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The Effect of Membrane Material and Surface Pore Size on the Fouling Properties of Submerged Membranes

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Abstract: We aimed to investigate the relationship between membrane material and the development of membrane fouling in a membrane bioreactor (MBR) using membranes with different pore sizes and hydrophilicities. Batch filtration tests were performed using submerged single hollow fiber membrane ultrafiltration (UF) modules with different polymeric membrane materials including cellulose acetate (CA), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) with activated sludge taken from a municipal wastewater treatment plant. The three UF hollow fiber membranes were prepared by a non-solvent-induced phase separation method and had similar water permeabilities and pore sizes. The results revealed that transmembrane pressure (TMP) increased more sharply for the hydrophobic PVDF membrane than for the hydrophilic CA membrane in batch filtration tests, even when membranes with similar permeabilities and pore sizes were used. PVDF hollow fiber membranes with smaller pores had greater fouling propensity than those with larger pores. In contrast, CA hollow fiber membranes showed good mitigation of membrane fouling regardless of pore size. The results obtained in this study suggest that the surface hydrophilicity and pore size of UF membranes clearly affect the fouling properties in MBR operation when using activated sludge.

Keywords: membrane bioreactor (MBR); membrane fouling; hollow fiber membrane; hydrophilicity; hydrophobicity; wastewater treatment

1. Introduction

Membrane bioreactors (MBRs) are a new technology that combines several typical operations (primary sedimentation, activated sludge aeration and sedimentation, and tertiary media filtration) into a single treatment step [1]. MBR has excellent potential for use in a wide range of applications including municipal and industrial wastewater treatment, solid waste digestion, and odor control. Moreover, this technology has many attractive advantages over conventional wastewater treatment processes due to its small footprint, high effluent quality, high volumetric loading, and reduced sludge production [2].

Membranes (flat sheets and hollow fibers) and membrane systems for MBRs are mainly produced by Japanese manufacturers such as Kubota, Tory, Asahi Kasei, and Mitsubishi-Rayon and North American companies such as GE and Koch Membrane Systems. Hollow fibers are mostly used in large plants (>10,000 m^3/d) because of their high surface areas and excellent mass transfer properties, while flat sheet membranes are employed for small plants (<5000 m^3/d). Thus, the use of hollow fiber membranes in MBR processes has grown recently [3,4].

For these reasons, the use of MBRs for research, technology, and commercial applications is rapidly advancing across the world. The global MBR market had an estimated value of around US $425.7 million in 2014, and the market is rising at a compound annual growth rate (CAGR) of 13.2% and is expected to reach US $777.7 million by 2019, while the Asia-Pacific market segment reached US $121.5 million in 2014 and should reach US $270.6 million by 2019, with a CAGR of 17.4% between 2014 and 2019 [5]. It can be seen that MBR technology has shown remarkable growth in the Asia-Pacific region, including Japan. However, membrane fouling is a major hindrance to the wider application of MBRs as it results in a sharp decrease in the quantity of produced water, as well as an increase in the energy demand and transmembrane pressure (TMP) [6].

Up to now, many studies on membrane fouling in MBR processes have focused on sludge characteristics, such as mixed liquor suspended solids (MLSS) and extracellular polymeric substances (EPS) [6–9]. Additionally, MBR fouling is affected by operating parameters such as solids retention time (SRT), hydraulic retention time (HRT), dissolved oxygen (DO), food-to-microorganism ratio (F/M), and permeate flux [9–11]. These parameters can indirectly affect membrane fouling by altering the sludge properties [6]. Various methods have been proposed to reduce membrane fouling in MBRs, including chemical and physical cleaning, the use of different membrane geometries (e.g., flat sheet, hollow fiber, and tubular membranes), effective membrane module and reactor design (e.g., membrane packing density and aerator position), membrane surface modification (e.g., hydrophilicity and roughness), and biological antifouling strategies such as quorum quenching and enzymatic disruption [12]. Among these strategies, membrane geometry and surface modification to reduce biofouling have attracted much attention [13,14]. In particular, membrane characteristics, such as membrane material, pore size, and hydrophilicity are important factors for membrane fouling because they affect interactions between the membrane surface and the mixed liquor in the bioreactor. It is believed that hydrophilic membranes allow greater membrane fouling mitigation than do hydrophobic membranes [15,16]. However, contradictory results have been reported. For example, Matar et al. [17] studied the effect of hydrophobic and hydrophilic membrane surfaces in MBR, and their results showed that fouling behavior in MBR processes are much less dependent on hydrophilicity than previously thought. Choi et al. [18] reported that pore structure had a greater influence on the development of membrane fouling than the hydrophilicity of the membrane surface. As such, it is still debatable whether or not the hydrophilicity of the membrane affects membrane fouling mitigation. In our previous work, we reported the effect of different polymeric membrane materials (polyvinylidene fluoride (PVDF), cellulose acetate butyrate (CAB), and polyvinyl butyral (PVB)) on the relationship between membrane pore size and the development of membrane fouling in a MBR. The membrane fouling of a PVDF hollow fiber membrane decreased as the membrane pore size increased, whereas CAB membranes with smaller pores showed less fouling than those with larger ones [19].

