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Electrospun AOPAN/RC blend nanofiber membrane for efficient removal of heavy metal ions from water

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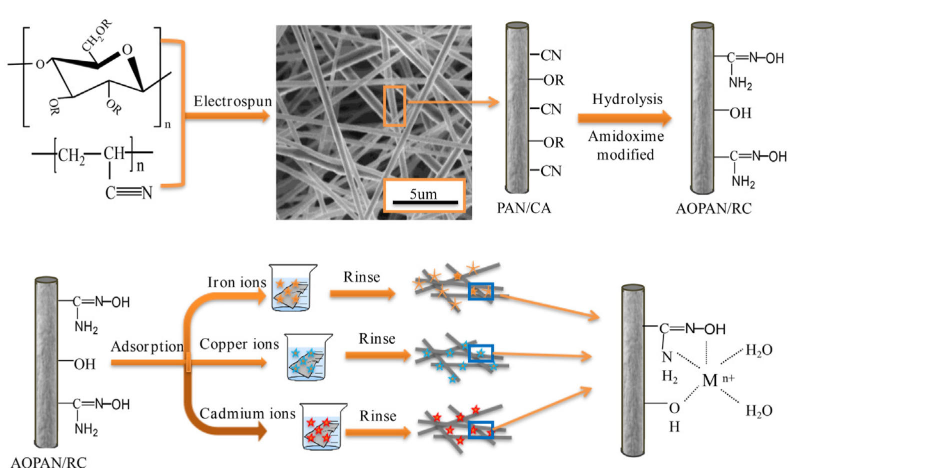
HIGHLIGHTS

- Electrospun AOPAN/RC blend nanofiber was prepared and studied as innovative carrier for adsorption of metal ions.
- The membrane's adsorption amount of Fe(III), Cu(II) and Cd(II) ions reached 7.47, 4.26 and 1.13 mmol/g, respectively.
- The adsorption equilibrium was obtained within 5, 20, and 60 min for Fe(III), Cu(II) and Cd(II) ions, respectively.
- The electrospun AOPAN/RC blend nanofiber membrane has excellent regeneration capability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an innovative nano-material was prepared, which was ultilized to removal of heavy metal ions from wastewater. Polyacrylonitrile/cellulose acetate (PAN/CA) composite nanofibrous membranes were generated by the electronspinning technique first, and then amidoxime ployarcylonitrile/regenerate cellulose (AOPAN/RC) composite nanofibrous membranes were prepared by combining hydrolysis and amidoximation modification. The modification of composite nanofibers (AOPAN/RC) were consequently used in heavy metal ions adsorption. The characterizations of various different nanofibers were analyzed using scanning electron microscopy, Fourier transform infrared spectroscopy, surface area and pore size distribution analyzer and energy dispersive X-ray spectroscopy. Meantime, the adsorption equilibrium studies were studied. In addition, the saturation adsorption amount of nanofibrous membranes (at 25 °C) for Fe(III), Cu(II) and Cd(II) of 7.47, 4.26 and 1.13 mmolg^{-1}, respectively. The effects of pH value of solution, adsorption time and ions concentration on adsorption capacity were also investigated. Furthermore, the composite nanofibrous membranes after five times consecutive adsorption and desorption tests, the desorption rate of the Fe(III), Cu(II) and Cd(II) mental ions maintained more than 80% of their first desorption rate, AOPAN/RC composite nanofibrous reflected excellent resuability.

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1. Introduction

Nowadays, water pollution has become a major environmental concern; and how to efficiently remove heavy metal ions (*e.g.*, the ions of Cd, Pb, Cr, Cu, Fe) has been of significant research interests. In general, the methods for removal of these ions from water include reduction-precipitation, membrane separation, ion exchange, coagulation-flocculation, flotation, and adsorption. Although different methods have different advantages, adsorption is one of the most important methods due to cost-effectiveness and operational simplicity/stability. In recent years, the electrospun nanofiber membranes have been explored as innovative adsorption and filtration media and widely used in the field of filtration because of their large specific surface area and high porosity/permeability; furthermore, electrospun nanofibers can be surface-functionalized to possess various coordination/chelation groups [1–5]. Li and coworkers prepared a controlled pore size composite filter material by electrospinning technique, and then the nanofiber membranes used as a packed bed exhibited fairly good dynamic adsorption capacity for Cr (VI) ions [6]. Zhao et al. [7] found that the bPEI grafted electrospun PAN fiber adsorbent possessed an excellent adsorption capacity toward Cr(VI). Moreover, the batch adsorption and dynamic filtration could also make the Cr(VI) concentration notably decrease from 10 mg/L to below 0.05 mg/L. The technique of electrospinning provides a facile while versatile approach for preparing continuous fibers with diameters in the range from tens of nanometers to several micrometers (commonly known as electrospun nanofibers) [8]. Among numerous polymers that have been successfully electrospun into nanofibers [8], polyacrylonitrile (PAN) is of particular interest to adsorption of heavy metal ions; this is because the nitrile ($-C\equiv N$) groups in PAN can be easily converted into amidoxime ($-C(NH_2)=NOH$) groups *via* the room temperature reaction with hydroxylamine in aqueous solution [9–11], and the generated amidoxime groups have strong capability to adsorb heavy metal ions through formation of coordination/chelation bonds [12–14]. Nevertheless, the amidoximation degree of electrospun PAN nanofibers is difficulty to precisely control; if it is too high, the resulting nanofibers are sticky (*i.e.*, the resulting polymer has relatively high water solubility) thus the morphology of nanofibers mat/membranes cannot be retained in water (*i.e.*, the nanofibers are likely to fuse/conglutinate together into a porous film). In consequence, the water permeability is reduced; and the adsorption capacity is decreased.

