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Low-pressure highly permeable polyester loose nanofiltration membranes tailored by natural carbohydrates for effective dye/salt fractionation

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ABSTRACT

With the continuous pressure of water contamination caused by textile industry, loose nanofiltration (LNF) membranes prepared by green materials with an extraordinary water permeability are highly desirable for the recovery and purification of dyes and salts. In this work, low-pressure LNF membranes with ultrahigh permeability were fabricated via one-step interfacial polymerization (IP), in which inexpensive natural carbohydrate-derived sugars with large size and low reactivity were utilized as aqueous monomers to design selective layer. A systematic characterization by chemical analysis and optical microscopy demonstrated that the formed polyester film features not only loosen the structure, but also results in a hydrophilic and negatively charged surface. The optimized sucrose-based membrane (Su0.6/TMC0.1) with an excellent water permeability of 52.4 LMH bar⁻¹ was found to have a high rejection of dyes and a high transmission of salts. In addition, the sugar-based membrane manifested an excellent anti-fouling performance and long-term stability. Furthermore, the non-optimized Gl0.6/TMC0.1 and Ra0.6/TMC0.1 membranes also shown a high water permeability while maintaining a competitive dye/salt separation performance, which confirmed the universal applicability of the membrane design principle. Therefore, the proposed new strategy for preparing next-generation LNF membranes can contribute towards the textile wastewater treatment.

1. Introduction

According to the World Bank, approximately 20% of water pollution globally comes from the textile industry (Kant, 2011). The wastewater from the textile industry contains various contaminating wastes typically dyes, inorganic salts (Na₂SO₄, NaCl), solvents, acids, and certain auxiliary chemicals, all collectively making the effluent highly toxic (Holkar et al., 2016; de de de Oliveira Neto et al., 2019). The presence of these compounds makes the textile wastewater treatment extremely challenging due to the high temperature (21–62 °C), high pH (6–11.8) and the presence of non-biodegradable chemicals (surfactants, color, salt, formaldehyde, etc.) of mill effluent (Kehinde and Aziz, 2014; Ghaly et al., 2014; Yaseen and Scholz, 2019). Without proper wastewater

treatment, the discharge of this textile wastewater will create significant hazards to the environment and human health (Verma et al., 2012; Shannon et al., 2010). Different methods such as adsorption, biological degradation, electrochemical oxidation, chemical coagulation and membrane filtration have been proposed to treat textile wastewater (Dasgupta et al., 2015; Jegatheesan et al., 2016; Abdelhamid and Zou, 2018; Jin et al., 2020b; Werber et al., 2016). Nonetheless, most of these methods do not respond to the concept of sustainable development, since they suffer from difficulties to recycle valuable resources (dyes and inorganic salts) from the textile wastewater (Jin et al., 2021a; Guo et al., 2021). It is estimated that up to 1.5 kg of salts and 40 kg of water are required to produce 1 kg of dyed textile (Allegre et al., 2006). Therefore, it is a win-win situation for the textile industry when effective separation

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Received 28 January 2021; Received in revised form 18 July 2021; Accepted 20 July 2021 Available online 23 July 2021 0304-3894/© 2021 Elsevier B.V. All rights reserved. processes to recover and reuse valuable dyes and salts are developed.

Pressure-driven membrane technology is extensively used due to its modular design, compact equipment, low cost, high efficiency and simplicity, high productivity, and selectivity (Jin et al., 2020a; Van der Bruggen et al., 2003; Elimelech and Phillip, 2011). Nanofiltration (NF) is broadly applied in the purification and recycling of saline water and wastewater (Tan et al., 2018a; Liang et al., 2020). Conventional charged NF membranes with a molecular cut-off range of 200–1000 Da, reject uncharged compounds via size sieving (Deen, 1987; Feng et al., 2019), while they reject multivalent salts by electrostatic repulsion (Donnan, 1995), so that they are unsuitable for the separation of dye/salt mixtures. Loose nanofiltration (LNF) membranes have received extensive attention due to their higher permeation of inorganic salts and high rejection of organics with low molecular weight, which allows to recover and reuse valuable materials from textile wastewater (Guo et al., 2021).

