Design, fabrication and evaluation of intelligent sulfone-selective polybenzimidazole nanofibers

Adeniyi S. Ogunlaja [a], Carol du Sautoy [b], Nelson Torto [a], Zenixole R. Tshentu [c],*

[a] Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown 6139, South Africa
[b] Analytical Technology, Sasol Technology (Pty) Limited, P.O. Box 1, Sasolburg 1947, South Africa
[c] Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port-Elizabeth 6031, South Africa

ABSTRACT

Molecularly imprinted polybenzimidazole nanofibers fabricated for the adsorption of oxidized organo-sulfur compounds are presented. The imprinted polymers exhibited better selectivity for their target model sulfone-containing compounds with adsorption capacities of 28.5 ± 0.4 mg g^{-1}, 29.8 ± 2.2 mg g^{-1} and 20.1 ± 1.4 mg g^{-1} observed for benzothiophene sulfone (BTO$_2$), dibenzothiophene sulfone (DBTO$_2$) and 4,6-dimethyldibenzothiophene sulfone (4,6-DMDBTO$_2$) respectively. Molecular modeling based upon the density functional theory (DFT) indicated that hydrogen bond interactions may take place between sulfone oxygen groups with NH groups of the PBI. Further DFT also confirmed the feasibility of π–π interactions between the benzimidazole rings and the aromatic sulfone compounds. The adsorption mode followed the Freundlich (multi-layered) adsorption isotherm which indicated possible sulfone–sulfone interactions. A home-made pressurized hot water extraction (PHWE) system was employed for the extraction/desorption of sulfone compounds within imprinted nanofibers at 1 mL min^{-1}, 150 °C and 30 bar. PHWE used a green solvent (water) and achieved better extraction yields compared to the Soxhlet extraction process. The application of molecularly imprinted polybenzimidazole (PBI) nanofibers displayed excellent sulfur removal, with sulfur in fuel after adsorption falling below the determined limit of detection (LOD), which is 2.4 mg L^{-1} S, and with a sulfur adsorption capacity of 5.3 ± 0.4 mg g^{-1} observed for application in the fuel matrix.

1. Introduction

The challenge of fulfilling the world's growing transportation fuel energy needs is no longer simple since the vast reservoirs of crude oils are sour (high sulfur content), and the growing concern over operational and environmental issues has increased over years [1]. Desulfurization of fuels is one of the main processes used in petroleum refinery to reduce sulfur concentration so as to meet environmental protection sulfur standards of 10–15 mg L^{-1} in fuels [1,2]. The conventional hydrodesulfurisation (HDS) process currently employed to remove sulfur suffers limitations such as the inability to efficiently eliminate refractory organosulfur compounds specifically dibenzothiophenes and the alkyl substituted dibenzothiophenes. On this account, the oxidative desulfurization (ODS) technique was proposed as a complementary desulfurization step to HDS as it eliminates refractory organosulfur compounds in hydrotreated fuels [2]. The ODS technique involves the oxidation of sulfur compounds

followed by the extraction of the oxidized sulfur products (sulfonated compounds) [2]. The extraction of sulfonated compounds from oxidized fuels using solvents such as acetonitrile and dimethylsulf-oxides (DMSO) eliminates other important compounds with similar chemical properties, consequently resulting in fuel properties and compositions falling outside the required specifications. Hence, the need to develop smart polymer nanofiber-based adsorbents [molecularly imprinted polymers (MIPs)] with large surface area-to-volume ratio for the selective removal of sulfonated compounds in fuels [2].

Electrospinning is a well-established technique for the production of nanofibers with diameters from nano-to-micrometer scale which possess very large surface area-to-volume ratio and high porosity [3–4], through the application of high voltage on polymer solution. It is an ancient technique, which was first observed by Rayleigh in 1897 as reported by Zeleny [5]. Zeleny, in 1914, studied electrospraying of liquids and the process was further developed and patented by Formhals [6] in 1934. However, Taylor's work [7] on electrically driven jets laid the foundation for electrospinning, since the findings were able to explain most of the processes governing nanofibers production. Over years, several applications of electrospun nanofibers have been reported. Burger et al. [8] and
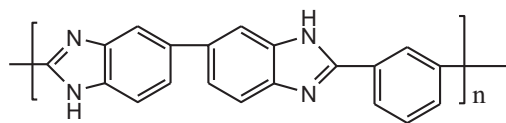
Fig. 1. Structure of polybenzimidazole (PBI).

