Ultrafiltration Membranes Functionalized with Polydopamine with Enhanced Contaminant Removal by Adsorption

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Keywords: Polysulfone membrane, polydopamine, ultrafiltration, adsorption.

Abstract: We investigated the performance of polymeric ultrafiltration membranes functionalized with polydopamine to couple depth adsorption of contaminants with the typical surface rejection characteristics of the membrane. Two approaches were deployed to achieve this functionalization: in a two-steps method, the ultrafiltration membranes were initially fabricated by phase inversion, then followed by coating with polydopamine; in a more facile and advantageous one-step method, the membranes were subjected to phase inversion in a water solution containing dopamine, so that polymer precipitation and polydopamine functionalization occurred at the same time. Methylene blue was used as representative target contaminant to study the enhancement of membrane adsorption behavior, and its removal was investigated both in batch and under filtration conditions. The sorption capacity increased with increasing polydopamine coating time and was higher for the membranes fabricated via the one-step protocol. The amount of methylene blue adsorbed per unit of membrane mass was large (roughly 5-10 mg/g) and the kinetics of adsorption were fast. These characteristics would allow to operate these materials effectively and for long times in membrane filtration processes before stopping the system for regeneration. The saturated membranes were completely regenerated and reused without loss of performance by cycling in acidic and alkaline solutions.

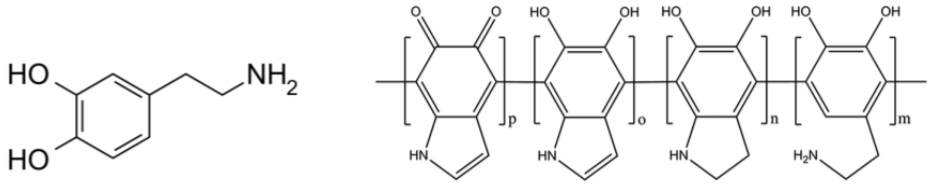
1. Introduction

Separation technologies based on polymeric membranes are becoming one of the most studied and implemented technologies both in industry and in academia. In particular, porous polymeric membranes are highly investigated in micro- and ultrafiltration, two separation processes able to remove pathogens, colloids, and large macromolecules from feed water [1]. There are several ways to prepare porous polymeric membranes, but the majority of them are prepared by controlled phase separation of a polymer solution into two phases, one with higher and one with lower polymer concentration. In this process, the polymer solution is cast as a thin film and is subsequently immersed in a non-solvent bath. Precipitation occurs because the solvent of the polymer solution is exchanged for the non-solvent. Among numerous polymers, polysulfone (PSU) is widely employed to prepare microfiltration and ultrafiltration membranes due to its high mechanical strength and resistance against a broad range of chemicals [2].

We have recently fabricated ultrafiltration membranes by adding an acrylic crosslinker to a PSU-based formulation; this modification allowed us to obtain chemically stable crosslinked membranes without affecting their flux performance [3]. In fact, by keeping the acrylic content as low as 10 wt. %, we achieved a porosity that guaranteed high performance in ultrafiltration, comparable to those of pristine PSU membranes. In this work, we expand the functionality of these membranes by adding a layer of polydopamine (PDA) on their surface, to allow for the removal of contaminants not solely based on size exclusion but also on specific membrane/contaminant interactions.

PDA layers have been deposited on all types of inorganic and organic substrates with controllable thickness, by inducing oxidation of dopamine under mildly alkaline conditions (pH typically between 7.5 and 8.5), using oxygen as the oxidant [4]. Under these conditions, the self-polymerization of dopamine monomers into PDA occurs spontaneously. The chemical structure of PDA includes catechol, amine and imine functional groups (see Figure 1) [5]. PDA coatings have been also added in the past to several polymeric materials, including polyethylene terephthalate

(PET), polytetrafluoroethylene (PTFE), polydimethylsiloxane, polyetheretherketone, polyimides, and polyurethanes [6, 7].



(a) dopamine (b) polydopamine

Figure 1. Structure of (a) dopamine and (b) polydopamine

PDA coatings are especially interesting for membrane applications due to their zwitterionic behavior: at low pH, the PDA layers are positively charged and allow small positively charged molecules to go through, while at high pH PDA is negatively charged and retains positively charged molecules [8]. This behavior may be exploited to remove the contaminants and easily regenerate the PDA functionalized membranes. McCloskey et al. studied the influence of PDA deposition conditions on pure water flux and foulant adhesion resistance of reverse osmosis, ultrafiltration, and microfiltration membranes [9]. These authors investigated PTFE, polyvinylidene fluoride, and polypropylene microfiltration membranes, PSU ultrafiltration membranes, and polyamide desalination membranes. Miller et al studied the influence of PDA deposition conditions on fouling, in particular in terms of pressure drop during the filtration of proteins and microorganisms, for the prevention of biofouling [10]. Similar works on membrane coating were conducted by Choi et al. [11] and Wei et al. [12]. Despite all this work showing the excellent properties of PDA-coated micro- and ultrafiltration membranes, so far no one has shown a PDA-coated membrane in use. All the experiments described in the previous papers, in fact, were performed in bulk, i.e. by studying the changes in membrane performance under static conditions.

This paper discusses the filtration performance of a membrane that combines the typical size exclusion of ultrafiltration with the additional removal of contaminants thanks to the PDA layer performing depth filtration in the membrane cross-section. This combination allows the separation

of different types of contaminants simultaneously: large colloids and macromolecules will be rejected at the membrane/feed solution interface, while smaller molecules will be removed due to adsorption within the pores of the membranes. We use high performance UV-crosslinked PSU-based membranes [3] as a substrate, and we investigate two procedures to functionalize these membranes with PDA. In a two-steps method, the UV-crosslinked PSU membrane are subjected to phase inversion followed by PDA coating. An advantageous one-step method is also investigated, in which UV-crosslinked PSU membranes are subjected to phase inversion in a water solution containing dopamine, so that phase inversion and PDA functionalization occur at the same time. These functionalized membranes are fully characterized with evaluation of their surface properties, morphology, water flux, and selectivity. Methylene blue is employed as a representative dye and positively charged contaminant. Its removal with the proposed membranes is extensively studied both in batch and during filtration.

