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Polydopamine/Cysteine surface modified isoporous membranes with self-cleaning properties

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Abstract

The major challenge in membrane filtration is fouling which reduces the membrane performance. Fouling is mainly due to the adhesion of foulants on the membrane surfaces. In this work, we studied the fouling behaviour of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) isoporous membrane and the mussel inspired polydopamine/L-cysteine isoporous zwitterionic membrane. Polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) isoporous membranes were fabricated via self-assembly and non-solvent induced phase separation method. Subsequently, the isoporous membrane was modified by a mild mussel-inspired polydopamine (PDA) coating; the isoporous surface structure and the water flux was retained. Zwitterionic L-cysteine was further anchored on the PDA coated membranes via Michael addition reaction at pH 7 and 50°C to alleviate their antifouling ability with foulants solution. The membranes were thoroughly characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and zeta potential measurements. Contact angle and dynamic scanning calorimetry (DSC) measurements were carried out to examine the hydrophilicity. The pH-responsive behaviour of the modified membrane remains unchanged and antifouling ability after PDA/L-cysteine functionalization was improved. The modified and unmodified isoporous membranes were tested using humic acid and natural organic matter model solutions at 0.5 bar feed pressure.

Keywords

Block copolymer membranes, self-assembly, polydopamine, zwitterionic surface modification, antifouling, filtration

1. Introduction

Water is one of the world's most valuable natural resources. The scarcity of water is increasing substantially worldwide because of population growth, water pollution, industrialization, and climate change [1,2]. The water sources such as rivers, lakes and ground water are being contaminated continuously through the indirect or direct discharge of pollutants from various type industries [1,3]. Therefore, efficient, low-cost and robust methods are required for purification of contaminated water [2,4]. Owing to high process efficiency, low energy consumption and easy scale-up, membrane filtration processes for production of fresh water have been extensively applied [3,5]. However, membrane fouling is a severe problem for many applications of membrane based filtration processes.

Fouling occurs via non-specific interactions between the foulants and the hydrophobic membranes [6-9]. The foulants including organic biological substances are susceptible for deposition on the membrane surface or inside the membrane pores during the contaminated water filtration. Membrane fouling leads to a decline in permeability and an increase in operation cost as well as to a deterioration in membrane performance [10,11]. Ultrafiltration membranes are used for filtration of proteins, viruses, or natural organic matter (NOM) contaminated water at known pH and constant feed pressure. Commercial ultrafiltration membranes suffer from trade-off between their permeability and selectivity [12]. Highly permeable and selective membranes with improved antifouling performance are needed for water purification and filtration applications.

Self-assembled block copolymer isoporous membranes have high water flux and selectivity due to their narrow pore size distribution and high porosity [13-15]. The isoporous membranes are produced through a one-step procedure by combining self-assembly of amphiphilic block copolymers (e.g. PS-*b*-P4VP) and non-solvent induced

phase separation, sometimes called self-assembly and non-solvent induced phase separation (SNIPS) method. The SNIPS method results in isoporous membranes composed of a uniform nanoporous surface (the separation layer) supported by a spongy macroporous sublayer [15-17]. Qiu *et al.* fabricated positively charged isoporous membranes from the self-assembly of amphiphilic polystyrene-*b*-poly-4-vinylpyridine block copolymer via the SNIPS method. The heterogeneous quaternization reaction was then conducted using 2-chloroacetamide to introduce charge in the barrier layer of the membrane. The selectivity of the membranes in separation of bovine serum albumin from haemoglobin in a mixture model solution was 10 times higher than the selectivity of conventional UF membranes [15].

Membranes with high molecular weight cut-off (MWCO) show generally a strong flux decline during the filtration of foulants containing solutions [18]. The same problem occurs when isoporous membranes are used in ultrafiltration of foulants containing solutions. Therefore, it is highly desirable to improve the antifouling ability of the isoporous membranes without disturbing their morphology through the hydrophilic modifications and subsequent functionalization with low fouling molecules. Hydrophilic modifications of membranes can be carried out through surface grafting or surface coating methods [19]. Surface coating is a simple approach to improve membranes hydrophilicity. However, coatings adhere often weakly to the surface of membranes and can be detached rapidly during filtration [20]. Thus, the adhesion of coatings to the surface of membranes should be robust so that the modified membranes can be used efficiently in filtration processes. PDA coating has received significant attention for surface modification of substrates and membranes. The formation of a PDA layer on the surface of any substrate/membrane occurs through the oxidative self-polymerization of dopamine in a weak alkaline tris-buffer solution [11,20,21]. The thin layer of PDA adheres firmly on the substrates or membranes in wet condition by covalent and non-covalent interactions such as π - π stacking, hydrogen bonding and electrostatic interactions [21,22]. In addition, the thin layer of PDA is not delaminated from the surface of various coated substrates even after a strong ultrasonication treatment [23].

The water flux of PDA modified membranes is enhanced due to the increased hydrophilicity caused by the hydroxyl groups on their surfaces [20,24,25]. Amine or thiol groups containing biomolecules can be attached covalently onto the PDA modified membranes either by Schiff-base or Michael addition reaction at elevated

temperature [26,27]. L-cysteine has been explored to reduce adsorption of protein on the membranes and simultaneously improve their antifouling ability. L-cysteine belongs to a zwitterionic type material which contains both amine ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups [27,28]. For example, Li et al. grafted zwitterionic L-cysteine on PDA coated poly(ethylene terephthalate) membranes by conducting a Michael addition reaction at 80°C . The antifouling ability of modified membranes with protein solutions in a static adsorption was improved after anchoring L-cysteine [27].

In the view of the beneficial facts mentioned above, efforts were made to fabricate antifouling and high flux PS-*b*-P4VP isoporous membranes via surface modification with PDA coating and subsequently L-cysteine functionalization using a Michael addition reaction. We hypothesize that the coating of a PDA layer followed by the grafting of L-cysteine would lead to enhanced water flux and antifouling performance of PS-*b*-P4VP isoporous membranes. The surface composition of the modified and unmodified membranes was analyzed with X-ray photoelectron spectroscopy (XPS). The fabricated membranes were characterized in detail by scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angles and zeta potential measurements. The water fluxes and antifouling performances of the membranes were determined by ultrafiltration of foulants solution and subsequent cleaning with DI water. The fully characterized membranes were further tested in ultrafiltration experiments of humic acid and natural organic matter contaminated solutions at constant feed pressure.

