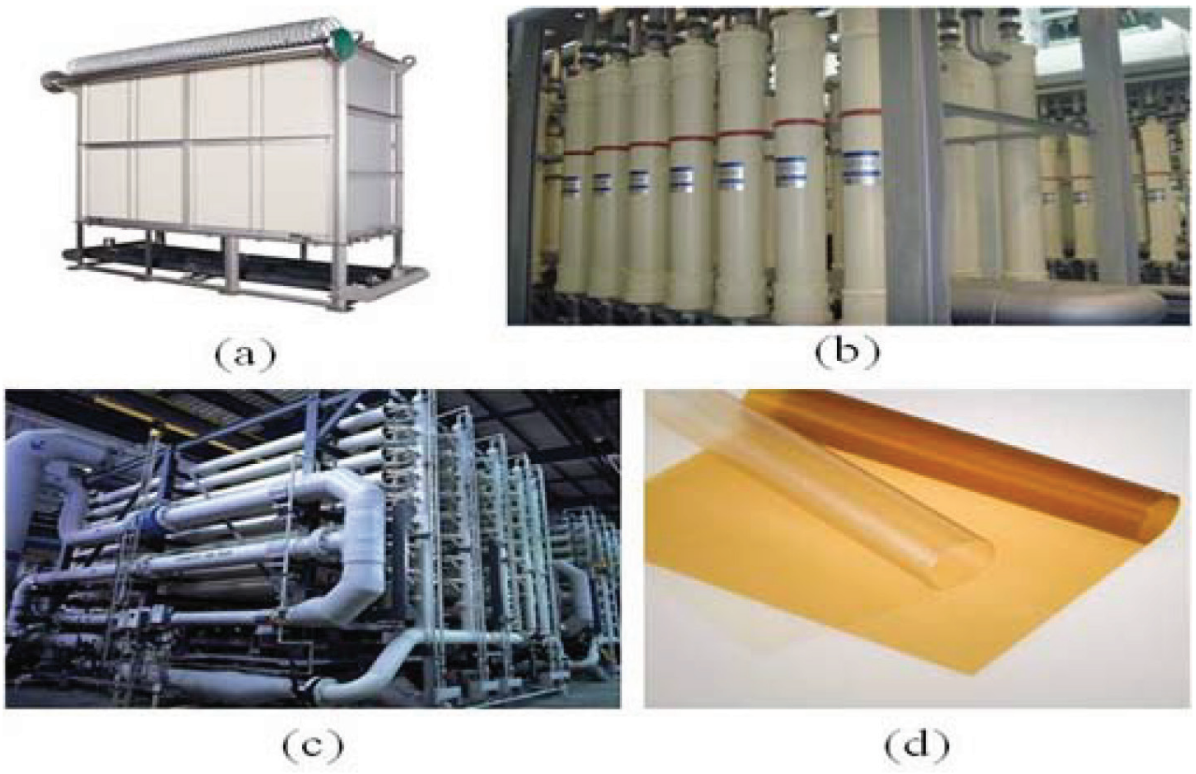

Figure 1. Various applications of water treatment membranes. (a) MBR process (Toray Industries, Inc.), (b) water treatment process (Yeongdeungpo water purification center), (c) desalination process (Doosan heavy industries & construction), (d) ion exchange membrane (Tokuyama America, Inc.).

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The separation membrane has a selective filtration function that selectively passes a specific component, as well as selective permeability capable of separating dissolved substances or mixed gases dissolved in a liquid [5–7]. Membrane separation technology comprehensively means various separation processes using such selective permeability of the membrane. As shown in **Figure 2**, the separation membrane used for water treatment produces clean water by allowing the water (B) to pass but not allowing the suspended material (A) to pass through. Membranes can be divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) depending on the pore size [8–10]. **Figure 3** shows the separation performance according to the pore size of the membrane, and **Table 1** shows the membrane characteristics of various process parameters [11].

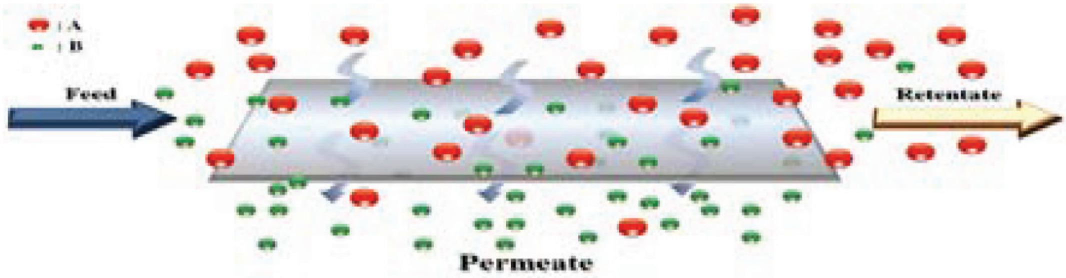

Figure 2. Schematic of membrane filtration process.

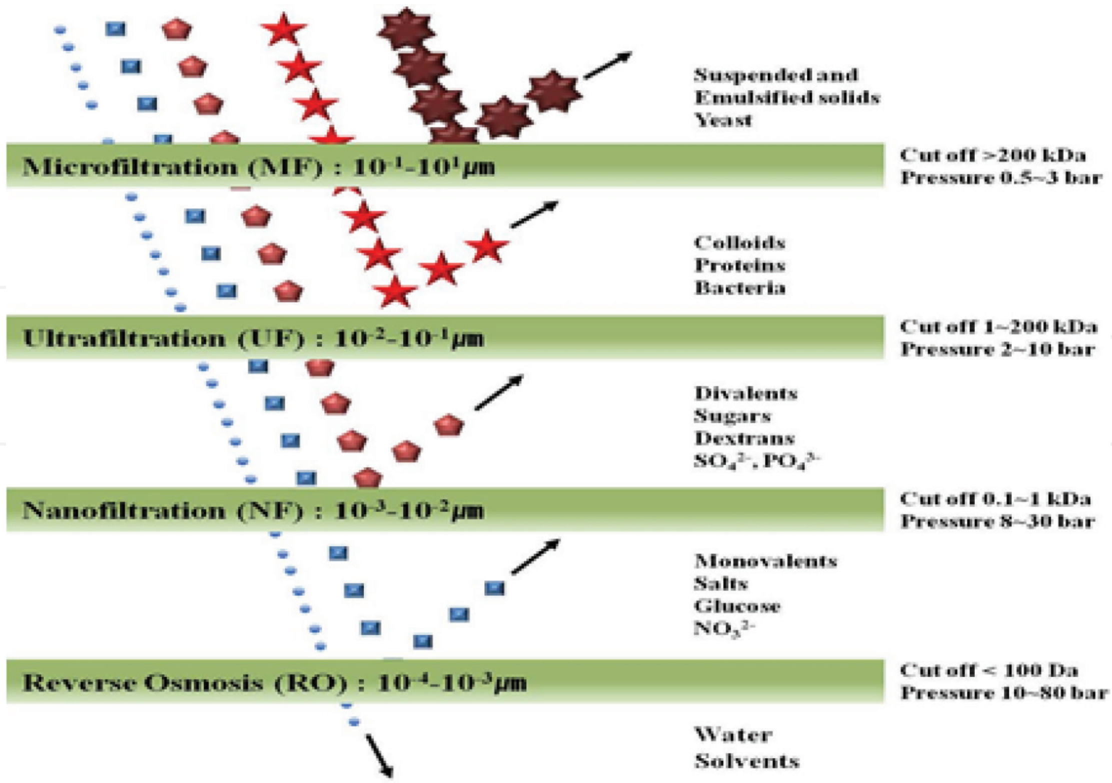

Figure 3. A scheme of the membrane for water purification processes.