2. Experimental

2.1 Materials

Polysulfone (PSU, Mn = 22,000 g/mol), solvents N,N,-dimethyl formamide (DMF, Anhydrous, 98.8%), acetone (99.9 %) and acrylic monomer bisphenol-A-ethoxylate (2EO/phenol) diacrylate (BEDA, Average Mn=512 gmole^{-1} inhibited with 1000 ppm MEHQ) were purchased from Sigma–Aldrich. The photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phoshineoxide (BAPO) was kindly provided by BASF. Dopamine hydrochloride, Tris(hydroxymethyl)aminomethane (TRIS) base and methylene blue (MB) was purchased from Sigma–Aldrich.

2.2 Preparation of UV cured PSU based membranes

The polysulfone-based membranes were prepared via UV curing followed by non-solvent induced phase separation method (NIPS). A 15 wt. % solution of PSU in DMF was prepared by continuous stirring at 60 $^{\circ}$C for 7 hr. The solution was then cooled down overnight and 10 wt. % of BEDA was

added as acrylic crosslinker, together with the photoinitiator (Irgacure 819) at 3 wt. % with respect to the amount of the acrylic resin. After obtaining a homogenous solution, a film of 100 µm thickness was cast onto a glass plate. Membrane formation was obtained by UV curing for one minute under nitrogen (using a mercury medium pressure lamp) followed by NIPS. The energy dose utilized to cure the membranes was 10.05 J/cm^2. During casting and NIPS, the temperature of the air was 25 ± 3 ^{o}C and the relative humidity was 40 ± 10 %.

2.3 Polydopamine functionalization of crosslinked membranes

PDA coating was not conducted to increase the hydrophilicity or the antifouling properties of UF membranes, but to provide a large density of sorption sites for contaminant removal during cross-sectional depth filtration. As such, functionalization must guarantee the effective formation of a PDA layer coating the inner pores of the membrane all across the membrane thickness. We followed two different strategies for the preparation of these multifunctional membranes; see Figure 2. In the two-steps method (Figure 2a), phase inversion and PDA coating were performed in two different and independent stages. After curing, the membrane was immersed for 24 hr in a non-solvent bath, containing distilled water, to achieve NIPS. Subsequently, the membrane was coated by immersion into a dopamine solution under alkaline conditions (dopamine 2.0 g/L in 50 mM TRIS-HCl buffer, pH 8.5) and gently stirred at 50 °C. Different immersion times were investigated (3 hr, 6 hr, 12 hr, or 24 hr), to understand the effect of the extent of PDA coating on the performance of the membranes. After the functionalization, the membrane was washed with gentle stirring in a deionized water bath for 24 hr in order to remove the residual PDA that had not adhered to the membrane.

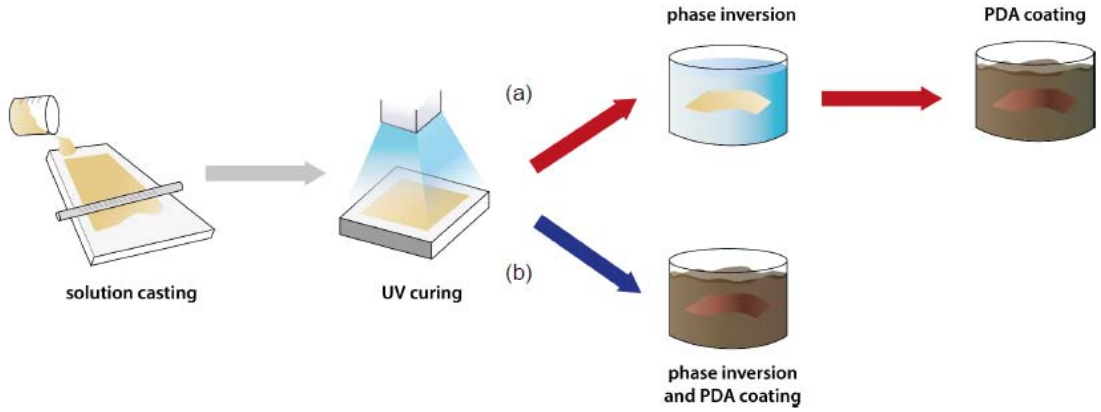


Figure 2. Schematic representation of the two-steps (**a**: NIPS for 24 hr followed by PDA coating in dopamine solution) or the one-step (**b**: NIPS in dopamine solution) synthetic approach for UV-Cured PSU-based membrane functionalization with PDA.

The advantageous one-step method consisted of a single stage in which NIPS of the UV-cured membranes was performed directly inside a dopamine water solution (Figure 2b). In this case, the membrane was immersed for different times (3 hr, 6 hr, 12 hr, or 24 hr) in a water bath, containing dopamine under alkaline conditions (dopamine 2.0 g/L in 50 mM Tris-HCl buffer, pH 8.5) and gently stirred at 50 °C. After this stage, the membrane was washed in a deionized water bath for 24 hr. The formulations of all the membranes functionalized with PDA are summarized in Table 1. Control pristine PSU membranes were also fabricated and referred to as M0, while control crosslinked membranes in the presence of acrylic monomers are referred to as M01.

Table 1. Composition of membrane casting solutions and PDA coating methodologies. All membranes were cast using a solution of 15 wt.% PSU. All the membranes were cross-linked with 10 wt.% BEDA acrylic monomer and a photoinitiator at 3 wt.% with respect to BEDA.~~For the crosslinked membranes, the polymer solution also comprised 10 wt.% BEDA acrylic monomer and a photoinitiator at 3 wt.% with respect to BEDA~~.

membrane	PDA functionalization time (hr)	two-steps method	one-step method
M1-3	3		✓
M2-3	3	✓	
M1-6	6		✓
M2-6	6	✓	
M1-12	12		✓
M2-12	12	✓	
M1-24	24		✓
M2-24	24	✓	

2.4 Characterization of PDA coated BPEDA modified PSU membranes

A Thermo Electron spectrophotometer was used for Fourier transform infrared spectroscopy (FTIR) and attenuated total reflectance (ATR) – FTIR analysis to evaluate the degree of crosslinking. The instrument is equipped with an ATR accessory containing a diamond crystal internal reflection element. The analysis was carried out with a resolution of 4 cm^{-1} and samples were scanned 32 times in the wavenumber range between 650 and 4000 cm^{-1}. The conversion of acrylate double bonds was calculated following the decrease of the area of the peak relative to C=C stretching group at 810 cm^{-1}, normalized by the area of the $\nu_{C=O}$ peak at 1730 cm^{-1}.

