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Removal of aniline from air and water by polymers of intrinsic microporosity (PIM-1) electrospun ultrafine fibers

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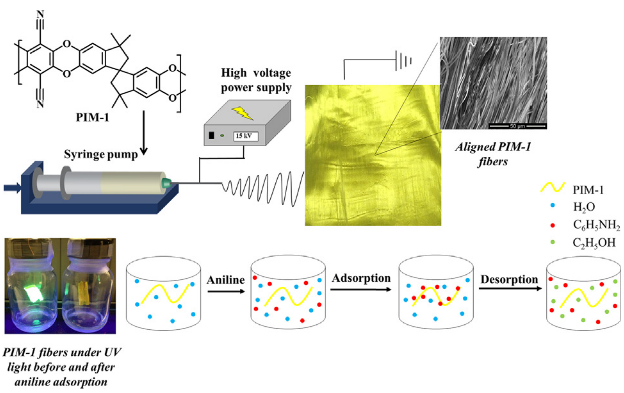
GRAPHICAL ABSTRACT



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ABSTRACT

This research aims to investigate the possibility of electrospun fibers from Polymers of Intrinsic Microporosity (PIM-1) as an alternative adsorbent for aniline removal from both air and aqueous solution. Adsorption properties of electrospun PIM-1 fibers were compared with powder and film form of PIM-1. While electrospun PIM-1 nanofibrous mat can adsorb 871 mg g^{-1} aniline from air, it can also adsorb 78 ± 5.4 mg g^{-1} aniline from aqueous environment when 50 mg L^{-1} aniline solution is used. The experimental maximum adsorption capacity of electrospun PIM-1 fibers was found as (q_e) 138 mg g^{-1}. Langmuir and Freundlich isotherm models have been studied and Langmuir model found more appropriate for aniline adsorption on electrospun PIM-1 fibers. The study reveals that self-standing electrospun fibrous mat of PIM-1 has shown potential to be used as an efficient adsorbent material for the adsorption of VOCs from air and aqueous system thanks to its fast kinetic and high adsorption capacity.

1. Introduction

Air and water pollutions are major problems faced by today's world. The situation is further aggravated by industrialization as the pollutants released into environment without proper treatment methods [1,2]. Aniline is an important organic compound that is widely used as an intermediate in the production of pharmaceuticals, dyes and pesticides [3,4]. Aniline is a common volatile

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organic compound (VOC) that can contaminate both air and aquatic environment [5]. The presence of aniline may cause serious environmental and health problems because of its toxicity [6,7]. Hence, removal of aniline from air and water has attracted serious attention from researchers. A number of processes including oxidation [8], biodegradation[9], membrane separation [10], adsorption [11] and some other processes can be applied for removal of aniline [12]. From the technical and economical points of view, adsorption is regarded as one of the most promising method for aniline removal [13].

Recently, Polymers of intrinsic microporosity (PIMs), a new class of polymer, attracted significant interest due to their unusual structural feature with a backbone composed of fused rings and site of contortion [14,15]. PIMs behave as molecular sieves and show high free volume as they cannot pack space efficiently [16]. PIMs have attracted widespread attention as material for sensor [17,18], catalysis [19,20], membrane separation [21,22], adsorbents [23] and other applications. Although a number of PIMs have been synthesized, the first member of this class, PIM-1, received the main focus as it shows great separation performance in the gas separation [24,25]. PIM-1, has high surface area, high thermal and chemical stability and, is soluble in common organic solvents such as tetrahydrofuran and chloroform, and can be processed in the forms of powders, membranes and fibers. PIM-1 is an organophilic polymer that is selective towards organic compounds and it shows extremely high CO_2 permeability along with moderate selectivity in the membrane form. Moreover, PIM-1 membranes employed successfully in pervaporation systems to separate VOCs from aqueous system as the system has the same mass transfer mechanism with the gas separation system [26,27]. It was also studied in organic solvent nanofiltration system [28]. Recently, comparative study has been conducted by using high free volume polymer including PIM-1, poly(1- trimethylsilyl-1-propyne) (PTMSP) and poly(4-methyl-2-pentyne) (PMP). PIM-1 showed great sorption selectivity along with sorption ability for neutral dye (Solvent 35) in ethanolic solution compared to other polymer [29]. Later on, the possibility of using PIM-1 as an adsorbent and membrane material was investigated using combined process of solvent swing adsorption with solvent recovery by nanofiltration [30]. In addition to membrane form, PIM-1 has also been produced in the form of hollow fibers showing similar performances in gas separation [31,32]. The fiber form can also be produced by electrospinning method which is fairly simple and versatile way to produce three-dimensional porous adsorbents for various applications [33–39]. Electrospinning of PIM-1 is a fairly new concept that was investigated recently [40–43]. Bonso et al. [40] was first used tetrachloroethane solution to produce electrospun PIM-1 fiber mat. Following this, PIM-1 mat was carbonized and used successfully as an electrode for supercapacitors. Then, the preparation of PIM/POSS fibrous membranes were developed and their oil/water separation performances have been studied by Zhang et al. [42]. The same group also have investigated the adsorption of dyes from non-aqueous media by electrospun PIM-1 [41]. Lasseuguette et al. [43] employed different solvent system for the fabrication of electrospun PIM-1 by using tetrahydrofuran/dimethylformamide mixture.