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Mechanism or separation	Sieving	Sieving	Sieving + solution/diffusion + exclusion	Solution/diffusion + exclusion
Materials	CA, CE, PAN, PC, PE, POF, PP, PS, PTFE, PVDF	CA, CE, PA, PAN, TFC, PS, PVDF	CA, PA, TFC	CA, PA, PS, TFC
MWCO (Da)	>100,000	>2000–100,000	300–1000	100–200
Structure	Porous isotropic	Porous asymmetric	Finely porous asymmetric/ composite	Nonporous asymmetric/ composite
Law governing transfer	Darcy's law	Darcy's law	Fick's law	Fick's law
Pore size range (μm)	0.1–10	0.01–0.1	0.001–0.01	<0.001
Rejects	Particulates, clay, bacteria	Macromolecules, proteins, polysaccharides, viruses	HMWC, mono-, di-, and oligosaccharides, polyvalent anions	HMWC, LMWC, sodium chloride, glucose, amino acids, proteins
Operating pressure (psi)	1–30	3–80	70–220	800–1200
Fluxes (L/m^2 h)	500–10,000	100–2000	20–200	10–100

Table 1. Correlation of membrane features with ranges of separation [6].

Microfiltration is a membrane separation process for separating a solute having a solute size of about 0.1–10 μm. It is preferable that the membrane used at this time is about 0.01–10 μm in pore size and the pore accounts for about 80% Do. As for the material of the membrane, cellulose-type, nylon, PVC, polytetrafluoroethylene (PTFE), and various other polymer materials are suitable. In a microfiltration process, propulsion is represented by a pressure difference, where the pressure difference is typically 1–30 psig. The separation effect of this membrane is fundamentally dependent on the pore size of the membrane and the size of the substance to be separated. If the size of the substance to be separated is smaller than the pore size, it does not pass through the entire membrane but the substance to be separated is adsorbed on the membrane or is not transmitted by steric hindrance near the pore. The biggest problem of the microfiltration process is the deposition of colloidal material on the membrane surface, which reduces the flow rate by blocking the pores, which can be replaced or regenerated to restore the original state [12–15].

Ultrafiltration is a membrane separation process that separates macromolecules or colloidal particles with molecular sizes ranging from 10 to 1000 Å. The pore size ranges from 20 to 500 Å. This method uses a differential pressure as a thrust for the separation operation similar to the reverse osmosis method. The pressure differential used in ultrafiltration is usually in the range of 10–100 psig because particles with a high molecular weight have relatively low osmotic pressure and thus do not require high pressure to apply pressure above osmotic pressure. Ultrafiltration is the same as reverse osmosis in mathematical modeling but fundamentally different from reverse osmosis. The reverse osmosis is largely governed by the correlation between the membrane and the dissolved salt, whereas ultrafiltration is dominated by the solute and pore size. In other words, ultrafiltration has a separation effect by the steric hindrance at the micropore inlet and the frictional resistance between the solute and the pore wall in the pore. The molecular weight cut off (MWCO) in the ultrafiltration method is an important item. The closer the slope is to infinity, the narrower the fractional molecular weight distribution which can be regarded as an excellent filter membrane. Ultrafiltration has a wide range of industrial applications in the middle of reverse osmosis and microfiltration in terms of the size of the separation object. The membrane material is the same as the material of the reverse osmosis membrane and has only a large pore size in terms of being hydrophilic [16–18].

Nanofiltration is the process of treating hundreds to thousands of molecules with medium molecular weight, the range of treatment of reverse osmosis membranes and ultrafiltration membranes. Nanofiltration is used for separation of small solvent molecules due to deformation of reverse osmosis membrane, but even large molecules of polysaccharides such as sugar can be separated. Nanofiltration membranes usually have a fractional molecular weight of 20–70% NaCl and organic solvents of 200–500. This fractional range corresponds to a diameter of about 10 Å, or 1 nm, of the molecule. This membrane is used for seawater treatment in the pressure range of 0.4–0.7 MPa which is 1/4–1/2 of the reverse osmosis pressure. The exclusion mechanism is similar to reverse osmosis and is widely applied to the separation of salt and organic matter of appropriate molecular weight. The nanofiltration membranes can be used at a rate of 50–97.5% at the same time and are used to replace the ion exchange method in the water softening process [19–21].

Reverse osmosis is a membrane separation process that separates solutes smaller than 10 Å in size of ions and molecules and was industrialized in seawater desalination and wastewater treatment in the 1970s. The membranes are composed of asymmetric cellulose acetate or aromatic polyamide which is formed as an active layer for a separating effect on the supporting layer. Recently, a composite membrane capable of removing up to 99% of dissolved salts has been developed. The composite membrane is formed of a polymer thin film having a high salt removal effect on the support layer. The support membrane is mainly composed of polysulfone having high mechanical strength and chemical resistance, and cellulose triacetate and cross-linked polyether are mainly used as the separation layer. Since the reverse osmosis membrane has almost no pores, it can be regarded as a nonporous membrane, which is permeated through the gap between micelles forming organic polymers or micelles. In the reverse osmosis method, since the dielectric constant of the organic polymer is low, the dissolved salt is not adsorbed to the membrane. In addition, in high pressure (800–1500 psig), water, which is a solvent, permeates in proportion to the osmotic pressure difference. The separation effect is increased. Since the reverse osmosis is not a separation operation according to the molecular size, deposition of organic substances such as microfiltration and ultrafiltration is less and consequently, the lifetime of the membrane is increased. Reverse osmosis membranes are being used not only for separation and removal of dissolved salts but also for separation of organic and aromatic hydrocarbons with low molecular weight [22–24].

Treatment and the reusing of wastewater are mainly based on the activated sludge process. In the activated sludge process, the amount of generated sludge is large, the treatment cost is high, and it is vulnerable to impacts such as biological oxygen demand (BOD) overload and toxicity, and problems such as sludge bulking occur. However, the membrane bioreactor (MBR) does not need to regulate the amount of microorganisms in the reactor and does not cause the sludge expansion phenomenon. In addition, it has excellent durability against load generated in the operation such as impact, toxicity, and organic load. It is expected that the technology of the MBR process will increase gradually because of the advantages of this separation membrane process [25, 26].

