Tight ultrafiltration membrane: preparation and characterization of thermally resistant carboxylic cardo poly (arylene ether ketone)s (PAEK-COOH) tight ultrafiltration membrane for dye removal

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Abstract

Cardo poly (arylene ether ketone)s bearing hydrophilic carboxylic acid groups (PAEK-COOH) was successfully synthesized by condensation polymerization of 2-[bis(4-hydroxyphenyl)methyl] benzoic acid and 4,4'-bisfluorodiphenylketone. TGA and DSC analyses demonstrated that the material has an initial decomposition temperature and glass transition temperature of 360°C and 220°C respectively, which revealed the excellent thermal stability of PAEK-COOH. Then PAEK-COOH was employed to fabricate tight ultrafiltration membrane by the nonsolvent induced phase inversion process (NIPS). The water contact angle of the prepared membrane is 61.5°, indicating its good hydrophilicity. The PAEK-COOH tight ultrafiltration membrane possesses a pure water flux of $119.6 \pm 2.6 \text{ L m}^{-2} \text{ h}^{-1}$, dye permeation flux of $100.9 \pm 4.3 \text{ L m}^{-2} \text{ h}^{-1}$ and rejection of $99.8 \pm 0.33\%$ for Congo red at dye concentration of 100 ppm and operation pressure of 0.4 MPa. Membrane has a molecular weight cut off of 9260Da and gives complete penetration of monovalent inorganic salt NaCl but a slight rejection of divalent inorganic salt Na₂SO₄ (less than 10%). Thus, the membrane could be used in the decolorization of wastewater or fractionation of dye

and salt mixture for dye purification. The membrane also exhibits excellent antifouling performance and anti-dye adsorption properties with a flux recovery ratio of 91.5% for BSA and dye adsorption rate below 5.0% for four kinds of studied dyes, respectively.

1. Introduction

The amount of textile wastewater produced by dyeing industry has increased yearly. The wastewater is usually generated in the process of dyeing, rinsing and cleaning, which is usually of high temperature and involves high toxicity because of the high concentration of azo dyes and inorganic salts involved in it[1]. A lot of efforts have been made for the removal of dissolved organic dyes from the colored wastewater, including chemical coagulation, biological treatment, electrochemical oxidation, ozonation and adsorption by activated carbons, as well as membrane filtration process[2]. Membrane separation process is the most prevailing method for its low energy consumption, involving no chemical reaction, being easy to scale-up, high efficiency and simplicity[3], and the separation membrane, as the most essential component, determines the cost of and efficiency of separation process. Tight ultrafiltration membrane, such as UH004[4] which could reject 99.8% of dyes (Congo red, direct red 23, direct red 80, and reactive blue 2) while permeate 98% of salts (NaCl and Na₂SO₄), indicating its potential application in fractionation of dye and salt mixture. Membrane that possesses good salt permeation property could not only maintain high flux originating from the low osmotic pressure, but also improve the separation efficiency.

Kinds of polymeric materials have been applied to the fabrication of water process membranes, such as polyacrylonitrile (PAN)[5], cellulose acetate (CA)[6], poly(vinylidene fluoride)(PVDF)[7], polysulfone (PSf)[8, 9] and polyethersulfone (PES)[10, 11], yet most of them could hardly be used for the fabrication of thermally resistant membrane to deal with hot streams, especially the high temperature effluent. In practical operation process, the temperature of the wastewater could be as high as 95 °C which exceeds the resistant temperature of most polymeric membranes. Therefore some heat exchange units are included into the filtration procedure, which

only leads to the increase of energy consumption and equipment operation cost[12]. Hence, it's crucial to develop thermally resistant material for the handling of streams that are of high temperature.

Currently available materials such as poly(arylene ether ketone)s (PEEK), poly(phthalazinone ether nitrile ketone)(PPENK) are proven to have excellent thermal stability. However, industrial grade PEEKs, being hydrophobic and semi-crystalline polymers, is uneasy to fabricate membranes by the NIPS method for its poor solubility in common polar aprotic solvents. PPENK, composed of rigid phthalazinone and aromatic structure, has good thermal stability and reasonable solubility[13]. Nevertheless, the hydrophilicity of that category of materials is poor due to the lacking of hydrophilic substituent groups. Thus, membranes made from those materials are prone to be fouled in operation process. Therefore, the selection of proper materials that possess both temperature-resistant property and good hydrophilicity for the fabrication of high performance membrane is really necessary.

Phenolphthalein based poly (arylene ether ketone)s is a novel kind of high-performance PEKs with excellent solubility, mechanical toughness, thermal stability and property of being easy to be functionalized[14], which make the materials of this category good candidates for the fabrication of separation membranes, including gas separation[15], water purification and ion exchange membranes[14, 16, 17]. Moreover, researches show that the introduction of carboxylic acid group could improve the solubility and hydrophilicity of material. Vankelecom et al found that the introduction of valeric acid group into the polymer backbone could enhance its solubility and thus it can be used to prepare solvent resistant nanofiltration membrane by crosslinking the valeric acid group with diamine[18]. Park et al carboxylated polysulfone by direct chemical functionalization and then used this material to prepare hydrophilic, mechanically stable microporous support membranes for forward osmosis (FO) membrane. The introduction of carboxylic acid group into hydrophobic polymer backbone greatly improved the hydrophilicity of PSF without sacrificing its mechanical strength. Carboxylated polysulfone-based FO membranes showed significant higher fluxes than PSF-based

FO membranes[19]. Wang et al have found that the introduction of pendent carboxylic acid group into poly(arylene ether ketone) copolymers could prepare good antifouling ultrafiltration membranes[20]. We can conclude from the above that the carboxylated materials not only possess good solubility and high hydrophilicity, but also have anti-swelling property and dimension stability, when compared with other hydrophilic materials, such as sulfonated polymers which are difficult to be dissolved in solvent and susceptible to swelling in water at high sulfonation degree[21, 22]. Consequently, the fabrication of water purification membranes by using carboxylated phenolphthalein based poly (arylene ether ketone)s (PAEK) is very promising.