The effects of membrane hydrophilicity on fouling claimed in the reported papers are summarized in Table 1. The objective of this study is to assess the role of membrane surface hydrophilicity and surface pore size in MBR systems. Many research groups have investigated the development of fouling on the surface of microfiltration (MF) membranes, as shown in Table 1. In our study, we fabricated ultrafiltration (UF) hollow fiber membranes with various pore sizes using three different membrane polymeric materials: PVDF, polyether sulfone (PES), and cellulose acetate (CA). The development of membrane fouling on each membrane was investigated by batch filtration testing with activated sludge using a laboratory-scale MBR.

Table 1. Membrane properties used in previous work and claims regarding the effect of membrane surface hydrophilicity on fouling.

Membrane Material	Average Pore Size (μm)	Hydrophilicity	Configuration	Affected by Hydrophilicity	References
PVDF	0.047	Hydrophobic	Flat sheet	Yes	[30]
PVDF/PMMA-g-PEG	0.053–0.089	Hydrophilic			
PVDF	0.02–0.3	Hydrophobic	Flat sheet	No	[28]
PE	0.3	Hydrophilic			
PC	0.1–2.5	Hydrophilic			
PETE	0.1	Hydrophobic	Flat sheet	No	[18]
PCTE	0.1	Hydrophobic			
PTFE	0.1	Hydrophobic			
PVDF	0.08	Hydrophobic	Flat sheet	Yes	[31]
PTFE	0.3	Hydrophobic			
PTFE	0.3	Hydrophilic			
PVDF	0.02–0.4	Hydrophobic	Hollow fiber	No	[19]
PVB	0.02–0.15	Hydrophobic			
CAB	0.04–0.2	Hydrophilic			
PVDF	0.02–0.09	Hydrophobic	Hollow fiber	Yes	This work
PES	0.03–0.14	Hydrophobic			
CA	0.03–0.09	Hydrophilic			

2. Materials and Methods

2.1. Materials

CA (Mw = 30,000, Sigma-Aldrich, St. Louis, MO, USA), PES (Mw = 65,000, Ultrason®E6020P, BASF, Tokyo, Japan), and PVDF (Mw = 322,000, SOLEF6020, Solvay, Japan) were used as polymeric membrane materials. Dimethylacetamide (DMAc) and lithium chloride (LiCl) were purchased from Wako Pure Chemical Industries. Polystyrene latex particles with diameters of 20, 50, 100, and 200 nm were purchased from Duke Scientific Corporation (Palo Alto, CA, USA). A LIVE/DEAD BacLight Bacterial Viability kit was purchased from Thermo Fisher Scientific (Waltham, MA, USA) and used to stain bacteria. A Pierce BCA Protein Assay kit was purchased from Thermo Scientific. Deionized water (18.2 MΩ cm, Merck Millipore, Billerica, MA, USA) was used to prepare all aqueous solutions and for rinsing. All chemicals were used without further purification.

