Journal of Materials Chemistry A

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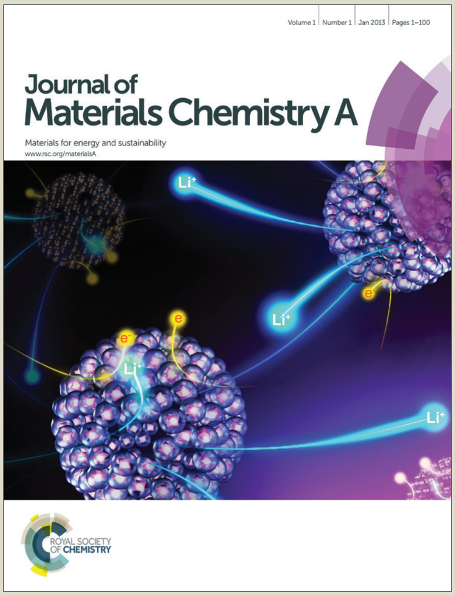

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ARTICLE

Co-deposition of Catechol/Polyethyleneimine on Porous Membranes for Efficient Decolorization of Dye Water

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Mussel-inspired chemistry has been broadly exploited for multifunctional coatings in the surface modification of applied materials. Polyphenols are ubiquitous in plant tissues and far less expensive than polydopamine for mussel-inspired chemistry. Herein, we report a facile and effective method to modify porous membranes via the co-deposition of catechol (CCh) and polyethyleneimine (PEI). The membrane structures and properties were investigated by ATR/FTIR, XPS, FESEM, zeta potential, water contact angle and pure water flux measurements. Results reveal that the membranes deposited with a CCh/PEI mass ratio of 1:0.25 show excellent hydrophilicity, ultrahigh water permeation flux and distinguished surface charges. These membranes were used to decolorize anionic dye solutions during filtration with superior removal efficencies of over 99%. Moreover, they have good reusability over repeated operations with simple regeneration process.

Introduction

Water pollution and water shortage are becoming a major challenge for the sustainable development of worldwide economy and society. Printing and dyeing of textiles discharge huge wastewaters polluted by various dyes. These dye wastewaters constitute only a small proportion of aquatic pollution, but they are highly undesirable. The increased color concentrations contaminate the water for domestic or industrial use and many of the dyes are toxic in nature with potential carcinogenic and genotoxic effects.[1-5] However, the treatment of dye effluents has been proven pretty intractable as the majority of commercial dyes are of complex aromatic structures that resist degradation.[6, 7] Therefore, they are recalcitrant to decolorize when exposed to light, aerobic digestion and many oxidizing agents.[4, 8-10] It is of vital environmental significance for the development of cost-effective methods to remove dye molecules from colored sewage.

Various approaches have been developed to treat dye wastewaters, which include ozonation,[11] adsorption,[12] coagulation-flocculation,[13] electrochemical techniques,[14] and membrane filtration.[15-26] It has attracted much attention to integrate membrane filtration into dyeing process, because this process has minor energy requirement, facile operate condition and relatively low investment and maintenance costs.[15-17,20,23] In most cases, nanofiltration (NF) membranes were used to isolate dye molecules (200-1000 Da) continuously from effluent with high removal efficiency, allowing the reuse of water, dyes and other valuable waste constituents.[18-20] Typical problem is that the NF membranes are confronted with severe fouling by the accumulation of dye molecules and concurrent concentration polarization, which lead to a prominent decline of permeation flux.[15,21] Meanwhile, dye wastewater always possesses high salinity and an increase in ionic strength will considerably decrease the dye rejection as a result of the shielding effect and attenuation of Donnan effect.[22,23] In comparison, microfiltration (MF) membranes are featured with high flux, low operating pressure, and much tolerance toward fouling by micromolecules. However, due to their oversize pore structures, MF membrane processes are generally believed unable to deal with soluble dyestuffs except being employed as the mere pretreatment for subsequent nanofiltration.[24] It has been scarcely reported for exerting microfiltration as the central technology for dye wastewater treatment. LEE *et al.*[26] adopted a submerged-type hollow fiber MF membrane to separate the suspended particles of sorbent-dye composite after the step of adsorption with powdered active carbons. This adsorption-membrane hybrid system achieved superior rejection (99%) for reactive dyes, but the involved multiple stages are inefficient and the membrane has to be severely contaminated. Meanwhile, active carbon lacks economic attraction due to its regeneration difficulty.[27] Porter *et al.*[28,29] investigated the feasibility of removing soluble dye straightforwardly using ceramic TiO_2 and polypropylene microfilters with pore diameter of 0.2 μm. They confirmed the charge or ionic nature of membrane surfaces were effectual for dye retentions. However, the rejection performances were mediocre, especially for organic polypropylene