With the implementation of the sustainable development goals, the demand for highly performant LNF membranes has further increased. At present, four main methods are employed to prepare highly performant LNF membranes: co-deposition of polyphenol-inspired monomers (Li et al., 2019), blending of nanoparticles within matrices (Tavangar et al., 2020), in situ self-assembly (Li et al., 2018), and interfacial polymerization (IP) (Li et al., 2020). Although these methods yield an excellent LNF performance, there are still some impediments that limit industrial applications, such as the cumbersome preparation process, expensive raw materials, agglomeration of nanofillers, and the poor compatibility between filler and matrix. Among the above-mentioned technologies for developing LNF membranes, IP is one of the most established and important methods (Mohammad et al., 2015). The structure and functional groups of monomers play a decisive role in the separation performance of the TFC membrane prepared via IP reaction. Therefore, the separating membrane can be tailored by selecting the appropriate monomer suitable for a specific separation. The traditional polyamide NF membranes prepared by amine-based monomers (piperazine, m-phenylenediamine, amine derivatives), widely applied in commercial TFC membrane and having high rejections to salts and dyes, are unfortunately not suitable for textile wastewater treatment (Mah et al., 2019; Yuan et al., 2020; Chowdhury et al., 2018; Zhao et al., 2020). Because in textile wastewater treatment, it is increasingly needed to separate, recycle, and reuse dye/salt mixtures as resources rather than remove them completely as waste. Besides amine-based monomers, hydroxyl-containing monomers (e.g., polyols, polyphenols) have also

been used to synthesize polyester NF membranes with better antifouling ability (Jin et al., 2021a; Seman et al., 2010; Arribas et al., 2020) and chlorine resistance (Xue et al., 2019; Cheng et al., 2017) than polyamide NF membranes. Some studies have demonstrated that hydroxyl-containing monomers with lower reactivity and larger size can result in a polyester selective layer with less cross-linking and larger pore size (Scheme 1); thus, obtaining polyester LNF membranes suitable for resource recovery from textile wastewater (Guo et al., 2021). For example, in our previous study, a novel polyester membrane with unprecedented water permeability was developed via IP, in which meso-erythritol (ME, a zero-calorie sweetener which can replace conventional sucrose to prepare zero-calorie beverages) was utilized as an aqueous monomer (Jin et al., 2021a). The optimized polyester LNF membrane with high water permeability of 53.2 LMH bar⁻¹ and excellent antifouling performance maintained a competitive dye/salt separation performance. Besides, Jiang's group prepared a polyester NF membrane via IP reaction between cyclodextrin with hydroxyl groups and trimesoyl chloride (TMC) (Xue et al., 2019). The resultant membrane with superior chlorine resistance can be used for textile wastewater treatment. Overall, these hydroxyl-containing monomers (such as ME, cyclodextrin, etc.) can be utilized to improve the LNF membranes performance for textile wastewater treatment; unfortunately, the difficult to obtain in nature and poor water solubility limit their application in LNF membrane fabrication on an industrial scale.

Inexpensive, renewable and natural carbohydrate-derived sugars (sucrose, glucose, raffinose) widely extracted from fresh fruits, honey and plants with excellent water solubility, lower reactivity (hydroxyl groups) and larger size, show a huge potential in the fabrication of LNF membranes. To the best of our knowledge, polyester LNF membranes prepared with natural carbohydrate-derived sugars have not been reported yet.

Herein, we introduce natural carbohydrate-derived sugars (sucrose, glucose, raffinose) to design novel carbohydrate-based polyester lowpressure LNF membranes with high selectivity for dyes/salts mixtures, excellent anti-fouling performance expected on account of the abundant hydrophilic hydroxyls, long-term stability, and high flux due to the larger pore size and lower crosslinking degree caused by carbohydrate with lager size and lower reactivity. Different contents of sucrose and different carbohydrate-derived sugars (sucrose, glucose, raffinose) were utilized to achieve the optimal polyester LNF membranes. The prepared polyester membranes were extensively characterized to confirm the successful membrane preparation and evaluate the pore structure and



Scheme 1. Strategy and mechanisms to enlarge the pore size of LNF membrane prepared through IP with hydroxyl-containing monomers.

surface characteristic of the polyester thin layers.

2. Experiments

2.1. Chemicals and materials

Polyethersulfone (PES) (Ultrason E3000P) provided by BASF Co. (Germany), Dimethyl sulfoxide (DMSO, 99.5%) purchased from Sigma-Aldrich were used to prepare dope solution for ultrafiltration (UF) membrane fabrication. Glucose (Gl, 99.5%), Sucrose (Su, 99%), Raffinose (Ra, 99%), and NaOH (97%) purchased from Sigma-Aldrich were used as aqueous phase reactants. Trimesoyl chloride (TMC, 98%) and n hexane (95%) purchased from Sigma-Aldrich were employed to prepare the organic phase solution.