The morphology of membrane surfaces and cross-sections was analyzed through field emission scanning electron microscopy (FESEM). The instrument was the MERLIN model by ZEISS, equipped with state of the art GEMINILIS column ensuring accurate control of spot and current. The operational voltage was adjusted for each sample based on its properties and on the desired magnitude. The samples were snapped after immersion in liquid nitrogen and mounted onto SEM stubs. For cross-sectional analysis, the samples were clamped with edges in upward position. The samples were sputter coated with a layer of chromium (8.0 nm) to prevent charging.

The hydrophobicity of the membranes was determined at room temperature via static contact angle measurements through a KRUSS DSA – 100 apparatus. This system makes use of different methods to obtain drop shape analysis across three phases: dry membrane/air/water drop. The sessile drop fitting method was chosen to measure the contact angle and the results were also verified by other methods: tangent method–I and tangent method–II. All the contact angles were measured in equilibrium mode in replicates and the average values are presented here.

2.5 Batch adsorption

Batch adsorption experiments were performed using methylene blue (MB), a cationic dye chosen as a model contaminant. A piece of coated membrane (20-30 mg) was immersed into a solution with known concentration of MB and the concentration of MB in solution was monitored by UV spectrophotometer at the wavelength of 664 nm. To calculate the amount of dye adsorbed on the membranes, a simple mass balance was carried out taking into account the values of the dissolved dye in the beginning and at the end of the test. Initial experiments were conducted by leaving samples functionalized for different coating times (namely, 3, 6, 12 and 24 hr) in the MB solution at pH 10 for 24 hr, to study the influence of coating time on the maximum amount of dye adsorbed. Then, the effect of pH was studied by immersing the membranes functionalized with a coating time of 24 hr in MB solutions of pH 4, 6 and 10. The initial adsorption rate at pH 10 was estimated by monitoring the amount of MB adsorbed as a function of time. Finally, the reusability of the membranes was tested by regenerating the membrane under acid conditions following saturation with MB solution at pH 10. Solutions of HCl at pH 3 were used to promote desorption of MB and to regenerate the membrane. The desorption was carried out for 12 hr, followed by a rinsing step in distilled water for 12 hr. The same membrane piece was used to perform ~~7~~seven adsorption-desorption cycles.

2.6 Filtration tests

The tests to measure the permeability adsorption characteristics of the membranes were conducted in a stirred cell apparatus, Amicon 8010 (Millipore Co.), with samples having a diameter of 1 inch. The cell was initially pressurized with N_2(g) to reach a pressure drop of 15 psi, monitored using a pressure gauge. At this pressure, the membranes were subjected to pre-compaction for 10 minutes. Thereafter, the pressure was reduced to 8 psi and the flux through the membranes was determined by collecting the permeate and by measuring the change in mass over time after the system reached steady-state. The experiments were conducted using deionized water obtained from a Milli-Q water purification system. The permeability was calculated as the flow rate divided by the membrane area and by the applied pressure, and it is reported in L $m^{-2}h^{-1}bar^{-1}$. The ultrafiltration rejection properties of the membrane were tested with polystyrene latex beads with a nominal diameter from TEM measurements of 27±4 nm, suspended in deionized water. Rejection of colloids was based on size exclusion, thus providing information on the average size of the pores at the membrane active surface (membrane/feed interface), which should not change upon functionalization with PDA. A spectrophotometer was used to measure the absorbance of both the feed solution (c_f) and the permeate solution (c_p) at a wavelength of 260 nm. A previously obtained linear correlation allowed calculation of the particle concentration from the value of absorbance. The rejection of latex particles, *R*, was then calculated through the following equation: $R = 1 - \frac{c_p}{c_f}$.

MB depth adsorption tests were conducted in the same filtration system. In this case, separation does not occur at the membrane/feed interface as it is not based on size exclusion. Instead, it occurs within the pores of the UF membranes for contaminants that were not initially rejected by the membrane. Initially, a solution of deionized water at pH 10 was filtered for 1 hr through the membrane at an applied pressure of 10 psi in order to clean the sample and to remove the PDA in excess. Subsequently, the feed was substituted with a 0.5 g/L solution of MB at pH 10. The solution was allowed to flow through the membrane for 3 hr. Permeate samples were collected continuously at fixed intervals of approximately three minutes and their absorbance was measured to evaluate the

concentration of MB, using a spectrophotometer at a wavelength of 664 nm. A previously obtained linear correlation allowed calculation of the dye concentration from the value of absorbance. A tracer test was conducted as follows: after saturation of the membrane with the dye during the adsorption experiment, the ultrafiltration system and the membrane were flushed using a dye-free solution at pH 10. No significant release of the previously adsorbed dye was observed during this step. Subsequently, the initial feed solution containing 0.5 g/L MB was again filtered through the already saturated membrane. Because all PDA sites were saturated with the dye, the hypothesis is that the dye did not interact with the membrane, thus this second filtration step can be used as tracer filtration. Permeate samples were collected and analyzed with the same procedure used for the previous adsorption test. At the end of this tracer filtration, the membrane was removed from the cell and rinsed in deionized water at pH 10. A dye desorption test was thus conducted by leaving the membrane sample in a batch containing deionized water at pH 3 for 24 hr with gentle stirring. The absorbance of this solution was measured to estimate the amount of dye that desorbed from the membrane.

3. Results and Discussion

In this study, we combine the ultrafiltration performance of a UV-cured solvent stable PSU-based membrane with the adsorption behavior of PDA used to functionalize the cross-sectional pores of the membrane.

3.1 Membrane preparation and characterization

The degree of crosslinking of the PSU-based membrane was evaluated previously, reaching a final conversion of about 85% after one minute of irradiation [3]. The PDA coating was confirmed by ATR analysis: the spectra of the membranes M1-6, M2-6, M1-24 and M2-24 are compared with that of the pristine PSU membrane (M0) and cross-lined PSU-based membrane (M01) in Figure 3.