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† Electronic Supplementary Information (ESI) available: Chemical structures of eight dyestuffs used in this work (Fig. S1); Weight gain of the membranes modified by immersing in CCh/PEI solution for 7 h with different mass ratios (Fig. S2); FT-IR/ATR spectra of the membrane surface modified with different CCh/PEI ratios for 7 hr deposition (Fig. S3); Digital pictures of the modified PPMMs (Fig. S4); Water contact angle (a) and pure water flux (b) of the modified membranes (Fig. S5); Pseudo-first order kinetic of DR80 adsorption on the modified membranes (Fig. S6); UV-vis spectra of the dye solutions before and after membrane treameats (Fig. S7); The concentration of rodamine in the filtrates with operation time and different AB/RD mass ratios (Fig. S8); Influence of ionic strength on the treating capacity of (a) orange ii and (b) x-3b by the CCh-PEI modified membranes (Fig. S9). See DOI: 10.1039/x0xx00000x

membranes (only 40-60%). Therefore, novel MF membranes or membrane processes are still required for more facile, effective and hypo-cost treatment of dye wastewaters.

In recent years, self-polymerization of dopamine into melanin-like polydopamine (PDA) coating[30] is becoming a versatile and attractive method for the surface modification of polymer membranes, which significantly promotes surface hydrophilicity, water permeation flux and antifouling property of the nascent membranes.[31] Our previous work revealed that the co-deposition of PDA with polycationic polyethyleneimine (PEI) could endow polypropylene membrane with noticeable surface charges capable of adsorbing opposite-charged SiO_2 sols.[32] We presume that this kind of positively-charged microfiltration membrane with high permeability may be applicable for the treatment of anionic dyestuffs. However, the molecular diversity of PDA precursors are quite limited (dopamine, norepinephrine, and DOPA) and their high costs are not desirable for practical applications. Tannin-like coatings derived from (poly)phenols, which are ubiquitous in plant tissues,[33-35] can be used to replace PDA-based substances. Specifically, Wang *et al.*[36] reported the co-deposition of catechol/polyamines on polypropylene separators as a facile method of hydrophilic modification. Herein, we report this plant-inspired approach to facilely construct superior hydrophilic and distinguished charged surfaces for polypropylene microfiltration membranes (PPMMs). The optimized membranes are useful in simple filtration experiments to realize a fast decolorization of anionic dye wastewaters.

Experimental

1. Materials

PPMM was a commercial product from Membrana GmbH (Germany) with an average pore size of 0.40 μm and a relatively high porosity of about 75%. All membrane samples were cut into rounds with a diameter of 45 mm, washed by acetone for 4 h to remove impurities adsorbed on the membrane surfaces and then dried in a vacuum oven at 40 °C to a constant weight. Catechol, polyethyleneimine (PEI, Mw = 600 Da) and eight dyestuffs (chemical structures are shown in **Fig. S1, ESI†**) were all purchased from Aladdin (China). Tris (hydroxymethyl) aminomethane (Tris) was acquired from Sinopharm Chemical Reagent Co. Ltd, China. Other reagents were of analytical grade and used as received.

2. Preparation of the catechol/PEI modified PPMMs

Catechol and PEI with designed mass ratios were dissolved in Tris buffer solution (pH = 8.5, 10 mM) and the concentration of catechol was fixed at 1.0 mg/mL. PPMM samples were pre-wetted thoroughly by ethanol and then immersed into the freshly prepared reaction solutions. After incubated at room temperature for 7 h under gentle vibration, the modified membranes were taken out, rinsed with ultrapure water for three times and dried under vacuum at 40 °C to a constant weight.