2. Experimental

2.1. Materials

Polystyrene-*b*-poly-4-vinylpyridine block copolymer P9957-S4VP (PS-*b*-P4VP 139,000-*b*-40,000 g/mol; PDI = 1.1) was purchased from Polymer Source, Inc., Canada and dopamine hydrochloride (98.5%) was procured from Alfa-Aesar. Bovine albumin serum (BSA), L-cysteine (Cys), humic acid (HA) and sodium alginate (SA) were obtained from Sigma-Aldrich. *N,N*-dimethylformamide (DMF), 1,4-dioxane, ethanol (96%), nitric acid (HNO_3) ammonium hydroxide (NH_4OH) and tris(hydroxymethyl) aminomethane (Tris) were acquired from Sigma-Aldrich. Tetrahydrofuran (THF) was received from Fischer Scientific. All chemicals were used without any further purification. The 10 mM Tris-buffer solution was prepared

according to the previously reported protocol in the literature [29]. Deionized (DI) water purified with a Milli-Q system (Millipore, Inc.) was used in this study.

2.2. Membrane fabrication

The isoporous membrane was prepared from a polymer solution containing 16.6 wt% PS-*b*-P4VP block copolymer in a ternary mixture of 27.8 wt% DMF, 27.8 wt% 1,4- dioxane and 27.8 wt% THF. PS-*b*-P4VP was dissolved in the mixture of solvents by continuous mechanical stirring for 24 h at room temperature (RT). The solution was then cast on a glass plate using a casting knife with a gate height of 200 μ m. The glass plate along with polymer solution film was left for 10 s at RT to partially evaporate solvents and then immersed in a DI water coagulation bath until the membrane was detached. The membranes were taken out and subsequently stored in DI water bath for 24 h to remove traces of solvents. The membranes were finally dried at RT for further characterizations and modifications.

2.3. Modification of isoporous membranes

The modification of the membranes was carried out in two steps via polydopamine coating and Michael addition reaction at elevated temperature [21,27,30]. For thin layer coating of PDA, membrane pieces (25 mm in diameter) were immersed in 25 ml of 10 mM Tris-buffer solution of pH 8.5 containing 2 mg/ml dopamine hydrochloride for 24 h at RT under constant stirring. The PDA coated membranes were taken out and washed thoroughly with DI water to remove loosely bound PDA. The cleaned membranes were dried in a vacuum oven at 25°C and the PDA coated membranes were then functionalized with L-cysteine by performing a Michael addition reaction at 50°C. PDA coated membranes were immersed into a round bottom flask containing 25 ml of 1 mg/ml L-cysteine solution in DI water. The reaction was carried out for 12 h at 50°C. The reaction mixture along with the membranes was cooled down to RT and removed. The obtained membranes were rinsed properly with DI water for further use and characterization. The membranes are denoted as M1; PS-*b*-P4VP, M2; PS-*b*-P4VP-PDA and M3; PS-*b*-P4VP-PDA-Cys.

2.4. Membrane characterization

The surface morphology of the modified and unmodified membranes was observed using a field emission scanning electron microscopy (FESEM). The dried

membrane samples were fixed on a SEM sample holder by a double-sided carbon tape, sputtered with iridium for 60 s at 5 mA current in an argon atmosphere. The samples were then moved to the SEM stage and the images were recorded on a FEI Quanta 200, scanning electron microscope at an accelerating voltage of 30 kV with varied magnifications. AFM images were done with a multimode Nasoscope system (Agilent, Model 5400) using a resonance frequency in the range from 76 to 263 kHz under tapping mode. The scan size to record the AFM image was kept $1\ \mu\text{m} \times 1\ \mu\text{m}$. XPS analysis was conducted by using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical Ltd, UK) equipped with a monochromated Al K α X-ray source (1486.6 eV) and hemispherical analyzer with a resolution from 0 to 0.5 eV. All spectra were recorded at an aperture slot of $700 \times 300\ \mu\text{m}$. The zeta potential measurements were carried out to determine the surface zeta potential (ζ) of the membranes in the pH range from 3 to 10 using an Anton Parr SurPass Electrokinetic Analyzer (Anton-Paar, GmbH, Austria). For all experiments, a 10 mM solution of NaCl was used as the background electrolyte and the solution pH was adjusted automatically by addition of 10 mM HCl or NaOH. The streaming current was measured and the surface zeta potential was calculated by utilizing the Helmholtz–Smoluchowski equation [31].

To elucidate the water binding capacity of the membranes in detail, the free and bound water fraction values (%) were obtained from DSC thermograms of the membranes in wet state. The peak due to the presence of freezable water for unmodified (M1) and modified membranes appear in the range from -4 to -6°C . The obtained endothermic peaks for the membrane are clearly visible (Fig. S1, Supporting Information). The free water fraction (φ_f , %) in the membranes was determined using eqn (1) [32,33]:

$$\varphi_f(\%) = \frac{\Delta H_m}{Q_m} \times 100 \quad (1)$$

where, ΔH_m is the melting enthalpy for freezable water in the membrane; the details are reported in previously published papers [32,33]. The bound water fraction (φ_b , %) was then determined by subtracting the free water fraction (φ_f , %) from the water uptake (φ , %). The procedure to determine water uptake of the membranes is described in Section S1, Supporting Information. The hydrophilicity of the membranes was characterized by determining their contact angle values using a contact angle

goniometer (FM40, Kruss GmbH, Germany) equipped with a video capture. For static and dynamic contact angle measurements, 5 μL of DI water was dropped onto the membrane surface and the sessile drop method was applied to obtain contact angle values. Images of the water droplets were captured using a video camera (Stingray model, Allied Vision Technology, USA). To minimize the experimental errors, the contact angle was taken at least four random locations of the membrane and the average values were then reported. The surface free energy was further calculated using the Young–Dupre equation (eqn (2)) [34]:

$$-\Delta G_{SL} = (1 + \cos\theta)\gamma_L^T \quad (2)$$

where, θ is the measured water contact angle (deg.) and γ_L^T is the surface tension of water (72.8 mJ m^{-2}).

