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Polydopamine-assisted deposition of polypyrrole on electrospun poly (vinylidene fluoride) nanofibers for bidirectional removal of cation and anion dyes

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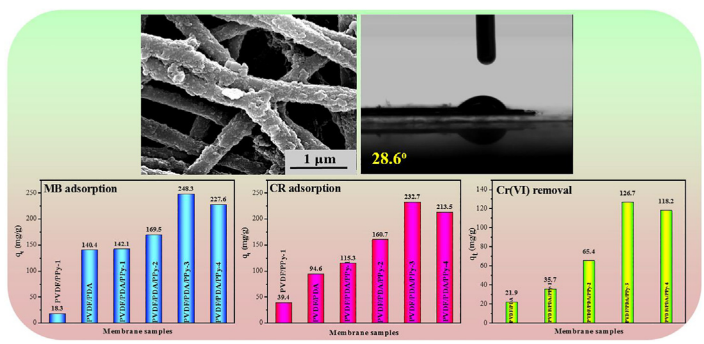
HIGHLIGHTS

- PPy particles were deposited on electrospun PVDF fibers with the aid of PDA.
- The composite fibers showed bidirectional removal ability toward cation/anion dyes.
- The composite fibers showed excellent removal ability toward Cr(VI).

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, novel composite nanofibers which exhibited 'core–shell'-like structure were fabricated through the deposition of polypyrrole (PPy) particles on the electrospun poly(vinylidene fluoride) (PVDF) nanofibers with the aid of polydopamine (PDA). First, the PVDF/DA electrospun nanofibers were prepared. Then, the self-polymerization of PDA was triggered in a Tris–HCl buffer solution. After that, the pyrrole monomer was added into the distilled water containing the PVDF/PDA fibrous membrane and the chemical oxidation polymerization of PPy was triggered by adding $FeCl_3$. Morphological characterization confirmed that the electrospun PVDF/PDA nanofibers were homogenously coated by PPy particles. Largely enhanced hydrophilicity of the fibrous membrane surface was achieved due to the presence of many nitrogen-containing groups and the increased surface roughness of nanofibers. The adsorption abilities of the composite nanofibers were investigated using Methylene Blue (MB) and Congo Red (CR) as the probe dyes. The results showed that the composite nanofibers exhibited excellent adsorption abilities toward cation and anion dyes simultaneously, and the maximum adsorption capacities were 370.4 and 384.6 mg/g for MB and CR adsorption, respectively. The adsorption behaviors toward the two dyes could be well described by the pseudo second-order adsorption model and the Langmuir adsorption model. Further results showed that the adsorption abilities of the composite nanofibers were greatly dependent upon the pH values of the solution. Furthermore, the composite nanofibers exhibited good regeneration ability. The removal ability toward Cr(VI) was also measured and the experimental adsorption capacity was 126.7 mg/g.

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The excellent adsorption abilities toward cation/anion dyes and heavy metal ions endow the composite nanofibers with great potential application in wastewater treatment.

1. Introduction

As one of the conjugated polymers, polypyrrole (PPy) exhibits various promising properties, such as easy preparation, excellent redox properties, tunable electrical conductivity, good biocompatibility and excellent environmental stability and therefore, it exhibits wide application in many fields ranging from biological detection, supercapacitor, antistatic material and microelectronic devices to electrodes of battery [1–5]. The synthesis of PPy is relatively easy compared with other conductive polymers [6,7]. Generally, it can be synthesized through the common chemical oxidation method which involves the oxidation of pyrrole monomer in aqueous medium using an oxidizing agent, such as ferric chloride ($FeCl_3$) [8] and ammonium persulfate ($(NH_4)_2S_2O_8$) [9]. PPy prepared through this method is usually electrically conductive and in the black powder state, and the electrical conductivity of PPy is greatly influenced by several factors, including the ratio of pyrrole monomer and oxidant [10], the presence of other polymers such as codopants and additive [11], the polymerization time and temperature [12,13], etc. The other synthesis method, which is also widely used, is relating to the electrochemical oxidation of pyrrole monomer on the electrically conductive substrate [14,15].

Recent researches have shown that PPy exhibits an ability to remove various heavy metal ions from wastewater, such as Hg(II) [16], Cu(II) [17], Zn(II) [18], Pb(II) [19], Cr(VI) [20], etc. The removal mechanism is believed to be mainly related to the presence of nitrogen atoms in the PPy molecular chains [21]. Among these heavy metal ions, the removal of Cr(VI) is relatively complicate, which is relating to the adsorption of Cr(VI) on the surface of PPy through the anion exchange by replacing the doped anion of PPy with Cr(VI) and the reduction of the highly toxic Cr(VI) to the less toxic Cr(III) through the redox property of PPy originated from the $–NH^+$ group in the pyrrole ring [22–24]. However, the removal efficiency of PPy toward Cr(VI) is greatly dependent upon the diffusion ability of the dopant anions from PPy material, which is usually related to the accumulation state and specific surface area of PPy [25]. Therefore, to enhance the removal efficiency of PPy, much wok has been carried out to deposit PPy particles on the other substrates, such as carbon nanotubes (CNTs) [26], magnetic iron oxide (Fe_3O_4) nanoparticles [23], cellulose [27], graphene oxide (GO) [28], etc.