Ramakrishna et al. [9] reported a very broad range of use of nanofibers, which includes adsorption [10,11], organ regeneration [12–15], electrospun scaffolds [16–21], fuel cells membrane [22], and catalyst supports [23–25].

Polybenzimidazole (PBI), a heterocyclic polymer with excellent chemical and thermal stability properties, was commercially developed by Celanese Corporation in 1983 for use as fire-retardant material and composite material reinforcement [26] due to the good molecular alignment [27,28]. Likewise, Sherrington et al. [29–31] as well as other researchers [32–35] have exploited the use of PBI as a support for a range of different metal-catalyzed reactions with great success. PBI comprises of repeating units of benzimidazole –NH groups (Fig. 1) which allows for hydrogen bonding interactions with polar compounds such as sulfones produced in the oxidation of organosulfur compounds in fuels [2,36–39].

Besides the possibility of PBI being a good adsorbent, desorption or extraction of isolated compounds from the adsorbent should generally be less problematic for material reusability. A safer desorption process that required the use of less hazardous solvents led to the evolution of green chemistry [40]. Green chemistry technology using subcritical fluids (pressurized hot water) for extraction and sample-preparation processes has proven to be a faster and more environmentally friendly process [40,41]. King et al. [42] reported that varying the temperature of water over a range of 25–250 °C under high pressure, changes its dielectric constant from 78 to less than 30, thereby attaining solvent polarities normally associated with polar organic solvents. Sulfone compounds display similar polar organic properties as pressurized hot water; thus, the latter will be a suitable and more economical candidate for sulfone extraction.

We describe for the first time, the fabrication of molecularly imprinted PBI nanofibers using benzothiophene sulfone (BTO$_2$), dibenzothiophene sulfone (DBTO$_2$), and 4,6-dimethyldibenzothiophene sulfone (4,6-DMDBTO$_2$) as templates. Absorption studies on model oxidized organosulfur compounds and oxidized hydrotreated diesel [36] were investigated in an attempt to produce ultra-pure fuels. This article also reports on the development of a simple pressurized hot water extraction method for desorption of the adsorbed sulfone compounds within the nanofibers matrix.

2. Experimental

2.1. Materials

Polybenzimidazole (PBI) was purchased from PBI performance products (Charlotte, USA) with intrinsic viscosity of 0.8 dL/g. Lithium bromide (LiBr) and Triton X-114 were purchased from Sigma Aldrich, Germany. Sulfur in diesel standards was purchased from Matheson Tri-Gas, Texas, USA. Sulfur standards produced by Matheson Tri-Gas have direct traceability to NIST SRM 2723a/SRM 2770 and are laboratory certified to ASTM D5453. *N,N*-dimethylacetamide (DMAc), acetonitrile (HPLC grade) and methanol (HPLC grade) were purchased from Merck, South Africa.

2.2. Sulfone compounds synthesis

Sulfone compounds (oxidized organosulfur compounds) were synthesized from the catalyzed oxidation of model organosulfur compounds such as benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene using poly[VO(allylSB-co-EGDMA)] and poly[VO(sal-AHBPD)] as oxidation catalysts [2,36].