2.2. Hollow Fiber Membrane Preparation

Hollow fiber membranes were prepared using a batch-type wet spinning machine via non-solvent induced phase separation (NIPS) [20]. The preparation conditions are summarized in Table 2. CA and DMAc were mixed for 12 h at 25 °C, and then left in the solution tank for 2 h to remove air bubbles. Hollow fibers were extruded from a spinneret with inner and outer tube diameters of 0.8 and 2 mm, respectively. Eventually, they were transferred into a coagulation bath, which induced phase separation and caused membrane formation, and the membrane was wound on a take-up winder. The prepared hollow fiber membranes were kept in pure water until they were characterized. PES and PVDF membranes were prepared in the same way.

Table 2. Preparation conditions for hollow fiber membranes.

| Material	CA			PES			PVDF		
Pore size	<10–30 nm	<50 nm	<90 nm	<10–30 nm	<50 nm	<140 nm	<10–20 nm	<40 nm	<90 nm
Polymer solution	CA-DMAc			PES-DMAc		PES-DMAc 4 wt % water	PVDF-DMAc	PVDF-DMAc 4 wt % LiCl	PVDF-DMAc 4 wt % LiCl-2 wt % water
Polymer concentration (wt %)	22	20	16	16	14	14	14	14	14
Solution temperature (°C)	Room temperature			Room temperature			Room temperature		
Polymer solution flow rate (g/min)	3.8	2.08	4.0	2.78	4.2	1.92	2.78	4.2	1.92
Inner coagulant (DMAc:Water)	8:2	6:4	6:4	6:4	6:4	6:4	6:4	6:4	6:4
Inner coagulant flow rate (g/min)	2.96	3.5	2.96	3.49	3.42	3.05	3.49	3.42	3.05
Air gap (mm)	60	50	50	25	25	60	25	25	60
Take-up speed (m/s)	0.034	0.025	0.046	0.024	0.03	0.027	0.024	0.03	0.027

2.3. Air Bubble Contact Angle Measurement

The air bubble contact angle of each membrane was measured using a contact angle goniometer (Drop Master 300, Kyowa Interface Science Co., Saitama, Japan). A sample was placed in a glass cell filled with deionized water, an air bubble (1 µL) was then released below the sample, and the contact angle between the air bubble, and the surface was measured automatically upon contact [21].

2.4. Polystyrene Particle Rejection Test

To estimate the pore sizes of the membranes, a polystyrene particle rejection experiment was performed using the cross-flow method with a single hollow fiber membrane. The polystyrene particles were monodispersed polystyrene latex particles with diameters of 20, 50, 100, and 200 nm. The feed solution was prepared by adding the latex particles to an aqueous nonionic surfactant (0.1 wt %, Triton X-100), which was forced to permeate through the membrane at a pressure of 0.05 MPa. The polystyrene particle concentrations of the feed and the filtrate were measured using a UV-Vis spectrophotometer (U-2000, Hitachi Co., Tokyo, Japan) at a wavelength of 385 nm. Particle rejection was calculated using the following equation: $R (\%) = (1 − C_P/C_f) \times 100$. Here, R was the rejection, and C_P and C_f were the polystyrene particle concentrations of the permeate and the feed, respectively. We used the particle diameter when the rejection was 90% as the pore size of each membrane.

2.5. Batch Filtration Test Using Single Membrane Module

Batch filtration tests were conducted to understand the fouling propensity and flux behavior of the membranes in a laboratory-scale MBR. A schematic diagram of the experimental apparatus is shown in Figure 1. Single membrane modules with a membrane fiber length of 7 cm were prepared using CA, PES, and PVDF hollow fiber membranes. The single membrane modules were installed in a small filtration apparatus with an effective volume of approximately 120 mL. The inside of the filtration apparatus was filled with wastewater supplied by the Shizuoka Prefecture industrial wastewater treatment plant in Japan. The membrane modules were operated under a constant flux of 0.23 m³/m²/day. The MLSS, polysaccharide, and protein concentrations were approximately 4000 mg/L, 14 mg/L, and 150 mg/L, respectively, while the SRT was set and maintained at 15 days. An aqueous solution of 0.85 wt % NaCl was fed into the reactor to prevent concentration of the MLSS. The batch filtration tests were carried out using raw activated sludge without treatment. A detailed procedure has been reported in our previous research [19].
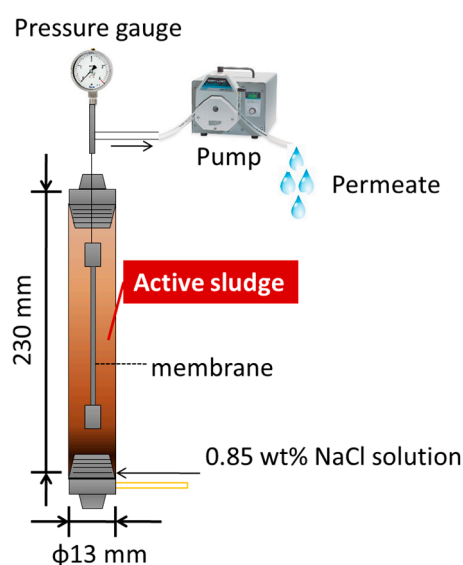
Figure 1. Schematic diagram of the experimental apparatus used in lab-scale batch filtration test.