In this study, we successfully synthesized cardo poly (arylene ether ketone)s bearing hydrophilic carboxylic acid groups (PAEK-COOH) by condensation polymerization of 2-[bis(4-hydroxyphenyl)methyl] benzoic acid and 4,4'-bisfluorodiphenylketone in DMSO. Thermal analyses demonstrate that the polymer has a decomposition temperature of 360 °C and glass transition temperature of 220 °C, which suggests that the polymer is well qualified for preparing membranes to deal with hot water without temperature controlling. Then this material was used to prepare tight ultrafiltration membrane by the NIPS method. The resulted membrane was hydrophilic in nature and can be applied to wastewater discoloration and dye purification. Its filtration performance towards negatively charged dyes was investigated in detail. Besides, membrane salt-influenced performance, temperature-dependent performance and antifouling performance have also been studied.

2. Experimental section

2.1. Materials and reagents

Phenolphthalein (PPH) was purchased from Beijing Chemical Reagent Company. 2-[bis(4-hydroxyphenyl)methyl] benzoic acid (PPH-COOH) was obtained by reducing industrial raw material phenolphthalein with sodium borohydride (NaBH_4) in water, then being washed and recrystallized in ethanol, with purity of 99.9%. And 4,4'-bisfluorodiphenylketone (BFDPA) was purchased from Sinopharm Group Chemical Reagent, dried at 80 °C for 12h before polymerization. NaBH_4 and K_2CO_3 were obtained from Aladdin. The detail information and properties of dyes are

presented in Table 1. All other chemicals were obtained from commercial sources and used as they were received.

Table 1 The characteristics of negatively charged dyes studied.

Dye	Obtained source	Molecular structure	Molecular weight (g mol ⁻¹)	purity	Charge	Max. absorption wavelength (nm)
Congo red (CR)	Alfa Aesar		696.08	Indicator grade	-2	488nm
Coomassie brilliant blue (BBR)	Amresco		840.27	Ultrapure grade	-1	556.5nm
Direct red 23 (DR23)	Aldrich		813.72	Dye content 30%	-2	508.0nm

Evans blue Alfa Aesar
(EB)

959.98

Not given

-4

608.5nm

2.2. Synthesis of carboxylated cardo poly (arylene ether ketone)

Carboxylated cardo poly(arylene ether ketone)s (PAEK-COOH) was prepared by condensation polymerization of 2-[bis(4-hydroxyphenyl)methyl] benzoic acid (PPH-COOH) with 4,4'-difluoro diphenylmethanone (DFPM) in DMSO solution catalyzed by K_2CO_3 at 180 °C with the initial molar ratio of PPH-COOH, DFPM and K_2CO_3 at 1:1:1.7. The reaction was conducted after 15h heating and then was cooled down to room temperature. After that, the viscous polymer solution was poured into diluted hydrochloric acid solution to remove salts and convert the basified COOK group to COOH form. The precipitated fibrous polymer was collected and washed with distilled water several times prior to being dried under vacuum at 120 °C to produce the final product. The finally obtained yield was 99%.

Scheme 1 Synthesis procedure of PAEK-COOH

2.3. Fabrication of tight ultrafiltration membrane

The asymmetric tight ultrafiltration membrane was fabricated by using the nonsolvent induced phase inversion process (NIPS). Firstly, PAEK-COOH was dissolved at 60 °C in a component solvent of NMP (N-methyl-2-pyrrolidone) and DO (1,4-dioxane) at a predetermined polymer concentration of 18 wt% and solvent mixture ratio of $m_{NMP}/m_{DO} = 8/2$. Then the homogeneous polymer solution was degassed and left to stand for about 10h to completely remove air bubbles. Finally, the viscous polymer solution was cast onto the non-woven fabrics with a knife gap of 150 μ m at the standard

humidity condition (40%), and the original film was subsequently immersed into the deionized water horizontally at 25 °C for taking the phase inversion process. The as-prepared membrane was kept at deionized water for one day before being tested.

2.4. Characterization

¹H NMR spectra of the polymer was recorded by Bruker Avance 300 MHz spectrometer.

Thermal stability analysis: the glass transition temperature and thermal decomposition temperature are two critical parameters for the characterization of the thermal properties of a material. Differential scanning calorimetry (DSC) experiment was carried out using a TA Instruments DSC Q20 (USA) from 50°C to 350°C under an N₂ atmosphere at a heating rate of 10°C min⁻¹; the thermal gravimetric analysis (TGA) of PAEK-COOH was performed under nitrogen on a PerkinElmer TGA-2 thermo gravimetric analyzer from 50°C to 800°C at a heating rate of 10°C min⁻¹.

Scanning electron microscope (SEM, XL 30 ESEM FEG, FEI Company) was employed for membrane morphology observation. Membrane for surface morphology observation was fixed on a metal support and that for cross section morphology was obtained by peeling off the membrane from supporting polyester fabric, then was cryogenically broken in liquid nitrogen. The coupon was freeze-dried and gold sputtered before testing.