Congo red (CR, dye content: 40%), direct red 23 (DR23, dye content: > 30%), and reactive blue 2 (RB2, pure) from Sigma-Aldrich were tested separately for dye rejection performance at an inlet concentration of 200 ppm; the chemical structure of these dyes is shown in Table S1. Sodium chloride (NaCl, 99%), sodium sulfate (Na₂SO₄, 99%), magnesium sulfate (MgSO₄, 99%), and magnesium chloride (MgCl₂, 99%) were purchased from Sigma-Aldrich and used to assess the salts' permeation at an inlet concentration of 1.0 g/L. Polyethylene glycols (PEG, AR, Merck) with different molecular weights (200 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da) were purchased from Sigma-Aldrich to measure the molecular weight cut-off (MWCO) of membranes. Unless specified, all aqueous solutions were prepared in deionized water (Milli-Q ultrapure unit).

2.2. Membrane preparation

2.2.1. Preparation of PES UF and polyester TFC NF membranes

PES UF substrate membranes (water permeance, around 1200 LMH bar⁻¹) were prepared according to our previous work (Jin et al., 2021b). In short, the PES substrate membranes were made by casting a dope solution (PES/DMSO, 15/85%) on a non-woven fabric using a casting knife with a thickness of 250 μ m via a non-solvent (water) induced phase separation method.

2.2.2. Preparation of polyester TFC NF membranes

The polyester TFC NF membranes were prepared via IP between Su and TMC catalyzed by NaOH on the surface of PES substrate at a room temperature of 25 $^{\circ}\text{C}$ \pm 3 $^{\circ}\text{C}$ and a relative humidity of 33% \pm 3%. Firstly, the PES substrate was kept in a glass holder and the surface was covered with aqueous Su/NaOH solution (10 mL, with Su concentration ranging from 0.4% to 1.0% w/v while NaOH was fixed at 0.5% w/v) for 6.0 min. The aqueous solution was then removed from the holder and the residual water on the PES substrate surface was gently blown by an air gun. Secondly, the n-hexane solution containing 0.05-0.20% w/v of TMC was poured onto the Su-saturated membrane surface for 2.0 min which resulted in the formation of a polyester active layer over the PES substrate. Finally, the prepared membranes were rinsed with hexane to remove unreacted TMC, then stored in DI water at 4 °C before use. The denotation 'Sux/TMCy' represents a Su-TMC membrane prepared from an aqueous solution with Su concentration of x % w/v and an organic solution with TMC concentration of y % w/v. In this work, 1% w/v and 10 mg/mL are equivalent.

In order to highlight the universal applicability of natural carbohydrates for preparing polyester LNF membranes, Gl0.6/TMC0.1 and R0.6/TMC0.1 polyester LNF membranes have also been prepared via the same fabrication process as the Su-TMC membrane.

2.2.3. Membrane characterization

The membrane morphology was inspected by FESEM (Philips XL30 FEG, the Netherlands). The membranes were sputtered with gold (Au) to enhance the conductivity before SEM observation. The surface roughness of the membranes was observed by a dimension 3100 AFM device

(Bruker USA) under atmospheric air with 5 × 5 μ m² scanning area. The elements content and the chemical constitution of the membranes were characterized by NEXUS670 Fourier transform infrared (FTIR) spectrometer and x-ray photoelectron spectroscope (XPS, X-Max, Germany). To obtain the hydrophilicity of membranes, the water contact angle (WCA) was measured using a contact angle goniometer (OCA20, Dataphysics Instruments, Germany) with 2 μ L water droplets at 5 different locations. The electrical properties of the membrane surface were investigated using an Electrokinetic Analyzer (SurPASS 3, Anton Paar, Austria) via the streaming potential method. Before characterization, all the membranes were dried in a vacuum chamber at room temperature for over 48 h.

2.3. Membrane performance test

A dead-end apparatus (HP4750 stirred cell, Sterlitech Crop., Kent, WA, USA) with an effective area of 14.6 cm^2 and a trans-membrane pressure of 2 bar was used to evaluate the membrane performance (i. e., water permeance, salt and dye rejections). Membranes were prepressurized with DI water for 30 min at 6 bar to attain a steady water flux prior to filtration. After compaction, the water permeability (WP, LMH bar⁻¹) was calculated by the following equation: WP = $V/(A \cdot \Delta t \cdot \Delta p)$, where V represents the volume of permeate liquid (L) collected over a period of sampling time Δt (h), A is the effective membrane area (m²), Δp is the trans-membrane pressure (bar). The selectivity of membranes was separately characterized by solutions containing salts (NaCl, Na₂SO₄, MgCl₂ and MgSO₄ 1 g/L) and dyes (CR, DR23, and RB2, 200 ppm). To estimate the MWCO of the membranes, PEG molecules with different molecular weights were chosen as the solutes in the aqueous solutions. The rejection of different solutes was calculated using $R = (1 - C_p/C_f) \times 100\%$, where C_p and C_f (g L⁻¹) are the concentrations of the solute in the feed and permeate solutions respectively. The rejection of salts (NaCl, Na₂SO₄, MgCl₂ and MgSO₄ 1 g/L), dyes (CR, DR23, and RB2, 200 ppm) and PEG molecules (200, 600, 1000, 1500, and 2000 Da, 1000 ppm) was separately tested at 2 bar and room temperature. All dye concentrations in the feed and permeate were characterized by a UV-spectrophotometer (Shimadzu, Japan). The single salt concentrations were tested with a conductivity meter (Thermo Scientific Orion Star A212). For dye/salt mixture solutions, the residual dyes in the permeate were completely adsorbed with activated carbon, then salt concentrations were measured. The concentration of PEG molecules was examined by a TOC analyzer (TNM-L ROHS, Shimadzu, Japan).