3. Characterization

UV-vis absorption of the solution was measured with an ultraviolet spectrophotometer (UV 2450, Shimadzu, Japan) from 700 nm to 250 nm. FT-IR/ATR spectra were obtained by an infrared spectrophotometer (Nicolet 6700, USA) equipped with an ATR accessory (ZnSe crystal, 45°). XPS analyses were performed on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA) with Al Kα radiation (hν = 1486.6 eV). Surface morphologies were observed by a field-emitting scanning electron microscope (FESEM, Hitachi S4800, Japan) after sputtered with a 10-20 nm gold layer. Water contact angles (WCA) were determined with a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd., China). Pure water flux was evaluated by a high-pressure method in a dead-end filtration cell (Millipore, USA). The membrane was compacted by filtering water through it at 0.3 MPa for 15 min and subsequently at 0.1 MPa for another 15 min, then the flux of pure water was measured every 5 min until reaching a stable value. Zeta potentials were measured for the membrane surfaces by an electrokinetic analyzer with an integrated titration unit for solid surface analysis (Anton Paar, SurPASS, Austria). Pore sizes of the membranes were determined with an automatic mercury porosimeter (AutoPore IV 9510).

4. Decolorization of anionic dye solutions

The experiments were carried out in a home-made filtration unit where a membrane deposited with 1:0.25 of catechol/PEI was sandwiched between two silicon gaskets. Dye solution (25 mg/L) with certain pH was filtered through the membrane driven simply by gravity. Filtrates were collected every 5 min until the removal efficiency was lower than 99%. For each dye solution, the experiment was repeated 3 times with a same membrane. And during all experiments, the height of water column was re-added to 8 cm every 5 min. Treating capacity (Tc, mg/g) and flux (F_d, L/m^2h) are defined as follows:

$$\mathrm{Tc} = \frac{\mathrm{c} \cdot \mathrm{V_d}}{\mathrm{m}} \qquad (1)$$

where c, V_d and m represent the concentration of dye solutions, the total volume of filtrates and the mass of effective membrane area, respectively.

$$\mathrm{F}_d = \frac{V}{\mathrm{A} \cdot \mathrm{t}} \qquad (2)$$

where V, t and A represent the volume of filtrates, operation time and effective membrane area, respectively. And removal efficiency was determined by measuring the dye content in feed and in corresponding filtrate via UV-vis spectrophotometer.

Results and discussion

1. Co-deposition of CCh-PEI aggregates on PPMMs via an oxidation process

Solution oxidation in the air atmosphere has been developed as a useful protocol to prepare melanin-like materials.[35-37] As an polyphenol, CCh can be oxidized to quinoid form and then react with PEI by Michael addition or Schiff base reaction (**Fig. 1a**) in an alkaline Tris buffer solution.[38,39] The reactions gradually form CCh-PEI aggregates in the solution and then deposit onto the membrane surfaces. This process is similar to that of dopamine self-polymerization for the surface modification of various materials.[40-42]

Fig. 1b depicts that the colorless solution turns brown after 7 h oxidation and show gradient color depth with the increase of CCh/PEI ratio from 1:0 to 1:2. The reaction solutions were further analyzed by UV-vis spectra. **Fig. 1c** shows two broad peaks at around 316 nm and 480 nm and the absorption at the whole region increases with the CCh/PEI ratio in the solution, which has been suggested as an evidence for the cross-linking reaction.[32] And it can be inferred that increased amount of PEI intensifies the formation of CCh-PEI aggregates by cross-linking.

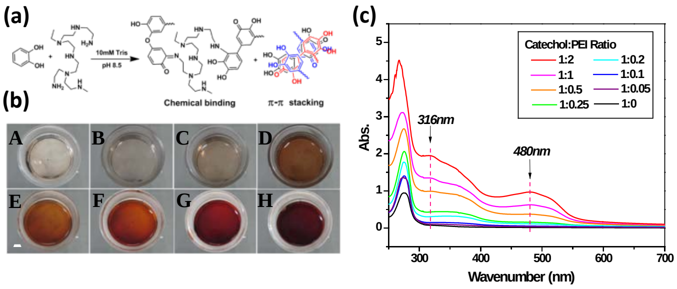

Fig. 1 (a) Schematic illustration for the possible polymerization mechanism of CCh and PEI; (b) Color of solutions with different CCh/PEI ratios after 7 h reaction: A) 1:2, B) 1:1, C) 1:0.5, D) 1:0.25, E) 1:0.2, F) 1:0.1, G) 1:0.05, H) 1:0; (c) UV-vis spectra of CCh and PEI solutions after 7 h deposition.