2.6. Membrane Morphology Observations

A field emission scanning electron microscope (FE-SEM) (JSF-7500F, JEOL Co. Ltd., Akishima, Japan) was used to observe the surface morphology of the membranes. The membranes were fractured into small pieces in liquid nitrogen and then dried overnight in a freeze dryer (FDU-1200 EYELA, Tokyo Rikakikai Co. Ltd, Tokyo, Japan). The dried samples were coated with osmium tetroxide (OsO_4) prior to SEM analysis in order to minimize sample damage due to the electron beam and to obtain clear images.

2.7. Microbial Floc Attachment Test

To evaluate the propensity of microbial flocs to attach to the surface of each membrane, batch attachment tests were carried out. Thin films (thickness: 500 μm) without any pores were prepared by casting films of CA, PES, and PVDF with an applicator and drying them. The films were soaked in 10 mL of a mixed liquor suspension for 1 h, and then rinsed with a pre-sterilized 0.85 wt % aqueous solution of NaCl to remove any suspended solids that had accumulated on the film surface. After that, the bacteria attached to the film surface were stained with a LIVE/DEAD BacLight Bacterial Viability Kit (Life Technologies, Carlsbad, CA, USA). The stained films were then observed using a confocal laser scanning microscope (CLSM, FV1000D, Olympus, Tokyo, Japan) at pH 7.0.

3. Results and Discussion

3.1. Properties of Hollow Fiber Membranes

Figure 2 shows SEM images of CA, PES, and PVDF hollow fiber membranes prepared using the NIPS process. As shown in Figure 2b, skin layers formed on the outer surfaces of the CA, PES, and PVDF hollow fiber membranes, while the cross-sections shown in Figure 2a indicate that macrovoid structures formed in all the membranes. These macrovoids are typical structures for membranes prepared via NIPS [22]. The three hollow fiber membranes had pores on the inner surfaces, as shown in Figure 2c. Thus, these hollow fiber membranes had asymmetric structures. The pure water permeabilities of the three membranes are shown in Table 3, with CA, PES, and PVDF hollow fiber membranes showing water permeabilities at one bar of 215, 331, and 233 LMH, respectively. Thus, the water permeability properties of the three membranes were similar.
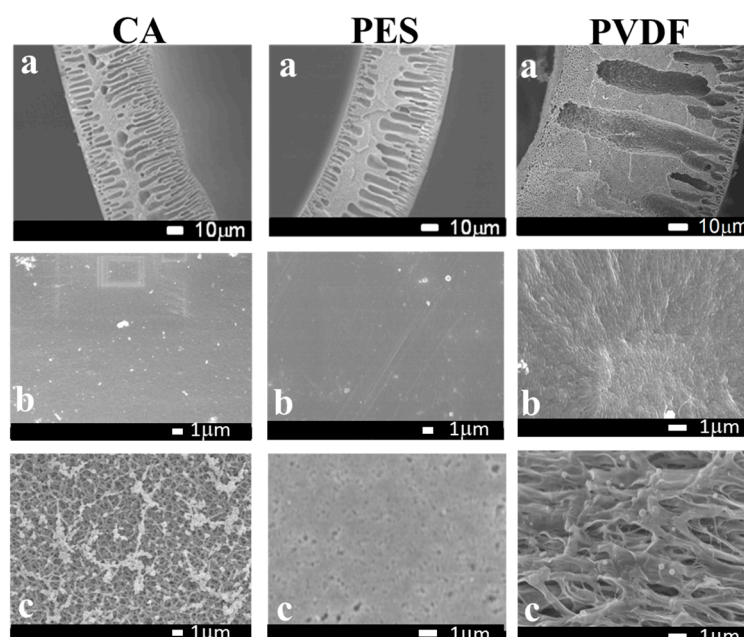