All performance tests were repeated at least three times to ensure experimental repeatability.

2.4. Antifouling and stability properties test

The fouling behavior of polyester TFC LNF membranes was explored with CR, RB2, and DR23 solutions (200 ppm) at room temperature and 2 bar. The initial pure water flux test was carried out for 1 h and the average water flux was recorded every 10 min as $J_{w,1}$. Then, the dye solution (200 ppm) was filtered for another 1 h and the average value of permeate flux was recorded as J_p . The fouled membrane was then rinsed with DI water for 30 min. Afterwards, the pure water flux after cleaning $J_{w,2}$ was measured again at the same conditions. The above protocol of antifouling properties for each membrane was repeated for 2 cycles. The fouling behavior of membranes was explored by the flux recovery ratio (FRR) and the total fouling ratio (R_t): *FRR* = $(J_{w,2}/J_{w,1}) \times 100\%$; *R*_t = $(1-J_p/J_{w,1}) \times 100\%$. Reversible fouling (Rr) can be used to explore the fouling caused by concentration polarization using the following equation: $R_r = (J_{w,2} - J_p)/J_1 \times$ 100%. Irreversible fouling (R_{ir}), which is closely related to the adsorption or deposition of molecules, can be expressed by $R_{ir} = R_t - R_r$.

The stability of the Gl0.6/TMC0.1 membrane was studied through a

75 h filtration test at 2 bar with a feed solution containing 200 ppm DR 23 and 1 g/L Na_2SO_4 . Then, permeability and solution rejection were measured as mentioned above.

3. Results and discussion

3.1. Characterization of the Su/TMC LNF membrane

As a proof-of-concept, the sucrose, one of the carbohydrates, was employed to prepare polyester selective layers on PES supports (Fig. 2a). Sucrose was chosen for its low-cost availability, low reactivity, and large molecular size that can possibly increase the formation of less crosslinking and larger pores during IP. Sodium hydroxide, which can control the hydroxyl groups of sucrose to deprotonate and form more reactive alkoxide ions, was chosen as a key parameter to form the polyester films. With the Su-NaOH solution, IP was conducted with a TMC/hexane solution to form the polyester thin selective layers. FTIR with expected characteristic peaks and XPS analysis of the variations in the content of elements were deployed to verify the presence of the polyester thin selective layer on the PES substrate. Different from the PES substrate, the FTIR spectrum of Su0.6/TMC0.1 exhibited a new peak at 1732 cm^{-1} (C=O), which should correspond to the vibration of the ester group (Fig. 1a), indicating the formation of ester bonds through IP between the hydroxyl groups from Su and the acid chloride groups from TMC (Jin et al., 2021a; Xue et al., 2019). The XPS spectrum (Fig. 1b) showed that the emission peaks of S 2 s (233.3 eV) and S 2p (167.8 eV)

derived from the PES substrate substantially weakened for the Su0.6/TMC0.1 membrane, further confirming the presence of polyester layers on the substrate. The C 1 s core spectrum of the Su0.6/TMC0.1 membrane exhibited three peaks of O–C=O, C–O, and C=O groups (Fig. 1c), which confirms that the polyester layer was successfully formed. As shown in Table S2, C, O, and S elements are present in these two membranes. The Su0.6/TMC0.1 membrane has a higher O/C ratio than the PES substrate, which further confirms the formation of a polyester layer.