Peaks at 1600 and 1450 cm^{-1} are evident after PDA functionalization and due to the $\nu_{C=C}$ from phenyl groups and δ_{N-H} from amino groups, respectively, present on PDA. The signal at 1730 cm^{-1} is related to the $\nu_{C=O}$ from the acrylate crosslinker.

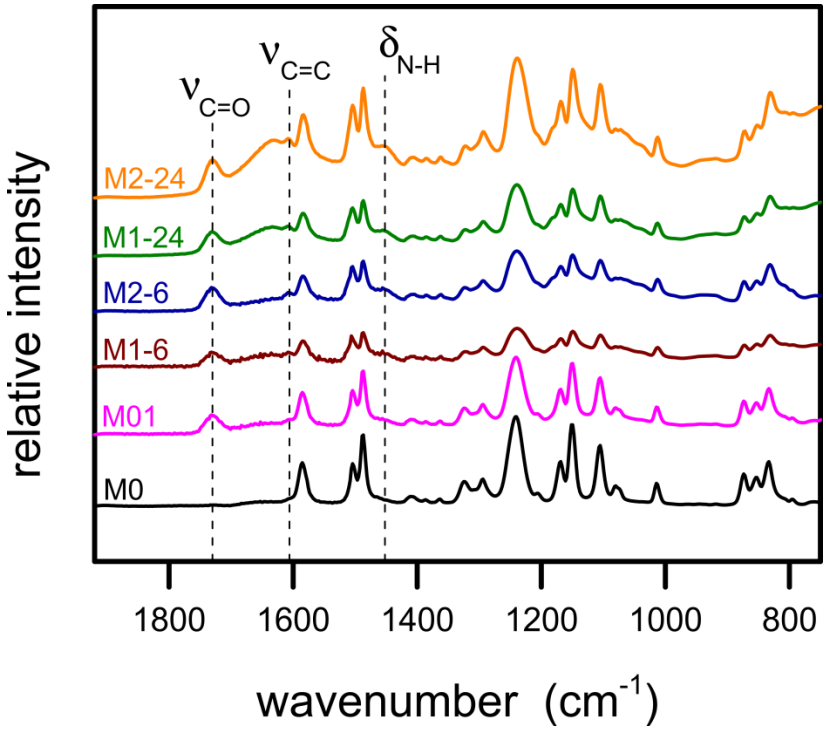
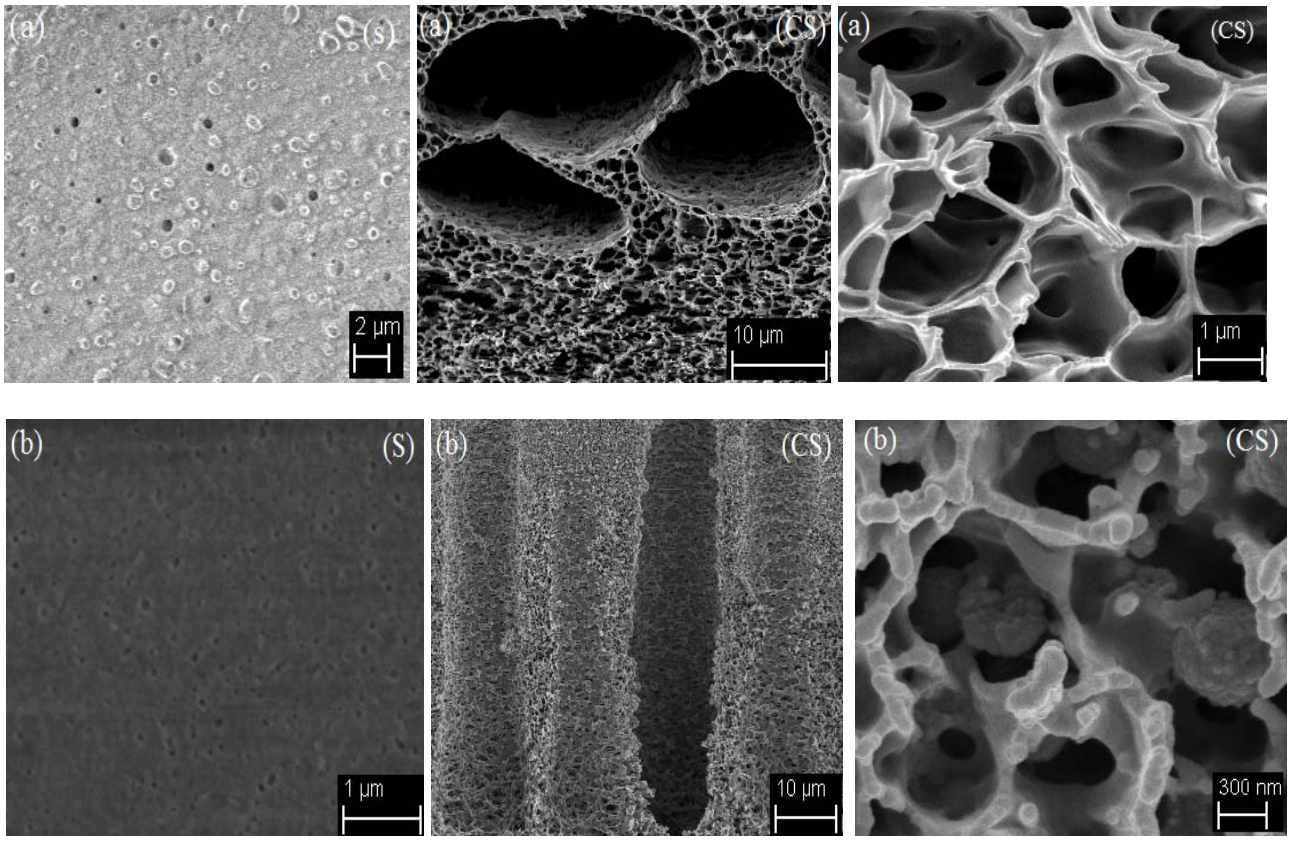


Figure 3. ATR-FTIR spectra of pristine PSU (M0), cross-linked PSU-based membrane (M01), and PDA-coated crosslinked PSU based membranes.