In this study, we have prepared electrospun PIM-1 fiber and the aniline removal ability of electrospun PIM-1 was compared with powder and film form of PIM-1 from air and water. The study revealed that all forms of PIM-1 have the ability to adsorb aniline from air within 24 h. Moreover, PIM-1 fiber shows considerable aniline adsorption from aqueous system up to 138 mg g^{-1} (q_e). While powder and fiber forms of PIM-1 show higher adsorption capacity than film form, fiber form of PIM-1 found more applicable in aqueous system as powder form dispersed in water and it needs additional filtration for analysis. On the other hand, fiber PIM-1 shows better stability and it maintains the fiber morphology that provides practical advantage in adsorption and reuse of adsorbent.

2. Experimental

2.1. Materials

5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI, 98%, Alfa Aesar) was dissolved in methanol and reprecipitated from dichloromethane before use. Tetrafluoroterephthalonitrile (TFTN, 98%, Aldrich) was purified by sublimation; pure product collected without vacuum. Anhydrous potassium carbonate (K_2CO_3, 99.0%, Fisher) was dried in an oven at 110 °C overnight before use. Dimethylacetamide (DMAc), toluene, dimethylformamide (DMF), methanol (MeOH), chloroform ($CHCl_3$), tetrahydrofuran (THF), dichloromethane (DCM) and 1,1,2,2, tetrachloroethane (% 98) were purchased from Sigma Aldrich and were used as received.

2.2. Synthesis of PIM-1

Synthesis of PIM-1 was performed as reported previously [44]. Yield: 62 g (90%). GPC: M_n = 106,000, M_w = 189 000, M_w/M_n = 1.78. ^1H NMR (400 MHz, $CDCl_3$, d, ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26–2.09 (4H, dd), 1.40–1.10 (broad, 12H). ATR-IR (cm^{-1}): 2995, 2864, 2239, 1605, 1446, 1264. Anal. calcd for $C_{29}H_{20}N_2O_4$ (wt%): C: 75.64, H: 4.37, N: 6.08 found: C: 74.6, H: 4.4, N: 5.9.

2.3. Film preparations

PIM-1 (0.2 g) was dissolved in $CHCl_3$ (8 mL) and stirred overnight to ensure a homogenous casting solution. The casting solution was filtered through glass wool into a glass dish. The cast solution was covered by glass funnel and left for 48 h to allow solvent evaporation. The freshly formed film was removed from the glass dish with the help of an ethanol/water mixture (1:1). Then it was dried in an oven at 110 °C overnight.

2.4. Electrospinning

PIM-1 powder was dissolved in 1,1,2,2-tetrachloroethane at the concentration of 23% (w/v). The PIM-1 solution was stirred at 60 °C for 1 h and left stirring overnight at room temperature and degassed for 15 min prior to use. Following that, about 2 mL of the PIM-1 solution was placed in a 3 mL syringe, which was equipped with a blunt metal needle with an inner diameter of 0.5 mm and the syringe was positioned horizontally on the syringe pump (K_D Scientific, KDS 101). Metal plate collector was covered by an aluminum foil then placed across the syringe to collect microfibers. Extensive optimization studies have been performed for the electrospinning and the applied parameters were as: flow rate of the polymer solution; 0.5 mL h^{-1}, applied voltage; 11–12 kV and tip to collector distance; 18 cm, rotation speed of the collector; 2000 rpm. Then, the collected fibers were detached from the aluminum surface by spraying MeOH on fiber surface to ease the stress on fibers and inhibit the immediate stretching. Finally, the PIM-1 fiber was dried in an oven at 130 °C under vacuum for overnight.

2.5. Methods

The molecular weight of PIM-1 was measured by an Agilent gel-permeation chromatograph (GPC) equipped with a ZORBAX PSM 300-S column, which was calibrated using polystyrene standard samples·THF was used as mobile phase at a flow rate of 1 mg