In most of the domestic large and medium-sized water purification facilities, using river water or lake water as a water source, problems occur periodically. However, the conventional water treatment methods such as coagulation, sedimentation, filtration, and disinfection processes are inferior in taste and odor. There is a limit in effectively controlling harmful organic substances and the like. In order to overcome the limitations of this conventional treatment method, microfiltration or ultrafiltration using a membrane has been shown to be a breakthrough technology that can replace the existing rapid sand filtration system because it completely removes turbidity and pathogenic microorganisms. In addition, it can easily combine with the existing unit-altitude water treatment process such as ozone-activated carbon to optimize the process configuration suitable for the characteristics of raw water and water quality, and it is more compact and easier to maintain than the existing water treatment method [27, 28].

Techniques for converting seawater to fresh water include conventional coagulation, coagulation, sedimentation, single- or two-phase granular filtration, dissolved air flotation, and low-pressure membrane filtration techniques using microfiltration or ultrafiltration membranes. Conventional pretreatment processes are generally used in seawater desalination, but it is difficult to completely remove float or colloidal particles, which makes it difficult to supply water in a stable manner. However, when the membrane is pretreated, it has the advantage of reducing the cost required in the desalination process, such as increasing the permeation flow rate, reducing the washing cycle, reducing the use of washing chemicals, reducing energy consumption, and reducing maintenance costs [29, 30].

A membrane electrode assembly (MEA), which is one of the most important components among the separation membranes used in the ion exchange process, includes a proton exchange membrane fuel cell (PEMFC). The membrane consists of two electrodes, cathode and anode, which determine the performance of the fuel cell [31–33]. Currently, the most widely used hydrogen ion exchange membranes are produced by DuPont's nafion® as well as Dow Chemical, 3 M, and others. The perfluorinated proton exchange membrane has been applied to most commercial fuel cell devices due to its high chemical/mechanical stability and excellent hydrogen ion transfer ability. However, since the production process requires high temperature/high pressure conditions, the production cost has increased. The limitation is that it has a pollution problem, and there is a problem that performance is reduced at high temperature due to low glass transition temperature [34, 35]. Therefore, research on the production of a hydrocarbon-based proton exchange membrane having a relatively high manufacturing cost and high thermal stability has been actively pursued as an alternative thereto [36–39].

In this review, the water treatment membranes are divided into wastewater treatment membranes, water treatment membranes, seawater desalination membranes, and ion exchange membrane separators. Through analysis of domestic and foreign patent information and publication of papers, technical trends and recent technology trends, And to analyze the trend of technology development of water treatment membranes by summarized graphs.

2. Analysis of patents and articles on water treatment membranes

In this chapter, we show all patents and papers for water treatment membranes. In the past 20 years (1995–2014), we have divided membranes for wastewater treatment, separation membranes for water treatment, and seawater desalination membrane trends. In evaluating the competitiveness of patent technology, patents filed after 2015 are analyzed only as valid patents before 2015 except for the fact that they were undisclosed. The patent database of WIPS was used for the analysis of the patent. The patent data were searched through the keyword search and the secondary classification was performed using the library method for noise and pattern removal. Finally, a final classification was carried out by experts in each field. The patent activity index (PAI), the patent intensity index (PII), the patent market-power index (PII), the patent market power index (PMI), and patent citation index (PCI) were the categories. These terms can be defined as follows. Patent activity is defined as the absolute number of patent applications based on the number of public/patent publications issued by the Patent Office. Patent concentration refers to providing information about the technological innovation activities that a country concentrates on relative to other countries. The patent market power refers to the use of patents as an indicator of the patentability of patents when the number of family patents is large, because patents are applied only when they are in commercial profit or for technology competition in the relevant country. Finally, patent impact is the measure of the impact of the patent on future patents, and the US patent with patent information for the patents is targeted [40–43].

The number of patent applications has been evaluated in the 10 countries, including Korea, the USA, Japan, China, and Europe, which are the major developing countries, for patent technology competitiveness. A total of 4629 patent applications were searched. 1144 patents were related to separation membranes for wastewater treatment, 734 patents related to water treatment membranes, 668 patents related to seawater desalination membranes, and 2083 patents related to membranes for ion exchange processes. **Figure 4** shows the patent application trends by technology in the last 20 years.

The thesis has been published in the past 20 years (1997–2016), and it has been evaluated for technical competitiveness. 13,506 papers are related to the separation membrane for wastewater treatment, 7958 papers are related to the separation membrane for water treatment, 9524 papers related to separation membrane for desalination, and 16,254 papers related to separation membrane for an ion exchange process. **Figure 5** shows the trend of publications by technology in the past 20 years. The database used to analyze the technological competitiveness of the paper is the Scopus paper retrieval system, which collects information by category and country and uses the Bibliometric Activity Index (BAI), Bibliometric Citation Index (BCI), and Bibliometric Intensity Index (BII). These terms can be defined as follows. The thesis activity is the number of absolute dissertations, which shows the corresponding country for the technology divided by the total number of countries. The impact of a paper is defined as an index that provides information that can be compared with other countries in terms of the quality of the paper. Finally, the thesis density can be defined as an index that provides information on the

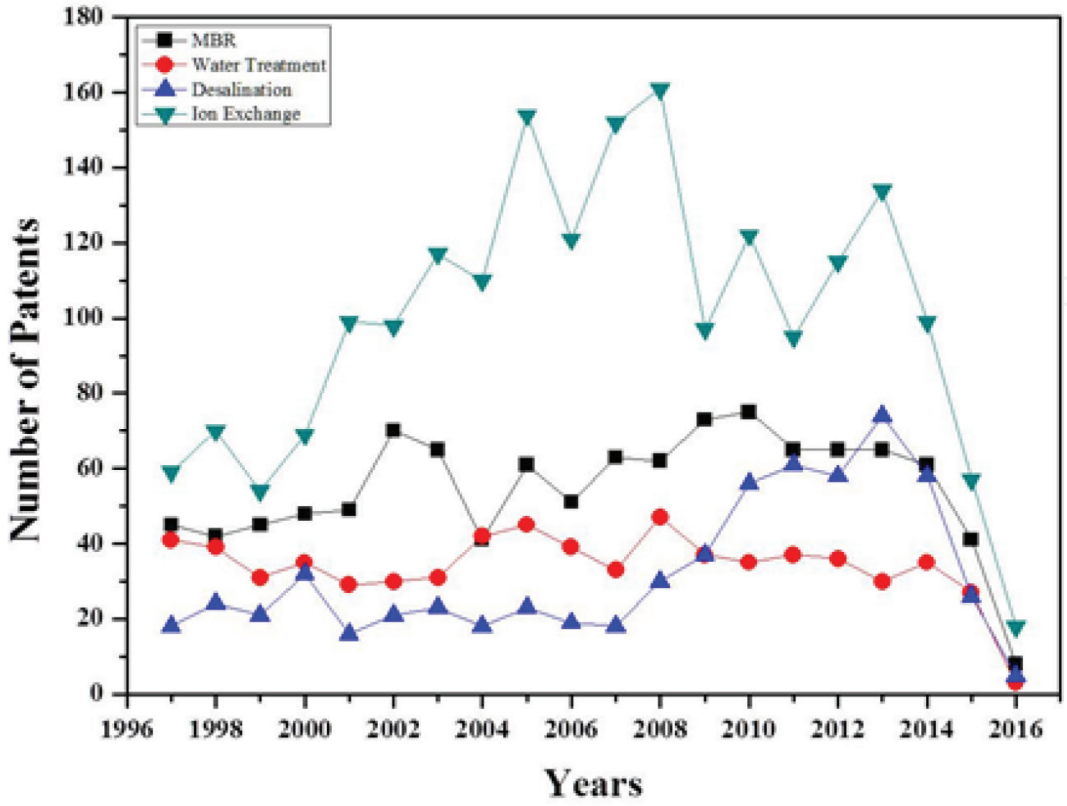

Figure 4. Patent applications 1996–2016 in membrane related technology.

