Applied Surface Science 453 (2018) 220–229

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Amine modified electrospun PIM-1 ultrafine fibers for an efficient removal of methyl orange from an aqueous system

Bekir Satilmis[a,b,*], Tamer Uyar[a,*]

[a] Institute of Materials Science & Nanotechnology, UNAM-National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey
[b] Department of Chemistry, Faculty of Science and Arts, Ahi Evran University, Kirsehir 40100, Turkey

ARTICLE INFO

Keywords:
Electrospinning
Amine PIM-1
Membrane
Nanofibers
Dye adsorption
Wastewater treatment

ABSTRACT

Polymers of Intrinsic Microporosity (PIM-1) is a promising material for adsorption and separation applications. While PIM-1 displays high affinity for neutral species, it shows lack of interaction with charged molecules in an aqueous system due to non-polar nature of it. Functionalization of PIM-1 provides an advantage of tailoring the interaction ability as well as the adsorption performance of PIM-1 towards target pollutants. In this study, electrospun Polymer of Intrinsic Microporosity (PIM-1) fibrous membrane (PIM-FM) was reacted with borane dimethyl sulfide complex to obtain amine modified PIM-1 fibrous membrane (AM-PIM-FM). Furthermore, PIM-1 film, which is referred as PIM-1 dense membrane (PIM-DM), was also modified under the same conditions as a control material. Structural analyses have confirmed that nitrile groups of PIM-1 have been fully converted to amine group as a result of the reduction reaction. Average fiber diameter of parent PIM-1 fibers was found $2.3 \pm 0.3\,\mu m$, and it remained almost the same after the amine modification. In addition, no physical damage has been observed on fiber structure based on the SEM analysis. Both amine modified PIM-1 dense and fibrous membranes became insoluble in common organic solvents. Before the modification, water contact angle of PIM-FM was $138 \pm 2°$ which also remained almost the same after the modification, showing water contact angle of $131 \pm 8°$. The insolubility along with amine functionality make membranes promising materials for adsorption of anionic dyes from wastewater. Here, dye (i.e. Methyl Orange) removal ability of AM-PIM-FM from an aqueous system was investigated and compared with parent PIM-1 (PIM-FM) as well as dense membrane form (AM-PIM-DM). AM-PIM-FM shows extremely higher adsorption capacity than that of PIM-FM and AM-PIM-DM. The maximum adsorption capacity of AM-PIM-FM was found $312.5\,mg\,g^{-1}$ for Methyl Orange. Langmuir isotherm model was found more favorable for the adsorption. AM-PIM-FM was employed effectively in continuous adsorption/desorption studies for several times without having any damage on fiber morphology using batch adsorption process. Furthermore, AM-PIM-FM was successfully used as a molecular filter for the removal of methyl orange from an aqueous system. The results indicate that AM-PIM-FM could be a promising adsorbent for removal of anionic molecules from an aqueous system.

1. Introduction

Water pollution has raised a global concern, and tremendous research has been performed on the removal of hazardous materials including heavy metals, aromatic compounds and dyes [1,2]. Several industries utilize dyes and most of the dyes are released into the environment without proper discharging method, leading to detrimental effects on the biological system and human body [3,4]. Therefore, their elimination from an aqueous waste would be of significant concern to handle wastewater issues. A number of treatment methods have been developed for dye removal from wastewater including adsorption, chemical reduction [5], oxidation [6], coagulation [7], biological treatment [8] and membrane separation [9]. Among all, adsorption is the most attractive method due to its efficiency and applicability on a large scale as well as having the potential of reusability of adsorbents [10]. Electrospinning is a simple and effective method to produce desirable adsorbents, having a high surface area to volume to ratio and highly porous structure. A variety of materials particularly polymers can be electrospun into fibers from nanometers to micrometers diameter [11–15].