Figure 2. SEM images of cellulose acetate (CA) (30 nm), polyethersulfone (PES) (30 nm), and polyvinylidene fluoride (PVDF) (20 nm) hollow fiber ultrafiltration membranes: (**a**) cross-sections; (**b**) outer surfaces; (**c**) inner surfaces.

Table 3. Properties of CA, PES, and PVDF hollow fiber membranes.

| Membrane	CA	PES	PVDF
Pure water permeability (L/m²·h·bar)	215 ± 7	331 ± 22	233 ± 71
Mean pore size (nm)	<10–30	<10–30	<10–20
Air bubble contact angle (°)	121	115	94

The rejection properties of the prepared hollow fiber membranes were evaluated using polystyrene latex particles with diameters of 20, 50, 100, and 200 nm. Figure 3 shows the polystyrene particle rejection curves for the hollow fiber membranes. All three membranes showed similar rejection tendencies, and high rejections were obtained even for 30 nm polystyrene latex particles. Therefore, these membranes were classified as UF membranes. According to the criteria used, the CA, PES, and PVDF hollow fiber membranes showed mean pore sizes of <30, <30, and <20 nm, approximately, respectively. These three membranes with similar water permeabilities and pore sizes were used for the following fouling filtration tests.
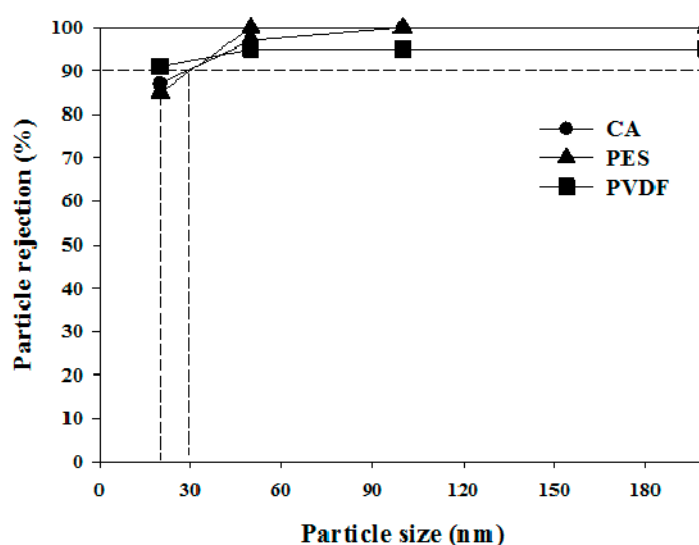
Figure 3. Polystyrene particle rejection results for the prepared membranes.

3.2. Fouling Behavior in Batch Filtration Tests

As mentioned in the introduction, whether or not the membrane hydrophilicity affects the mitigation of membrane fouling is still open for debate. In many cases, membranes with different hydrophilicities, water permeabilities, and pore sizes were used for the comparison of fouling properties. Since the water permeability and pore size can also affect the fouling properties, membranes with similar water permeabilities and pore sizes must be used to more accurately examine the effect of membrane hydrophilicity. In this work, three types of hollow fiber membranes (CA, PES, and PVDF) with similar water permeabilities and pore sizes were used to evaluate the effect of material hydrophilicity. The air contact angles of CA, PES, and PVDF were 121°, 115°, and 94°, respectively (Table 3). Thus, the hydrophilicities of the materials increase in the order CA > PES > PVDF. Figure 4 shows the membrane fouling results obtained for the three membranes used for MBR water treatment of raw activated sludge. When using the CA membrane, TMP was almost constant and was below 5 kPa throughout the test. On the other hand, the development of membrane fouling with the PES and PVDF membranes increased remarkably. After 60 min, the TMPs decreased in the order of PVDF > PES > CA, which is in agreement with the hydrophobicities of the membranes. Thus, it is clearly shown that hydrophilic membrane materials are preferable for reducing membrane fouling. Major membrane foulants are believed to be EPS from bacterial cell lysis, microbial metabolites, and unmetabolized wastewater components [23], including proteins, polysaccharides, nucleic acids, and other polymers [23–25]. Of these major foulants, we believe that hydrophobic