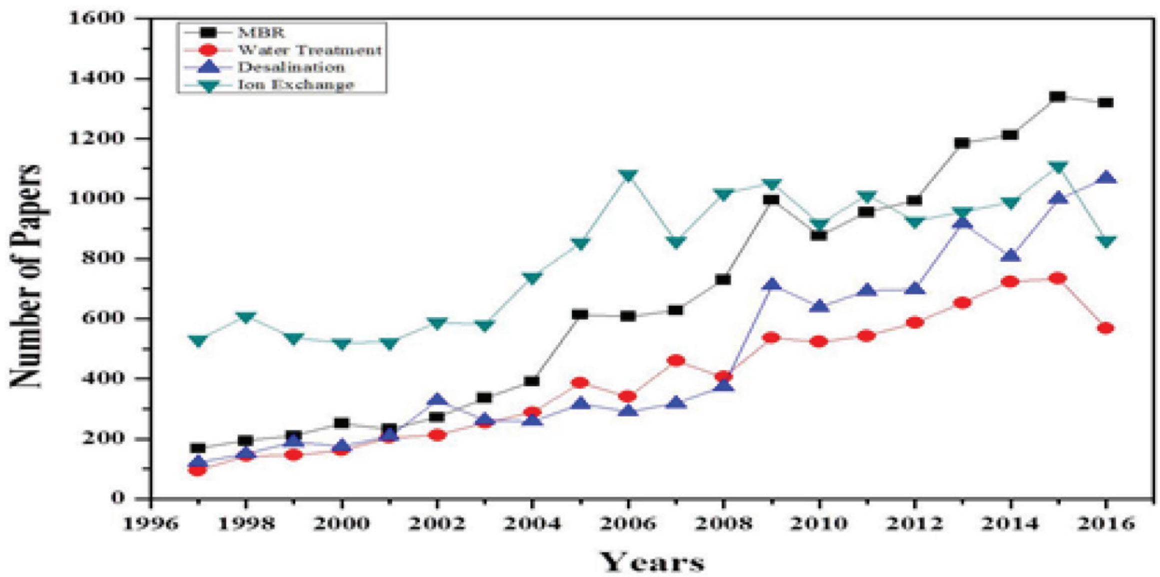

Figure 5. Papers publications 1996–2016 in membrane related technology.

relative concentration of a technological innovation activity in a given technology sector relative to other countries in terms of the number of relative papers published. Major countries participating in the analysis of information are the top 13 countries such as Korea, the USA, Japan, China, and Europe (**Figure 6**).

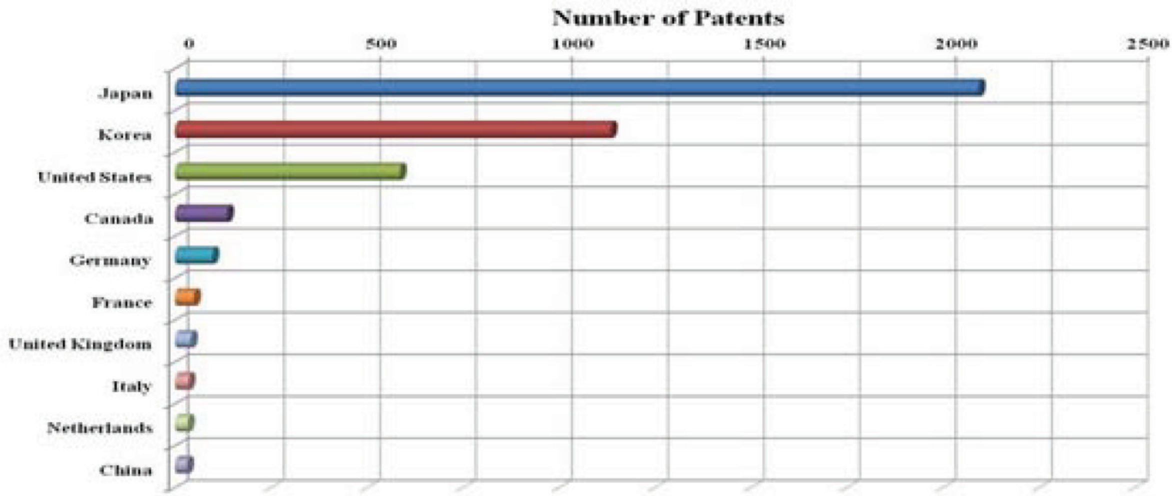

Figure 6. Top countries with the highest number of patent application.

2.1. Evaluation of patent technology competitiveness of water treatment membranes

As a result of analyzing the number of applications for separation membrane-related patents, the following results were obtained: Japan (2093 cases), Korea (1134 cases), the USA (585 cases), Canada (135 cases), Germany (97 cases), France (49 cases), Italy (35 cases), the Netherlands (33 cases), and China (31 cases). As for the patent activities, Japan was overwhelmingly ranked high (0.49), followed by Korea (0.27), the USA (0.14), Canada (0.03), and Germany (0.02). **Table 2** and **Figure 7** show the patents' utilization rate, patent concentration, patent market power, and patent influence by country.

In terms of the degree of patent concentration in each country, Japan tends to concentrate most on water treatment membranes (1.20), Korea on wastewater treatment membranes (1.72), and the USA on ion exchange membranes (1.13)—1.37, 1.39, 1.32, and 1.86 for Canada, Germany, the United Kingdom, and Italy, respectively, for the ion exchange membrane, 1.25 for the wastewater treatment membrane for France and 1.77 and 1.25 for the water treatment membranes.

As a result of analyzing the number of family patents of separation membrane-related patents, the following results were obtained: Japan (5651 cases), the USA (3328 cases), Korea (1743 cases),

Index of evaluation	KR*	JP	US	CA	DE	FR	GB	IT	NL	CN
PAI**	0.27	0.49	0.14	0.03	0.02	0.01	0.01	0.01	0.01	0.01
PII	4.46	3.92	3.76	3.42	3.13	3.59	3.91	2.76	3.85	3.98
PMI	0.46	0.81	1.71	2.02	2.64	2.66	3.12	3.49	2.06	1.23
PCI	0.51	0.50	1.18	1.87	0.67	0.51	1.02	2.40	0.66	0.14

*ISO code: KR, Korea; JP, Japan; US, United States of America; CA, Canada; DE, Germany; FR, France; GB, United Kingdom; IT, Italy; NL, Netherlands; CN, China.