Recently, Polymers of intrinsic microporosity (PIMs) have generated significant interest due to their high surface area and packing inefficiency as a result of their rigid and contorted structure [16,17]. PIM-1 is the most studied member of this class and it was utilized in various

* Corresponding authors at: Department of Chemistry, Faculty of Science and Arts, Ahi Evran University, Kirsehir 40100, Turkey (B. Satilmis).
E-mail addresses: bekir.satilmis@ahievran.edu.tr (B. Satilmis), uyar@unam.bilkent.edu.tr (T. Uyar).

https://doi.org/10.1016/j.apsusc.2018.05.069
Received 18 February 2018; Received in revised form 7 May 2018; Accepted 9 May 2018
Available online 16 May 2018

applications including adsorption [18], separation [19], catalysis [20] and several other applications in the form of powder, membrane and fibers since its solution processable, and it displays selectivity for some certain organic compounds [21–23]. PIM-1 exhibits outstanding gas separation performance in the dense membrane form [17,24]. It also shows selective adsorption for neutral species from non-aqueous system in the powder and dense membrane form [23,25]. Although powder and membrane form of PIM-1 is widely studied, fiber form is comparably a new concept, which can be obtained by electrospinning technique. Recently, electrospinning of PIM-1 has been performed, and very few studies have been reported related to fiber production [22,26], energy storage applications [22], adsorption of aniline from an aqueous system and air [27], and adsorption of oil soluble (neutral) compounds from non-aqueous system [28,29]. Functionalization of PIM-1 is also of interest as it offers the possibility of altering the interaction ability of PIM-1 with its surrounding, especially in an aqueous system [30–33]. However, modification may cause a serious damage on structure and the membrane forming ability of polymer. Recently, we have devoted some efforts to the modification of PIM-1 in order to alter the adsorption ability of PIM-1 against charged molecules such as cationic and anionic species in an aqueous system. Our previous results demonstrated that while hydrolyzed PIMs exhibit high adsorption capacity against cationic species, amine and ethanolamine modified PIMs show high uptake for anionic species [25]. Even though we have managed to obtain several modified PIM powders with an improved adsorption selectivity along with an enhanced adsorption capacity, they can only be employed as a powder adsorbent that limits the potentials of these materials in broader applications due to the handling difficulties. Therefore, producing more convenient form is necessary to overcome the handling difficulties. Recently, Zhang et. al.[34] has reported the hydrolysis of electrospun PIM-1 fiber to improve the cationic dye adsorption performance of electrospun PIM-1. However, post-modification of electrospun fiber has caused serious structural damage on fibers. Afterwards, we have reported a facile method to produce hydrolyzed electrospun PIM-1 ultrafine fibers for an effective removal of cationic dye (methylene blue) from an aqueous system [35]. Moreover, electrospun fibrous membrane was successfully used as a filter to remove methylene blue from aqueous system. These two examples are the only two modified electrospun PIMs reported so far and they can only be selective for cationic species. Producing selective fibrous PIM membrane for anionic species has not been achieved yet. In general, amine functionalization is an effective way to tune the adsorption ability of material and to empower selectivity against anionic species [36,37]. Previously, amine modification of PIM-1 has been reported by our group [31], and the powder form of amine PIM-1 showed enhanced selectivity and high adsorption capacity against anionic species from an aqueous system [25]. As aforementioned, although amine PIM-1 powder is a good adsorbent, handling difficulty limits the applications of the material. To overcome this problem, producing the amine PIM-1 in the form of a membrane is more beneficial, since membranes can be employed in different applications including adsorption, membrane separation and sensor applications. Even though the dense membrane (film form) of amine PIM-1 has been reported previously [31], it has been only employed in gas separation. Thus, no study has revealed the adsorption ability of amine modified PIM-1 membrane from an aqueous system yet. Furthermore, the amine modification of electrospun PIM-1 fibrous membranes and their adsorption properties from an aqueous system has not been reported yet, to the best of our knowledge.