The morphology of the surface and of cross-sections of the membranes was investigated by FESEM. Figure 4 presents representative micrographs of the pristine PSU membrane, the crosslinked membrane, and the PDA coated membranes obtained after 24 hr of functionalization time with both methods. As also shown in our previous study [3], the cross-sectional structure of the membrane crosslinked using acrylic monomers (Figure 4b) showed a denser sponge-like structure compared to the pristine PSU membrane (Figure 4a). On the other hand, the density and the size of the pores at the active surface did not change significantly, thus allowing high water flux; see Table 2. A qualitative evaluation of Figure 4 suggests that ~~While~~ PDA coating did not visibly change the cross-sectional porosity of the membranes, while a lower density of smaller pores was

observed at the surface; see Figure 4c, d. This decrease in surface porosity is in agreement with the observed reduction of the water flux values, which decreased of about one order of magnitude for the PDA-coated membranes compared to the non-functionalized membranes (Table 2). The presence of macrovoids in the cross-section of the membranes functionalized with PDA may reduce the contact opportunities between the fluid and the functionalized polymer structure, thus decreasing the kinetics of contaminant adsorption. However, a dense cross-sectional structure would further decrease the permeability of the membrane, which might not be suitable for ultrafiltration if fluxes are too low. The ideal pore structure is such that would allow appropriate water productivity while maintaining high contaminant adsorption kinetics.



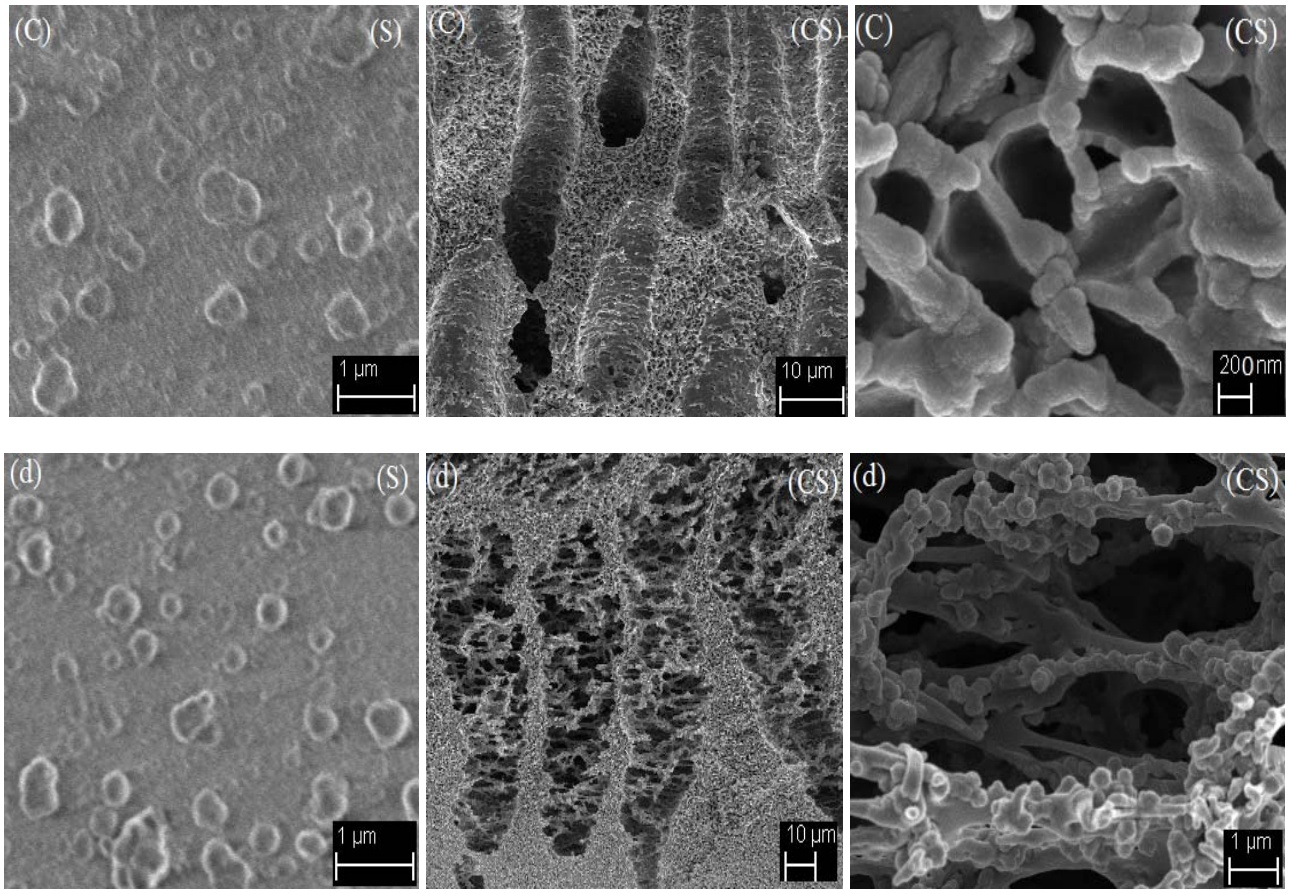


Figure 4. FESEM micrographs of surface (S) and cross-section (CS) of: **(a)** pristine PSU (M0), **(b)** cross-linked PSU based membrane (M01), **(c)** UV-cured films coated with PDA for 24 hours via the one step procedure (M1-24), **(d)** UV-cured films coated with PDA for 24 hours via the two step procedure (M2-24).

High rejection was maintained for particles with diameter of 27 nm (Table 2). Minor differences in terms of morphology were observed for the membranes functionalized following the one-step process and the two-step process, the former showing a slightly denser sponge-like structure. While the presence of PDA during NIPS did not significantly change the precipitation pathway of the polymer, these results may explain the somewhat lower water flux measured with the one-step membranes. Values of contact angle indicate that the functionalization also caused a marginal increase in wettability, induced by the PDA, but probably not sufficient to cause changes in water flux.