Atomic force microscopy (AFM, Dimension Icon SPM, Bruker) is employed for microscopic investigation of membrane surface roughness. The specimens of samples were frozen dried under vacuum for about 5 hours before testing in order to maintain the archetypal surface morphology of the membranes. Small pieces of the prepared membranes (approximately 1 cm²) were attached on a silicon wafer and imaged in tapping mode in air.

The dynamic water contact angle of membrane was measured using a Drop Shape Analysis Dataphysics OCA 20 at ambient temperature.

The charge property of tight ultrafiltration membrane surface was determined by streaming potential measurement with a SurPASS electrokinetic analyzer ((SurPASS, Anton Paar GmbH, Austria). The streaming potential measurement was carried out

using Ag/AgCl electrodes in a 0.01M KCl background electrolyte solution. The pH of the solution was accommodated using the 0.1M HCl and 0.1M NaOH acid-base adjust-pair. The surface zeta potential ξ was calculated by the Helmholtz-Smoluchowski equation[23]:

$$\xi = \frac{\Delta E}{\Delta P} \frac{\eta \kappa}{\varepsilon \varepsilon_0} \quad (1)$$

where ΔE is the streaming potential of the membrane, ΔP is the applied pressured, ε is the dielectric constant of the streaming solution, ε_0 is the vacuum permittivity, η is the solution viscosity, and κ is conductivity of bulk solution.

2.5. Filtration experiments

The filtration experiment was carried out in a cross-flow filtration system. All membranes were precompacted by deionized water at 0.4 MPa and 25 ± 2 °C for 2h to obtain a steady filtration performance. The dyes used in the separation experiment was Congo red (CR), coomassie brilliant blue R250 (BBR), Direct red 23 (DR23) and Evans blue (EB). Membrane separation performance towards dyes was accomplished by dissolving a single dye into deionized water. Membrane filtration experiment of multi-component solutions consisting of dyes and inorganic salts was conducted at 100 ppm dye concentration in the presence of variable amount of salts with the concentration at 5, 10, 20, 30, 40 g L⁻¹ in deionized water. The filtration flux of deionized water and dye solution were calculated from:

$$F = \frac{V}{A \times t} \quad (2)$$

where V is the permeation volume (L), A is the effective membrane area (cm²), and t is the filtration time (h). Protein rejection (R) is calculated as follow:

$$R = \left[1 - \frac{C_p}{C_f} \right] \times 100\% \quad (3)$$

where C_p and C_f are the concentrations of dyes in the permeation and feed solution respectively. Dyes concentration of the permeation and feed solution were measured by a UV-vis spectrophotometer at the biggest absorption peaks of each dye.

Besides, the membrane performances at different temperatures were measured by determined Congo red solution permeation flux and its rejection at each temperature in the range of 20 °C to 95 °C at an interval of 20 °C at an operation pressure of 0.3

MPa.

2.6. Molecular weight cut off (MWCO) and pore size distribution

The MWCO of membrane was conducted by filtrating a series of polyethylene glycols (PEGs) with average molecular weight of 2000, 4000, 6000, 8000 and 10000 Da at a concentration of 100 ppm and 0.4 MPa. The concentration of PEGs was measured by the total organic carbon (TOC) at (TOC-VCPHSHIMADZU). All the measurements were based on three samples and the average values were adopted. Rejection determination of PEGs was similar as dyes using Equation (3). The MWCO of membrane has been defined as the molecular weight of PEG which has 90% rejection rate, and the mean effective pore size (μ_p) has been defined as the Stokes radius (d_s) of a neutral solute at 50% rejection rate. The Stokes radius of PEG could be calculated on the basis of its average molecular weight[24, 25]:

$$d_s = 16.73 \times 10^{-12} \times M_{\text{PEG}}^{0.557} \quad (4)$$

The relationship between pore size distribution and solute Stokes radius was mathematically fitted by an exponential probability density function on the hypothesis that there are no hydrodynamic and electrostatic interactions between neutral solutes and membrane pores.

$$\frac{dR(r_p)}{dr_p} = \frac{1}{r_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln r_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (5)$$

where r_p is the pore radius and μ_p is the mean effective pore size, and σ_p is the geometric standard deviation, which is the ratio of r_p at 84.13% rejection rate over that at 50%.

2.7. Antifouling performance evaluation

The antifouling performance of membrane was tested in BSA model protein solutions. 1000 ppm of BSA in 10 mmol L⁻¹, pH=7.4 phosphate buffer solution (PBS) at room temperature was used as the feed solution for antifouling study. Membranes were compacted at 0.2 MPa for 1h. Then the operation pressure was turned down to 0.1 MPa to measure the initial pure water flux, which was recorded as $J_{w,1}$, according to equation (2). After the flux measurement, the operation cells were refilled with model protein solution and kept for 1h, and the flux of BSA solution was recorded as J_p .

