Reviving of embedded MOFs in electrospun nanofibers by solvent swelling for arsenate removal in water

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**ABSTRACT**
Nanoparticles coated with electrospun fibers cannot fully exert their inherent properties. Therefore, it is critical to develop a method to enhance the intrinsic performances of the composite fibers. In this work, UIO-66/PAN composite nanofiber membranes with good physicochemical properties were prepared by electrospinning, and a swelling method was developed to improve its performances. The adsorption performance for arsenate was improved by 19.9% or 49% after swelling by nitrobenzene or pyridine solvent, respectively. The swelling process did not change the morphologies and structures of the fibers. The pyridine solvent as the swelling agent improved the adsorption performance of the nanofiber membrane by about 45% in 1 hour. There was no detectable leached Zr in the remaining solution, indicating that the composite membrane was stable during the course. This work provides a new strategy for functional promotion of electrospun nanofiber membrane and will be helpful for environmentally friendly applications of nanocomposites in water remediation.

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Electrospun nanofibers; swelling; metal organic frameworks; arsenic removal

1. Introduction

A large number of pollutants such as heavy metals have been discharged into aquatic environment and resulted in serious water pollution [1,2]. The dissolved heavy metals can cause toxic effects and diseases to organisms [3,4]. Many technologies have been developed to remove heavy metals from water, including ion exchange [5], chemical precipitation [6], membrane separation [7], reverse osmosis [8], electrodialysis [9], adsorption [10], and so on. Among them, the adsorption method is considered to be a very attractive and universal choice due to its advantages of high removal efficiency, simple operation and low cost [11].

Nanomaterials have been regarded as one of the most effective adsorbents for pollutants removal. However, there are two unresolved challenges during applications [12]. Firstly, the instability of nanomaterials is easy to cause shedding during use, which can not only discount their intrinsic performances but also cause secondary pollution. Secondly, the material is not possible to be collected for reuse, which increases the total cost. Electrospinning technique is a facile and flexible route to fabricate ultrathin fiber membrane with unique hierarchical (microporous/nanofibrous) morphology and outstanding versatile functions [13]. Nanomaterials with excellent functions can be electrospun into the fibers to fabricate the multifunctional composites. This strategy can provide a stable and repeatable utilization route for nanomaterials by polymer capsule and coating, and minimize the possible secondary pollution caused by falling off in water treatment. But, unfortunately, the intrinsic functions of the capped nanomaterials will also inevitably be weakened. Therefore, it is very significant to promote the intrinsic performances of the capped materials inside the fibers.

In this study, a stable nanocomposite was synthesized by electrospinning and applied to remove arsenate in water. A swelling method was successfully developed to improve the intrinsic performances of UIO-66 inside the fibers. The solvents used for swelling were compared and optimized, and the influence of swelling time was also studied. The polymer macromolecular chain can be opened and provide more active sites via swelling without loss of MOF particles from the fibers. The newly proposed swelling method can effectively promote the intrinsic functions of nanomaterials inside the fibers.

2. Materials and methods

2.1 Reagents
Zirconium chloride (ZrCl₄), nitrobenzene, iodine, potassium iodide and pyridine were purchased from Macklin. 1,4-Benzenedicarboxylic acid (BDC), N,
N-Dimethylformamide (DMF), methanol, ethanol, sodium hydroxide, hydrochloric acid and nitric acid were purchased from Tianjin Kernel Chemical Reagent. Polyacrylonitrile (PAN, Average M.W. 150,000) was obtained from Beijing J&K Scientific Co., Ltd. Deionized water was prepared by Genie purist (Shanghai Lefeng Biotechnology Co., Ltd.). The arsenate (As(V)) standard solution was obtained from the resource platform of the national standard material. Unless otherwise stated, all reagents were of analytical grade and used as received.

2.2 Preparation of the UiO-66 and UiO-66/PAN nanofibers

UiO-66 was synthesized in the previously reported manner [14]. In short, after mixing 512 mg of ZrCl₄, 327 mg of BDC and 25 mL of DMF under ultrasonic for 1 h, the mixture was transferred into a 50 mL Teflon autoclave and heated at 120°C for 24 h. The obtained materials (MOFs) were washed with deionized water and DMF for several times and then soaked in methanol for 3 days for activation. The activated samples were dried in vacuum at 80°C for 6 hours.