As shown in Fig. 1d, the concentration of Su and TMC was found to influence the hydrophilicity of the membranes. As there are more hydroxyl and carboxylic groups in polyester membranes prepared by IP than in PES substrate, the surface of the polyester membranes is slightly more hydrophilic than that of the PES substrate. The WCA varied from 58.3 ° to 50.2° when the Su concentration increased from 0.4% w/v to 1.0% w/v. The reason is that the content of hydrophilic hydroxyl groups increased with increasing Su concentration, causing a more hydrophilic membrane surface (Liu et al., 2020). Furthermore, the hydrophilicity of the surface of the membranes tends to be strengthened with increasing TMC dosage. Apparently, the increased unreacted acid chloride groups would be hydrolyzed to form more hydrophilic carboxyl groups, which was responsible for this phenomenon (Tian et al., 2020). The zeta potential results (Fig. 2e) revealed that the polyester membranes have a negatively charged surface over a wide pH range (3.0-9.0) (Qian et al., 2020).



Fig. 1. (a) FTIR spectra of PES and Su0.6/TMC0.1 membranes; (b) XPS survey spectra of PES and Su0.6/TMC0.1 membranes; High-resolution XPS spectra of (c) C 1s for Su0.6/TMC0.1 membranes; (d) WCA of fabricated membranes with different Su and TMC concentrations.



Fig. 2. (a) Schematic representation of Su-based polyester LNF membranes; the SEM and AFM images for (b) PES substrate and (c) Su0.6/TMC0.1; (d) the change tendency of MWCO as a function of Su concentration; (e) the zeta potential of PES and Su0.6/TMC0.1 membranes.

3.2. Morphological characterization of Su/TMC LNF membranes

SEM and AFM images demonstrate that the PES substrate comprised a typical smooth surface (Fig. 2b). After the polyester film was formed on the PES substrate, the membrane morphology changed considerably. As can be seen from Fig. 2c, microsphere structures, formed by Su diffusion from the PES substrate into the organic phase to react with TMC, appear on the surface of the Su/TMC membrane (Jin et al., 2021b). More microsphere structures are present as the Su concentration increases (Fig. S1). This is primarily ascribed to the accelerated diffusion of Su as its concentration increased since IP is a self-limiting process (Liu et al., 2018). In addition, the microspheres can increase the effective filtration area of the prepared membranes and thus increase the membrane permeability (Tan et al., 2018b). Furthermore, the cross-sectional structure of Su/TMC LNF membranes that has some relation of permeable properties is also present in Fig. S1.

3.3. Optimization of separation performance

The separation performance of the resultant polyester membranes was optimized by changing Su and TMC concentrations separately. This allows to explore whether the prepared membranes can effectively purify the dye while achieving a high salt permeability. Single component dyes (CR, DR23, RB2) at 200 ppm or salts (Na₂SO₄, NaCl, MgSO₄, MgCl₂) at 1000 ppm were employed in filtration experiments. Fig. 3 presents the effect of the Su concentration on water permeability, single dye, and single salt rejections. With increasing Su concentration, from 0.4% to 1.0% w/v, the water permeability diminished from 89.3 to 30.8 LMH bar⁻¹, but the rejection of CR (99.3–99.5%), DR23 (98.5–99.5%), RB2 (97.2-99.0%), Na₂SO₄ (3.8-42.6%), NaCl (0.9-23.0%), MgSO₄ (0-4.1%), MgCl₂ (0-2.7%) improved (Fig. 3a, b and c). As confirmed by the MWCO results (Fig. 2d and S3), the MWCO decreased from 893 Da to 493 Da, which demonstrated that the polyester layer reduced the tunnels and strengthened the cross-linking degree, induced by the increase of the Su concentration in the aqueous phase. This decrease in the tunnels and increase in the cross-linking degree, caused by a high monomer concentration, results in a decrease of water permeability and an increase of solute (dyes and salts) rejection. According to the Donnan effect, a highly negatively charged surface should have a better rejection to anionic dyes and ions. However, the polyester membranes have a low rejection for Na₂SO₄, NaCl, MgSO₄, MgCl₂. This is because size exclusion should also be considered for LNF membranes with a larger pore size. As mentioned above, the MWCO of the Su-based membrane was large (Fig. 2d and S3), so even if the polyester membrane has a strong negatively charged surface, the salt rejection is still low. In contrast, the polyester membrane has an excellent rejection to negatively charged dyes with large molecules. An excellent dye rejection of polyester membranes, mainly associated with size exclusion and Donnan effect, was observed, with the following order: CR(696.6 Da) > DR23 (813.2 Da) > RB2 (774.2 Da). It is interesting that the highest rejection was observed for CR, which has a low molecular weight compared to the other dyes. This is attributed to the formation of large clusters by dyes in aqueous solutions (Li et al., 2020; Jin et al., 2021b).