After that, the membrane was rinsed thoroughly with pure water for 1h. Then the pure flux of the cleaned membrane was measured again, recorded as $J_{w,2}$. The filtration test was performed on three coupons and the antifouling test was operated for two cycles for each membrane. Then the obtained average values were employed for antifouling performance evaluation. The flux recovery ratio (FRR) and total fouling ratio (R_t) were calculated.

$$FRR = \frac{J_{w,2}}{J_{w,1}} \times 100\% \quad (6)$$

$$R_t(\%) = \left(1 - \frac{J_p}{J_{w,1}}\right) \times 100\% \quad (7)$$

In fact, the total fouling of membrane can be divided into two parts: reversible fouling (R_r) and irreversible fouling (R_{ir}). The reversible fouling of membrane was caused by concentration polarization while the irreversible fouling could be ascribed to the adsorption and deposition of proteins on membrane surface. R_r and R_{ir} were evaluated using the following equation.

$$R_r(\%) = \left(\frac{J_{w,2} - J_p}{J_{w,1}}\right) \times 100\% \quad (8)$$

$$R_{ir}(\%) = \left(\frac{J_{w,1} - J_{w,2}}{J_{w,1}}\right) \times 100\% \quad (9)$$

3. Results and discussion

3.1. Synthesis and characterization of polymer PAEK-COOH

Fig.1. The ^1H NMR spectra of PAEK-COOH

PAEK-COOH was synthesized by the aromatic nucleophilic substitution (SNAr)

polycondensation of 2-[bis(4-hydroxyphenyl)methyl] benzoic acid (PPH-COOH) and 4,4'-difluoro diphenylmethanone (DFPM) as shown in Scheme 1 and the chemical structure of the target material was confirmed by ^1H NMR spectroscopy in DMSO as shown in Fig.1. Particularly, the peak at $\delta = 13.0$ ppm could be assigned to the chemical shift of protons of carboxylic acid group. The resulting polymer has an intrinsic viscosity of 0.55 which was measured by an Ubbelohde capillary viscometer in DMAc at $30 \pm 0.02^\circ\text{C}$ at a polymer concentration of 0.5 g dL^{-1} , suggesting that the obtained polymer has a high molecular weight.

Fig.2. The DSC and TGA curves of PAEK-COOH.

Fig.2. is the DSC and TGA curves of PAEK-COOH. PAEK-COOH is a relatively thermal stable material with a glass transition temperature of 220°C and an initial decomposition temperature of 360°C , which suggests that the polymer is qualified for the preparation of thermal resistant ultrafiltration membranes for dye removal.

3.2. Preparation and characterization of membrane

PAEK-COOH was dissolved in component solvent pair of NMP/DO, of which NMP is an ideal solvent and DO is a volatile co-solvent, respectively. The introduction of DO is crucial for the formation of a tight skin layer, because co-solvent DO has lower water affinity than NMP. The addition of DO in casting solution would decrease the nonsolvent in-flow speed during the convection diffusion process. Relatively high solvent out-flow speed and low nonsolvent in-flow speed in the convection diffusion process may lead to the formation of a dense skin layer[26]. Then PAEK-COOH tight ultrafiltration membrane was prepared by the NIPS method using deionized water as

coagulation bath at 30°C and 30%-40% relative humidity.

Fig.3. Characterization of membrane morphology. (a) Surface morphology, (b) 3D AFM image, (c) and (d) cross section morphology of membrane.

Fig.3. shows the morphology of PAEK-COOH membrane. The membrane has a ridge-and-valley structure (Fig.3b) yet no obvious macrovoids in the surface (Fig.3a), which provides a rough surface morphology having an average roughness of 12.8 nm. The cross section morphology (Fig.3c) of membrane composes of an integrally skinned thick top layer and an irregular finger-like porous supporting layer. In the filtration experiment, the dense top layer could act as the separation layer which determines the separation performance of membrane. Membrane rejection of PEGs that have different molecular weight is used to characterize the molecular weight cut off (MWCO) and pore size distribution of membrane, as shown in Fig.4.

Fig.4. The MWCO and pore size distribution of membrane.

Fig.4. is the MWCO and pore size distribution of membrane. The MWCO of membrane is 9260 Da and mean effective pore size is 1.761 nm, respectively, which suggests the PAEK-COOH membrane is a tight ultrafiltration membrane.

Fig.5. Zeta potential and water contact angle of PAEK-COOH membrane.

Fig.5 (a) is the zeta potential of PAEK-COOH membrane, which is a function of pH, indicating that the membrane is slightly negatively charged in pH range of 4.0 to 10.0, and the isoelectric point is pH = 3.7. Zeta potential measurement suggests that the net charge density on membrane surface was very low, because COOH group has weak acidity; its dissociation constant is similar to benzoic acid, about 6.4×10^{-5} , which means only 0.8% of the carboxylic group is dissociated at neutral condition. Fig.5 (b) is the time-dependent water contact angle of membrane, which reaches its equilibrium state within 3 seconds at 61.5° , suggesting the inherent hydrophilic property of membrane material.

3.3. Separation performance of membrane

3.3.1. Filtration of dye solution

Fig.6. Membrane permeates flux of pure water, dye solutions and membrane rejection for dyes. (Dye concentration: 0.1 g L⁻¹.)