The CCh/PEI ratio also influences the deposition behavior on the membrane surfaces. Results indicate that the deposition gain increases with the ratio from 1:0 to 1:0.25, and then decreases with the ratio from 1:0.25 to 1:2 (**Fig. S2, ESI†**). ATR/FT-IR spectra of the membrane surfaces follow the same trend with this ratio (**Fig. S3, ESI†**). The membrane appearance also reflects the deposition amount (**Fig. S4, ESI†**). It seems that 1:0.25 is the most efficient ratio for forming CCh-PEI aggregates to deposit on the membrane surfaces. As mentioned above, PEI accelerates the cross-linking of CCh-PEI to form aggregates which continuously deposit to the membrane surfaces.[44] However, excessive amount of PEI is likely to suppress the covalent binding among aryl rings[45] and π–π stacking[46] of catechol via oxidation, thus to disintegrate the aggregates formation for deposition.

2. Surface structures and physical properties of the CCh-PEI modified PPMMs

XPS and FESEM were applied to characterize the morphology and chemical composition of the membrane surfaces. **Fig. 2a** depicts typical FESEM images from the membrane surface of nascent (A) and CCh-PEI modified PPMMs with different CCh/PEI mass ratios (B-D). At the ratio of 1:0, the membrane surface is as smooth as the nascent one. Whereas, the membrane surface is covered with massive granular and even lumpish aggregates at 1:0.25. In comparison, merely a small quantity of particles can be observed when the ratio is raised to 1:2. The cross-section images of the above membranes are not differentiable, so the membranes were further treated with silver nitrate. Silver ions can be reduced by polyphenols[47] and EDX mapping of the silver element of the membrane cross-sections confirms that the CCh-PEI coating is distributed throughout the membranes (**Fig. S5, ESI†**). Meanwhile, the average pore sizes of membranes decreases from 404 nm (blank) to 341 nm (1:0.25) after modification (**Fig. S6, ESI†**). XPS analyses (**Fig. 2b**) show that the nascent PPMM gives a single peak at around 284.2 eV attributed to the binding energy of C 1s. Peaks of O 1s and N 1s can be detected for the CCh-PEI modified membranes and the peak intensity corresponds with the deposition weight. Despite that, N/O ratio increases distinctly with PEI concentration (**Table S1, ESI†**). It is noted that a tiny N 1s peak is observed for the membrane modified with CCh alone. This can be rationalized by the fact that primary amines in Tris molecules would take participation in the oxidation polymerization process of CCh.[48]

The blank PPMMs are highly hydrophobic, while the membrane surfaces are significantly hydrophilized by CCh-PEI deposition, as illustrated by the values of water contact angle and pure water flux (**Fig. S7, ESI†**). Meanwhile, CCh-PEI aggregates contain quantities of residual amine or imine groups liable to be protonated under acidic condition, thus endowing the membrane with positively charged surfaces. The surface potentials were measured at pH = 3 and the results are shown in **Fig. 3**. Under the experimental conditions, the nascent membrane has a few positive charges (26.1 ± 0.8 mv). The zeta potential of the CCh-PEI modified PPMM increases to 115.7 ± 1.6 mv with the CCh/PEI ratio and then decreases to 52.7 ± 0.5 mv, roughly in accordance with the deposition gain of CCh-PEI aggregates. These positively charged membranes should be useful for anionic dye adsorption, and typical results reveal that the membrane deposited with 1:0.25 of CCh/PEI shows the fastest adsorption rate and maximum capacity to anionic direct red 80 (DR80, **Fig. S8 and Table S2, ESI†**). Thus, this membrane can be used for the decolorization of dye water.

