

Designing high flux and solute selectivity in hydrogel-modified cellulose triacetate membranes for forward osmosis

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Forward osmosis (FO) has attracted intensive attention in liquid separation since it is less energy-consuming as compared to the pressure-driven separation processes, but the lack of high-performance membrane limits its application [1,2]. In this paper, novel FO membranes were fabricated by generating three methacrylate-based hydrogels (methyl-, ethyl- and butyl-methacrylate; MMA, EMA and BMA) on the cellulose triacetate (CTA) surface via the solution drop-casting method. The characterization results show that the hydrogels were chemically crosslinked with the porous CTA substrate and improved the hydrophilicity of membranes. As a result, all the hydrogel-modified CTA membranes showed higher pure water flux than the bare CTA and commercial HTI-CTA membranes. The modified FO membranes also exhibited higher solute selectivity and salt retention as the hydrogels acted as the active barrier. In addition, antibacterial study demonstrated that hydrogel modifications conferred antibacterial properties to the CTA membranes, which is indicative of better anti-fouling feature. The outstanding separation performance indicates the hydrogel-modified CTA membranes have great potentials for the industrial application.

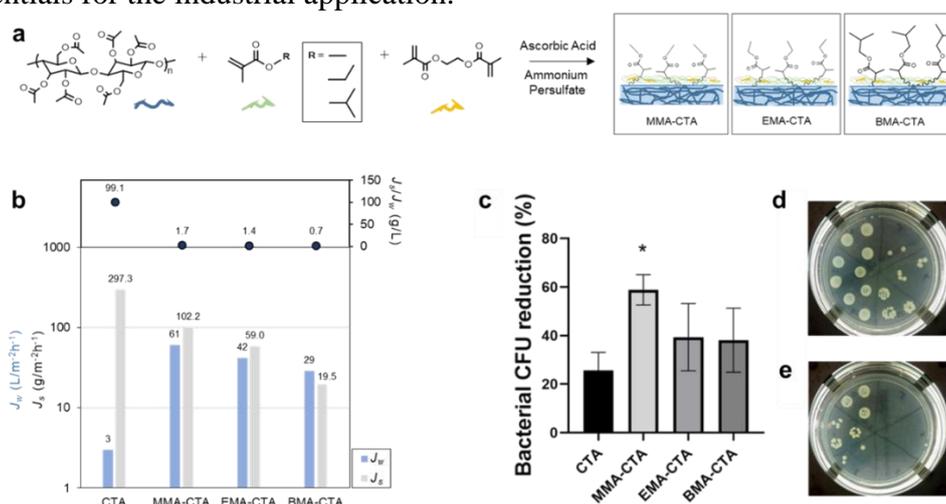


Fig. 1 (a) Schematic diagram of the hydrogel modified CTA membranes. (b) Pure water flux, J_w , and reverse salt flux, J_s , of the CTA and hydrogel modified CTA membrane along with specific reverse salt flux J_s/J_w ratio (top figure). Antibacterial effect of CTA membranes. (c) Reduction in *Pseudomonas* fluorescence colony forming units (CFU) incubated with unmodified CTA and modified MMA-CTA, EMA-CTA and BMA-CTA membranes, respectively, and example bacterial colonies on control plate (d) and modified membrane samples (e).

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Enhancement of antifouling properties using Poly (vinylidene fluoride) membranes modified with Cellulose Acetate/PEG

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Poly(vinylidene fluoride) (PVDF) is one of the most prominent base polymer for the fabrication of membranes in water treatment. However, due to its hydrophobic nature it has a poor membrane performance i.e. antifouling property and efficacy of water permeability is very low. In this study, to obtain high permeability, surface porosity and good pore structure, PVDF asymmetric membrane was blended with cellulose acetate (CA) and then poly ethylene glycol (PEG) is added as a pore forming additive to improve its hydrophilicity. The pristine PVDF membrane and modified PVDF membranes were prepared via phase inversion method with Dimethyl formamide (DMF) as solvent in casting solution. The prepared, pure PVDF, PVDF/CA and PVDF/CA/PEG membranes were characterized by SEM and AFM to evaluate the surface morphology, which exhibited good surface pore structure with interconnected surface pore. Also the topography shows good surface roughness in the modified membranes. Hydrophilicity of the membranes was determined via contact angle measurements. Then, the permeability studies were carried out by measuring pure water flux. The modified membrane (PVDF/CA/PEG) shows high permeability (379.86 L/m²h) rate than pure PVDF (7.84 L/m²h). Further, membranes antifouling properties and rejection studies were also carried out using bovine serum albumin protein. From the results, it was observed that PVDF membranes incorporated with CA and PEG showed better permeability and antifouling property.

