

Novel Polymeric Membranes Preparation and Membrane Process

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Polymer-based membranes have advanced or novel functions in the various membrane separation processes for liquid and gaseous mixtures, such as gas separation, pervaporation (PV), reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and in other critical applications of membranes such as water purification, solvent concentration, and recovery. In recent years, advanced membrane technologies, including new membrane materials, membrane preparation technology, and membrane processes, have been at the forefront of research.

This Special Issue of *Separations*, “Advances in Novel Polymeric Membranes and Membrane Process”, aims to provide an update on recent trends in novelty polymeric membrane preparation and modification to readers already familiar with this topic and hopefully spark the curiosity and the attention of more membrane separation experts toward the importance of this topic.

This Special Issue collates seven impressive contributions that describe the new development of polymeric membrane preparation and membrane technologies, from novel polymeric materials for specific separation to developing high-performance membranes for enhanced separation efficiency and prospective applications. One review article describes the fouling problems in the membrane technology for use in water and wastewater treatment, as well as the methods of both initial treatment and the least-advanced technologies in treatment processes, such as introducing nanochemistry into the area of water treatment [1]. Six research papers illustrated high-performance NF membrane for the lithium recovery from brine [2], molecular dynamics (MD) simulation of gas transporting in polydimethylsiloxane (PDMS) membrane [3], zeolite molecular sieve SAPO-34/polydimethylsiloxane (PDMS) mixed matrix membranes (MMMs) preparation to recover propane [4], polyvinylidene fluoride (PVDF)-pressurized ultrafiltration membrane on the treatment of steel wastewater and analyzing [5], poly (vinyl alcohol) (PVA)-based MMMs preparation for high ethanol dehydration performance [6], hydrophilizing the polytetrafluoroethylene (PTFE) microfiltration membrane combining of surfactants and cross-linked co-deposition double-layer self-assembly method [7].

Mervette El Batouti and coworkers at the Alexandria University (Egypt) reviewed the fouling problems in the membrane technology for use in water and wastewater treatment and overviewed various factors affecting membrane fouling and strategies for mitigation of fouling [1]. This article reported the membrane fouling mechanism that occurred in membrane processes. The fouling in RO systems includes particulate/colloidal fouling, scaling, organic fouling, and biofouling. After a chemical pretreatment, the physical cleaning with DI and bubbling air could achieve 100% flux recovery [8]. In NF, the pretreatment with coupled aluminum (Al) EC-MF reduces the colloid and organic fouling in the NF process of inland natural brackish surface water [9]. Adding GO, vanillin and molecular sieving



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to the polymeric matrix considerably increases fouling resistance and membrane performance [10]. A dynamic membrane (DM) is a layer of particles deposited on a conventional membrane by permeate drag, and the deposited particles serve as a secondary membrane. The presence of DMs, which operate as an adsorbing, protecting the layer against foulants, aids in the reduction of PM fouling [11]. Membranes modified using more straightforward methods, such as coating, will be used to mitigate membrane distillation (MD) operational problems in large-volume processes, such as desalination or water recovery from industrial discharges. Antifouling properties, resistance in long-term operations, and self-cleaning capability will be required in these cases, which may be achieved through coating. Separations involving high-value-added products that require robust membranes, on the other hand, will gravitate toward more robust techniques, such as electrospinning and plasma, wherein desirable features can be highly controlled and achieved quickly. This review work also proposed new membrane treatment approaches, such as ultrasonic waves, the coupling of applied electric fields in membrane systems, and the creation of conductive membranes for electrically improved fouling mitigation, which show great promise. Thus, this review article offers the reader a clearly defined viewpoint on various antifouling strategies that minimize the fouling phenomenon in membrane processes [1].

Shijie Xu et al. contribute their work to the antifouling modification of PTFE microfiltration membranes [7]. They use a combination of surfactants and a cross-linked co-deposition double-layer self-assembly method to hydrophilize the PTFE microfiltration membrane. In this paper, the PTFE membrane is pretreated with a polyethylene glycol laurate (PEGML) solution in order to reduce its surface tension and initially enhance the wettability of the PTFE microfiltration membrane. In order to better anchor PEGML to the membrane surface, they used PVA and green non-toxic CA crosslinked to form a three-dimensional network structure with hydrophilic groups deposited and wrapped around the fibers and nodes of the membrane. At the same time, the modification conditions were optimized, and the anti-fouling properties and hydrophilic coating stability of the modified membranes were investigated. PTFE microfiltration membranes modified by the optimal conditions achieved a water flux of $396.9 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ (three times that of the original membrane) at low operating pressures (0.05 MPa), and the contact angle decreased from 120° to 40° . Meanwhile, the modified PTFE microfiltration membrane has improved contamination resistance and good stability of the hydrophilic coating.