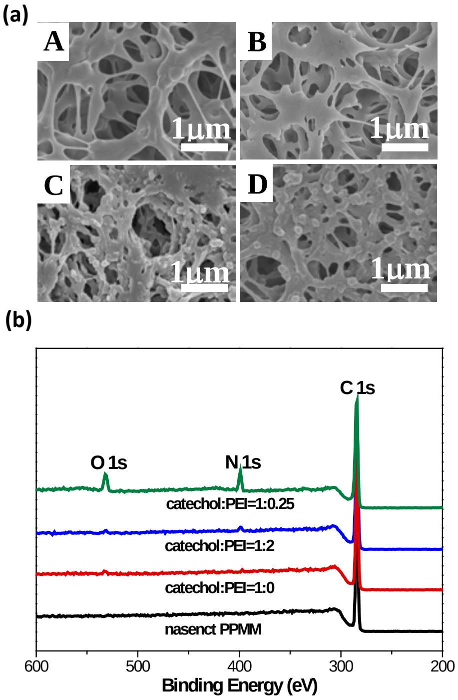

Fig. 2 (a) Surface morphologies and (b) XPS spectra of the modified membranes with different CCh/PEI ratios after 7 h deposition: A) nascent PPMM, B) 1:0, C) 1:2, D) 1:0.25, respectively.

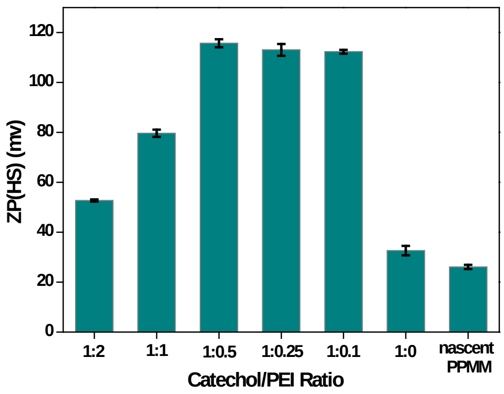

Fig. 3 Zeta potentials of the membrane surfaces before and after modification.

3. Decolorization of anionic dye water with the CCh/PEI modified PPMMs

The CCh-PEI modified PPMMs are featured with high water permeation flux and positively charged surfaces. This kind of materials can be applied in dye wastewater treatment through membrane process. Therefore, the decolorization of dye water was carried out with a home-made filtration unit (**Fig. 4a**), where water permeates through the membrane simply driven by gravity. In this case, the pristine PPMM is too hydrophobic for water to penetrate through. But for the modified one, the average flux is approximately 150 L/m^{2}h under the pressure of 80 mm water column. This “filtering” operation works quite well, as shown in **Fig. 4a** and **4b**, for water samples containing a series of anionic dyes. **Fig. 4b** depicts that the filtrated water is visually colorless. UV-vis analyses also indicate that those specific absorption peaks of dye molecules are completely vanished after the dye water was filtrated by the CCh-PEI modified PPMMs (**Fig. S9, ESI†**).

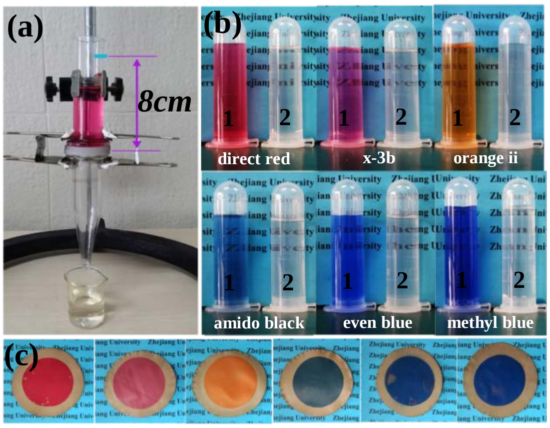

Fig. 4 (a) Treatment of dye solutions by CCh-PEI modified membranes in normal pressure; (b) Feeds (1) and filtrates (2) after the filtration process by CCh-PEI modified membranes; (c) Color of the contacting membrane area after filtration.