Keywords: Poly (vinylidene fluoride), Cellulose Acetate, Poly ethylene glycol, Bovine serum albumin.

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Preparation and characterization of low-cost NaA zeolite membrane on Kaolinite support for dehydration of alcohols

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In the last two decades, zeolite membranes have attracted a lot of interest, not only for their well-defined channels structure and uniform pore size, but also for their high thermal and excellent chemical stability. Additionally, zeolite membranes are characterized by high performance in terms of selectivity and separation factor, which make them very demanded in industrial applications, such as dehydration of acids and alcohol, organic/organic and gas separation, as well as desalination [1].

However, the estimated cost of zeolite membranes for industrial applications is estimated between 1000 and 3000 €/m², noting that 80% of this cost is related to the support and only 20% dedicate to zeolite layer itself [2]. For this, there is a great interest in using local materials that are abundant and cheaper for the preparation of the support that provides the mechanical strength of the membrane.

In this work, a systematic approach is described for the preparation of NaA zeolite membrane on inexpensive ceramic kaolinite support through hydrothermal synthesis. Firstly, ceramic support was prepared from local kaolinite clay via uniaxial pressing method, followed by sintering. Secondly, the zeolite layer was grown on the substrate via in-situ crystallization and secondary growth methods. The prepared membrane was deeply characterized using several techniques in order to investigate the layer deposition as well as the membrane hydrophobicity.

To evaluate its performance, NaA zeolite membrane was tested for alcohol dehydration via pervaporation process. It is worth to mention that preliminary results showed that zeolite membrane exhibited high permeate flux and selectivity. Thus, the prepared membrane proved to be promising for ethanol/water separation

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Crosslinked terpolymer anion exchange membranes for selective ion separation and acid recovery

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Anion exchange membrane (AEM) is useful for the removal of salts via electrodialysis (ED) process. AEM is also used for the recovery of acid from an aqueous feed containing acid and metal ion through diffusion dialysis (DD). However, for the selective separation of monovalent and divalent ions, special type of AEM is required.

Herein, we report the preparation of poly(acrylonitrile-*co*-*n*-butyl acrylate-*co*-polydimethylamino ethyl methacrylate) (PAN-*co*-PnBA-*co*-PDMA) terpolymer-based crosslinked AEMs for the separation of monovalent ion from bivalent ion via ED process and recovery of hydrochloric acid (HCl) from aqueous feed of HCl and FeCl₂ through DD. The slowing down the movement of bivalent anion under electrical potential, and hindering the diffusion of metal ion are the key factors for the optimization of the membranes. The tuning the polarity of the microenvironment of quaternized nitrogen (from DMA moieties) of the terpolymer by changing the length of alkyl chain gave membranes with different monovalent to bivalent anions selectivity, and separation factor for acid recovery. AEM-TP-C1, AEM-TP-C4 and AEM-TP-C10 membranes were prepared by quaternizing the DMA moieties (C1 to C10 denote length of alkyl) of the terpolymer followed by crosslinking.

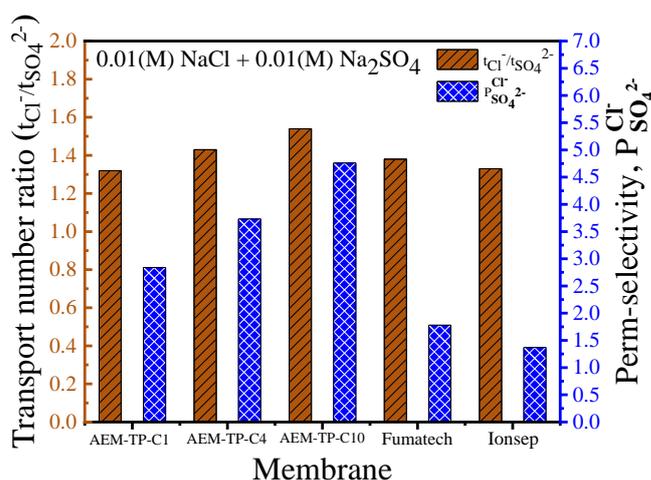


Fig. 1 $P_{SO_4^{2-}}^{Cl^-}$ for the AEM-TP-C1, AEM-TP-C4, AEM-TP-C10, Fumatech, and Ionsep. membranes.