**PAI: Patent Activity Index, PII: Patent Intensity Index, PMI: Patent Market-power Index, PCI: Patent Citation Index.

Table 2. An analysis table about PAI, PII, PMI, and PCI by each country.

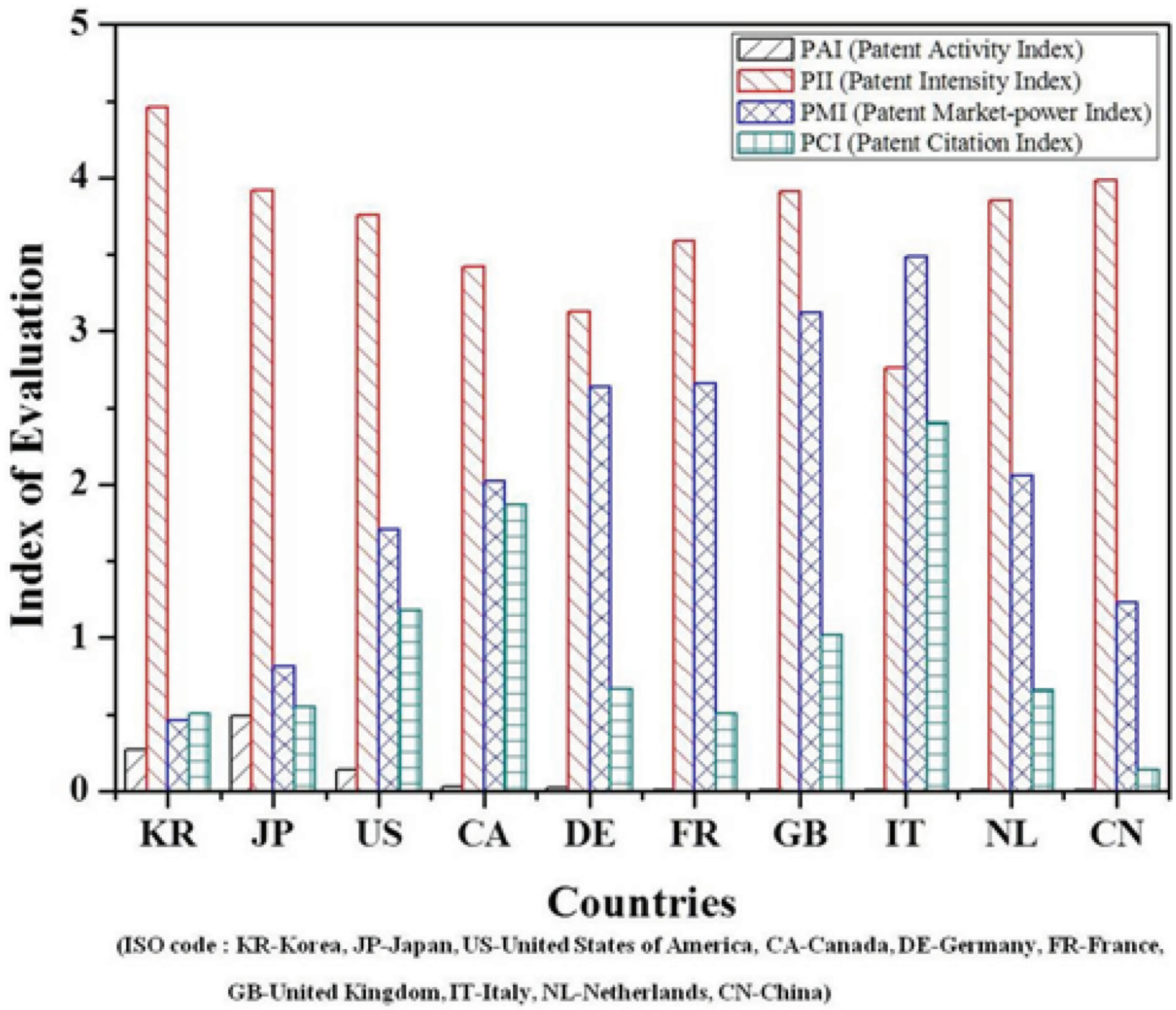

Figure 7. An analysis graph about PAI, PII, PMI, and PCI by each country.

Canada (910 cases), Germany (852 cases), France (426 cases), Italy (407 cases), the Netherlands (226 cases), and China (127 cases). (11.63), Britain (10.39), France (8.86), Germany (8.78), Netherlands (6.85), Canada (6.74), the United States (5.69) and China (4.10), Japan (2.70), and Korea (1.54). The results of this study are as follows: Italy (3.49), Britain (3.12), France (2.66), Germany (2.64), the Netherlands (2.06), Canada (2.02), the USA (1.71) (0.81), followed by Korea (0.46).

As a result, the total number of patents for separator-related patents was derived from the USA (4238 cases), Canada (1537 cases), Japan (979 cases), Germany (267 cases), Italy (163 cases), France (101 cases), the Netherlands (96 cases), and China (11 cases). The number of registered patents related to membranes was 271 in the USA, 147 in Japan, 62 in Canada, 30 in Germany, 26 in Korea, 15 in France, 12 in the UK, (31.86), Canada (24.79), the United States (15.64), and the United States (15.64), followed by the United States), Britain (13.58), Germany (8.90), Netherlands (8.73), Korea and France (6.73), Japan (6.66) and China (1.83). The results of this study are as follows: Italy (2.40), Canada (1.87), the USA (1.18), the UK (1.02), Germany (0.67), the Netherlands (0.66), Korea and France (0.51), and China (0.14). Among them, Korea ranked 2nd place in patent activity, 10th place in patent market power, and 7th place in patent efficacy, and patent concentration tended to be concentrated on wastewater treatment membrane (1.72) (**Figure 8**).

2.2. Evaluation of technology competitiveness of water treatment membranes

As a result of analyzing the number of published papers related to membranes, the results obtained were as follows: the USA (11,435), China (9235), Japan (3183), Korea (3013), Germany (3005), Canada (2370), the United Kingdom (2312), Spain (2296), Australia (2260), Italy (1710), and the Netherlands (1422). Therefore, in the activity of the thesis, the USA (0.24) was the highest, followed by China (0.20), Japan (0.07), Korea (0.06), and Germany (0.06). **Table 3** and **Figure 9** show the activities of each country, the influence of the thesis, and the concentration of the thesis.

As a result, the total number of citations for the membrane-related papers was found to be 351,996 in the US, 125,276 in China, 84,777 in Japan, 69,354 in Japan, 66,727 in the UK, 66,492 in Canada, (66,239), Australia (61,057), Korea (60,156), Netherlands (43,128), Spain (41,663), Italy (41,281) and India (40,121), Followed by the United States (0.31), China (0.11), Germany (0.08), Japan / France / Canada / Britain (0.6).