Another polymer that has been electrospun into nanofiber mat/membrane for adsorption applications is cellulose. Cellulose is a natural polymer with limited solubility in common solvents; fortunately, cellulose fibers can be readily produced from cellulose acetate (CA). Unlike cellulose, CA is soluble in many solvents; thus it can be electrospun into nanofibers. After electrospun CA nanofiber membrane undergoes hydrolysis/deacetylation upon simply immersed in NaOH aqueous solution at room temperature, the regenerated cellulose (RC) nanofiber membranes are produced [15,16]; note that during this process, the fibers morphology can be retained without appreciable differences. The repeating unit of cellulose macromolecule has three hydroxyl ($-OH$) groups, which can be utilized to adsorb heavy metal ions; furthermore, cellulose can be chemically modified to enhance the adsorption performance/capability. For example, Zhou and coworkers reported that, the cellulose modified with β-cyclodextrin and quaternary alkyl ammonium groups would exhibit excellent adsorption performance/capability for removal of chromium (VI) ions from water [17]; while Anirudhan and coworkers prepared the iron(III)-coordinated amino-functionalized poly(glycidyl methacrylate)-grafted cellulose for efficient removal of arsenic (V) ions from aqueous solutions [18]. However, it is important to note that the adsorption performance/capability of cellulose and chemically modified cellulose is substantially lower than that of PAN after amidoximation (AOPAN), whereas the morphological stability of electrospun cellulose-based nanofibers is significantly higher than that of electrospun AOPAN nanofibers.

The aim of this researtch is to prepare and charcaterize electrospun AOPAN/RC blend nanofibers membranes for efficient removal of heavy metal ions from water. The hypothesis is that AOPAN/RC blend nanofibers would exhibit superior adsorption performance/capability owing to the synergistic effect between amidoxime and hydroxyl groups towards coordination/chelation of heavy metal ions. Additionally, it was expected that the morphology of nanofiber membranes could be well-retained during the chemical conversion of PAN/CA blend nanofiber mat/membrane into AOPAN/RC blend nanofiber mat/membrane. Note that electrospun polymer blend nanofibers have not been widely studied due to the concerns over immiscibility of different polymers and/or micro-scale phase separation in spinning solution. However, during the electrospinning process (particularly during the bending instability [19]), a jet/filament is typically elongated by thousands of times and the solvent evaporation occurs extremely fast; hence, electrospun PAN/CA blend nanofibers are expected to possess two co-continuous and randomly dispersed phases with the overall fiber diameter being hundreds of nanometers and with dispersed phases being continuous “strings” on the order of several to tens of nanometers each. Furthermore, upon the chemical conversion of PAN/CA blend nanofibers into AOPAN/RC blend nanofibers, the miscibility beween two relatively hydrophilic polymers of AOPAN and RC is expected to be improved. Therefore, the AOPAN and RC components in the AOPAN/RC blend nanofibers might be random (despite some degree of micro-scale phase separation might still exist); such a situation would facilitate the synergistic adsorption of heavy metal ions through the formation of coordination/chelation bonds with neighboring amidoxime and hydroxyl groups, leading to high adsorption capacity and fast adsorption rate.

During this research as schematically depicted in Fig. 1, electrospun PAN/CA blend nanofiber membranes were prepared first; subsequently, this membranes were chemically converted into AOPAN/RC membranes upon immersion in NaOH aqueous solution and then hydroxylamine hydrochloride aqueous solution. Finally, the adsorption performance of AOPAN/RC blend nanofiber membranes were evaluated to remove Fe(III), Cu(II), and Cd(II) ions from their respective aqueous solutions. And various influential factors/effects (*e.g.*, *p*H value, contact time, ion concentration, and adsorption equilibrium isotherm) were also investigated on adsorption performance/capability. This study demonstrated for the first time that, electrospun AOPAN/RC blend nanofiber membranes might be a highly promising and efficient adsorption medium for the removal of heavy metal ions from water.

2. Experimental

2.1. Materials

Polyarcylonitrile (PAN, $M_w \sim 90000$ g/mol) and cellulose acetate (CA, $M_w \sim 131000$ g/mol) were provided by Sinopharm Chemical Reagent Co. (Shanghai, China). NaOH, $FeCl_3$, $CuSO_4$, $CdCl_2$, Na_2CO_3, *N,N*-dimethylformamide (DMF), and hydroxylamine hydrochloride (NH_3OHCl) were purchased from Aldrich. All of the chemicals were used without further purifications.

2.2. Preparation of electrospun AOPAN/RC blend nanofibers membranes

Prior to electrospinning, PAN (2.31 g) and CA (0.99 g) were dissolved in DMF (26.7 g) at 40 °C under the stirring condi-