Fig.6. shows membrane permeates flux of pure water and dye solutions, as well as membrane rejection for different dyes. The pure water flux of membrane is 119.8 L m⁻² h⁻¹ at 0.4MPa, permeate flux of CR is 104.5 L m⁻² h⁻¹. The permeate flux of dyes fluctuates with dye species, which is ranked in the order of $F_{CR} > F_{DR23} > F_{BBR} > F_{EB}$, and the rejection of all dyes are higher than 99.0%. The flux of membrane declines with the increasing of charges that dye occupied, from two-charged dyes, CR and DR23, to four-charged dye EB, excluding the one-charged dye BBR. The osmotic pressure of dye solution caused by dyes is proportional to dye charges and the more the charges a dye possesses, the higher the osmotic pressure to be. However, membrane flux would decline with the increasing of osmotic pressure. The flux for CR and DR23 is close for they both possess two negative charges, so the osmotic pressure of them is also similar and they have closer flux. For four-charged dye EB, its osmotic pressure is the biggest among all the dyes, so it has the lowest dye permeate flux. BBR is an individual for its flux is not regular like that of others. BBR has only one negative charge, but a relatively high molecular weight, the electrostatic interaction between dye molecules, as well as dye molecule and membrane surface is smaller, so dye aggregation and dye adsorption trend are promoted, which induces

membrane fouling. Therefore the permeate flux of BBR is the lowest.

Table 2 summarizes the filtration performances of commercially available and literature reported dye separation membranes. In this study, we focus on high permeability and dye/salt selectivity, the as-prepared membrane has relatively high flux, dye rejection and salt permeation, therefore the membrane can be a candidate for decolorization of wastewater or fractionation of dye and salt mixture for dye purification.

Table 2 Comparisons of the performance of PAEK-COOH tight ultrafiltration membrane with that of commercially available and literature reported dye separation membranes.

Membrane	PWF ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) ^a	DPF ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) ^b	Dye rejection (%)	Operating conditions		Ref.
				pH limitation	Max. temp.(°C)	
Commercial Sepro NF 2A	10.5	9.6	99.98	3.0-10.0	50	[27]
Commercial Sepro NF 6	13.7	13.2	99.95	3.0-10.0	50	[27]
UH004 (hydrophilic PES)	27.5	27.0	98.9	0-14.0	95	[4]
SIO ₂ -PIL/PES blending NF	21.2	null	90-93	--	--	[28]
GO-PSBMA/PES blending NF	12.5	8.8	95	--	--	[29]
Zwitterion-hydrotalcite incorporated PES	20.1	null	86.7	--	--	[30]
PAEK-COOH	29.5	25.0	95	1.0-10.0	95	This work

^aPWF, pure water flux, ^bDPF, dye permeate flux. Operation pressure: 0.4MPa.

3.3.2. Filtration of dye/salt mixtures

Fig.7. Filtration performance of dye/salt mixture. (Dye: BBR, the background salt is Na_2SO_4 .)

Wastewater in dyeing and textile industry usually composes of high concentration of salts and dyes. As a byproduct from dye synthesis or additive in dying process, salts have negative impacts on dye permeate flux and rejection during membrane filtration process. Fig.7. shows the filtration performance of membrane for BBR at different salt concentrations. The permeate flux of dye/salt mixture decreases with the increasing of salt concentration in solution, which is in agreement with the study done by Arnot et al[31]. This result can be explained by the reduction of the net driving pressure due to the difference in osmotic pressure between the retentate and permeate streams, especially in high salt concentrations, despite that most of salt has penetrated. The rejection of BBR increases when a small amount of salt (salt concentration < 0.5wt %) is introduced, and the figure reaches to a steady value when more salt was added in dye solution. The introduction of background electrolytes in dye solution can promote dye aggregation, because anionic dye would aggregate under the influence of mental ions. This is because the presence of counterions in the aggregates would offset the Coulombic repulsive forces, so the effect, as well as the dye hydrophobicity is accelerated by the addition of electrolytes to dye solution [32, 33]. BBR has one negative charge and a molecular weight of 840Da with a triangle molecular

configuration, so the charge-to-mass ratio is very lower; dye aggregation effect of dye molecules induced by salts is notable. Therefore membrane rejection increases with the increasing of salt concentration.

3.3. Effect of solution pH on membrane performance

Solution pH could affect the ionization degree of PAEK-COOH, which in turn influences the membrane filtration performance towards dyes and salts.

Fig.8. Effect of solution pH on membrane dye filtration performance. Test conditions: CR-water solution, dye concentration of 100 ppm and operation pressure of 0.4MPa, in the pH range of 2 to 13, and the pH of the system was adjusted by HCl and NaOH and stabilized at each pH point for at least 20min before test.

Fig.8. shows the effect of solution pH on membrane flux and rejection of CR. In the pH range of 2 to 11, membrane performance fluctuates with the pH of solution media; the flux of membrane has maximum value and the rejection also gets its optimal state at pH=5 to 7. In acidic conditions, dye permeation flux decreases and rejection increases. At lower pH value, sediments of dye occur and color of dye solution becomes dark blue. CR has sulfonated acid groups and the protonation of those groups decreases the polarity and solubility of CR, resulting in dye aggregation and precipitation. The flux decreases because of membrane fouling from precipitated dyes on membrane surface, while rejection increases due to the aggregation of dye molecules. In basic conditions, both the dye permeation flux and rejection would

decline as solution pH increases. Increasing the pH of filtration media would promote acid-base reaction between COOH group and NaOH, which leads to the ionization of membrane surface and the swelling of membrane material, and in turn greatly increases membrane hydrophilicity. Membrane material swelling could also affect membrane structure, which probably thickens the surface separation layer of membrane due to the swelling effect of elastic polymer networks[30], and finally decreases membrane flux. At higher pH value, the electrostatic interaction between membrane surface and dye molecules decreases for the reason that it is screened by excessive hydroxyl ions, just like the screening effect of salt[34] that could decrease membrane rejection. On the other hand, membrane swelling could widen the pore diameter distribution of membrane, during which the small pores become smaller and large ones become larger. Seen from Fig.4, small pores of membrane count for a large percent. According to Maxwell–Stefan model, the flux of small pores reduces to a higher degree than the larger pores, but the rejection is determined, to a larger extent, by bigger pores and reduces when membrane swelled[35].