2.5. Pure water flux measurement and antifouling performance

The pure water flux of the membranes was measured using a stirred dead-end ultrafiltration cell (Amicon 8010, Millipore Co., USA) at 0.5 bar feed pressure. The ultrafiltration cell was connected to a reservoir of 1 L capacity, which was pressurized by N_2 gas from a cylinder. A circular piece of the membrane (25 mm diameter) was fixed in the cell and DI water was then passed for 15 min at 0.5 bar feed pressure. The weight of the collected DI water was measured on a digital balance (Mettler Toledo Inc., UK). The water flux was calculated as follows:

$$J_w = V/A \times t \quad (3)$$

where, V is the volume of DI water (L), t is the permeation time (h) and A is the membrane area.

The antifouling ability of the membranes was assessed in details by static adsorption and dynamic ultrafiltration of 100 ppm foulant solution. BSA, HA and SA were selected as model foulants because these are major constituents of natural organic matters [35,36]. Circular membrane pieces (1.54 cm^2 effective area) were immersed into vials containing 10 ml solution of foulant (1 mg ml^{-1}). The vials were then kept on a shaker for 24 h and the concentration of foulant in supernatant solution was analyzed using a UV-Vis spectrophotometer (Nano-Drop™ 2000/2000C, Thermo Fisher Scientific) at $\lambda_{\text{max}} = 280$; BSA; 253 nm; HA and 220 nm; SA, respectively. The

adsorbed amount of the foulant per square cm of the membrane (Q ; $\mu\text{g cm}^{-2}$) was estimated according to the eqn (4).

$$Q = \left(\frac{C_0 - C_1}{A} \right) \times V \quad (4)$$

where, C_0 and C_1 are the concentration of foulant before and after adsorption (mg/L) and V is the volume of the foulant solution (L).

Furthermore, the dynamic ultrafiltration of 100 ppm solution of individual foulant was performed as follows: DI water was initially passed through the membrane for 30 min at 0.5 bar and afterwards, DI water was replaced with 100 ppm foulant solution. The ultrafiltration of foulant solution was performed using the membranes at 0.5 bar for 2 h with a stirring speed of 400 rpm. The flux of the membranes for foulants solution (J_{W1} ; $\text{L/m}^2 \text{ h bar}$) was determined (*cf.* above). After filtering the foulant solution, the membrane was flushed with DI water for 30 min to remove weakly adhered foulant. The water flux of the cleaned membranes (J_{W2}) was measured again by passing DI water for 15 min. The flux recovery ratio (FRR) was calculated using eqn (5):

$$FRR(\%) = \frac{J_{W2}}{J_{W1}} \times 100 \quad (5)$$

The rejection (R ; %) capacity of the membranes for individual foulant was determined using the eqⁿ (6):

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (6)$$

where, C_p and C_f are the concentrations of the foulant in permeate and feed solutions (mg/ml).

2.6. Ultrafiltration of humic acid and natural organic matter solutions

Ultrafiltration of HA solutions was conducted in a dead-end stirred ultrafiltration cell using the membranes at varied feed concentrations (5, 10, 20, 50 and 100 ppm), pH 7 and 0.5 bar feed pressure. HA solution of known concentration with pH 7 was filled into the reservoir and then passed through the membranes for 1 h. The concentration of HA in the feed and the permeate solutions was determined after the end of each experiment. The membranes were also tested in ultrafiltration experiments of a synthetic solution of NOM in DI water for assessing their practical application. The synthetic solution of NOM was prepared according to the previously reported protocol in the literature *i.e.*, the foulants (BSA, SA and HA) of 10 mg/ml

concentration were dissolved in DI water containing 1 mM CaCl₂ and 7 mM NaCl [35]. The synthetic solution of NOM was further filtered using the membranes for 1 h at pH 7 and 0.5 bar feed pressure with a stirring speed of 400 rpm. Thereafter, backwashing of the used membranes was carried out with DI water for 10 min to remove weakly adhered fractions of NOM. The water flux of the cleaned membranes was measured again. Antifouling ability of the membranes with a synthetic solution of NOM was analyzed using the resistance-in-series model as shown in equation (eqn (7)) [35]:

$$R_t = R_m + R_r + R_{ir} = \frac{\Delta P}{\mu J} \quad (7)$$

The R_m , R_r , R_{ir} and R_t values were calculated using eqn (8), (9), (10) and (11) [35]:

$$R_m = \frac{\Delta P}{\mu J_w} \quad (8)$$

$$R_r = \frac{\Delta P}{\mu J_{w1}} - \frac{\Delta P}{\mu J_{w2}} \quad (9)$$

$$R_t = \frac{\Delta P}{\mu J_{w1}} \quad (10)$$

$$R_{ir} = R_t - R_m - R_r \quad (11)$$

where, R_m , is the intrinsic membrane resistance (m⁻¹), R_r is the reversible resistance (m⁻¹), R_{ir} is the irreversible resistance (m⁻¹), R_t is the total membrane resistance (m⁻¹), ΔP is feed pressure (kPa) and μ is the dynamic viscosity of feed solution (Pa s).

3. Results and discussion

The highly ordered self-assembled pores perpendicular to the membrane surface are accountable to obtain high flux and sharp molecular weight cut-off isoporous membranes [13,15-17]. Therefore, highly ordered isoporous membranes were fabricated from PS-*b*-P4VP block copolymer by the SNIPS method [13,17]. The fabricated membrane was first coated with a mussel-inspired polydopamine by dip coating in an aqueous solution of dopamine. The dopamine in aqueous solution containing dissolved oxygen gets oxidized at pH 8.5 and forms 5,6-dihydroxyindole. Then the 5,6-dihydroxyindole undergoes intramolecular oxidative polymerization and noncovalent self-assembly to produce PDA particles/aggregates which deposits on the surface of the membranes [11,21]. The PDA coated layer on the membrane surface was confirmed from the change in membrane color from off-white into dark

brownish. The modified membranes were further functionalized with L-cysteine via a Michael addition reaction to obtain high flux and antifouling membranes (Scheme 1).