The AEM-TP-C10 membrane exhibited best selectivity (4.76) during desalination of sodium chloride and sodium sulfate mixture (0.01M, 0.01M) via ED process (Fig. 1). Best performance in terms of acid recovery was obtained with AEM-TP-C4 membrane with dialysis coefficient of 0.031 m/h and separation factor of 38 during acid recovery. The length of alkyl and the hydrophobicity of the environment of the quaternized nitrogen is a governing factor for deciding the performance of the AEMs. This work provides an insight to design crosslinked AEMs for selective separation and acid recovery. The tertiary amine presence in the terpolymer may be quaternized with varieties of halide compounds to further correlate the structure of quaternized amine and property of the AEMs.

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Preparation process optimization of phosphate/kaolinite membrane using response surface methodology. Application for treatment of textile wastewater

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As well known, ceramic membranes exhibit many advantageous characteristics in comparison to polymeric membranes namely good mechanical strength, excellent thermal resistance, high chemical stability, long-life performance and minimal pollution impact. However, commercial ceramic membranes are prepared from metals oxides that are expensive and require high energy for sintering. Therefore, it is very promising to use local geomaterials such as phosphate, pozzolan and clays to prepare low-cost ceramic membranes more or less similar to available commercial membranes. Economically, it is highly expected that this approach leads to fabricate competitive membranes.

This work aims to study the effect of incorporation of kaolinite clay on phosphate for the preparation of a low-cost ceramic microfiltration membrane. The phosphate/kaolinite membrane was prepared via dry pressing method followed by sintering. Box-Behnken design was used to evaluate the effect of preparation conditions such as added clay, sintering temperature, time of sintering on membrane features especially permeability and mechanical strength. In order to assess its performance, the optimized membrane was subjected to the filtration of industrial wastewater. Finally, the fouling mechanism and the flux recovery studies were also performed.

Analysis of various pretreatments to mitigate fouling and scaling in membrane distillation

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Membrane Distillation (MD) has shown the potential for the treatment of the high salinity wastewater like produced water resulted from unconventional oil and gas explorations. The driving force of the MD is the partial vapor pressure across the hydrophobic membrane which salinity at feed has negligible effect. The low operating temperature compared with commercial technology allow MD to harvest the low-grade heat like waste heat from power plant. However, one of the major challenges in MD is the fouling and scaling of the minerals and organics. The complexity of the real produced water with high concentrations of suspended solids and organic matter makes the MD treatment even more challenging. To tackle the issue regarding the scaling and fouling, pretreatment should be investigated to mitigate the fouling and scaling. In this talk, we present some of our results regarding pretreatment of produced water for membrane distillation, including oxidation, filtration, dissolved air flotation, and coagulation. Vacuum Membrane Distillation (VMD), which has shown to have the highest potential for fouling and scaling was chosen as the configuration that was tested in our filtration experiments. Membrane surface and water chemistry were comprehensively characterized, and a baseline is proposed for proper treatment of produced water for MD treatment.

Hydrated zirconium dioxide/Graphene oxide nanoparticles incorporated polyamide membranes

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Today polymeric membranes are the most used in processes for separation because they are widely available but characterized of short life of exploitation. They are not strong for chemical cleaning and high temperature conditions, besides organic membrane have seriously disadvantage – well-known problem of fouling.

Composite polymeric membranes has attractive interest for separation due to the probability to improve existing properties of pristine polymeric matrix. The development of polymeric membranes with nanoparticles is under attention because there is the way to hydrophilization for solving problem of fouling, to give selectivity and to extend operating conditions for membranes. The work is focused on modification polyamide membranes with inorganic/carbon modifier for baromembrane process of purification. The aim of this work was to develop ultrafiltration membranes with nanoparticles for improvement of pore characteristics for separation of solutions containing protein compounds.