Table 2. Parametric analysis and performance evaluation of pristine and PDA coated membranes

membrane	average water contact angle	water permeability ($L\ m^{-2}h^{-1}bar^{-1}$)	rejection of 27 nm particles (%)
M0	53 ± 3	338 ± 15	-
M01	54 ± 4	239 ± 14	92 ± 4
M1-6	53 ± 6	16 ± 1	95 ± 4
M2-6	43 ± 5	24 ± 2	96 ± 3
M1-24	45 ± 6	15 ± 2	89 ± 3
M2-24	50 ± 7	28 ± 1	91 ± 2

3.2 Adsorption of methylene blue

The PDA coating was performed with the goal to adsorb charged molecules during their depth filtration and combine the ultrafiltration properties of PSU membranes with the adsorption properties of PDA. At pH 10, PDA is negatively charged, and should attract positively charged molecules such as the cationic dye MB. We initially evaluated the adsorption of MB in batch experiments. ~~These experiments suggested that adsorption of MB is not an equilibrium-driven process but that it is quantitative until saturation.~~ In fact, at liquid concentrations lower than those necessary to achieve saturation of the membrane, all MB molecules were adsorbed on the membranes, as confirmed by measurement of negligible light absorbance of the solution following contact with the PDA-functionalized materials. Therefore, MB adsorbs onto the membrane until saturation is achieved. These experiments suggested that adsorption of MB is not an equilibrium-driven process, or in any case that equilibrium would be reached in times much longer than experimental or operational times.

Figure 5 shows the mass of adsorbed dye normalized by the total mass of the membrane, defined as specific adsorbed mass, at saturation as a function of PDA coating time during membrane fabrication. The adsorption capacity increased with increasing PDA coating time, although this increase was not linear for longer functionalization times. The membranes functionalized following the one-step method were capable of adsorbing a larger amount of dye compared to those fabricated via the two-step approach. A trade-off was thus observed between water flux and adsorption capacity for the two different fabrication approaches investigated in this study. The amount of PDA available for adsorption for the membranes functionalized for 24 hr was estimated to be roughly 2 mg for each g of membrane, based on the values of MB adsorbed at saturation. The actual amount of PDA may be larger, but not all the monomers may be exposed or accessible for contaminant adsorption.

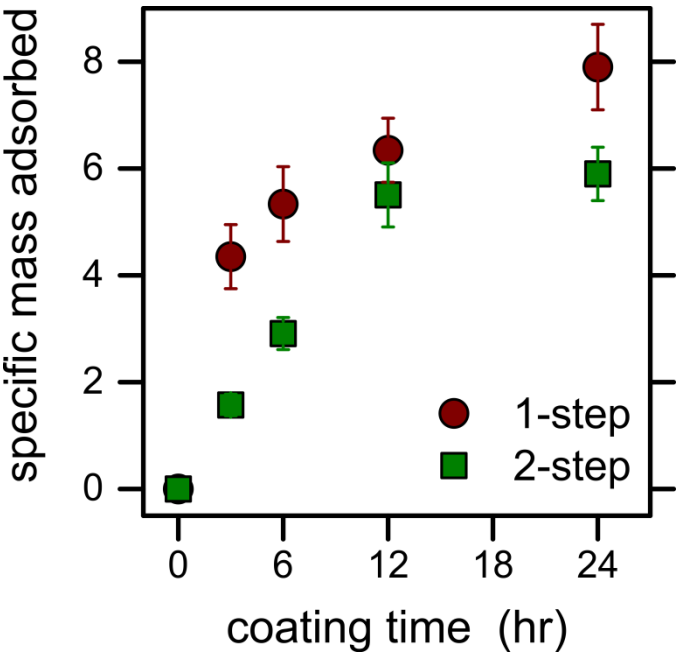


Figure 5. Mass of methylene blue adsorbed per mass of membrane as a function of PDA coating time, for membranes fabricated in (red circles) one step and (green squares) two steps. Experiments were performed with an initial mass of dye in solution and for an amount of time as to allow complete saturation of each of the various membranes. The temperature was fixed at 23 °C and the pH at 10.

The kinetics of adsorption was then evaluated for these materials (Figure 6). Membrane samples were immersed in 10 mL of a solution of 12.5 mg/L of MB; the light absorbance of this solution was monitored over time and used to calculate the mass of dye going from the liquid to the solid phase. The data confirm that both the capacity and the kinetics of adsorption were higher for the membranes obtained via the one-step coating process. However, both membranes had a large number of sites available for interaction with the dye and the observed force driving adsorption was of high magnitude in all cases.

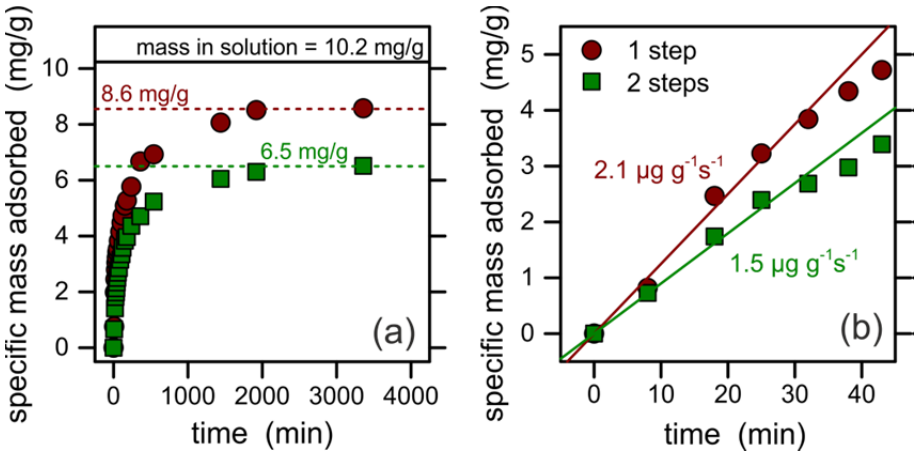


Figure 6. Mass of methylene blue adsorbed per mass of membrane as a function of time, for membranes fabricated in (red circles) one step and (green squares) two steps. (a) Complete sets of data, also showing (horizontal continuous line) the total amount of dye in solution normalized by the membrane mass and (horizontal dashed lines) the values of specific adsorbed mass at saturation for both types of membranes. (b) Enlargement of the initial part of the curves with linear fittings used to calculate the adsorption kinetics coefficients. Experiments were performed in ~~20~~12.5 mg/L methylene blue, at pH 10, and at a temperature of 23°C.