Scheme 1. Reaction route for modification of PS-*b*-P4VP isoporous membrane through an adhesion of polydopamine layer followed by Michael addition reaction at 50°C.

3.1. Surface morphologies of the membranes

The surface SEM images of the membrane PS-*b*-P4VP; M1, PS-*b*-P4VP-PDA; M2 and PS-*b*-P4VP-PDA-Cys; M3 are shown in Figure 1. The membrane M1 has an asymmetric structure with highly ordered pores perpendicular to the membrane surface with high pore density and a non-ordered spongy sublayer (Fig. 1a). A slight change in the surface morphology and pore size of PDA coated membrane M2 was observed. This could be attributed to adhesion of the PDA on the membrane surface after modification.

Fig. 1. The top surface SEM images at low and high (inset) magnifications for membrane: (a) M1 (b) M2 and (c) M3.

The membrane surface became smoother and the isoporous structure was retained when the PDA coated membrane was functionalized with L-cysteine (Fig. 1c). Furthermore, the average pore size of M1 and M3 was calculated from their surface SEM images using Image J software for at least 200 pores [17]. The average pore size for membrane M1 was 38.7 nm ($\sigma = \pm 6.6$ nm) and for membrane M3 was 32.05 nm ($\sigma = \pm 7.1$ nm).

Two and three dimensional AFM images of the unmodified and modified membranes are presented in Fig. 2. These images are clearly indicating that the surface morphologies of the modified membranes did not change.

Fig. 2. Two and three dimensional AFM images for membrane: (a) M1 (b) M2 and (c) M3.

The surface roughness parameters (the average roughness; R_{av} , the root mean square roughness; R_{rms} and the maximum roughness; R_{max}) were obtained from AFM images using Gwydion software. The obtained values are tabulated in Table S1, Supporting Information. The R_{av} , R_{rms} and R_{max} values for the unmodified membrane M1 were 8.5, 10.6 and 10.6 nm,

respectively, which are higher values than those obtained for modified membranes (*cf.* Table S1). R_{av} values for membranes were decreased after coating of the PDA and subsequent functionalization with zwitterionic L-cysteine. For the PDA coated membrane M2, the R_{av} value was 5.8 nm which is lower than the R_{av} value (8.5 nm) of unmodified membrane M1. This is attributed to uniform deposition of PDA on the surface of isoporous membrane M1 (Fig. 1). In addition, R_{av} value declined further to 5.4 nm after anchoring L-cysteine onto the PDA modified membrane M2. This was possible due to the good attachment of L-cysteine on the surface of the membrane M2. These results are in agreements with previously reported observations [37]. The surface roughness affects membranes fouling and their antifouling ability is enhanced with decrease in surface roughness [37,38]. Thus, the membrane M3 would be suitable for filtration of solution containing NOM at known pH and constant feed pressure.

3.2. Membrane surface composition and charge characteristics

XPS analysis was explored to determine the surface composition of unmodified and modified membranes. The XPS spectra and the elemental compositions of the membranes are

presented in Fig. 3 and Table 1. Compared with the unmodified membrane M1, the peak intensities and atomic percentage (%) of both O1s and N1s were enhanced after PDA adhesion *i.e.*, membrane M2 (Fig. 3b and Table 1).

Fig. 3. XPS spectra for unmodified and modified membrane: (a) M1 (b) M2 and M3.

Table 1. The surface elemental composition of the unmodified and modified membranes.

Membrane	C (%)	O (%)	N (%)	S (%)
M1	93.3	3.2	3.5	ND

M2	86.4	7.7	5.9	ND
M3	68.7	16.2	9.2	5.9

ND: not detected.

The obtained results demonstrated successful coating of PDA on the membrane *via* self-oxidative polymerization of dopamine at alkaline pH 8.5. Two new peaks (S2s and S2p) appeared in the XPS spectrum of L-cysteine functionalized membrane M3 (Fig. 3c). The atomic percentage (%) of O1s and N1s on the surface of membrane M3 further increased to 16.2 and 9.2%. The total atomic percentage of sulfur atoms for membrane M3 was 5.9%. The appearance of sulfur peaks S2s and S2p confirmed grafting of L-cysteine through a Michael addition reaction [27,30]. The surface zeta potential values (Fig. 4) provide information on the charge characteristics of the unmodified and modified membranes.

The surface zeta potential of the unmodified membrane M1 was positive in acidic pH from 3 to 5 and then altered to negative as the pH changed from 5 to 9. This is ascribed to the preferential adsorption of cations (Na^+ or H^+) in acidic pH or adsorption of anions (Cl^- or OH^-) on the membrane in alkaline pH [17,39]. The surface zeta potential of PDA coated membrane M2 was positive (below the isoelectric point) and negative (above the isoelectric

point of the membrane M2) due to the amphoteric nature of PDA [40]. The positive/negative surface zeta potential values for membrane M2 were significantly lower than that of the membrane M1, which could be due to the retardation in the adsorption rate of anions or

cations to the surface of membrane M2 by the hydrophilic PDA [33]. Moreover, the positive/negative surface zeta potential values of L-cysteine functionalized membrane M3 were noticeably increased in the studied pH. The surface zeta potential values (-43.9 mV, -37.3 and -56.7 mV) are demonstrating the negatively charged nature of the unmodified and modified membranes at pH 7.

Fig. 4. The surface zeta potential values for unmodified and modified membranes at varied pH.