Combined with the effect of the TMC concentration on the



Fig. 3. (a) DI water, (b) dye, and (c) salt solution permeability and rejection of membranes with different concentrations of Su monomer; (d) schematic representation of dye/salt separation of Su/TMC polyester membrane.

membrane performance as shown in Fig. S4, when the Su and TMC concentration was fixed at 0.6% and 1.0% w/v, respectively, the Su0.6/TMC0.1 membrane reached an optimal separation performance, i.e., water permeability of 52.4 LMH bar⁻¹ with a high rejection of dyes and a high transmission of salts, the schematic representation of dye/salt separation can be found in Fig. 3d. In this case, the rejection of Su0.6/TMC0.1 membrane was high for CR (99.4%), DR23 (98.8%), RB2 (98.2%), and low for Na₂SO₄ (11.2%), NaCl (3.3%), MgSO₄ (0.9%), and MgCl₂ (1.8%). These results indicate that the polyester membrane has an excellent LNF performance, i.e., high dye rejection and low salt rejection, due to the tuned pore size, between the size of organic dyes and salt ions using the aqueous monomer Su with large size and low reactivity (Scheme 1).

The anti-fouling performance of polyester membranes was also explored, and the results showed that the flux recovery ratio (FRR) for three different dye solutions' cycling tests was superb under the circumstances of almost complete dye rejection (Fig. 4). The excellent antifouling with dyes was due to the hydrophilic and electronegative nature of the polyester membrane, which can form a water layer between dyes and the hydrophilic surface and enhance repulsion between negatively charged dyes and the surface; thereby, improving the anti-fouling performance (Vatanpour et al., 2011; Zinadini et al., 2014). Furthermore, textile wastewater contains some inorganic salts (Na2SO4, NaCl) and acid/alkali compounds (NaOH, HCl), which pose a challenge to the stability of the polyester LNF membrane. A long-term (75 h) test for purifying DR23/Na₂SO₄ mixture proved the extraordinary salt tolerance of the prepared polyester membrane and the practical application ability in the separation of dye/salt mixtures (Fig. 5). It can also be confirmed from the results in Fig. 5 that most of the initial flux was recovered (FRR



Fig. 4. The normalized flux of Su0.6/TMC0.1 membrane before and after the filtration of Congo red (pH=6.3), reactive blue 2 (pH=6.6) and direct red 23 (pH=6.7) solutions, separately. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

> 92.0%), and the surface fouling is basically reversible and can be removed by simple washing. Similarly, pH stability is also challenging for the polyester LNF membrane, of which the ester group can be



Fig. 5. Long-term stability of the prepared polyester LNF membrane,0.2 g/L DR 23 + 1 g/L Na_2SO_4.

hydrolyzed under strong alkaline conditions (Jin et al., 2021b). To explore the acid resistance of the prepared membranes, the Su0.6/TMC0.1 membrane was immersed in weakly acidic DI water with pH of 4.5 for 10 days then evaluated by filtrating weakly acidic DR23/Na2SO4 salty dye solutions (pH=4.5), the Su0.6/TMC0.1 membrane retains a stable filtration performance during 75 h measurement (Fig. S9). Therefore, textile wastewaters need to be adjusted to neutral or acid before using polyester LNF membrane technology to treat them.

3.4. The formation mechanism of sugar-based loose nanofiltration membranes

Generally, traditional NF membranes prepared by highly active amine monomers (such as PIP and MPD) via the IP process can have a high salt rejection. It was assumed that hydroxyl-containing monomers with larger size and lower reactivity were able to form the polyester selective layer with less cross-linking and larger pore size (Scheme 1); such properties are prerequisite for LNF membranes that are suitable for resource recovery from textile wastewater (Guo et al., 2021; Li et al., 2020). It is noteworthy that many natural renewable sugars (sucrose, glucose, raffinose) are such monomers, indicating that the above suggestion exhibits great potential in industrial application.

To investigate the formation mechanism of polyester LNF brought by hydroxyl-containing monomers, three sugar-based membranes, i.e., Gl0.6/TMC0.1, Su0.6/TMC0.1, and Ra0.6/TMC0.1, were prepared under the same conditions of an optimal Su/TMC membrane (i.e., 0.6% w/v Su and 0.1% TMC). The optimal conditions of Gl/TMC and Ra/TMC membranes were different from that of a Su/TMC membrane, so the separation performance of the three membranes differed, but they all possessed excellent water permeability and maintained a competitive dye/salt separation performance. The prepared sugar-based membranes were extensively characterized to confirm the successful fabrication of polyester LNF membranes and to further evaluate its mechanism.