Graphene oxide (GO) have a great potential due to their unique structure: high theoretical value of specific surface, hydrophilic and hydrophobic properties, in addition GO particles modifier able to embed in polymer pore structure. Inorganic ion-exchange component hydrated zirconium dioxide (HZD) is characterized by developed surface with functional hydroxyl groups are located. It was found amphoteric properties of HZD with point zero charge near 7. Co-precipitation of HZD together with GO particles in the active layer of the polymeric matrix affects selectivity, stability and surface charge of the membrane.

Modification of commercial polymeric polyamide-based membrane (PAN) was prepared via sol stage and two-component modifier (HZD+GO) was used. The amount of the carbon GO component was 0.5 mass %. Co-precipitation of this two-component modifier was carried out exclusively in the active layer of the polymeric membrane, namely without treatment of macroporous fibrous support.

It was found that the contact angle for the pristine PAN membrane is 55° degrees and contact angle for the modified PAN (HZD+GO) membrane is 50°, indicating enhancement of hydrophilicity. Porous characteristics both membranes were measured by the method of nitrogen adsorption. The degree of rejection of the protein ovalbumin for the pristine and modified membrane (HZD+GO) measured 95-97% and 99% respectively. Composite polymeric membranes could find application for effective ultrafiltration processes of colloid solutions.

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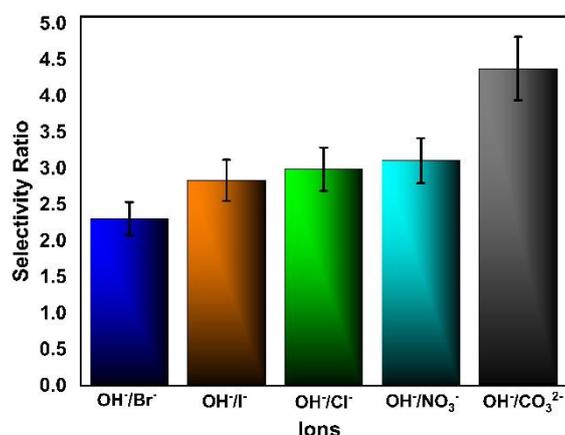
Low Humid Transport of Anions in Layered Double Hydroxides

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Lithium carbonate and lithium hydroxide are two compounds used for producing battery cathodes, however, lithium hydroxide is favored in producing battery compounds as it possesses very high electrochemical potential and low density. As a result, there is substantial demand for development of anion-selective membranes capable of selecting hydroxide over carbonate.

Membranes made of two-dimensional (2D) materials have a great potential to be used for ion separation [1]. Layered Double Hydroxides (LDHs) have the potential to conduct ions because of their positively charged nanosheets. Here we show LDH membranes can form a highly conductive hydroxide-selective membrane. Measuring the conductance of the membrane under different electrolytes with matching ionic strength demonstrated the excellent hydroxide selectivity of the membrane over other anions. The in-plane ion conductance of the membrane for different ions is $\text{OH}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^- > \text{Cl}^- > \text{CO}_3^{2-}$ with corresponding selectivity ratios of OH^- to Br^- , I^- , NO_3^- , Cl^- , CO_3^{2-} found to be 2.30, 2.83, 2.99, 3.11 and 4.38 respectively.



Molecular dynamics (MD) simulations revealed that the small nanochannels of LDH increase its diffusion barrier against ion permeation and cause the partial dehydration of ions. We showed that ions move inside the LDH nanochannels in a semi-dry transport manner so that they attract to the surface more than water molecules inside the nanochannels. Selectivity predictions from MD simulations were in excellent agreement with the experimental data, confirming our hypothesis about ion transport in LDH nanochannels. This work takes advantage of the semi-dry transport mechanism of anions in the narrow nanochannels of LDHs to produce a hydroxide selective membrane applicable in the production of LiOH for the new generation of Li-ion batteries.

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Metal organic frameworks based mixed matrix membranes in wastewater treatment