Besides the excellent removal ability toward heavy metal ions, the adsorption ability toward organic dyes of PPy is also worthy of noting. First, the $–NH^+$ may interact with the organic dyes through an electrostatic interaction. Second, the pyrrole ring may exhibit π–π interaction with some organic dyes which also have the C=C structure. However, compared with the intensive investigation about removing heavy metal ions from aqueous solution, less attention has been payed to investigate the adsorption behavior of the PPy or PPy-based materials toward organic dyes. To date, only several researches have been carried out. Chafai et al. [29] comparatively investigated the adsorption abilities of PPy and polyaniline (PANI) toward Congo Red (CR) dye from aqueous solution and they found that the maximum adsorption capacities were 250.0 and 66.7 mg/g for PANI and PPy, respectively. Xin et al. [30] synthesized PPy nanofibers and the adsorption measurements toward Methyl Orange (MO) showed that the maximum adsorption capacity was 169.6 mg/g. Li et al. [31] prepared PPy/CNTs-$CoFe_2O_4$ magnetic nanohybrid composites and the adsorption behaviors toward Methyl Blue, MO and Acid Fuchsin (AF) were investigated. The results showed that the maximum monolayer adsorption capacities were 137.0, 116.1 and 132.2 mg/g for Methyl Blue, MO and AF, respectively.

Electrospinning technology is rapidly emerging as a simple fabrication method used to prepare nanofibers of various polymers. The nanofiber morphology and microstructure can be well controlled through changing the compositions of the polymer solution and the electrospinning parameters [32]. Specifically, the non-woven fabric via the random stacking of nanofibers is a promising membrane with high porosity, high surface area and high pore interconnectivity compared with the membranes prepared through the common thermal-induced phase inversion method [33]. This indicates that the fibrous membrane fabricated through the electrospinning technology exhibits great potential application in wastewater treatment if the membrane material has adsorption ability or removal ability toward organic pollutants and heavy metal ions. Factually, much work has been carried out to investigate the application of the electrospun fibrous membrane in wastewater treatment [34]. To date, several researches about the fabrication of PPy nanofibers through electrospinning technology have been carried out [35,36]. However, compared with other polymers that are widely used to prepare the electrospun nanofibers, it is relatively difficult to prepare the pure electrospun PPy nanofibers due to the inherently poor solubility in common solvents [37]. In most cases, other polymers, such as poly(ethylene oxide) (PEO) [36], sulfonated-poly (styrene-ethylene-butylene-styrene) (S-SEBS) [38], polyacrylonitrile (PAN) [39], poly(vinylidene fluoride) (PVDF) [40], etc. were used as the carrier to improve the processability of PPy during the electrospinning processing. Recently, using the other electrospun polymer nanofibers as the substrate and promoting the synthesis of PPy on the nanofiber surface through chemical oxidation method [41,42] or a vapor-phase polymerization method [43,44] attracts much attention of researchers. This undoubtedly opens a window for the actual application of PPy-based materials in wastewater treatment.

In this work, we attempt to prepare the PPy-coated electrospun PVDF nanofibers and investigate the potential applications of such composite nanofibers in wastewater treatment, such as organic dye adsorption and heavy metal ions removal. The electrospun PVDF fibrous membrane is used as the substrate to provide the deposition of PPy particles. As a typical semicrystalline polymer, PVDF is thought to be one of the most appropriate membrane materials due to its good comprehensive mechanical properties, high thermal stability, excellent chemical stability and good processing ability such as film-forming ability [45]. To insure the deposition of PPy on the nanofiber surface, the electrospun PVDF nanofibers were firstly modified by polydopamine (PDA) through the blend-electrospinning technology of PVDF and dopamine monomer accompanied with the subsequent self-polymerization of PDA on the nanofiber surface as reported in our previous work [46]. After that, many polar groups are introduced on the nanofiber surface, which is believed to be favorable for the deposition of PPy nanoparticles on the PVDF/PDA nanofiber surface. It is surprising to observe that the PPy-coated PVDF/PDA (PVDF/PDA/PPy) composite nanofibers exhibit excellent adsorption abilities toward anion and cationic dyes and Cr(VI) simultaneously.

2. Experimental part

2.1. Materials

PVDF (Kynar 720) was obtained from Arkema (France) and it has a weight average molecular weight of 1.05×10^5 g/mol and a density of 1.78 g/cm^3. Dopamine (DA) monomer was purchased from Aladdin Reagent Co. (China). Pyrrole monomer (analytical purity) and $FeCl_3$ (analytical purity) were obtained from Kelong Chemical Reagent Co. Ltd. (China).