XPS and FTIR spectroscopy results confirmed the successful formation of polyester selective layers for the three sugar-based membranes (Fig. S2, S5). Fig. 6 summarizes a comparison test for the permeability and rejection performance of the three sugar-based membranes. The water permeability of Gl0.6/TMC0.1, Su0.6/TMC0.1 and Ra0.6/ TMC0.1 were 115.9 LMH bar⁻¹, 52.4 LMH bar⁻¹, 81.1 LMH bar⁻¹,



Fig. 6. (a) DI water, (b) dye, and (c) salt solution permeability and rejection of membranes prepared by different aqueous monomers (i.e., Gl, Su, and Ra); (d) the MWCO for Gl0.6/TMC0.1, Su0.6/TMC0.1, and Ra0.6/TMC0.1 membranes.

respectively (Fig. 6a). The hydrophilicity of three sugar-based membranes is beneficial to their excellent water permeability (Fig. S6). Furthermore, they depicted both a high rejection of dyes (Fig. 6b) and a low rejection of salts (Fig. 6c). The three sugar-based membranes showed negative zeta potential over a wide pH range (Fig. S7), which was the key to give better rejection to negatively charged molecules. Among the sugar-based membranes, the water permeability of Gl0.6/ TMC0.1 is better than it is for the other two, while maintaining high dye/salt mixtures separation performance. The SEM results illustrated (Fig. S8) that numerous microsphere structures were present on the surface of the three sugar-based membranes. Compared to the other two, Gl0.6/TMC0.1 developed more microsphere structures, which may have helped in grabbing higher water permeability. In addition, the MWCO in Fig. 6d is also higher for the Gl0.6/TMC0.1 than the other two given its looser structure of polyester selective layers. The different flux and MWCO of the three kinds of sugar-based membranes is different mainly caused by different aqueous monomer activity and monomer size. According to Scheme 1, the size order (Ra > Su > Gl) and reactivity order (Su \approx Ra > Gl) of the three sugar monomers can be known. Compared with Su and Ra with three secondary hydroxyl groups, Gl with only one secondary hydroxyl group possesses lower reactivity, due to the easier deprotonation of secondary hydroxyl groups determining the reactivity of sugars in the IP reaction (Villalobos et al., 2017; Shen et al., 2020). The activity of Su and Ra in IP process is similar; however, the size of Ra is larger than that of Su; thus, the Ra0.6/TMC0.1 membrane is looser, and its water permeability is higher. Gl with only one secondary hydroxyl group possesses the lowest activity to participate in IP reaction, so the Gl0.6/TMC0.1 showed the loosest structure and highest water

Table 1

Comparison of dye/salt filtration performance.