fouling materials such as proteins and microorganisms affect the development of fouling on hydrophobic membrane surfaces.
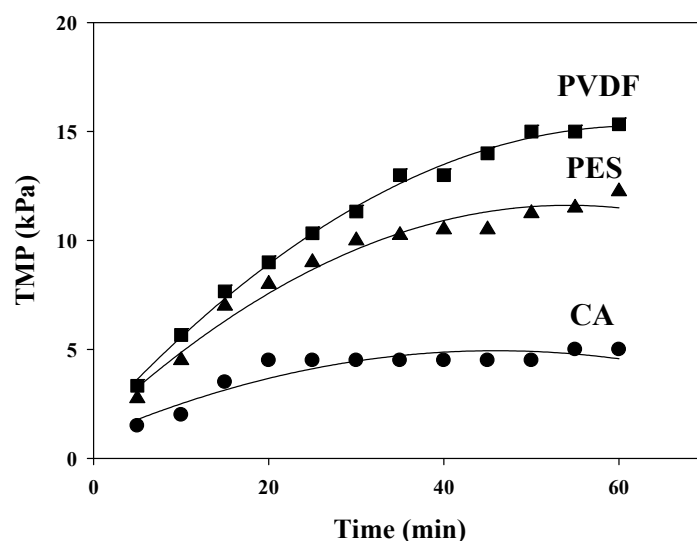
Figure 4. Transmembrane pressure (TMP) changes during batch filtration tests with activated sludge. The pore sizes of CA, PES and PVDF membranes were 30, 30, and 20 nm, respectively.

3.3. Visualization of the Biofouling on the Film Surfaces

To understand the attachment properties of the microbial flocs on the prepared films, batch attachment tests with activated sludge were performed. Figure 5 shows the CLSM images of the surface of each polymer film after the attachment test. The amount of fluorescent microbial flocs on the surface of the CA membrane was significantly less than seen for the PES and PVDF membranes. It is hypothesized that the hydrophilicity of the CA membrane play an active role in reducing microbial floc adsorption, which is expected to be beneficial for the antifouling properties of the membrane, as shown in Figure 4.
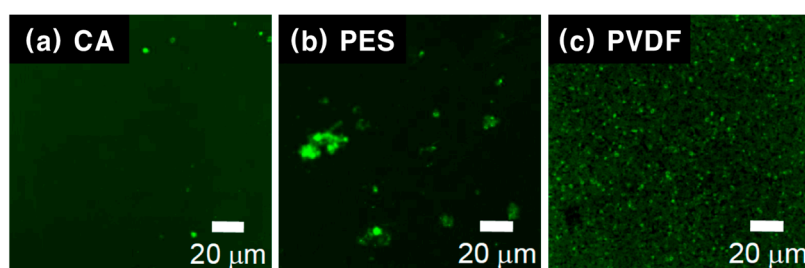

Figure 5. Confocal laser scanning microscope (CLSM) images obtained for the surfaces of thin films of (**a**) CA; (**b**) PES; and (**c**) PVDF after use in batch attachment tests with activated sludge. The surfaces of the films were stained with LIVE/DEAD stain.