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Abstract

In the 21st century, water pollution is one of the major concerns for sustainable development. Membrane-based separation processes are becoming the progressive solution for the treatment of wastewater. Polymeric membranes have been widely used for the rejection of undesirable constituents from water through selective membrane barrier. Nevertheless, there is trade-off between permeability and selectivity, which limits the membrane separation processes use in the various applications. Mixed matrix membranes (MMMs) were introduced to overcome these limitations and enhance the performance by incorporation of different additives. Metal-organic frameworks (MOFs) are the hybrid inorganic–organic materials that are used as novel fillers for incorporation in polymer matrix to form composite membranes [1]. Their exceptional and unique properties include adjustable pore size, high porosity and surface areas, flexibility, variable structures which makes MOFs compatible for the removal of heavy metals, pesticides, dyes, organic contaminants, etc., from various wastewater sources. For instance, Wang et al. [2] investigated the effect of polyamide (PA)/ZIF-8 membrane on the removal of Congo red dye from water by nanofiltration process and their findings highlighted that the flux significantly increased to two times that of pure PA membrane and rejection was nearly 100%. The current article will review the detailed insights of all the recently developed MOFs and their effects on the performance of MOFs based MMMs in water purification process. Moreover, most suitable preparation techniques, various challenges encountered and the future perspectives of MOFs based MMMs will be discussed.

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Title:

Forward Osmosis System Design and Optimization Using a Hollow Fibre Membrane Module for Energy Efficient Desalination

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Abstract:

The hollow fibre membrane module offers much higher packing density compared to the flat-sheet membrane modules. This study is aimed at developing system design models to simulate and optimize a full scale forward osmosis (FO) plant using a hollow fibre membrane module for energy efficient desalination. Mathematical models were developed to simulate the mass transport through the membrane considering the actual geometry of the hollow fibre membrane. Module scale performances were then computed by employing the mass transport models with the fluid conservation laws. Pilot scale experiments were also conducted employing a commercial CTA hollow fibre FO module to validate the theoretical models. Less than 10% difference between the simulation and experimental results were observed which validated the reliability of the developed simulation models. These mathematical models were then applied to simulate and design a 1,000 m³/day FO plant using 0.6 M NaCl as draw solution or DS (~seawater) and 0.02 M NaCl feed solution (~MBR effluent) to produce 0.25 M, 0.2 M and 0.15 M NaCl diluted seawater DS. For the full scale design, single element parallel module arrangement was found more suitable for this commercial hollow fibre membrane element tested in this study. Moreover, the maximum feed solution (FS) inlet flowrate was 3 LPM per hollow fibre element considering the maximum allowable FS inlet pressure. Finally, the numerical simulations revealed that to achieve 0.25 M, 0.20 M and 0.15 M final DS concentrations from the system, the optimum number of modules required were 370, 435 and 555 respectively considering the cost of membrane and energy. For the same final concentrations, the DS inlet flowrates to each module were found to be 0.8 LPM, 0.55 LPM and 0.32 LPM, whereas the FS inlet flowrates were 2 LPM, 2.5 LPM and 2.5 LPM respectively.

Fabrication and performance evaluation of polyvinylidene fluoride membranes for wastewater treatment

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Abstract

The objectives of the current study are to fabricate a polyvinylidene fluoride (*PVDF*) flat sheet membrane by electrospinning and evaluate its performance in treating industrial wastewater (i.e., organic dye waste “Methylene Blue, *MB*”). The experimental work is divided into two phases. Firstly, the effect of different membrane compositions (i.e., polymer concentration and inorganic additives) and electrospinning conditions (i.e., internal needle diameter, tip to collector distance, and feed flow rate) on the quality of the electrospun membrane was investigated by scanning electron microscope (*SEM*) to get the optimum conditions for the production of a free-beads *PVDF* membrane. Furthermore, characterizations by X-Ray Diffraction (*XRD*), Fourier Transform Infrared Spectrometer (*FTIR*), static water contact angle, surface zeta potential, porosity, fiber diameter, and pore size measurements were conducted for the beads' membrane to assess the impact of electrospinning on fibers elemental composition, hydrophobicity, surface charge and ensure the formation of submicron fibers with random alignment. Secondly, an experimental setup was developed in a flexible way to enable separate-and-integrated effects investigation of the membrane and the photocatalytic reactor, separately and simultaneously. Different variables as photocatalyst (*TiO₂*) concentration and methylene blue concentration were studied on dye removal and permeate flux. It was found that a photocatalytic membrane reactor (*PMR*) with a *PVDF* membrane is privileged by attaining pure permeate and 100% dye removal under certain operating conditions.

Separating 1-butanol from water with PU/ZSM-5 mixed matrix membranes

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Biofuels can provide a promising alternative to conventional liquid fuels. In the bioconversion of the biomass, the current separation process in place for the recovery of the desired products is distillation. However, distillation has proved to be extremely energy-intensive and economically unfavorable [1]. This is the case for biobutanol because the product is produced in very low concentrations (~13 g/L) due to product-induced toxicity during ABE fermentation [2]. In order to solve this issue, novel separation process, such as pervaporation, are necessary to improve the economic feasibility of biofuels.