In order to alleviate the water crisis, the recycling of industrial wastewater has become a meaningful way to increase the supply of water resources [12]. The iron and steel industry is one of China's five major water-consuming industries. However, treating wastewater from the iron and steel industry is difficult due to its complex and changeable characteristics. Yanggang Zhang et al. introduce the application of polyvinylidene fluoride (PVDF)-pressurized ultrafiltration membrane with low packing density produced via thermally induced phase separation (TIPS) in wastewater of iron and steel industry to study the effects of packing density of ultrafiltration membrane modules as well as the membrane performance under different operation conditions, in order to guide the subsequent development of other ultrafiltration applications in wastewater of iron and steel. The pilot test of SMT900-P80 PVDF hollow fiber ultrafiltration membrane module in the steel industry's wastewater treatment showed that the prolongation of filtration cycle and increase in operating flux during the operation would degrade the filtration performance of the membrane, and the percentage of irreversible fouling would increase significantly after long-term operation [5].

Lithium is known as "an energy metal in the 21st century", and its demand in the energy field (e.g., as batteries and nuclear energy) has been increasing in recent years [13]. Statistics reveal that over 60% of lithium reserves are present in continental brine, highlighting the importance of developing more efficient technology for recovering lithium from brine. Very often, brine is heavily loaded with Mg^{2+} compared to Li^+ due to their similar ionic properties, which undoubtedly makes it more challenging to recover lithium from the brine. Lei Ma et al. synthesized and characterized a positively charged NF membrane

with a sandwich structure that was successfully fabricated by depositing PDA-g-C₃N₄ as the interlayer on the surface of the PES membrane, followed by the IP process of PEI and TMC on the interlayer. Using PDA-g-C₃N₄ as the interlayer is conducive to the penetration and diffusion of water molecules on the membrane surface. The high permeance will not affect the salt rejection rate, mainly due to the pore size of the NF membrane and the strong electrostatic repulsion between the abundant positive charges and the polyvalent cations on the membrane surface. The final NF membrane also has good and stable separation performance for complex salt lake brine and antifouling property with the permeance of 10.19 L·m⁻²·h⁻¹·bar⁻¹ and 98.2% rejection of Mg²⁺ [2].

With the large-scale development of modern industry, environmental problems and the energy crisis are becoming more serious. Volatile organic compounds (VOCs) are essential atmospheric pollutants. The dense silicone rubber PDMS membrane has wide-ranging prospects for the separation and recovery of VOCs. It is suitable for nearly all kinds of VOCs and has the advantages of a high recovery rate, low energy consumption, no secondary pollution, etc. [14]. Two exciting reports [3,4] are included in this Special Issue, both of which are related to the use of dense silicone rubber PDMS membrane. They simulated gas transport in PDMS membranes using BIOVIA Materials Studio (MS, Accelrys Software Inc. San Diego, USA). The dissolution and diffusion properties of three different gases (C₃H₈, C₃H₆, and N₂) were simulated and analyzed in the membranes at different temperatures. The free volume fraction (FFV), cohesive energy density (CED), radial distribution function (RDF), diffusion coefficient, and solubility coefficient of C₃H₈, C₃H₆, and N₂ in PDMS membranes were calculated, and the permeability coefficients were calculated according to these values. In a C₃/N₂ mixed gas system, there is a synergistic relationship between gases in the diffusion process during competitive adsorption in the dissolution process. In the second paper [4], the n-Octyltrichlorosilane (OTCS)-modified SAPO-34 was then introduced into the PDMS to prepare SAPO-34 (OTCS)/PDMS MMMs. A propane/nitrogen mixture was employed to study the separation performance of the membrane. The surface roughness and hydrophobicity of the prepared membrane increased with the filling of zeolite molecular sieve SAPO-34, which was beneficial to the dissolution of propane. A small amount of SAPO-34 agglomeration occurred only when the loading was over to 20 wt%. When the loading of SAPO-34 (OTCS) was 15%, the separation factor reached 22.1, and propane permeance was 101 GPU. Compared with the unfilled membrane, the overall separation performance of SAPO-34 (OTCS)-filled PDMS membrane was greatly improved.

Ethanol dehydration via pervaporation (PV) has attracted increasing attention due to ethanol biofuel's rapid development and application [15]. Xia Zhan et al. reported another kind of MMMs for ethanol dehydration via pervaporation [6]. The relationship between the physical/chemical properties of graphene and pervaporation performance of MMMs was investigated by comparison of hydrophobic graphene (GR)/PVA and hydrophilic graphene oxide (GO)/PVA MMMs in microstructure and PV performance. The incorporation of GR/GO into PVA depressed the PVA membrane swelling degree, and the incorporation of GR showed a more obvious depression effect. The higher permeation flux of GO/PVA MMMs was ascribed to the facilitated transport of water molecules induced by oxygen-containing groups and exclusive channels provided by GO lamellae, while the much lower permeation flux and higher separation factor GR/PVA MMMs resulted from the smaller GR interplanar spacing (0.33 nm) and hydrophobicity as well as barrier effect of GR lamellae on the sorption and diffusion of water molecules.

Serving as guest editor of this Special Issue has been a very exciting experience. I would like to express my deepest gratitude to all of the authors for their brilliant contributions and invite the readers of Separations to take full advantage of all of the important information that this Special Issue provides, hoping that many of these strategies will be broadly applied in many membrane science and technology laboratories.

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