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Positively charged nanofiltration membranes via economically mussel-substance-simulated co-deposition for textile wastewater treatment

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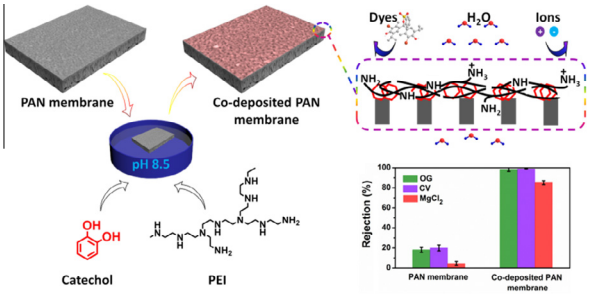
HIGHLIGHTS

- Co-deposition of catechol and PEI were utilized to obtain novel NF membranes.
- Positively charged NF membranes can be economically fabricated.
- The novel membrane exhibits excellent rejections toward cationic dye and metal ions.
- EtOH activation can greatly enhance the permeance with a factor of 1.8–2.4.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, a novel positively charged nanofiltration (NF) membrane has been facilely fabricated via a highly efficient one-step mussel-substance-simulated co-deposition of low-cost catechol and branched polyetheylenimine (PEI) onto substrates. The co-deposition behaviour, physicochemical properties and separation performances of resultant membranes can be readily tailored by varying PEI molecular weight. In particular, the catechol/PEI600 co-deposited NF membrane shows good removals toward dyes, common salts and heavy metal ions for textile wastewater treatment. Our membranes exhibit high removal efficiency toward cationic dye and metal ions due to the Donnon effect. In addition, EtOH activation process can greatly enhance the membrane permeance with a factor of 1.8–2.4 without compromising rejection. Especially, the novel membranes show stable long-term separation performance toward $MgCl_2$ removal, and the dye-fouled co-deposited membranes can be facilely regenerated and reused with a simple static immersion operation. The co-deposited membrane can perform well in alcohols solvents, indicating its excellent performance for practically environmentally-friendly usages. The facile strategy disclosed in our study can provide new opportunities to not only nanofiltration membrane modification but also the surface engineering of vast kinds of materials towards energy and environmental applications.

Abbreviations: PEI, polyetheylenimine; NF, nanofiltration; UF, ultrafiltration; RO, reverse osmosis; TFC, thin film composite; DA, dopamine; PDA, polydopamine; PAN, polyacrylonitrile; NMP, N-methyl-2-pyrrlione; Tris, tris(hydroxymethyl)aminomethane; BTB, Bromothymol Blue; OG, Orange G; CV, Crystal Violet; PES, polyethersulfone; GA, glutaraldehyde; QPEI, quaternized polyethylenimine; DAPP, 1,4-Bis(3-aminopropyl)piperazine; ECH, epichlorohydrin; AP(AN-r-OEGMA-r-GMA), amine-functionalized poly (acrylonitrile-r-oligo(ethylene glycol) methyl ether methacrylate-r-glycidyl methacrylate).

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1. Introduction

The worldwide pressing demand for quality and sustainable water has been on a continuous rise, and there has been particular concern on the environmentally-friendly decontamination and reuse of wastewater. The textile industry discharges enormous wastewaters containing many types of organic dyes, common inorganic salts, heavy metal ions and solvents [1]. These wastewaters are among the most aggressive pollutions of all the industrial sectors and can cause permanent damage to the aquatic ecosystems if discharged untreated. Techniques such as adsorption [2], coagulation [3], advanced oxidation [4] and biodegradation [5] have been developed for the treatment of wastewater. However, adsorption and coagulation usually generate intractable sludge, and oxidation and biodegradation are invalid to the heavy metal ion and inorganic salt removals. Thus, a thorough and effective technology for textile wastewater treatment is urgently desirable for sustainably environmental remediation.

Nanofiltration (NF) as an environmentally-friendly technology has attracted much attention for dynamic applications including food, pharmaceutical, petrochemical industries and wastewater treatment. Theoretically, it is much more efficient than ultrafiltration (UF) with regard to rejection and also shows the higher permeance than reverse osmosis (RO). NF can be readily screening low molecular weight organics (200–1000 g mol^{-1}), divalent ions and large monovalent ions in aquatic systems, realizing molecular-scale "green" separation with much less energy consumption. Despite the excellent rejection capabilities, most of available NF membranes are thin film composite (TFC) polyamide membranes which involve sophisticated multistep fabricating steps and suffer high cost of reactive monomer (especially trimesoyl chloride (TMC)) [6]. Besides, these membranes usually have a low value pH isoelectric point and are negatively charged at normal operating pH of 6 due to the existence of carboxyl groups arising from the hydrolyzation of residual acyl chloride groups during interfacial polymerization [7]. This has limited the number of studies on the fabrication of NF membranes which are positively charged at normal operating conditions. In fact, positively charged NF membranes are especially suitable for dealing with positively charged solutes such as cationic dyes and metal ions from textile wastewaters due to electrostatic repulsion (Donnan effect). Polyethyleneimine (PEI) as one of the most positively charged polymers has been employed to fabricate positively charged NF membranes via various approaches, such as in suit quaternary amination in casting solution [8], interfacial polymerization [9] and layer-by-layer deposition [10]. However, these works disclosed on positively charged NF membranes are still suffering some problems like involvement of toxic organochlorine, high cost raw materials and complicated multiple stages. Thus, an economic and facile approach to fabricate positively charged NF membrane with high-performance is highly desirable and represents a tough challenge.