3.4. Effect of operation temperature on membrane performance

PAEK-COOH is an excellent thermally stable material, so the effect of operation temperature on membrane flux and rejection of dyes could have practical and applicable significance.

Fig.9. Effect of operation temperature on the dye filtration performance of

PAEK-COOH tight ultrafiltration membrane in CR-water solution. Test conditions:

dye concentration of 100 ppm and operation pressure of 0.3MPa.

Fig.9. shows the effect of operation temperature on flux and rejection of CR. The dye permeates flux increases from $95 \text{ L m}^{-2} \text{ h}^{-1}$ to $138 \text{ L m}^{-2} \text{ h}^{-1}$, and its rejection decreases from 99.6% to 95.7% as the operation temperature varies from 20°C to 95°C with an operation pressure of 0.3MPa. When compared with the performance of membrane at room temperature, the dye permeates flux has an increment of 45.26%, while the rejection rate has a decrement of 3.91% at 95°C . That the dye permeate flux increases along with the increment of operation temperature can be ascribed to the corresponding increase in the mobility of water molecules with a simultaneous decrease in the viscosity of dye solution[36, 37]. As the flux of dye increases, the rejection decreases, which is consistent with the trade-off relationship between membrane flux and rejection[38].

The increasing of temperature could result in an increase in the diffusion of water and dye molecules. The decrement of dye rejection with increasing operation temperature indicates that the increase in mass transfer is greater for ionized dye molecules than for water, which make the permeation of dye slightly increase with the increment of dye permeate flux[31]. The small variation in membrane rejection could corroborate the conclusion presented by the DSC and TGA analyses with regards to the excellent thermal stability of PAEK-COOH. The excellent thermal stability of PAEK-COOH is due to the rigidity of polymer chain, which inhibits the longitudinal sliding displacement between inter-chains, thus prohibiting the tendency of membrane pores to collapse or expend with corresponding increment in the operation temperature. In the textile dying industry, the operation temperature range normally vary from 20°C to 90°C . This indicates that the membrane performance in the operation temperature range is quite acceptable and the temperature-dependent comprehensive performance of membrane could meet the requirements in industry application. Furthermore, using elevated temperatures could alleviate the disadvantage of low flux at room temperature by reducing solution viscosity, which could be particularly applicable to prepare time- and cost-effective membrane without the cooling procedure involved if

the effluent is generated at high temperature[34].

3.5. Membrane antifouling performance and dye adsorption properties

Membrane filtration performance and long-term stability depend greatly on membrane antifouling properties. The filtration properties of membrane used for wastewater treatment can be easily compromised or deteriorated from membrane fouling caused by protein adsorption on the hydrophobic membrane surface, which finally leads to the decrease of membrane operation efficiency. Therefore the antifouling performance is a critical aspect to evaluate the overall performance of membrane. In order to facilitate comparison, all permeate fluxes are normalized on the basis of initial pure water flux $J_{w,1}$.

Fig.10. (a) Time-dependent normalized flux and (b) Antifouling indexes of PAEK-COOH membrane for the filtration of BSA solution.

Fig.10. demonstrates the time-dependent normalized flux and antifouling indexes of membrane during the protein filtration procedure. The permeate flux decreases with a degree of 28.5% when the pure water is substituted by protein solution, which is a combined influence of concentration polarization and membrane fouling. After being rinsed with water for 1h, the permeate flux of the membrane recovers to 91.5% (FRR=91.5%). Therefore, the irreversible fouling and reversible fouling rate are 8.5% and 20%, respectively. In the second cycle, the protein solution permeate flux is almost equivalent to that in the first cycle, which indicates that the irreversible fouling caused by permanent protein adsorption reached to an adsorption–desorption equilibrium after protein filtration and rinsing process, and this does not have an

effect on the permeation of protein solution. The irreversible fouling counting for 8.5% of total flux declination is unavoidable and cannot be removed by facile washing or rinsing. In a word, the higher FRR suggests that PAEK-COOH membrane has a relatively better antifouling property.

Table 3 Dye absorption properties of PAEK-COOH membrane

UV-Vis absorption intensity	CR	BBR	DR23	EB
100ppm dye solution	6.290	2.610	1.988	24.976
Surface absorbance	0.031	0.129	0.98	0.048
Absorption rates (%)	0.49	4.94	4.93	0.19

Static dye absorption properties of membrane are also essential to evaluate its comprehensive performance and industrial applicable capacity[39]. Membrane coupons were immersed into 100 ppm of dye solution for 5h at room temperature, and then cleaned under ultrasonication for 10min to remove the deposited rather than adsorbed dyes. The UV-Vis absorption of the dye fouled-cleaned membrane surface is recorded and employed to assess membrane dye absorption properties and the results are illustrated in Table 3. The PAEK-COOH membrane exhibits excellent anti-dye adsorption properties with the dye adsorption rate below 5.0% for four kinds of studied dyes. This can be attributed to the good hydrophilicity of membrane, which reduces the hydrophobic interaction between dye molecules and membrane surface.