2.2.1. Benzothiophene sulfone synthesis

0.15 g (0.0011 mol) benzothiophene (BT) was placed in a 25 mL round bottom flask containing 10 mL mixture of toluene/hexane (1:4) and 0.015 g (0.0135 mmol) of oxidation catalyst. The mixture was heated to 40 °C with continuous stirring at 500 rpm in an oil bath. An oxidant-to-substrate ratio of 6.8 was then added to the mixture. The oxidation reaction was allowed to proceed for 6 h under continuous stirring after the addition of *tert*-butylhydroperoxide. A white precipitate of benzothiophene sulfone (BTO$_2$) observed was collected through filtration and washed with hexane to remove unreacted benzothiophene. Yield=81%. ^{1}H NMR (δ, ppm in DMSO) δ 7.83 (d, J=7.2, 1H), 7.69 (t, J=7.4, 1H), 7.62 (t, J=9.1, 3H), 7.34 (d, J=6.8, 1H). *Anal.* Calcd. (found) for C$_8$H$_6$O$_2$S (%): C, 57.81 (57.49); H, 3.64 (3.89); S 19.29 (19.02).

2.2.2. Dibenzothiophene sulfone synthesis

0.15 g, (0.00081 mol) dibenzothiophene (DBT) was dissolved in a 25 mL round bottom flask containing 10 mL mixture of toluene/hexane (1:4) and 0.015 g (0.0135 mmol) of oxidation catalyst. After which an oxidant-to-substrate ratio of 7.6 was added to the mixture and the oxidation reaction was allowed to proceed for 6 h under continuous stirring at 500 rpm at 40 °C. A white precipitate of dibenzothiophene sulfone (DBTO$_2$) was collected through filtration and washed with hexane to remove unreacted dibenzothiophene. Yield=98%. ^{1}H NMR (δ, ppm in DMSO): 8.22 (d, J=7.7, 2H), 8.00 (d, J=7.6, 2H), 7.82 (t, J=7.6, 2H), 7.67 (t, J=7.6, 2H). *Anal.* Calcd. (found) for C$_{12}$H$_{10}$O$_2$S (%): C, 66.65 (66.02); H, 3.73 (4.04); S 14.83 (14.83).

2.2.3. 4,6-Dimethyldibenzothiophene sulfone synthesis

0.15 g (0.00071 mol) 4,6-dimethyldibenzothiophene (4,6-DMDBT) was dissolved in a 25 mL round bottom flask containing 10 mL mixture of toluene/hexane (1:4) and 0.015 g (0.0135 mmol) of oxidation catalyst. After which an oxidant-to-substrate ratio of 7.6 was added to the mixture and the reaction was allowed to proceed for 6 h under continuous stirring at 500 rpm at 40 °C. A white precipitate of 4,6-dimethyldibenzothiophene sulfone (4,6-DMDBTO$_2$) was collected through filtration and washed with hexane to remove unreacted dibenzothiophene. Yield=87%. ^{1}H NMR (δ, ppm in DMSO): 7.98 (d, J=7.6, 2H), 7.66 (t, 2H), 7.44 (d, J=7.5, 2H), 2.48 (s, 6H). *Anal.* Calcd. (found) for C$_{14}$H$_{12}$O$_2$S (%): C 68.38 (68.38); H, 4.95 (5.25); S, 13.12 (12.83).

2.3. Instrumentation and methods

FT-IR spectra (4000–650 cm^{-1}) of PBI nanofibers were obtained on a Perkin Elmer 400 ATR-FT-IR spectrometer. Microanalysis was carried out using Elementar Analysen Systeme Vario® MICRO VI 6.2 GmbH. PBI nanofibers images and chemical characterization were carried out by using a TESCAN Vega TS 5136LM scanning electron microscopy (SEM) and an energy-dispersive spectroscopy (EDS) respectively. Before images were taken for SEM analysis, nanofibers were coated with a thin film of gold to prevent surface charging and also to protect the material surface from thermal damage by the electron beam. No surface coating was needed for EDS analysis. The BET surface area measurements of the nanofibers were performed by using a Micromeritics ASAP 2020 surface area analyzer. Prior to analysis, the nanofibers were degassed for 10 days at 50 °C. Nitrogen gas was employed as adsorption gas for the surface area measurements. High voltage power supply from Glassman High Voltage Inc., USA, was employed for the electrospinning of polymer solutions.