According to the concentration of each country, the USA tends to concentrate the most in the ion exchange process membrane (1.15), China in the wastewater treatment membrane (1.36), and Korea in the seawater desalination membrane (1.19). China, Spain, and Italy are the most

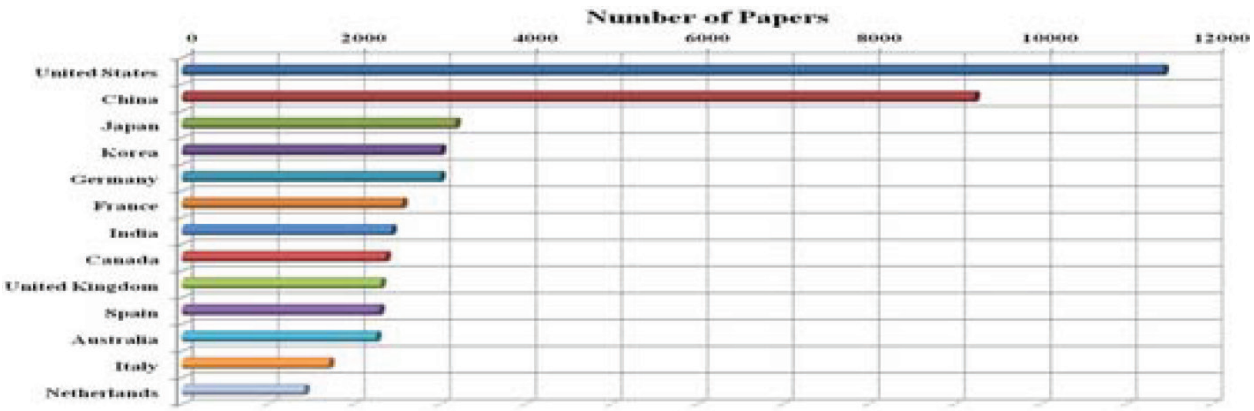

Figure 8. Top countries with the highest number of paper publications.

Index of evaluation	KR*	JP	US	CA	DE	FR	GB	IT	NL	CN	IN	CA	ES
BAI**	0.06	0.07	0.24	0.05	0.06	0.05	0.05	0.04	0.03	0.2	0.05	0.05	0.05
BCI	4.03	3.8	4.02	3.91	4.04	3.99	3.98	3.95	4.21	3.94	4.02	3.91	4.06
BII	0.05	0.06	0.31	0.06	0.08	0.06	0.06	0.04	0.04	0.11	0.04	0.06	0.04

*ISO code: KR, Korea; JP, Japan; US, United States of America; CA, Canada; DE, Germany; FR, France; GB, United Kingdom; IT, Italy; NL, Netherlands; CN, China; IN, India; CA, Canada; ES, Spain.

**BAI: Bibliometric Activity Index, BCI: Bibliometric Citation Index, BII: Bibliometric Intensity Index.

Table 3. An analysis table about BAI, BII, and BCI by each country.

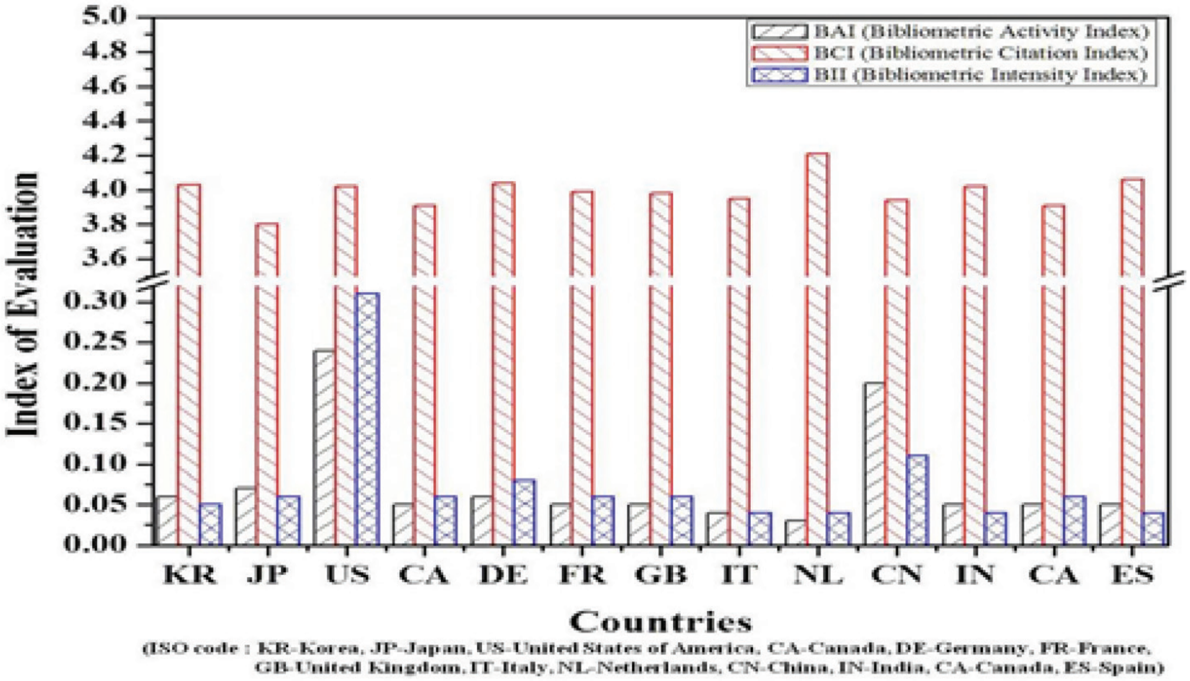

Figure 9. An analysis graph about BAI, BII, and BCI by each country.

important for separating membranes for wastewater treatment, Germany for water treatment membranes, Korea, India, the UK, Australia, and the Netherlands for seawater desalination membranes, USA, Japan, And the researcher.

3. Analysis of patent applicants and papers published by technology

In this chapter, we analyzed the top applicants and papers published by each technology and each classification (separation membranes for wastewater treatment, purification membranes for water treatment, separators for seawater desalination, and separation membranes for ion exchange processes). In the case of patents, applicants from all countries are categorized as applicants according to the section. The applicants are divided into three sections (1995–1999), two sections (2000–2004), three sections (2005–2009) (1997 ~ 2001), two sections (2002 ~ 2006), three sections (2007 ~ 2001), and three sections (2011 ~ 2016), and the changes in the top 13 countries were confirmed.

Looking at the top applicants by overall technology, although the overall strength of Japan can be seen, the number of Korean applicants for technology is gradually increasing (Korea Institute of Energy Research, Woongjin Chemical, LG Chem).

Toray Industries, Japan, ranked second place (31), second place (43), second place (43), and third place (48) (53 cases).

In the case of the thesis, if we look at the top publishing countries by overall technology, the overall strength of the USA is strong, but China and Korea are showing a sharp rise, and Japan is steadily declining. In Korea, it is ranked 13th place (130 cases) in one section, 7th place (538 cases) in two sections, 5th place (890 cases) in three sections, and 3rd place (1455 cases) in four sections.

Figures 10 and **11** and **Tables 4** and **5** show the top patent applicants and top papers published by technology in the last 10 years.