4. Conclusions

Poly (arylene ether ketone) with pendent carboxylic acid group (PAEK-COOH) was synthesized by the aromatic nucleophilic substitution (S_NAr) polycondensation of 2-[bis(4-hydroxyphenyl)methyl] benzoic acid (PPH-COOH) and 4,4'-difluoro diphenylmethanone (DFPM), and it was a membrane preparation material with good thermal and mechanical stability. Hydrophilic tight ultrafiltration membrane is prepared by this material using the NIPS method, which has a molecular weight cut off of 9260Da and effective pore size of 1.761nm. The membrane displays high permeation flux and good dye rejection, with a pure water flux of $119.6 \pm 2.6 \text{ L m}^{-2} \text{ h}^{-1}$, permeation flux of $100.9 \pm 4.3 \text{ L m}^{-2} \text{ h}^{-1}$ and rejection of $99.8 \pm 0.33\%$ for Congo

red at dye concentration of 100 ppm and operation pressure of 0.4 MPa, which can be used in wastewater decolorization and dye purification. Effect of operation temperature on membrane performance reveals that the membrane is thermally stable and suitable for high temperature filtration application. The antifouling performance and anti-dye adsorption properties of membrane are excellent, possessing a FRR of 91.5% for BSA and dye adsorption rate below 5.0 % for all the studied dyes, respectively.

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References

- [1] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, *Journal of environmental management*, 93 (2012) 154-168.
- [2] J. Dasgupta, J. Sikder, S. Chakraborty, S. Curcio, E. Drioli, Remediation of textile effluents by membrane based treatment techniques: a state of the art review, *Journal of environmental management*, 147 (2015) 55-72.
- [3] R.W. Baker, *Membrane Technology and Applications* (Second Edition). John Wiley & Sons Ltd., England, (2004).
- [4] J. Lin, W. Ye, M.-C. Baltaru, Y.P. Tang, N.J. Bernstein, P. Gao, S. Balta, M. Vlad, A. Volodin, A. Sotto, P. Luis, A.L. Zydney, B. Van der Bruggen, Tight ultrafiltration membranes for enhanced separation of dyes and Na₂SO₄ during textile wastewater treatment, *Journal of Membrane Science*, 514 (2016) 217-228.
- [5] W. Li, Z. Yang, Q. Meng, C. Shen, G. Zhang, Thermally stable and solvent resistant self-crosslinked TiO₂/PAN hybrid hollow fiber membrane fabricated by mutual supporting method, *Journal of Membrane Science*, 467 (2014) 253-261.
- [6] A. Idris, L.K. Yet, The effect of different molecular weight PEG additives on cellulose acetate asymmetric dialysis membrane performance, *Journal of Membrane Science*, 280 (2006) 920-927.

- [7] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, *Journal of Membrane Science*, 375 (2011) 1-27.
- [8] D.Y. Koseoglu-Imer, B. Kose, M. Altinbas, I. Koyuncu, The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): Physical properties, filtration performances, and biofouling resistances of membranes, *Journal of Membrane Science*, 428 (2013) 620-628.
- [9] R. Kumar, A.M. Isloor, A.F. Ismail, T. Matsuura, Performance improvement of polysulfone ultrafiltration membrane using N-succinyl chitosan as additive, *Desalination*, 318 (2013) 1-8.
- [10] H. Rajabi, N. Ghaemi, S.S. Madaeni, P. Daraei, B. Astinchap, S. Zinadini, S.H. Razavizadeh, Nano-ZnO embedded mixed matrix polyethersulfone (PES) membrane: Influence of nanofiller shape on characterization and fouling resistance, *Applied Surface Science*, 349 (2015) 66-77.
- [11] G. Ouyang, A. Hussain, J. Li, D. Li, Remarkable permeability enhancement of polyethersulfone (PES) ultrafiltration membrane by blending cobalt oxide/graphene oxide nanocomposites, *RSC Adv.*, 5 (2015) 70448-70460.
- [12] S. Barredo-Damas, M.I. Alcaina-Miranda, A. Bes-Piá, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, Ceramic membrane behavior in textile wastewater ultrafiltration, *Desalination*, 250 (2010) 623-628.
- [13] G. Wang, H. Zhang, B. Qian, J. Wang, X. Jian, J. Qiu, Preparation and characterization of electrospun poly(phthalazinone ether nitrile ketone) membrane with novel thermally stable properties, *Applied Surface Science*, 351 (2015) 169-174.
- [14] N. Gao, S. Zhang, Phenolphthalein-Based Cardo Poly(arylene ether sulfone) Preparation and Application to Separation Membranes, *Journal of Applied Polymer Science*, 128 (2013) 1-12.
- [15] Z. Wang, T. Chen, J. Xu, Novel Poly(aryl ether ketone)s Containing Various Pendant Groups. II. Gas-Transport Properties, *Journal of Applied Polymer Science*, 64 (1997) 1725-1732.
- [16] Q. Zhang, S. Zhang, L. Dai, X. Chen, Novel zwitterionic poly(arylene ether sulfone)s as antifouling membrane material, *Journal of Membrane Science*, 349 (2010)

217-224.

[17] Q. Zhang, Q. Zhang, J. Wang, S. Zhang, S. Li, Synthesis and alkaline stability of novel cardo poly(aryl ether sulfone)s with pendent quaternary ammonium aliphatic side chains for anion exchange membranes, *Polymer*, 51 (2010) 5407-5416.

[18] K. Hendrix, M. Van Eynde, G. Koeckelberghs, I.F.J. Vankelecom, Crosslinking of modified poly(ether ether ketone) membranes for use in solvent resistant nanofiltration, *Journal of Membrane Science*, 447 (2013) 212-221.