3.4. Effects of Membrane Pore Size on Membrane Fouling

To investigate the effects of membrane pore size on fouling behavior, MBR experiments were conducted using membranes with different pore sizes. Figure 6 shows the relationship between membrane pore size and fouling rate as determined in the batch filtration tests. In this figure, the fouling rates are denoted by the TMP after 60 min of filtration. For the CA hollow fiber membrane, the effect of pore size was unclear. This is because the fouling of the hydrophilic membrane was reduced, so the effect of the pore size was not significant. However, for PVDF and PES hollow fiber membranes, the fouling propensity decreased sharply with increased pore size. This is in agreement with other research results [18,26–28]. Marel et al. [29] reported that PVDF with large pores showed greatly reduced membrane fouling in submerged membrane bioreactors. They carried out fouling

filtration tests with flat sheet PVDF membranes with different pore sizes (0.03, 0.1, and 0.3 µm) to investigate the influence of pore size on fouling behavior. The membrane resistance sharply decreased with increasing pore size. Our previous research on PVDF MF membranes showed a similar trend [19]. The development of membrane fouling on PVDF membranes decreased in the order 0.02 > 0.25 > 0.4 µm. However, the results for the CAB hollow fiber membrane showed the opposite tendency [19]. This indicates that fouling behavior can be affected by complicated factors such as surface chemical properties, surface morphology, pore size, hydrophilic/phobic properties, and solution chemistry. These factors should be considered together for a definite understanding of the fouling behavior in MBR processes.
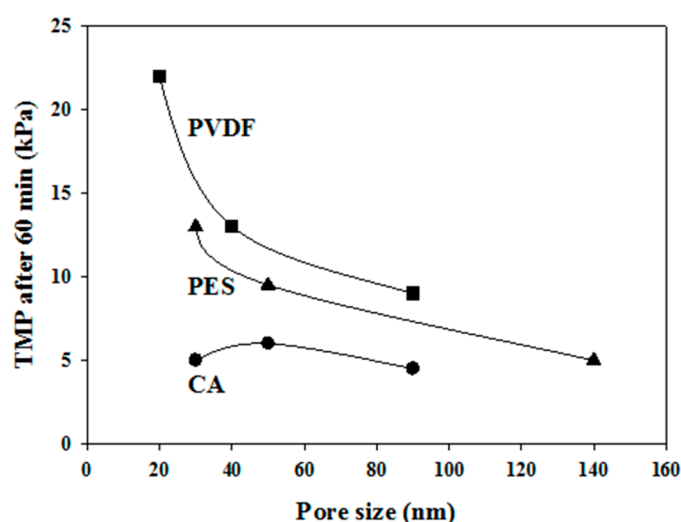
Figure 6. Relationship between membrane pore size and TMP for membranes using different polymer materials.

4. Conclusions

In this paper, we investigated the effect of membrane hydrophilicity and pore size on the development of UF membrane fouling in a MBR process. The membrane hydrophilicity was found to affect the membrane fouling. The hydrophilic CA membrane showed good mitigation of membrane fouling, while dramatic biofouling occurred on the PVDF and PES membrane surfaces due to interaction between hydrophobic foulants such as proteins and microorganisms and the hydrophobic membranes. For CA hollow fiber membranes, membrane pore size had no significant effect on fouling mitigation. In contrast, larger pores were found to contribute to the mitigation of membrane fouling for PVDF and PES hollow fiber membranes.

Author Contributions: Ryo Okamura, Toru Ishigami, and Saeid Rajabzadeh conceived and designed the experiments; Ryo Okamura and Toru Ishigami performed the experiments; Sungil Jeon, Saeid Rajabzadeh, Ryo Okamura, Susumu Hasegawa, and Noriaki Kato analyzed the data; Sungil Jeon, Saeid Rajabzadeh, and Hideto Matsuyama contributed to the writing of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BSA	bovine serum albumin
CA	cellulose acetate

CAGR	compound annual growth rate
CLSM	confocal laser scanning microscopy
DMAc	dimethylacetamide
DO	dissolved oxygen
EPS	extracellular polymeric substance
FE-SEM	field emission scanning electron microscope
F/M	food-to-microorganism ratio
HRT	hydraulic retention time
LiCl	lithium chloride
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids
NIPS	non-solvent induced phase separation
OsO_4	osmium tetroxide
PBS	phosphate buffer solution
PES	polyether sulfone;
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
SMBR	submerged membrane bioreactor
SRT	solids retention time
TIPS	thermally induced phase separation
TMP	transmembrane pressure
UF	ultrafiltration
WWTP	wastewater treatment plant

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