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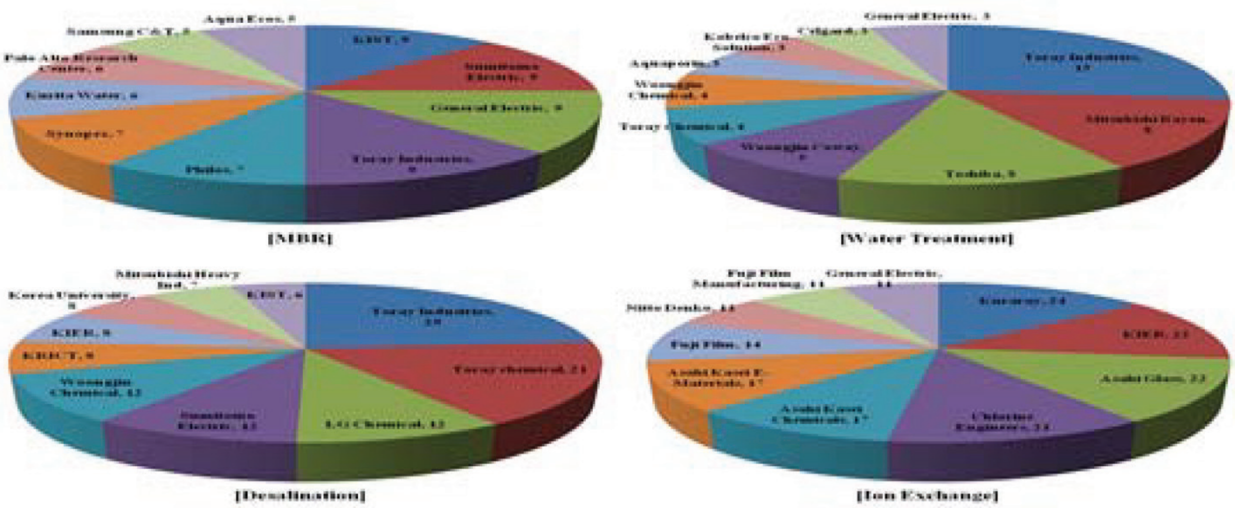

Figure 10. Comparison of total number of patent applications of global company in field of different membrane technology between the periods 2006 and 2016.

3.1. Top applicant and posting office of separation membranes for wastewater treatment

Japan is the main applicant of the separation membranes for wastewater treatment. In Korea, the rankings are gradually increasing over time. (Korea Institute of Science and Technology, Korea Advanced Institute of Science and Technology, Woongjin Chemical), 4 (Korea Institute of Science and Technology), 2 (Korea Institute of Science and Technology, Phylos, Sinopec, and Samsung C & T). Among them, Korea Institute of Science and Technology (KIST) ranked eighth place (4 cases) in two sections, third place (7 cases) in three sections, and first place (9 cases) in four sections.

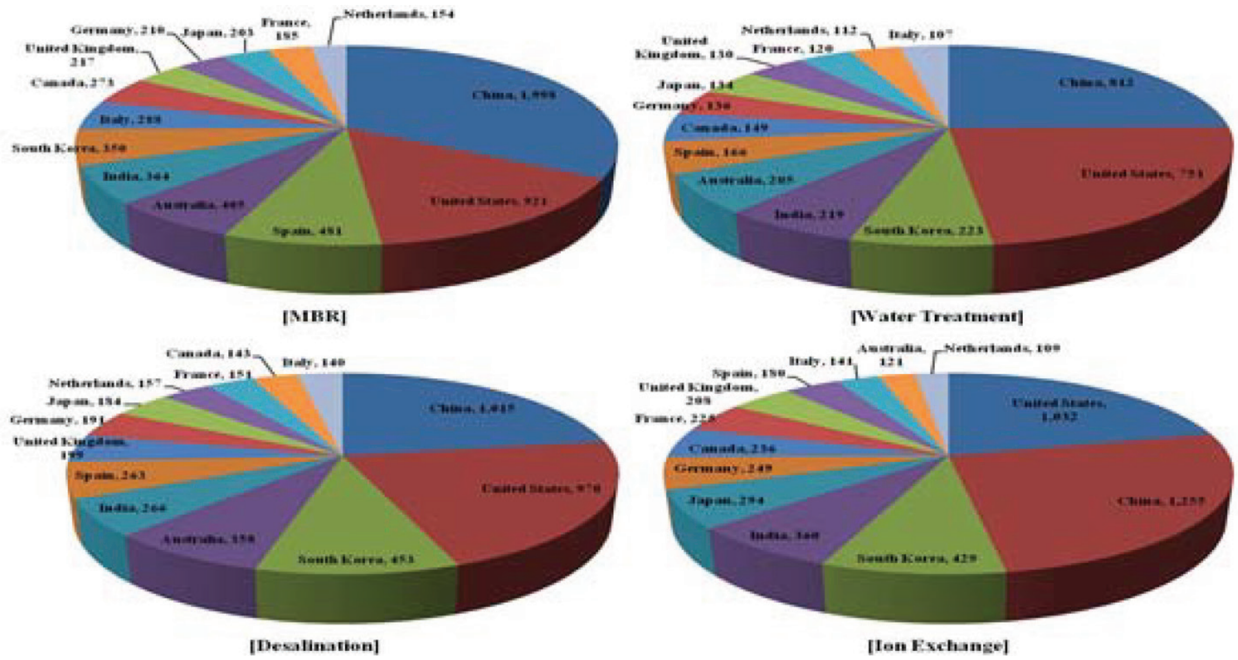

Figure 11. Comparison of total number of papers publications of global company in field of different membrane technology between the periods 2006 and 2016.

In the case of the top publishing countries, the USA is strong overall, but China has steadily climbed to the top of the four sections, and Japan is steadily declining. In Korea, Korea ranked eighth place (46 cases) in the first section, fourth place (179 cases) in the second section, sixth place (236 cases) in the third section, and sixth place (350 cases) in the fourth section.

3.2. Top applicants and posting authorities for separation membrane for water treatment

The top applicants of water treatment membranes are generally Japan, but in Canada and the UK in the second section, in Korea in the third section and in Korea and the United States and Denmark in the fourth section, It can be seen that patent applications are increasingly being made in various countries. Toray Industries in Japan has filed more than 10 patents in all segments and continues to apply for patents related to separation membranes for water treatment. The Korean applicant has applied for Woongjin Coway (fourth place, 6 cases) in three sections, Woongjin Coway (fourth place, 5 cases) and Woongjin Chemical (sixth place, 4 cases) Can be.

In the case of the top publishing countries, the overall strength of the USA is strong, but China and Korea have shown a sharp rise, and Japan is showing a steady decline. In Korea, there are 12 (17 cases), 1 (5 cases), 3 (7 cases), and 3 (223 cases).

3.3. Top applicant and posting office of seawater desalination membrane

The top applicant for seawater desalination membranes is Toray Industries, Japan, which has filed more than 10 applications in all segments, showing continuous applications for membrane-related desalination membranes. There are four applicants from Korea (Saehan), two from two sections (Saehan and KEPCO), four from three sections (Gwangju Institute of Science and Technology, Woongjin Chemical, Siontech and Hyosung) (LG Chem, Woongjin Chemical, Korea Research Institute of Chemical Technology, Korea Institute of Energy Research, Korea University, Korea Institute of Science and Technology).