To understand the role of PDA ionization on the adsorption of MB at saturation, experiments were also conducted at pH 4 and pH 7. The results are summarized in Figure 7a and suggest the importance of electrostatic interactions to drive adsorption of the oppositely charged dye. PDA displays a lower density of charges under acidic conditions, thus a lower amount of sites available

for interaction with the dye molecules in solution (Figure 8). Indeed, lower adsorption of MB was observed for both the one-step and the two-step membranes at lower pH. While at pH 10 the one-step membrane showed higher MB adsorption, as previously discussed (see Figures 6 and 7), at low pH values the MB adsorption on the one and two step membranes was only marginally different, possibly because in this pH range the electrostatic interactions are minimal.

To test the zwitterionic properties of the PDA coatings, the membranes were subjected to cycles of adsorption and desorption steps. Adsorption was performed at pH 10 for 24 hr until saturation, while desorption steps were conducted at pH 3 for 12 hr. At pH 3, PDA is positively charged and it released most of the previously adsorbed dye due to electrostatic repulsion. The data presented in Figure 7b suggest that the membranes were able to re-adsorb the same amount of dye in each of the seven adsorption cycles following dye release under acidic conditions. Therefore, these materials may be completely regenerated and reused without loss of performance by simple changes of pH. It is important to note that adsorption at a given pH was always irreversible under unchanged conditions; no dye desorption was detected after contacting the saturated membrane with a dye-free solution of the same ionic and pH composition.

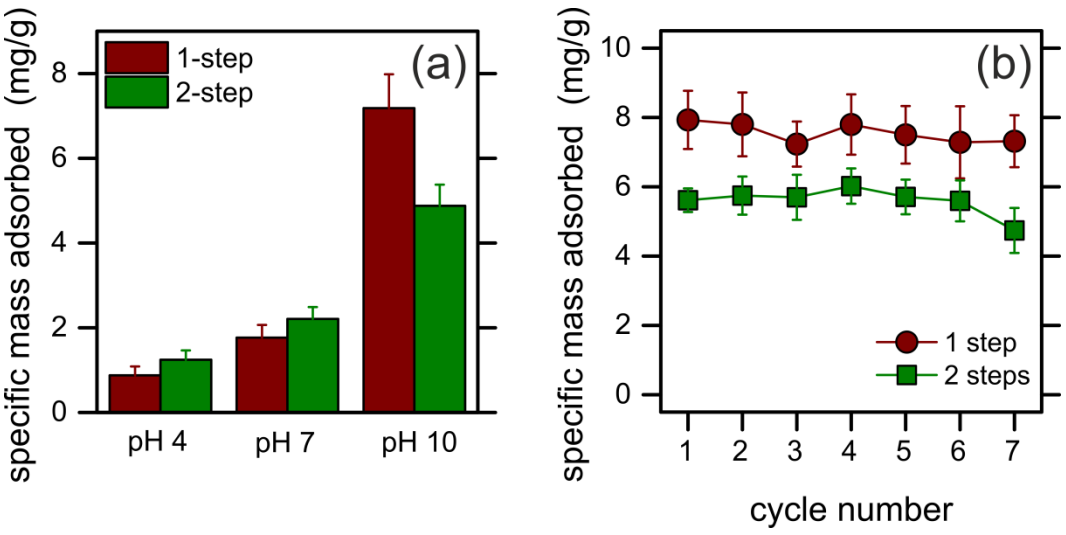


Figure 7. Mass of methylene blue adsorbed per mass of membrane (a) as a function of ~~time~~ pH and (b) for different cycles of adsorption following release at low pH. Data refer to membranes fabricated in (red bars

and red circles) one step and (green bars and green squares) two steps. All adsorption experiments were performed in 20 mg/L methylene blue for 24 hr, at pH 10, and at a temperature of 23°C. In (b), dye release between each adsorption cycle was performed in a dye-free solution of pH 3 for 12 hr at a temperature of 23 °C.

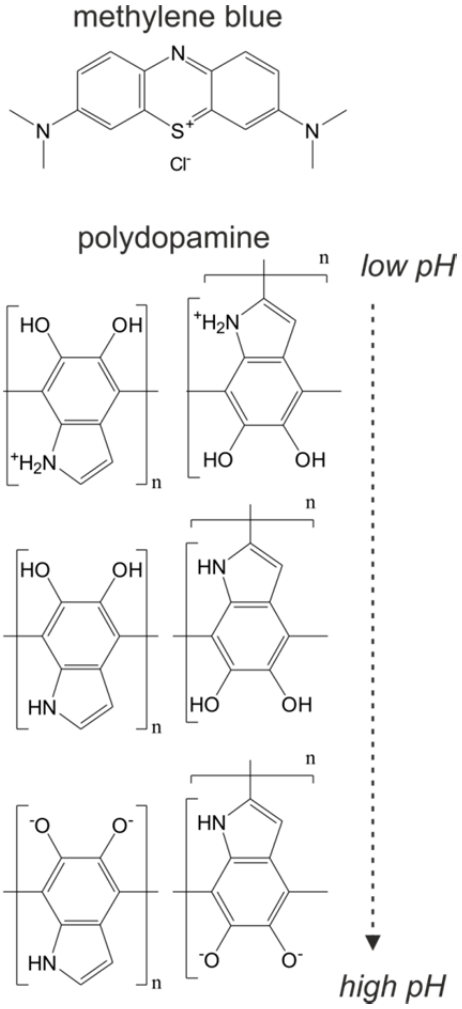


Figure 8. Schematic representation of the molecules of methylene blue and polydopamine under different ionization conditions as a function of pH.

3.3 Filtration of methylene blue

Depth filtration experiments were also conducted under ultrafiltration conditions. For these experiments, a solution containing 0.5 g/L of MB was filtered through the membranes functionalized with PDA and the concentration of dye was monitored over time in the permeate.

Figure 9 shows results obtained in a representative test using two-step membranes. The concentration of dye in the permeate, presented as circles, increased with increased volume of permeate collected, following the typical breakthrough curves of depth filtration processes, such as filtration of colloids or solutes through porous media. The normalized concentration in the permeate reached an asymptotic value of approximately 0.85; this results is rationalized with the expected ability of the membrane to marginally reject the dye with a rejection of roughly 15% under the test conditions. This observation is confirmed by the data collected during filtration of a tracer, which also reached the same plateau value as shown by the triangles in Figure ~~10~~9.