3.3. Hydrophilicity and water flux of the membranes

The hydrophilicity of the membranes was evaluated by determining their water uptake and water contact angle values. The water uptake values are presented in Table S2, Supporting Information. The θ value for unmodified membrane M1 was 125°, which is the lowest value. The θ values increased further after PDA adhesion and subsequent functionalization with L-cysteine. The highest θ value for the L-cysteine functionalized membrane M3 was achieved due to the water holding capacity of PDA and zwitterionic L-cysteine [11,27]. The bound water (ϕ_b , %) and free water (ϕ_f , %) fraction values of the membranes are presented in Table S2. The ϕ_f values were significantly decreased from 32.5 to 10.2%, while ϕ_b value increased from 92.5 to 115.6% after anchoring of PDA and L-

cysteine. The water contact angle, the surface free energy and snapshots of 5 μ l water droplet on the surface of the unmodified and modified membranes are illustrated in Fig. 5. The water contact angle of L-cysteine functionalized membrane M3 is much lower (40.5°) than the

contact angle of the unmodified membrane M1 and PDA coated membrane M2. This is attributed to the formation of a thick hydration layer on the surface of membrane M3 because L-cysteine can bind more water molecules through electrostatic/hydrogen bonding interactions [24,27]. The surface free energy increased and its highest value (128.2 mJ m^{-2}) was achieved for the L-cysteine functionalized membrane. Time-dependent water contact angle measurement also reveals the effect of PDA and L-cysteine functionalization on improving the membrane hydrophilicity (Fig. S2, Supporting Information). For unmodified and PDA modified membranes, the water contact angle values slowly declined to 33.1° and 23.7° after 80 s. On the other hand, the water contact angle value for the L-cysteine functionalized membrane became almost zero in 30 s. These results support an improvement in hydrophilicity of the modified membranes.

Fig. 5. Water contact angle and surface free energy for membrane M1, M2 and M3.

The water flux of the unmodified and modified membranes at 0.5 bar feed pressure is presented in Fig. 6a. It was found that the water flux of PDA coated membrane M2 and L-cysteine functionalized membrane M3 was comparable to the unfunctionalized membrane M1 even though the pore size of the modified membranes was reduced slightly.

Fig. 6. (a) Pure water and 100 ppm foulant solution flux and (b) % rejection of the foulants (BSA, HA and SA) by the unmodified and modified isoporous membranes during ultrafiltration at pH 7 and 0.5 bar feed pressure with a stirring speed of 400 rpm.

The water flux of the membranes increased with their hydrophilicity. The water flux of the unmodified and modified membranes at varied feed pressure was measured and the obtained

values are shown in Fig. S3, Supporting Information. The water flux linearly increased with feed pressure in the range from 0.5 to 2 bar. The linear increase in water flux with feed pressure indicates good adhesion of PDA to the surface of membrane M1 and pore blockage as well as leaching of L-cysteine from the functionalized membrane M3 was not observed. The water flux at varied pH is depicted in Fig. S4, Supporting Information. The pH responsive flux of the membranes remains unchanged after modifications. The foulants solution flux for unmodified and modified membranes is also presented in Fig. 6a. The foulants solution flux decreased when DI water was replaced with 100 ppm solution of the foulant. The reduction in flux of the foulants solution could be due to concentration-polarization and membrane fouling [41,42]. However, the flux reduction of foulant solution due to concentration-polarization was negligible because ultrafiltration of an individual foulant solution was carried out at a high stirring speed of 400 rpm. Thus, the membrane fouling by the adsorption of foulants led to the flux reduction. The rejection (%) of the foulants by the unmodified and modified membranes is shown in Fig. 6b, which depends on the size of foulants [36,41]. The rejection of SA was higher than the rejection of HA and BSA because of its larger size [41]. The L-cysteine functionalized membrane M3 shows rejection of 85.8 % of SA (conc. 100 ppm, pH = 7).

3.4. Antifouling capacity of the membranes

BSA, SA and HA were chosen to evaluate antifouling ability of the membranes in static adsorption and dynamic ultrafiltration of 100 ppm solution of the individual foulant. The foulant (BSA, SA and HA) adsorption results for unmodified and modified membranes at pH 7 are shown in Fig. 7a. The adsorbed amount of the foulants on the membranes was gradually decreased after PDA coating and L-cysteine functionalization. This is ascribed to an

improvement in hydrophilicity of the modified membranes (*cf.* Fig. 5).

Fig. 7. (a) Adsorbed amount of foulants and (b) FRR (%) for unmodified and modified membranes after ultrafiltration 100 ppm foulant solution followed by the subsequent cleaning with DI water.

The electrostatic repulsions between the negatively charged membranes and the foulants were also liable for the adsorption reduction (*cf.* Fig. 4). The adsorbed amount of foulants on the L-cysteine functionalized membrane M3 was lower in comparison with the PDA coated membrane M2 and the unfunctionalized membrane M1. Adsorption of foulants is reduced with the increased hydrophilicity of the membrane. The adsorbed amount of BSA, SA and HA on membrane M3 was 26.3, 32 and 4 $\mu\text{g cm}^{-2}$, which is the lowest adsorbed amount of the tested foulants. FRR values (%) of the unmodified and modified membranes are presented in Fig. 7b; FRR values were lowest for the unmodified membrane M1. Foulants solutions were filtered through this membrane at 0.5 bar feed pressure. The FRR values were improved

after PDA coating and L-cysteine functionalization. The highest FRR values were obtained for L-cysteine with the functionalized membrane M3 because the adhesion of the foulant molecules to the hydrophilic membrane surfaces could be suppressed during ultrafiltration of foulants solution [20,41,42]. Therefore, the foulants adhered loosely on the membranes and could be removed or detached by simple washing with DI water. The FRR values for the

modified membrane M3 were 80, 82 and 88.2% respectively. These results are confirming the improved antifouling ability of the membranes with foulants solution after grafting of PDA and L-cysteine functionalization. In addition, FRR values for membranes after ultrafiltration of 100 ppm solution and subsequently cleaning with DI water are significantly higher than other foulant (BSA or SA). Hence, the modified membranes are more suitable for ultrafiltration of either HA or NOM solutions.