[19] Y.H. Choa, J. Hanb, S. Hanb, M.D. Guiver, H.B. Park, Polyamide thin-film composite membranes based on carboxylated polysulfone microporous support membranes for forward osmosis, *Journal of Membrane Science*, 445 (2013) 220-227.

[20] J. Ren, Y. Liu, Y. Wang, Q. Wang, G. Wang, Synthesis and characterization of poly(arylene ether ketone) copolymers with pendant carboxylic acid groups for antifouling ultrafiltration membrane, *High Performance Polymers*, 25 (2013) 714-722.

[21] D. Song, J. Xu, Y. Fu, L. Xu, B. Shan, Polysulfone/sulfonated polysulfone alloy membranes with an improved performance in processing mariculture wastewater, *Chemical Engineering Journal*, 304 (2016) 882-889.

[22] J. Zhu, Q. Zhang, S. Li, S. Zhang, Fabrication of thin film composite nanofiltration membranes by coating water soluble disulfonated poly(arylene ether sulfone) and in situ crosslinking, *Desalination*, 387 (2016) 25-34.

[23] M. Hadidi, A.L. Zydney, Analysis of the effects of electrostatic interactions on protein transport through zwitterionic UF membranes using protein charge ladders, *Journal of Applied polymer science*, 41540 (2015) 1-8.

[24] P. Zhong, X. Fu, T.S. Chung, M. Weber, C. Maletzko, Development of thin-film composite forward osmosis hollow fiber membranes using direct sulfonated polyphenylenesulfone (sPPSU) as membrane substrates, *Environmental science & technology*, 47 (2013) 7430-7436.

[25] S. Singh, K.C. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, *Journal of Membrane Science*, 142 (1998) 111-127.

[26] I. Soroko, M. Makowski, F. Spill, A. Livingston, The effect of membrane

formation parameters on performance of polyimide membranes for organic solvent nanofiltration (OSN). Part B: Analysis of evaporation step and the role of a co-solvent, *Journal of Membrane Science*, 381 (2011) 163-171.

[27] J. Lin, W. Ye, H. Zeng, H. Yang, J. Shen, S. Darvishmanesh, P. Luis, A. Sotito, B. Van der Bruggen, Fractionation of direct dyes and salts in aqueous solution using loose nanofiltration membranes, *Journal of Membrane Science*, 477 (2015) 183-193.

[28] L. Yu, Y. Zhang, Y. Wang, H. Zhang, J. Liu, High flux, positively charged loose nanofiltration membrane by blending with poly (ionic liquid) brushes grafted silica spheres, *Journal of hazardous materials*, 287 (2015) 373-383.

[29] J. Zhu, M. Tian, J. Hou, J. Wang, J. Lin, Y. Zhang, J. Liu, B. Van der Bruggen, Surface zwitterionic functionalized graphene oxide for a novel loose nanofiltration membrane, *Journal of Materials Chemistry A*, 4 (2016) 1980-1990.

[30] J. Wang, Y. Zhang, J. Zhu, J. Hou, J. Liu, B. Van der Bruggen, Zwitterionic functionalized layered double hydroxides nanosheets for a novel charged mosaic membrane with high salt permeability, *Journal of Membrane Science*, 510 (2016) 27-37.

[31] M. Nilsson, G. Trägårdh, K. Östergren, The influence of pH, salt and temperature on nanofiltration performance, *Journal of Membrane Science*, 312 (2008) 97-106.

[32] K.W. Yeung, S.M. Shang, The influence of metal ions on the aggregation and hydrophobicity of dyes in solutions, *Coloration Technology*, 115 (1999) 228-232.

[33] S.M. Mooi, S.N. Keller, B. Heyne, Forcing aggregation of cyanine dyes with salts: a fine line between dimers and higher ordered aggregates, *Langmuir : the ACS journal of surfaces and colloids*, 30 (2014) 9654-9662.

[34] V. Freger, T.C. Arnot, J.A. Howell, Separation of concentrated organic/inorganic salt mixtures by nanofiltration, *Journal of Membrane Science*, 178 (2000) 185-193.

[35] G. Bargeman, J.M. Vollenbroek, J. Straatsma, C.G.P.H. Schroën, R.M. Boom, Nanofiltration of multi-component feeds. Interactions between neutral and charged components and their effect on retention, *Journal of Membrane Science*, 247 (2005) 11-20.

[36] J. Dasgupta, S. Chakraborty, J. Sikder, R. Kumar, D. Pal, S. Curcio, E. Drioli,

The effects of thermally stable titanium silicon oxide nanoparticles on structure and performance of cellulose acetate ultrafiltration membranes, *Separation and Purification Technology*, 133 (2014) 55-68.

[37] C. Wu, S. Zhang, C. Liu, D. Yang, X. Jian, Preparation, characterization and performance of thermal stable poly(phthalazinone ether amide) UF membranes, *Journal of Membrane Science*, 311 (2008) 360-370.

[38] A. Mehta, A.L. Zydney, Permeability and selectivity analysis for ultrafiltration membranes, *Journal of Membrane Science*, 249 (2005) 245-249.

[39] Z. Wang, J. Ma, C.Y. Tang, K. Kimura, Q. Wang, X. Han, Membrane cleaning in membrane bioreactors: A review, *Journal of Membrane Science*, 468 (2014) 276-307.

Filtration process

Membrane performance