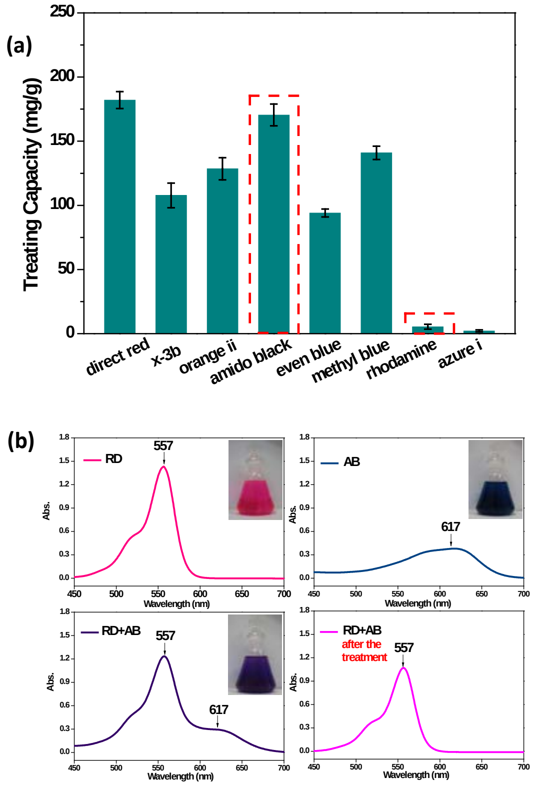

Fig. 5 (a) Treating capacity of a series of dye solutions by the treatment of CCh-PEI modified membranes; (b) UV-vis spectra of rodamine and amido black solutions.

The separation of dye molecules is based on the principle of adsorption so that the decolorization process is not permanent. Dye molecules will break through the membrane cross-section over a certain period of operation. **Fig. 5a** displays the treating capacities for the above anionic dyes, ranging from 95.9 ± 3.2 mg/g (even blue) to 182.1 ± 8.0 mg/g (direct red 80). And the adsorption rate for anionic dyes is about 0.44 mg/10 min, which is comparable to that of Fe_3O_4/carbon composite porous nanofiber memrbrane.[49] For comparison, the treating capacity is lower than 10 mg/g for cationic rhodamine and azure i. The interactions between dyes and membrane surfaces can be concluded as electrostatic interaction, Van der Waals forces and surface hydrogen bonds. And from the aforementioned results, it is demonstrated the adsorption is predominately caused by the electrostatic interactions between anionic dye molecules and positive CCh-PEI aggregates deposited on the membrane surfaces. Van der Waals forces and surface hydrogen bonds are probably responsible for the slight adsorption of cationic dyes to the modified membrane,[50] but obviously these interactions are not strong enough for continuous decolorization. However, the incompetence for cationic dyes is helpful for the separation of cationic and anionic dyes. As shown in **Fig. 5b**, rodamine (RD) can be recycled from its mixture with amido black (AB) by the CCh-PEI modified membranes. The concentration of RD in the filtrates decreases with time and AB/RD ratios (**Fig. S10, ESI†**).

pH of the dye solutions is a crucial variable affecting the adsorption process by influencing on both the surface charges of membrane[51] and dye structures.[27] In this study, the initial pH was adjusted to the desired values (i.e., 1, 2, 3, 4, and 5) with H_2SO_4 solution. **Fig. 6a** shows the effect of pH on the adsorption behavior of DR80 (25 mg/L). When pH decreases from 5 to 1, the treating capacity for DR80 increases from 156.7±7.5 mg/g to 223.3±4.4 mg/g. This pH effect may be explained by the reinforced protonation of amine or imine groups in co-deposited CCh-PEI, which provides enhanced charge density and thus strengthens the electrostatic interaction between the membrane surface and the dye molecule.

The effect of ionic strength was also investigated by using NaCl solutions from 0 g/L to 30 g/L at pH 3. As shown in **Fig. 6b**, the adsorption of DR80 (25 mg/L) is hardly affected by salt concentration and there exists no distinct variation in the treating capacity (around 183.1 mg/g). Compared with direct dye, the treating capacity decreases about 14% and 33% for acidic orange ii and reactive x-3b, respectively (**Fig. S11, ESI†**). It seems that the CCh-PEI modified membranes are more suitable for direct dyes when the effluents possess high salinity. Anyway, the system is relatively inert to ionic strength compared to numerous adsorbents.[8, 52, 53]