Fig. 8. The rejection of humic acid (%) by the modified membrane M3 at varied feed concentration.

3.5. Membrane performance in ultrafiltration of humic acid and synthetic NOM solutions

The L-cysteine modified membrane M3 was applied in ultrafiltration of HA solutions with varied concentration in the range from 5 to 100 ppm at pH 7 and 0.5 bar feed pressure. The obtained HA rejection (%) for membrane M3 is illustrated in Fig. 8. The HA rejection (%) by the modified membrane M3 was enhanced first with increase in feed concentration of HA solution from 5 to 10 ppm. The membrane M3 has a rejection of 80% HA of 10 ppm solution at pH 7 because the transport of the negatively charged HA molecules was hindered by the negatively charged membrane (*cf.* Fig. 4). However, the rejection of HA (%) for membrane M3 declined with increase in feed solution concentration from 10 to 100 ppm. This is related

to the charge density of the membranes for retaining HA molecules with the same charge.

Fig. 9. Normalized flux values for unmodified and modified membranes after ultrafiltration of NOM solution at pH 7 and 0.5 bar feed pressure with a stirring speed of 400 rpm and initial pure water flux of the membranes in inset figure.

The negatively charged M3 membrane surface (-56.7mV) rejected similar charged HA molecules [43]. However, the charge dependent exclusion ability of membrane M3 declined with increase in concentration of HA in feed solution. Hence, the L-cysteine modified membrane M3 was efficient in removal of HA from 10 ppm solution at pH 7. Furthermore, the well-characterized membranes (M1, M3 and M3) were used in ultrafiltration of synthetic solution of NOM to evaluate their suitability in water purification applications. The synthetic solution of NOM was passed through the unmodified and modified membranes for 1 h at pH 7 and 0.5 bar feed pressure. The used membranes were then cleaned by backwashing with DI water. Afterwards, the normalized flux of the membranes was determined and the values are presented in Fig. 9. The highest normalized flux value (0.68) was attained for the L-cysteine modified membrane M3. This could be due to the reduction in cake layer formation (the complexation of HA and SA with Ca^{2+}) on the hydrated surface of the membrane M3 [44,45]. This observation was supported by the change in the surface colour of the unmodified and modified membranes (Fig. S5, Supporting Information). The surface of the unmodified membrane M1 altered from off-white to reddish-brown colour when ultrafiltration of NOM solution was carried out and some fraction of the cake-layer remained even after backwashing with DI water. However, the reddish-brown colour of the modified membrane did not change and the cake-layer from the surface of membrane disappeared after backwashing with DI water. The modified membrane M3 was effective in ultrafiltration of NOM solution at pH 7. Additionally, the resistance in-series model was applied to determine various resistances parameters during ultrafiltration of NOM contaminated solution and the obtained parameters are illustrated in Table 2.

Table 2. Membrane resistance parameters for unmodified and modified isoporous membranes after filtration of NOM solution at pH = 7 and 1 bar feed pressure with a stirring speed of 400 rpm.

Membrane	$R_m (\text{m}^{-1})$	$R_r (\text{m}^{-1})$	$R_{ir} (\text{m}^{-1})$	$R_t (\text{m}^{-1})$	R_r/R_m	R_{ir}/R_m	R_t/R_m
M1	51.9	208.7	115.3	375.9	4.0	2.2	3.1

M2	57.4	61.4	64.6	183.4	1.1	1.1	2.5
M3	70.2	74.9	32.8	177.8	1.1	0.5	7.2

R_m : the intrinsic membrane resistance, R_r : the reversible fouling, R_{ir} : the irreversible fouling, R_t : the total fouling, R_{ir}/R_m : the nominalized irreversible fouling, R_r/R_m : the nominalized reversible fouling and R_t/R_m : the nominalized total fouling.

The reversible fouling ratio (R_r) and the irreversible fouling ratio (R_{ir}) values were significantly reduced after PDA/L-cysteine coating because of the increased hydrophilicity or the membrane surface. A similar trend was achieved for nominalized reversible fouling resistance (R_r/R_m) and the nominalized irreversible fouling resistance (R_{ir}/R_m) values of the modified membranes. The lowest R_r/R_m and R_{ir}/R_m values were observed for the highly hydrophilic membrane M3. These values also demonstrate the improved antifouling performance of the modified membrane M3 in ultrafiltration of NOM solution. These membranes can be applied efficiently in water purification and removal of NOM from the contaminated water.

4. Conclusions

PS-*b*-P4VP based isoporous membrane was fabricated by the SNIPS method and a PDA coating was applied at pH 8.5 and room temperature. L-cysteine was then anchored onto the PDA modified membranes through a Michael addition reaction. It was observed that the surface morphology of the unmodified and modified membranes did not change. The XPS analysis results confirmed a successful grafting of PDA and L-cysteine onto the membranes. All membranes were negatively charged at pH 7; the L-cysteine modified membrane M3 had the highest negative surface zeta potential (-56.7 mV). The hydrophilicity of the modified membranes was improved after anchoring PDA and L-cysteine. The high water flux and pH-responsive behavior of the membranes retained after the PDA/cysteine grafting. Because of the high hydrophilicity and the negative surface charge the modified membranes had improved antifouling performance with foulants (BSA, HA and SA) and NOM contaminated solutions during ultrafiltration. The FRR values for the PDA/cysteine functionalized membrane were 80, 82 and 88.2% after ultrafiltration of foulant solution. The reversible fouling ratio (R_r) and the irreversible fouling ratio (R_{ir}) values were significantly reduced when the membrane M3 was applied in ultrafiltration of NOM contaminated solution. Overall, the modified membrane M3 had self-cleaning ability and better performance in

ultrafiltration of either HA or NOM contaminated solutions. The modified membranes can be applied efficiently in water purification and removal of NOM from the contaminated water.