Membrane	Method	Permeability (LMH bar ⁻¹)	Types of dye	Dye rejection (%)	Types of salts	Salt Rejection (%)	Refs.
Su0.6/TMC0.1	IP	52.4	Congo red	99.4	Na_2SO_4	11.2	This work
			Direct red 23	98.8	NaCl	3.3	
			Reactive Blue	98.2	$MgSO_4$	1.8	
			2		MgCl ₂	0.9	
Gl0.6/TMC0.1	IP	115.9	Congo red	99.4	Na ₂ SO ₄	1.3	This work
			Direct red 23	98.3	NaCl	1.1	
			Reactive Blue	92.1	MgSO ₄	0.4	
Da0.6 (TMC0.1	ID	01.1	Z Comeo rod	00.4	MgCl ₂	0	This work
Ka0.0/ INICO.1	IP	01.1	Direct red 22	99.4	Na2504	2.4	THIS WORK
			Beactive Blue	96.8	MaSO.	0.9	
			2	50.0	MgCl ₂	0	
Tannic acid/PEI	Co-deposition	41.5	Congo red	99.5	Na ₂ SO ₄	6.00	(Li et al., 2019)
runne deld, r Er	ee acposition	1110	congo reu	5510	NaCl	8.00	(Li et uii, Lory)
EGCg/PEI	Co-deposition	19.0	Congo Red	99	Na_2SO_4	4.10	(L. Zhang et al., 2019; N. Zhang et al., 2019)
MoS2-PSBMA/PES	Blending	18.5	Reactive	98.20	Na_2SO_4	2.20	(Liang et al., 2019)
			black				
			Reactive	99.30	NaCl	1.10	
			green		MgCl ₂	1.20	
					MgSO ₄	0.30	
CuTz-1/GO	Vacuum filtration	40.2	Congo red	99.4	Na_2SO_4	19.6	(Zhou et al., 2021)
			Direct red	98.2	NaCl	0.3	
CO DODILL DEC	D1 1	11.00	Methyl blue	94.9	N. 60	10.00	
GO-PSBMA/PES	Blending	11.98	Reactive	99.2	Na_2SO_4	10.00	(Zhu et al., 2016)
			Reactive red	97.2			
CS-MMT	Blending	15.6	Reactive	95	NasSO	22	(Zhu et al. 2015)
	Dicitating	10.0	black 5	50	1402004	22	(End et di., 2010)
			Reactive red	87	NaCl	5	
			49				
Ag ⁺ -PEI@HPAN	In situ self-	10.6	Congo red	99.80	Na_2SO_4	12.80	(Liu et al., 2018a)
	assembly		Acid fuchsin	99.50	NaCl	9.60	
			Crystal violet	99.20	MgCl ₂	6.20	
					MgSO ₄	8.30	
PVDF/SMA/CNT-	Blending+IP		Congo red	99.9	NaCl	1.7	(Kang et al., 2021)
COOH			Methyl blue	96.7	MgCl ₂	4.5	
			Acid fuchsin	96.1	MgSO ₄	1.2	
Fe3 ⁺ -PEI@HPAN	In situ self-	6.0	Congo red	99.53	Na ₂ SO ₄	5.89	(Li et al., 2018)
	assembly		Methyl blue	99.92	NaCl	7.46	
			Acid fuchsin	98.99	MgCl ₂	30.51	
Chitogan@UDAN	In city colf	7.0	Crystal violet	92.80	MgSO ₄	20.57	(Lin et al. 2018b)
CIIItOSall@HPAN	accombly	1.2	Acid fuchein	99.00	Na2304	4.60	(Liu et al., 2010b)
TiO2-HMDI-PES/	In situ self-	26.0	Congo red	98.70	Naci Na-SO	60	(N. Zhang et al. 2010; J. Zhang
β-CD	assembly	20.0	Congo reu	<i>.</i> ,	1422004	0.0	et al., 2019)
Membrane fouling		32.1	Direct red 80	99.9	NaCl	12.4	(Shen et al., 2019)
LNFM-1	IP	87.13	Congo red	98.97	Na ₂ SO ₄	5.04	(Jin et al., 2021b)
			Direct red 23	93.39	NaCl	0	
			Reactive Blue 2	91.02			
LNFM-2	IP	53.23	Congo red	99.62	Na_2SO_4	11.00	(Jin et al., 2021b)
			Direct red 23	95.22	NaCl	5.60	
			Reactive Blue	99.55			
			4				

permeability out of the three sugar-based membranes, even if the size of Gl was the smallest. Compared to other LNF membranes, our natural carbohydrate-derived sugars loaded in LNF membranes displayed a remarkable performance in both water permeability and dye/salt mixtures separation, surpassing most established LNF membranes (Table 1). Therefore, aqueous monomers with larger size and lower reactivity can be introduced for membrane preparation; hence, IP can achieve loose packing and larger pores in the selective layer with excellent water permeability. The resultant membrane can eventually fractionate dye/salt mixtures effectively. Maltose (Ma) and meso-erythritol (Me) were employed to further confirm the concept of loose nanofiltration, membranes, i.e., Su0.6/TMC0.1, Ma0.6/TMC0.1, three and Me0.6/TMC0.1, were prepared under the same conditions of the optimal Su/TMC membrane (i.e., 0.6% w/v Su and 0.1% TMC). They all possessed excellent water permeability and maintained a competitive dye/salt separation performance (Fig. S11, S12 and S13).

4. Conclusions

In summary, an extendable strategy was developed utilizing natural renewable carbohydrates to prepare high performant LNF membranes for effective dye/salt fractionation. The methodology employed hydroxyl-containing sugars (Gl, Su, and Ra) with large size and low reactivity polymerized with TMC to form loose packing and larger pores of LNF membranes. The sugar-based membranes were developed with a polyester selective layer with loose structures, high hydrophilicity and negatively charged surface, validating the high-water permeability, excellent rejection of dyes, high transmission of salts, excellent antifouling ability and good stability. Most importantly, this designed strategy can be extended to other hydroxyl-containing natural materials to produce next-generation energy-efficient membranes for fluid precise purification to minimize environmental pollution.

CRediT authorship contribution statement

Pengrui Jin: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Sara Chergaoui:** Methodology, Writing – review & editing. **Junfeng Zheng:** Conceptualization, Methodology, Formal analysis, Resources, Writing – review & editing. **Alexander Volodine:** Resources, Methodology, Formal analysis. **Xin Zhang:** Resources, Methodology, Formal analysis. **Ziyuan Liu:** Resources, Methodology, Formal analysis. **Patricia Luis:** Writing – review & editing. **Bart Van der Bruggen:** Writing – review & editing, Resources, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126716.

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