Nature provides many interesting clues for human beings to develop advanced materials and technologies handling practically tough issues. Dopamine (DA) as a mussel-inspired material with catechol and amine groups discovered from Nature, can simulate the mussel protein to adhere onto almost all kinds of substrates and has attracted extensive interest in membrane surface modification. Co-deposition of DA and PEI [11], as well as PEI grafting onto polydopamine (PDA) [12,13], has been employed to fabricate positively charged NF membranes. However, the performances of these membranes toward heavy metal ions have not been investigated. What is more, the high cost of dopamine is undesirable in practical application. Recently, plant-derived phenols or polyphenols, containing a remarkable high content of catechol and gallic acid groups, have been reported capable of forming multifunctional coatings [14–16]. Intriguingly, such coatings have the excellent properties like dopamine-derived coatings by simulating a similar complex mechanism of reactions, but bear with much lower cost (less than 1/10 cost of DA). Some works have reported the applications of these coating in Li-ion batteries and dyes adsorptions. In particular, Wang et al. have fabricated hydrophilic modified polypropylene separators by the co-deposition of catechol and polyamine for Li-ion batteries [15]. Qiu et al. have reported the co-deposition of catechol and PEI onto microfiltration (MF) membranes for decolorization of dye water [16]. Due to the dye removal mechanism is based on the electrostatic interaction between dyes and membrane surfaces, only anionic dyes can be adsorbed. For the removal of cationic and neutral dyes, common inorganic salts and heavy metal ions, however, it is invalid.

Herein, for the first time, positively charged NF membranes were designed and facilely fabricated via the simple one-step mussel-substance-simulated co-deposition of catechol and PEI onto PAN substrate (Fig. 1). The effects of PEI molecular weight on co-deposition behaviour and the resultant membrane structure have been systematically investigated. The membrane exhibits excellent performances toward dyes, common inorganic salts and heavy metal ions removals. EtOH activation process greatly enhances the membrane permeance without compromising rejection. Moreover, the developed membranes also perform well in organic solvent. The much lower price of catechol (3.44 RMB per gram for a 100 g purchase, Sigma-Aldrich) than TMC (18.94 RMB per gram for a 100 g purchase, Sigma-Aldrich) and DA (38.21 RMB per gram for a 100 g purchase, Sigma-Aldrich), combined with the simplicity of fabrication strategy, make the co-deposited membranes more economic and easily prepared than TFC polyamide and dopamine-derived NF membranes. These are the most attractive features that can endow the novel NF membranes with great potential for sustainably environmental remediation.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN) powder (Mw = 75,000) contains 6% methyl methacrylate and 0.3% 2-methyl-2-propene-1-sulfonate as co-monomers was obtained from shanghai petrochemical company Ltd. PEG800 was purchased from Xilong Chemical Industrial Co., Ltd. N-methyl-2-pyrrlione (NMP), Tris(hydroxymethyl)amino methane (Tris) and Bromothymol Blue (BTB) were received from Sinopharm Chemical Reagent Co., Ltd. Catechol was purchased from Sigma-Aldrich. Branched polyethylenimine (PEI, with different average molecular weight of 600, 1800 and 10000), Orange G (OG) and Crystal Violet (CV) were purchased from Aladdin (China). Methanol (MeOH), ethanol (EtOH), isopropanol (iPrOH), $MgCl_2 \cdot 6H_2O$, $MgSO_4$, NaCl, Na_2SO_4, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were provided by Tianjin Kermel Chemical Reagent Co., Ltd. (China). All the chemicals were used as received. All used water was deionized.

2.2. Preparation of PAN UF membranes

PAN UF membranes were fabricated by a traditional non-solvent induced phase separation process. The PAN powder was first dried in an oven at 80 °C overnight to remove moisture before usage. 20.0 g of PAN and 1.0 g of PEG800 were dissolved in 79 g of NMP to form a dope solution. Then, the solution was then stored at 60 °C for 12 h to remove any air bubble. After cooled to room temperature, the dope solution was cast on a glass plate by using a casting knife with a thickness of 200 μm. The glass plate with