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References

- [1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301–310.
- [2] M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, *Energy Environ. Sci.* 4 (2011) 1946–1971.
- [3] M. Elimelech, W.A. Phillip, The future of seawater desalination: Energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [4] H.W. Liang, X. Cao, W.J. Zhang, H.T. Lin, F. Zhou, L.F. Chen, S.H. Yu, Robust and highly efficient free-standing carbonaceous nanofiber membranes for water purification, *Adv. Funct. Mater.* 21(2011) 3851–3858.
- [5] G.M. Geise, H.S. Lee, D.J. Miller, B.D. Freeman, J.E. McGrath, D.R. Paul, Water purification by membranes: the role of polymer science, *J. Polym. Sci. Part B: Polym. Phys.* 48 (2010) 1685–1718.
- [6] A. Asatekin, S. Kang, M. Elimelech, A.M. Mayes, Anti-fouling ultrafiltration membranes containing polyacrylonitrile-graft poly(ethylene oxide) comb copolymer additives, *J. Membr. Sci.* 298 (2007) 136–146.
- [7] E. Ostuni, R.G. Chapman, R.E. Holmlin, S. Takayama, G.M. Whitesides, A survey of structure-property relationships of surfaces that resist the adsorption of protein, *Langmuir* 17 (2001) 5605–5620.
- [8] B.T. McVerry, J.A.T. Temple, X. Huang, K.L. Marsh, E.M.V. Hoek, R.B. Kaner, Fabrication of low-fouling ultrafiltration membranes using a hydrophilic, self-doping polyaniline additive, *Chem. Mater.* 25 (2013) 3597–3602.
- [9] M. Kumar, M. Ulbricht, Novel ultrafiltration membranes with adjustable charge density based on sulfonated poly(arylene ether sulfone) block copolymers and their tunable protein separation performance, *Polymer* 55 (2014) 354–365.

- [10] J. Mansouri, S. Harrison, V. Chen, Strategies for controlling biofouling in membrane filtration systems: Challenges and opportunities, *J. Mater. Chem.* 20 (2010) 4567–4586.
- [11] J. Jiang, Z. Liping, L. Zhu, H. Zhang, B. Zhu, Y. Xu, Antifouling and antimicrobial polymer membranes based on bioinspired polydopamine and strong hydrogen-bonded poly(N-vinyl pyrrolidone), *ACS Appl. Mater. Interfaces* 5 (2013) 12895–12904.
- [12] A. Mehta, A.L. Zydney, Permeability and selectivity analysis for ultrafiltration membranes, *J. Membr. Sci.* 249 (2005) 245–249.
- [13] K.-V. Peinemann, V. Abetz, P.W. Simon, Asymmetric superstructure formed in a block copolymer via phase separation, *Nat. Mater.* 6 (2007) 992–996.
- [14] M.E. Warkiani, A.A.S. Bhagat, B.L. Khoo, J. Han, C.T. Lim, H.Q. Gong, A.G. Fane, Isoporous micro/nanoengineered membranes, *ACS Nano* 7 (2013) 1882–1904.
- [15] X. Qiu, H. Yu, M. Karunakaran, N. Pradeep, S.P. Nunes, K.-V. Peinemann, Selective separation of similarly sized proteins with tunable nanoporous block copolymer membranes, *ACS Nano* 7 (2013) 768–776.
- [16] H. Yu, X. Qiu, S.P. Nunes, K.-V. Peinemann, Self-assembled isoporous block copolymer membranes with tuned pore sizes, *Angew. Chem. Int.* 126 (2014) 10236 – 10240.
- [17] R. Shevate, M. Karunakaran, M. Kumar, K.-V. Peinemann, Polyanionic pH-responsive polystyrene-*b*-poly(4-vinyl pyridine-*N*-oxide) isoporous membranes, *J. Membr. Sci.* 501 (2016) 161–168.
- [18] H. Susanto, M. Ulbricht, High-performance thin-layer hydrogel composite membranes for ultrafiltration of natural organic matter, *Water Res.* 42 (2008) 2827–2835.
- [19] F. Liu, N. A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, *J. Membr. Sci.* 375 (2011) 1–27.
- [20] Z. X. Wang, C. H. Lau, N. Q. Zhang, Y. P. Bai, L. Shao, Mussel-inspired tailoring of membrane wettability for harsh water treatment, *J. Mater. Chem. A* 3 (2015) 2650–2657.
- [21] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, *Science* 318 (2007) 426–430.
- [22] J. Jiang, L. Zhu, L. Zhu, B. Zhu and Y. Xu, Surface characteristics of a self-polymerized dopamine coating deposited on hydrophobic polymer films, *Langmuir* 27 (2011) 14180–14187.
- [23] J. Ryu, S. H. Ku, H. Lee, C. B. Park, Mussel-inspired polydopamine coating as a universal route to hydroxyapatite crystallization, *Adv. Funct. Mater.* 20 (2010) 2132–

2139.