A total of 0.1 g of UiO-66 was uniformly dispersed in 10 g of DMF by sonication, and then 1 g of PAN was added into the solution and stirred at room temperature for 6 h until a homogenous solution formed. The solution was used as a precursor for electrospinning. The applied voltage, tip-collector distance and flow rate were 20 kV, 18 cm and 0.6 mL/h [14]. The synthesized UiO-66/PAN composite nanofiber membrane was dried in vacuum at 60°C for 6 h.

2.3 Swelling processes of UiO-66/PAN

Multiple nanofiber membranes (2 cm × 2 cm, about 0.05 g) were immersed in 20 mL of iodine-potassium iodide solution, DMF and water mixture, and nitrobenzene and pyridine solution, respectively. The nanofibers swollen in the corresponding solution were named as NFs-I, NFs-D, NFs-N and NFs-P, respectively. NFs-I, NFs-D, NFs-N and NFs-P were solvent-exchanged with acetone solution [15], deionized water, anhydrous methanol [16] and diluted hydrochloric acid [17], respectively. After that, the materials were washed with deionized water (about 60 mL) to neutral.

2.4 Characterization of UiO-66/PAN

The morphology was examined by scanning electron microscopy (SEM) with a Hitachi-S-4800 microscope (Japan). Molecular functional groups were characterized by Fourier transform infrared spectroscopy (FTIR-200, JASCO, Japan), and the samples were analyzed from 500 to 4000 cm⁻¹. X-ray diffraction patterns (XRD) of the samples were recorded using Bruker D8 Advance X-ray powder. In order to evaluate the stability of UiO-66 in the synthesized nanofibers after swelling, Zr in the solution was determined by ICP-OES instrument (5110, Agilent). An AFS-933 atomic fluorescence spectrometer (Beijing Jitian Instrument Co., Ltd.) was utilized to determine the concentration of arsenate in batch experiments throughout the experiment.

2.5 Arsenate adsorption by swelling-nanofibers

The adsorption experiments were conducted with 10 mL of As(V) at a concentration of 10 mg/L. The pH of the arsenate solution was adjusted to 7.0 ± 0.1 with diluted HCl (0.1 M) and NaOH (0.1 M). After 2 × 2 cm (about 0.05 g) of membranes were added to the solution and shaken at 250 rpm at 25.0 ± 1°C for 24 h. The test was performed in triplicate, and the mean value was reported.

The adsorption efficiency (η, %) of the material was derived from the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where $C_0$ (mg/L) and $C_t$ (mg/L) represent the initial and final concentration of arsenate in the solution.

The enhanced efficiency ($\eta'$, %) of arsenate adsorption by membrane before or after swelling was derived from the following equation:

$$\eta' = \frac{\eta_{swelling} - \eta_0}{\eta_0} \times 100\% \quad (2)$$

where $\eta_{swelling}$ (%) and $\eta_0$ (%) represent the adsorption efficiency of the swollen membrane and unswellened membrane, respectively.

3. Results and discussion

3.1 Membrane characterization

The successful syntheses of UiO-66 and UiO-66/PAN had been confirmed by XRD, FTIR and SEM-mapping characterizations in our previous study [14]. The SEM images of the UiO-66/PAN nanofibers (NFs), NFs-N and NFs-P were illustrated in Figure 1(a,b,c). The electrospun nanofibers were smooth and uniform, and their structures were not destroyed by nitrobenzene and pyridine. The results indicated that the electrospun membrane was stable enough, and nitrobenzene or pyridine could be used as the swelling reagents.

The XRD patterns and FTIR spectra of the UiO-66/PAN nanofibers (NFs), NFs-N and NFs-P were illustrated in Figure 2(a,b). The XRD characteristic peaks and functional groups of UiO-66/PAN (NFs) nanofiber membrane did not change obviously after swelling in pyridine or nitrobenzene.
### 3.2 Membrane performance