In this study, we have reported the modification of electrospun PIM-1 ultrafine fibers in the presence of borane dimethyl sulfide complex to Amine PIM-1 (AM-PIM) ultrafine fibers. Here, we have investigated the possible effect of the chemical modification on fiber morphology and we have compared the adsorption ability of dense and fibrous membranes of amine modified PIM-1 samples with parent PIM-1 polymer and with each other. Although borane dimethyl sulfide complex is a strong reducing agent, fiber structure of PIM-1 has not been affected from the reaction conditions. The self-standing amine PIM-1 fibrous membrane (AM-PIM-FMs) was obtained by modification of electrospun PIM-1 fibrous membrane that might be a useful material for adsorption applications due to the insoluble behavior and functionalized fibrous structure. Furthermore, the amine PIM-1 fibrous membrane has shown greater adsorption capacity towards anionic dye (i.e. Methyl Orange) compared with PIM-1 dense/fibrous membranes as well as dense amine PIM-1 membrane and low adsorption capacity against cationic dye (i.e. Methylene Blue) from an aqueous system. Moreover, amine modified fibrous membrane was successfully utilized to decolor Methylene Blue & Methyl Orange mixtures owing to affinity difference of amine PIM-1. Desorption of Methyl Orange was achieved by using basic alcohol solutions, and adsorbent was successfully used in several adsorption cycles without having any damage on fiber morphology. Besides, the application of AM-PIM-FM in filtration application was also investigated to provide further evidence for the convenience of the material.

2. Experimental

2.1. Materials

Tetrafluoroterephthalonitrile (97%, Alfa Aesar) and 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (98%, Alfa Aesar) were purified as reported previously [32]. Anhydrous potassium carbonate (K_2CO_3, 99.0%, Fisher) was dried overnight at 110 °C. Borane dimethyl sulfide complex solution (5.0 M in diethyl ether), 1,1,2,2, tetrachloroethane, dimethylacetamide (DMAc), methanol, ethanol, chloroform ($CHCl_3$), dimethylformamide (DMF), toluene, sodium hydroxide (NaOH) and Methylene Blue (molecular formula: $C_{16}H_{18}ClN_3S{\cdot}3H_2O$; molecular weight: 373.9) were obtained from Sigma Aldrich. Methyl Orange (molecular formula: $C_{14}H_{14}N_3NaO_3S$; molecular weight: 327.3) was purchased from Merck, and they were used without further purification.

2.2. Synthesis of amine modified PIM-1 fibrous membrane (AM-PIM-FM)

Synthesis and electrospinning of PIM-1 was performed as reported previously [27]. Highly aligned PIM-1 fibers were prepared using 1,1,2,2 tetrachloroethane as solvent at 2000 rpm rotating speed to avoid any wetting. Synthesis of amine PIM-1 was achieved according to previous method [31]. Fibrous membrane of PIM-1 (0.3 g) was placed in a flange reactor. Condenser and nitrogen inlet were fitted to reactor which was then placed in oil bath and was heated to 45 °C before the addition of borane-dimethylsulfide complex (10 mL, 5 M in diethyl ether). The reaction was performed overnight, and the excess borane was quenched by adding ethanol dropwisely. Fibrous membrane was soaked in 1 M methanolic HCl (100 mL) for overnight then transferred into 5% (*w/w*) aqueous sodium hydroxide (100 mL) for a further night to neutralize the membrane. Following that, membrane was washed with a copious amount of water and dried at 110 °C overnight to obtain golden yellow color.

2.3. Synthesis of amine modified PIM-1 dense membrane (AM-PIM-DM)

Dense membrane of PIM-1 (PIM-DM), which is used to express film form of PIM-1, was prepared by well-known solvent evaporation technique using chloroform as a solvent. Synthesis of amine modified PIM-1 dense membrane (AM-PIM-DM) was performed under the identical conditions with AM-PIM-FM sample.

2.4. Methods

FT-IR spectra of membranes were collected on a Bruker Vertex 70 spectrometer by mixing a piece of membrane with potassium bromide (KBr) which was then pressed to prepare pellet samples. Each sample