- [24] J.I. Clodt, V. Filiz, S. Rangou, K. Buhr, C. Abetz, D. Höche, J. Hahn, A. Jung, V. Abetz, Double stimuli-responsive isoporous membranes via post-modification of pH-sensitive self-assembled diblock copolymer membranes, *Adv. Funct. Mater.* 23 (2013) 731–738.
- [25] B.D. McCloskey, H.B. Park, H. Ju, B. W. Rowe, D.J. Miller, B.D. Freeman, A bioinspired fouling-resistant surface modification for water purification membranes, *J. Membr. Sci.* 413–414 (2012) 82–90.
- [26] H. Lee, J. Rho, P.B. Messersmith, Facile conjugation of biomolecules onto surfaces via mussel adhesive protein inspired coatings, *Adv. Mater.* 21 (2009) 431–434.
- [27] P. Li, X. Cai, D. Wang, S. Chen, J. Yuan, L. Li, J. Shen, Hemocompatibility and anti-biofouling property improvement of poly(ethylene terephthalate) via self-polymerization of dopamine and covalent graft of zwitterionic cysteine, *Colloids Surf. B Biointerf.* 110 (2013) 327–332.
- [28] S. Azari, L. Zou, Fouling resistant zwitterionic surface modification of reverse osmosis membranes using amino acid L-cysteine, *Desalination* 324 (2013) 79–86.
- [29] W. Cui, M. Li, J. Liu, B. Wang, C. Zhang, L. Jiang, Q. Cheng, A strong integrated strength and toughness artificial nacre based on dopamine cross-linked graphene oxide, *ACS Nano* 8 (2014) 9511–9517.
- [30] A. Vaish, D.J. Vanderah, L. J. Richter, M. Dimitriou, K.L. Steffens, M.L. Walker, Dithiol-based modification of poly(dopamine): Enabling protein resistance via short-chain ethylene oxide oligomers, *Chem. Commun.* 51 (2015) 6591–6594.
- [31] Z. Yi, C. J. Liu, L. P. Zhu, Y.Y. Xu, Ion exchange and antibiofouling properties of poly(ether sulfone) membranes prepared by the surface immobilization of bronsted acidic ionic liquids via double-click reactions, *Langmuir* 31 (2015) 7970–7979.
- [32] J. Ostrowska-Czubenko, M. Pierog, G. Gierszewska-Druzynska, Water state in chemically and physically crosslinked chitosan membranes, *J. Appl. Polym. Sci.* 130 (2013) 1707–1715.
- [33] X. Zhao, Y. Su, H. Dai, Y. Li, R. Zhang, Z. Jiang, Coordination-enabled synergistic surface segregation for fabrication of multi-defense mechanism membranes, *J. Mater. Chem. A* 3(2015) 3325–3331.
- [34] M.E. Schrader, Young-dupre revisited, *Langmuir* 11 (1995) 3585–3589.
- [35] L. Bai, H. Liang, J. Crittenden, F. Qu, A. Ding, J. Ma, X. Du, S. Guo, G. Li, Surface modification of UF membranes with functional MWCNTs to control membrane fouling

- by NOM fractions, *J. Membr. Sci.* 492 (2015) 400–411.
- [36] X. Zhao and C. He, Efficient preparation of super antifouling PVDF ultrafiltration membrane with one step fabricated zwitterionic surface, *ACS Appl. Mater. Interfaces* 7 (2015) 17947–17953.
- [37] G. Han, S. Zhang, X. Li, N. Widjojo, T. S. Chung, Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection, *Chem. Eng. Sci.* 80 (2012) 219–231.
- [38] E.M.V. Hoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* 188 (2001) 115–128.
- [39] G. Ye, J. Lee, F. Perreault, M. Elimelech, Controlled architecture of dual-functional block copolymer brushes on thin-film composite membranes for integrated “Defending” and “Attacking” strategies against biofouling, *ACS Appl. Mater. Interfaces* 7 (2015) 23069–23079.
- [40] B. Yu, J. Liu, F. Zhou, Pdop layer exhibiting zwitterionicity: A simple electrochemical interface for governing ion permeability, *Chem. Commun.* 46 (2010) 5900–5902.
- [41] X. Li, J. Li, B. Van der Bruggen, X. Sun, J. Shen, W. Han, L. Wang, Fouling behavior of polyethersulfone ultrafiltration membranes functionalized with sol–gel formed ZnO nanoparticles, *RSC Adv.* 5 (2015) 50711–50719.
- [42] Y. Li, Y. Su, X. Zhao, X. He, R. Zhang, J. Zhao, X. Fan, Z. Jiang, Antifouling, high-flux nanofiltration membranes enabled by dual functional polydopamine, *ACS Appl. Mater. Interfaces* 6 (2014) 5548–5557.
- [43] J. Shao, L. Zhao, X. Chen, Y. He, Humic acid rejection and flux decline with negatively charged membranes of different spacer arm lengths and charge groups, *J. Membr. Sci.* 435 (2013) 38–45.
- [44] J. Tian, M. Ernst, M. Jekel, Effect of different cations on UF membrane fouling by NOM fractions, *Chem. Eng. J.* 223 (2013) 547–555.
- [45] M. Hashino, T. Katagiri, T. Kubota, Y. Ohmukai, T. Maruyama, H. Matsuyama, Effect of membrane surface morphology on membrane fouling with sodium alginate, *J. Membr. Sci.* 366 (2011) 258–265.

Figure captions

Fig.. 1. The top surface SEM images at low and high (inset) magnifications for membrane: (a) M1; (b) M2 and (c) M3.

Fig. 2. Two and three dimensional AFM images for membrane: (a) M1 (b) M2 and (c) M3.

Figure 3. XPS spectra for unmodified and modified membrane: (a) M1; (b) M2 and M3.

Fig. 4. The surface zeta potential values for unmodified and modified membranes at varied pH.

Fig. 5. Water contact angle and surface free energy for membrane M1, M2 and M3.

Fig. 6. (a) Pure water and 100 ppm foulant solution flux and (b) % rejection of the foulants (BSA, HA and SA) by the unmodified and modified isoporous membranes during ultrafiltration at pH 7 and 0.5 bar feed pressure with a stirring speed of 400 rpm.

Fig. 7. (a) Adsorbed amount of foulants and (b) FRR (%) for unmodified and modified membranes after ultrafiltration of 100 ppm foulant solution followed by the subsequent cleaning with DI water.

Fig. 8. The rejection of humic acid (%) by the modified membrane M3 at varied feed concentration.

Fig. 9. Normalized flux values for unmodified and modified membranes after ultrafiltration of NOM solution at pH 7 and 0.5 bar feed pressure with a stirring speed of 400 rpm and initial pure water flux of the membranes in inset figure.

Table captions

Table 1. The surface elemental composition of the unmodified and modified membranes.

Table 2. Membrane resistance parameters for unmodified and modified isoporous membranes after filtration of NOM solution at pH = 7 and 1 bar feed pressure with a stirring speed of 400 rpm.

Graphical abstract

Self-cleaning isoporous membranes were prepared by surface coating with polydopamine and subsequent functionalization with zwitterionic L-cysteine.

Highlights

- Self-cleaning isoporous membranes with polydopamine and zwitterionic L-cysteine were prepared.
- High water permeability and pH responsive behavior was retained.
- Membranes antifouling property was significantly improved.
- The membranes were efficient for purification of NOM contaminated water.