Pervaporation is of great interest to the biofuel industry since it has the potential to make separation processes cheaper, to reduce waste footprints, and to improve efficiency. This practice is defined as a liquid mixture separation technique, driven by a partial pressure difference, that selectively permeates a desired product through a dense membrane [3]. In order to utilize pressure as the driving force, vacuum is pulled on the permeate side. Any liquid that passes through the membrane evaporates and must be condensed with a cold trap.

In this work, a mixed matrix membrane (MMM) was developed in which a ZSM-5 zeolite filler was dispersed throughout a polyurethane (PU) matrix for the purpose of pervaporation. Membranes with 0, 10, 15, 20, 25, and 30 wt% ZSM-5 loadings were first prepared and their performance at separating 1-butanol from water was evaluated at 60 °C. The 20% membrane performed best achieving a maximum selectivity of 6.86 ± 0.15 and a separation factor of 12.8 ± 0.03 . Once the optimal ZSM-5 loading was discovered the 20% membrane was tested at different temperatures, feed concentrations, and membrane thicknesses.

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Mechanistic understanding of the adsorption of natural organic matter by
heated aluminum oxide particles (HAOPs) via molecular dynamics
simulation

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Abstract

Membrane fouling caused by natural organic matter (NOM) in water is a pressing problem. To address this, heated aluminum oxide particles (HAOPs) have been used as dynamic membranes pre-deposited onto the primary membrane to effectively remove NOM and thereby significantly diminish the fouling potential. An in-depth understanding of the mechanisms underlying the superior performance of HAOPs remains amiss, which motivated this study. Molecular dynamics (MD) simulations were conducted to systematically compare the performance of HAOPs, which have been reported to be particularly effective for high molecular weight (HMW) NOM, with the conventional powdered activated carbon (PAC) adsorbent. Six NOM constituents, three of which have HMW and three have low molecular weight (LMW), were studied. Results indicate that the mechanisms underlying the effective removal of HMW NOM by HAOPs include: (1) higher foulant-HAOPs interaction energy; (2) greater hydration of the HMW NOM, which thereby increases the affinity to the more hydrophilic HAOPs; (3) diminished mobility of the foulant once adsorbed, which deters desorption; and (4) higher peak intensities in the radial distribution functions for multiple functional groups on the HMW NOM foulants. These results are expected to be valuable towards the better design of such materials for mitigating membrane fouling.

Dense hot-pressed polyelectrolyte complexes as novel monovalent-selective alkaline-stable anion exchange membranes

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Polymer-based ion-exchange membranes are being used in a myriad applications, and have come a long way since their inception[1]. They facilitate an array of processes ranging from desalination to electrolysis and fuel cells. Although they are widely used, several shortcomings such as stability in alkaline media, monovalent ion selectivity, high costs render them unsustainable for several processes.

Polyelectrolytes are polymers bearing a net charge, and have opened many doors in the recent past. Their applications have shown to be inexpensive, and sustainable alternatives to several existing materials.

This work showcases novel anion-exchange membranes that were made by hot-pressing a polyelectrolyte complex formed by mixing poly(diallyldimethylammonium) chloride (PDADMAC) and sodium salt of poly(styrenesulfonate) (Na-PSS). These oppositely charged strong polyelectrolytes combine in a specific ratio with excess cationic groups, which translates into the dense plastic film formed by applying pressure and temperature [2]. Free-standing films were made and a net charge on them allowed for the successful exploration of their prospects as ion-exchange membranes (IEMs).

Although novel, the performance of these novel plastics were comparable to commercial IEMs. Ion exchange capacity of 1.4 mmol g⁻¹, up to 97% permselectivity, water uptakes of 40%, and an electrical resistance of 2.3 ohm. cm² were observed. In addition to these key indicators, they are stable in extreme alkaline and acidic conditions for >60 days and display a good monovalent selectivity for chloride ions over sulfate ions. Also, these plastics have demonstrated good stabilities even at high salinities- up to 2M NaCl.

This work showcases non-porous saloplastics of Na-PSS and PDADMAC as very promising anion exchange membranes with several advantages such as low cost, eco-friendly, and scalability.

References:

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