#### 3.2.1 Swelling solvent selection

In order to optimize the swelling solvents, the swelling experiments of nanofiber membranes were carried out by using iodine-potassium iodide, DMF aqueous solution, pyridine and nitrobenzene as swelling solvents, and the swelling adsorbents were labeled as NFs-I, NFs-N, NFs-P and NFs-D, respectively. The arsenate solution (10 mg/L) was chosen as a model pollutant. As illustrated in Figure 3, the adsorption efficiency ($\eta$, 50.8%) observed by the unswollen membrane was used as the benchmark in our study. The adsorption efficiencies of NFs-P and NFs-N reached 75.7% and 60.9%, respectively. The enhanced efficiencies ($\eta'$) of 49% for NFs-P and 19.9% for NFs-N were obtained. The macromolecular chains of PAN were fluffed up by swelling solvents, allowing MOFs to have more space for interaction, which in turn provided more active sites for adsorption. The adsorption efficiency ($\eta$) of NFs-D (DMF: H$_2$O = 2:1) was similar to that of the membranes without swelling. However, the adsorption efficiency ($\eta$) of NFs-I decreased by 20%, which might be due to iodide ions adsorption, which reduced the number of active sites [18,19].

#### 3.2.2 Effect of swelling time

The adsorption efficiencies of NFs-N and NFs-P for As(V) were evaluated after swelling for 1, 2, 5, 10, 15, 20, 72 and 168 hours (Figure 4). The adsorption efficiency of the unswollen membrane (50.8%) was also used as the benchmark here. The adsorption efficiency increased by 45% after swelling for 1 h by pyridine solvent, and there was a slight increase with longer soaking time. The maximum efficiency was reached after 5 h swelling in

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**Figure 1.** SEM images of (a) NFs, (b) NFs-N and (c) NFs-P.

**Figure 2.** XRD patterns (a) and FTIR (b) spectra of nanofiber membrane before and after swelling by pyridine (NFs-P) or nitrobenzene (NFs-N).

**Figure 3.** Optimization of swelling reagents.

**Figure 4.** Adsorption efficiency (%) of NFs-I, NFs-N, NFs-P and NFs-D after swelling for various times.
Comparison

3.2.3 Stability

The stability of a nanofiber membrane is not only an important index to evaluate its practical applicability but also an important factor to maintain water security. In order to determine the possible loss of MOFs during swelling process, the inherent Zr in the fibers and the lost Zr in the swelling reagents were determined by ICP-OES (Table 1). The data showed that there was no detectable Zr in swelling reagents or working solution. The results demonstrated that the MOFs could be stably preserved in the composite nanofibers without detectable nanoparticle leaching during use, which would greatly minimize the possible secondary contamination to water ecosystem.

3.2.4 Comparison with other methods

In order to solve the problem that the performance of MOF materials cannot be fully utilized in electrospinning fiber composite, the in-situ growth method and layer-by-layer self-assembly method were also tried in the previous studies [20,21]. However, since the essence of these two methods was the growth of MOF on the surface of electrospun nanofiber membrane, it was inevitable that the agglomeration of MOF materials would occur in the synthesis process. At the same time, there was also a serious risk of secondary pollution caused by falling off during use. Our results showed that the swelling method could effectively enhance the intrinsic performances of the capsules nano-particles inside the fibers, and the swollen membrane had good stability during use without any secondary pollution.

4. Conclusion

In this study, UiO-66/PAN nanofibers were synthesized by electrospinning with good adsorption efficiency for As(V). The adsorption efficiency of nanofibers could be further increased by 49% through pyridine swelling. The swelling did not affect the structure and morphology of the original fibers without any loss of immobilized MOFs inside the fibers. Our study developed a new method for the performance promotion of electrospun composite nanofibers by swelling for the first time. The swelling method can significantly improve the removal efficiencies of nanofiber membranes while maintaining the integrity of the original fiber membrane structures during the swelling process. The composite membrane not only contributes to water security but also facilitates the reuse of the materials.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Authors’ contributions

Qi Guo: Formal analysis, Writing—Original draft preparation, Writing – Reviewing and Editing, Methodology. Yuan Li: Software, Methodology. Xiao-Yang Wei: Methodology, Validation. Yi-Wen Shen: Methodology. Xue-Lei Duan: Methodology. Kai-Qiang He: Methodology. Ke-Gang Zhang: Methodology. Chun-Gang Yuan: Conceptualization, Methodology, Writing – Reviewing and Editing, Funding acquisition.

Ethics approval and consent to participate

Not applicable.
Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this article.

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