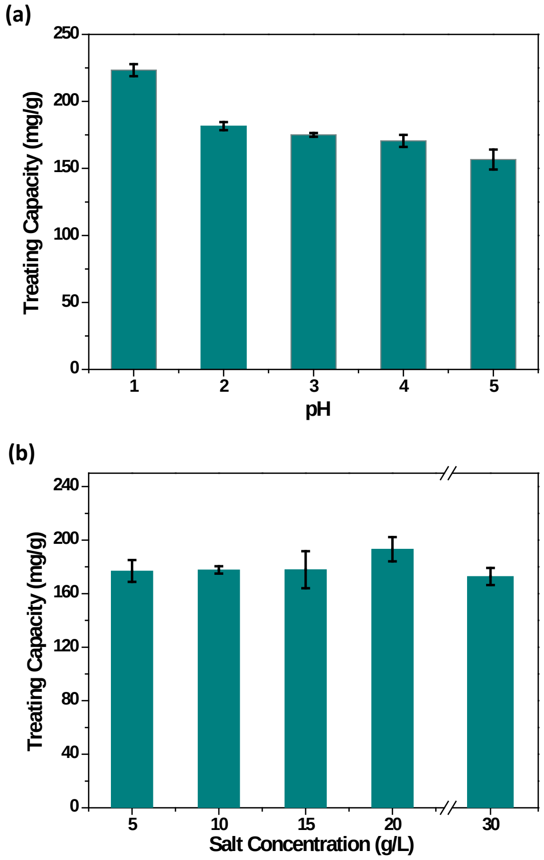

Fig. 6 Influence of (a) pH and (b) ionic strength on the treating capacity of DR80 by the treatment of CCh-PEI modified membranes.

The reusability of the modified membranes was further assessed with DR80 solution (25 mg/L). The filtrates are collected every 5 min. The removal efficiency and flux over three cycles of operation are illustrated in **Fig. 7**. Within a cycle, the dye molecules are probably retained successively from the top of membrane cross-section to the bottom, so the removal efficiencies remain over 99% with time. And when the break-through occurs at around 50 min, the membrane is regenerated facilely by rinsing with 10 mL NaOH solution (pH=12) for 30 s under mild vibration. Notably, no performance difference can be observed for the reused membrane considering removal efficiency (around 99.5%), permeation flux (around 145 L/m^{2}h) and corresponding treating capacity, which suggests the rinse is so thorough that few residual dye molecules hardly change the membrane structures and surface charges. And the rinse solution is capable of repeated use so as to concentrate the dyestuff for possible reuse. Furthermore, due to the limitation of treating capacity for a single piece of membrane, multiple layers of membranes can be integrated for the treatment of dyes with higher concentration (**Fig. S12, ESI†**). With 5 layers of membranes, DR80 solution with a concentration of 250 mg/L can be decolorized and the separation process is also recyclable (**Fig. S13, ESI†**).

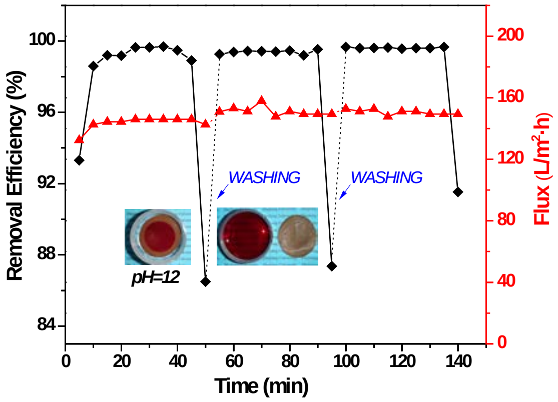

Fig. 7 Removal efficiency and permeation flux of DR80 by the treatment of CCh-PEI modified membrane over three cycles of operation.

Conclusions

In conclusion, we facilely modified commercial PPMMs via the co-deposition of CCh and PEI. The modification method is effective to endow the membranes with superior hydrophilicity and high surface charges. The modified membranes are capable of decolorizing anionic dye solutions with high treating capacity and good reusability. The method we reported may provide the prospect of treating dye wastewaters with microfiltration membranes and is more suitable to be applied as the secondary process after the first step of treatment, for example NF membrane separation. Meanwhile, the approach of co-deposition is also versatile, therefore applicable for diverse porous membranes.

Acknowledgement

This work is financially supported by the Zhejiang Provincial Natural Science Foundation of China (Grant No. LZ15E030001) and the National Natural Science Foundation of China (Grant No. 50933006).

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Porous membranes via the co-deposition of catechol and polyethyleneimine were fabricated with excellent hydrophilicity and distinguished surface charges for decolorizing anionic dye solutions.