In the case of the top publishing countries, the overall strength of the USA is strong but China and Korea have shown a sharp rise and Japan is showing a steady decline. Korea ranked 13th place (14 cases) in the first section, 13th place (53 cases) in the second section, 3rd place (203 cases) in the third section, and 3rd place (453 cases) in the fourth section.

3.4. Top applicant and posting office for separation membranes for ion exchange processes

Asahi Glass is ranked first place in the first section (28 cases), first place in the second section (41 cases), first place in the third section (76 cases) (22 cases), showing a slight decline. In addition, Chlorine Engineers ranked sixth (8 cases) in one section, fourth place (19 cases) in two sections, fifth place (19 cases) in three sections, and fourth place (21 cases) in four sections. The application rose steadily. 1 in the three sections (Samsung SDI) and one in four sections (Korea Institute of Energy Research) in the ion exchange process.

In the case of top publishing countries, the USA has shown a decline but China and Korea have shown a sharp rise. Korea ranked 13th place (53 cases) in the first section, 7th place (207

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Ranking	MBR			Water treatment			Desalination			Ion exchange		
	Company	Country	Number	Company	Country	Number	Company	Country	Number	Company	Country	Number
1	KIST	KR	9	Toray Industries	JP	15	Toray Industries	JP	29	Kuraray	JP	24
2	Sumitomo Electric	JP	9	Mitsubishi Rayon	JP	8	Toray chemical	JP	21	KIER	KR	22
3	General Electric	US	9	Toshiba	JP	8	LG Chemical	KR	12	Asahi Glass	JP	22
4	Toray Industries	JP	9	Woongjin Coway	KR	5	Sumitomo Electric	JP	12	Chlorine Engineers	JP	21
5	Philos	KR	7	Toray Chemical	JP	4	Woongjin Chemical	KR	12	Asahi Kasei Chemicals	JP	17
6	Synopex	KR	7	Woongjin Chemical	KR	4	KRICT	KR	8	Asahi Kasei E-Materials	JP	17
7	Kurita Water	JP	6	Aquaporin	DK	3	KIER	KR	8	Fuji Film	JP	14
8	Palo Alto Research	US	6	Kobelco Eco-Solution	JP	3	Korea University	KR	8	Nitto Denko	JP	11
9	Samsung C&T	KR	5	Celgard	US	3	Mitsubishi Heavy Ind	JP	7	Fuji Film Manufacturing	NL	11
10	Aqua Ecos	JP	5	General Electric	US	3	KIST	KR	6	General Electric	US	11

ISO code: KR, Korea; JP, Japan; US, United States of America; DK, Denmark; NL, Netherlands.

Table 4. Patent application company by each technology (past 10 years).

Ranking	MBR		Water treatment		Desalination		Ion exchange	
	Country	Number	Country	Number	Country	Number	Country	Number
1	China	1998	China	812	China	1015	United States	1032
2	United States	921	United States	751	United States	970	China	1255
3	Spain	481	South Korea	223	South Korea	453	South Korea	429
4	Australia	405	India	219	Australia	358	India	360
5	India	364	Australia	205	India	266	Japan	294
6	South Korea	350	Spain	166	Spain	263	Germany	249
7	Italy	288	Canada	149	United Kingdom	199	Canada	236
8	Canada	273	Germany	136	Germany	191	France	225
9	United Kingdom	217	Japan	134	Japan	184	United Kingdom	208
10	Germany	210	United Kingdom	130	Netherlands	157	Spain	180
11	Japan	203	France	120	France	151	Italy	141
12	France	185	Netherlands	112	Canada	143	Australia	121
13	Netherlands	154	Italy	107	Italy	140	Netherlands	109

Table 5. Papers application country by each technology (past 10 years).

cases) in the second section, 4th place (325 cases) in the third section, and 4th place (429 cases) in the fourth section.

4. Conclusion

The purpose of this review is to examine the progress of research on the water treatment membranes of each country by evaluating the technical competitiveness of the patent and thesis of the water treatment membranes. In order to evaluate the competitiveness of patent technology, we analyzed the technology using four evaluation items: patent activity, patent concentration, patent market power, and patent influence. Of the 4433 valid patents searched for in relation to water treatment membrane technology, Korea, which belongs to the top 10 countries, ranked second place in patent activity, 10th place in patent market power, and 7th place in patent efficacy, indicating a concentration tendency. As a result of analyzing the top applicants by technology and section, it is found that Japan is much stronger overall, among which Toray Industries, Nitto Denko, and Asahi Glass are among the top applicants. In recent years, however, applications have been actively being made in Korea, such as Korea Institute of Energy Research, Korea Institute of Science and Technology, and Saehan. In addition, some applications related to the technology have appeared in other countries such as the USA and Canada. The competitiveness of patent technology in Korea can be relatively low compared to Japan in relation to technology, but if the trend is steadily rising in the recent years, the competitiveness of patent technology in Korea will sufficiently increase in future.

In case of publishing the thesis, we analyzed the technical competitiveness of the thesis on the related technology by using three evaluation items, thesis activity, thesis influence, and thesis concentration. Among the 47,242 validated papers related to water treatment membrane technologies, Korea ranked among the top 13 countries in terms of thesis activities and ninth in terms of thesis influence, and the concentration of thesis was mostly on seawater desalination membranes (1.19). As a result of analyzing the top ranking countries by technology and sector, overall, the USA has shown stronger strength; China and Korea are rising sharply, and Japan has shown a declining trend. The technology competitiveness in Korea can be relatively low compared to the developed countries in the related technology, but if the trend is steadily rising in the recent years, the competitiveness of paper technology in Korea will sufficiently increase in future.

When the patent application and the publication of the papers are comprehensively judged, the activities of patents and theses are actively carried out, but the qualitative level (market power, influence, concentration) is lower than those of the competitors. Among the four water treatment membrane technologies, Ion Exchange Membrane has the highest concentration of patents, of 0.57, the lowest among the top 10 countries, and its market power and influence remain low. The results of the papers showed a similar tendency as the patent applications. Though the activities of the thesis were recorded in the top 13 of the top applications, the influence of the quality of the thesis was recorded at the lowest level (ninth place). Particularly, in the case of the Republic of Korea, the separation membrane for ion exchange process among the four water treatment membrane technologies has the highest activity rate but the least influence. This is considered to be a result of the high price formation, low durability, commercialization technology, and the formation of a supply system in the ion exchange membrane for the ion exchange process in the domestic market. In order to solve this problem (solar, wind, geothermal, etc.), technological internalization through technological advancement, as well as a system that can secure economic efficiency, is important. In addition, it is necessary to develop pro-market-type products suitable for demand sites such as urban areas and industrial complexes that can respond to the increase in social demand for greenhouse gas reduction and stability of the metropolitan area system. It is necessary to utilize it as a strategy to cope with climate change and power plants and to utilize renewable energy in the medium and long term. Will gradually increase..

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