Both tracer and adsorption data sets were thus fitted using an advection-dispersion model; see Supporting Information for details about the model. In the case of the tracer, no adsorption was implemented in the model, which allowed calculating the dispersivity and the porosity of our system. These values were then used to model the breakthrough curve obtained during adsorption. In this latter case, blocking was added to take into account that there is a maximum value of sites available for adsorption, related to membrane saturation. The value of the kinetics adsorption coefficient and that of the specific mass adsorbed at saturation were used as fitting parameters. In these calculations, the thickness of the membranes was fixed at 100 μm. The fitting procedure yielded accurate results and the model described the experimental data well; see Figure 9. The calculated values were 12 mg/g for the specific mass adsorbed at saturation and 0.01 1/s for the adsorption coefficient. These values are not far from the values calculated from batch experiments, suggesting that the data modeling was adequate. More importantly, both the adsorption capacity and the rate of adsorption were large: despite the use of a highly concentrated feed solution (0.5 g/L), the amount of dye in the permeate was negligible or low during the initial minutes of filtration.

Desorption of MB from the membranes carried out at pH 3 was complete after 24 hr, based on the concentration of the dye measured in the release solution. Similar results were obtained for the membranes functionalized with the one-step and with the two-step approaches. In a potential application, membranes would be operated by alternating cycles of adsorption and regeneration,

ensuring that only a negligible amount of targeted contaminant reached the permeate stream. The large adsorption capacity observed for these materials would allow ~~to operate~~operating the filtration for long time before stopping the process for cleaning. Based on our results, a typical 40 m^2 spiral-wound module, operated under 2 bar of applied pressure, would allow constant operation for roughly 15 min, obtaining approximately 300 L of permeate with a contaminant concentration always lower than 10% of the feed concentration, for a feed stream with an unrealistically high contaminant concentration of 0.5 g/L, as in our experiments.~~.~~

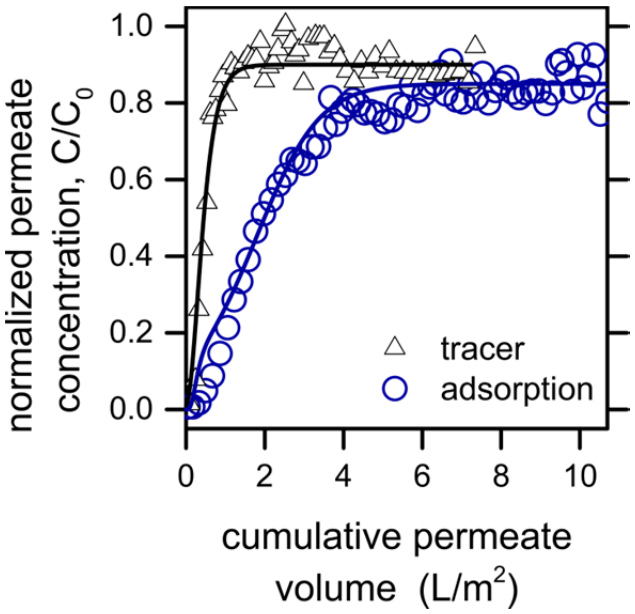


Figure 9. Breakthrough curves of methylene blue obtained in ultrafiltration tests for (blue circles) a clean membrane and (black triangles) an already saturated membrane. The concentration in the permeate was normalized by the concentration of dye in the feed and plotted against the collected volume of permeate. The data refer to a membrane functionalized following a two-step protocol. The experimental data were fitted using advection-dispersion models, and the results are shown as continuous lines in the graph. Experiments were conducted using a feed solution of 0.5 g/L methylene blue at pH 10, filtered using an applied pressure of 10 psi at a temperature of 23 °C.

4. Conclusions

In this paper, we investigated the preparation and the filtration performance of polymeric membranes that combine the size exclusion of ultrafiltration with the adsorption and contaminant removal ability of polydopamine (PDA). The polysulfone based ultrafiltration membranes were obtained in the presence of an acrylic crosslinker in order to achieve chemically stable crosslinked membranes maintaining good flux performance. Functionalization with PDA occurred either via a two-steps method, where the UV-crosslinked PSU membrane were subjected to phase inversion followed by PDA coating; or in a one-step method, where UV-crosslinked PSU membranes were subjected to phase inversion into a water solution containing dopamine, so that phase inversion and PDA functionalization occurred at the same time.

No visible differences in terms of morphology were observed for the membranes functionalized following the one-step process and the two-step process; however, lower water flux was measured with the one-step membranes. Data suggested that the presence of PDA during NIPS did not change the precipitation pathway of the polymer significantly, but that the coating of PDA achieved in the one-step method may be sufficiently thicker to reduce the size of the smaller pores of the asymmetric membrane near its surface. Methylene blue (MB) was employed as a representative dye and positively charged contaminant, and dye removal was investigated both in batch and under filtration conditions. The adsorption capacity, studied at pH 10, showed an increase MB removal with increasing PDA coating time. The MB dye adsorbed onto the membrane until saturation was reached. Both the capacity and the kinetics of adsorption were higher for the membranes obtained via the one-step coating process, thus implying a trade-off between water permeability and contaminant adsorption for the two different fabrication methods.

These results suggest that fabrication of these selective and reactive membranes may be designed depending on the application and on the desired performance. When contaminant removal is the concern, and not the productivity, fabrication does not need to comprise a cumbersome sequence of

two synthesis steps but may be conducted via traditional NIPS, simply by adding dopamine and adjusting the chemistry of the non-solvent solution.

The membranes were completely regenerated and reused without loss of performance, as they were able to re-adsorb the same amount of dye in several adsorption cycles following dye release under acidic conditions. The membrane adsorption capacity and the rate of adsorption were large also during filtration experiments. This study suggests that the functionalized membranes behave as suitable ultrafiltration membranes and that they may be successfully used to filter solution containing positively charged contaminants.

Acknowledgements

This research was partially supported by a Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) Fellowship (Mat4Treat, proposal n. 645551) within the H2020-MSCA-RISE-2014 European Community Call.

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TOC/GRAPHICAL ABSTRACT

Ultrafiltration Membranes Functionalized with Polydopamine with Enhanced Contaminant Removal by Adsorption

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