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Porous sulphur copolymer for gas-phase mercury removal and thermal insulation

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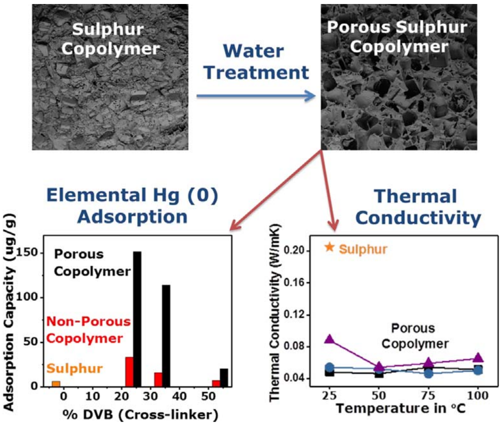
GRAPHICAL ABSTRACT



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ABSTRACT

Removal of gas-phase mercury is vital in gas processing industries. Herein, we report the preparation of porous sulphur copolymers for capturing elemental mercury (Hg(0)) in the gas phase. Porous sulphur copolymers were prepared using porogen and an inverse-vulcanisation technique. Sulphur powder was mixed with a water-soluble porogen (NaCl) and cross-linked with divinyl benzene (DVB) at 165 °C, and the porous structure was later obtained by dissolving the porogen in water. The porosity of the copolymer was controlled by varying the amount of salt and cross-linker. The effect of pore volume and temperature on the adsorption of mercury from gas phase has been estimated. Samples with larger pore volumes showed a significant increase in adsorption capacity, reaching approximately 151 µg/g at 60 °C. High sulphur content and the porous structure enhanced the adsorption capacity. Furthermore, the thermal conductivities of the porous copolymers were studied at a range temperature. Copolymers with relatively high cross-link densities showed the very low thermal conductivity of approximately 0.048 W/m K at 25 °C, which is much lower than that of pristine sulphur. Abundant availability of sulphur and a simple method of preparation could make porous sulphur copolymers potential candidates for mercury capture and thermal insulation.

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1. Introduction

There is an upward trend in the development of functional materials from renewable sources. Most of this research focuses on renewable feedstock from biomass. Developing functional materials from inorganic regenerables and waste remains underexploited. Elemental sulphur, a by-product from petroleum refining, can be classified as one such inorganic material. The sheer abundance and low cost of sulphur call for the initiation of new chemistry and processing techniques to develop novel functional materials. Inverse vulcanisation, first reported by Pyun et al. in 2013, has facilitated the production of high-sulphur loaded polymers by adding a small organic molecule, typically a diene [1]. This acts to cross-link the sulphur chain and provide stability against depolymerisation, creating a stable, functional material [2].

High sulphur content (wt% > 50) in these materials opens doors for various applications such as LiS batteries [3–6], IR-transparent lenses [7], hole transport materials in dye-sensitised solar cells (DSSC) [8], and mercury capture [9–11]. Recently, *Chalker et al.* illustrated a limonene-based inverse-vulcanised polymer for the sequestration of mercury and other heavy metals from waste water [10]. Though the results demonstrated potential for some applications, the material that was generated is a low molecular weight polysulphide, a waxy substance that could be challenging to employ as a functional filter [11]. Hasell et al. demonstrated an improvement in mercury adsorption by foaming a sulphur–1,3-diisopropenylbenzene (DIB) polymer using supercritical carbon dioxide ($scCO_2$) [11]. The foaming process led to a large increase in surface area, and the material showed superior performance in mercury ion capture from waste water streams. However, the foaming process involves the risk of using $scCO_2$ at high pressure and temperature in an autoclave. This could also restrict the scalability of the foaming process. *Hasell et al.* later overcame this issue by employing a salt-template method to obtain a robust sulphur foam that showed improved mercury capture from waste water [12]. Elemental mercury, Hg(0), is present in natural gas streams. Though low levels of mercury are found in natural gas streams (parts per billion), it can damage the aluminium heat exchangers in cryogenic, petrochemical, and liquefied natural gas (LNG) plants [13,14]. Thus, the removal of elemental mercury from the gas phase is essential. Owing to the poor thermal conductivity of elemental sulphur (~ 0.205 W/m K) [15], sulphur foams were used as roads subbase thermal insulators in cold regions to prevent frost penetration and thawing of permafrost in roads of Calgary [16–21].

To the best of our knowledge, we are the first to demonstrate the utilisation of porous sulphur co-polymers as reactive adsorbents for capturing Hg(0) from the gas phase and demonstrated the use of the porous copolymer as a potential candidate for thermal insulation.

2. Experimental

2.1. Materials

Elemental sulphur (S_8, sublimed powder, reagent grade), divinyl benzene (DVB, 80%) and sodium chloride (NaCl, 99%) were purchased from Sigma Aldrich, USA and used without further purifications.

2.2. Preparation of porous sulphur copolymer

The sulphur copolymer was prepared using a porogen and an inverse-vulcanisation technique. A representative method for the synthesis of the porous sulphur copolymer (SSD-7-3-3) is as follows. A mixture of sodium chloride (7 g) and sulphur (3 g) was ground into a fine homogeneous powder using a mortar and pestle and transferred to a 50-ml glass vial equipped with a magnetic stir bar. The vial was then placed in an oil bath preheated at 165 °C. The mixture appeared orange in 15–20 min. To this, DVB was slowly added under violent stirring. In 5–10 min the mixture solidified and appeared dark brown in colour. The reaction setup was kept undisturbed for approximately 1 h to ensure the completion of the cross-linking reaction. The material was recovered by breaking the glass vial. The resulting solid product was hammered into granules ranging from 3–8 mm in size. The pores were then obtained by simply dipping the granules in 50 ml of de-ionised water under constant stirring overnight at room temperature (27 °C). Finally, the product was dried at 50 °C overnight in a vacuum oven until a constant weight was achieved. Similarly, a series of samples were prepared by varying the sulphur, salt, and DVB ratio as shown in Table 1. The prepared samples were denoted as SSD-x-y-z, where x, y, and z indicates the amount in grams of salt, sulphur, and DVB, respectively.

Table 1
Compositions of the SSD-x-y-z series.

Sample name	Salt (g)	Sulphur (g)	DVB (g)
SSD 7-3-3	7	3	3
SSD 7-3-1.5	7	3	1.5
SSD 7-3-0.75	7	3	0.75
SSD 8-2-2	8	2	2
SSD 5-5-4	5	5	4
SSD 5-5-3	5	5	3

2.3. Characterisation

Fourier-transform infrared spectroscopy (FT-IR) was performed by a Bruker Vertex 70 from 500–4000 cm^{-1}. The samples were analysed in transmission by KBr technique. NMR spectra of obtained polymers were recorded on a Bruker Avance 400 Spectrometer in $CDCl_3$, and chemical shifts were given relative to tetramethylsilane as the internal standard. Diffraction (XRD) patterns were collected using analytical X'Pert PRO Powder Diffractometer (CuKa radiation 1.5406 A°, 40 kV, 40 mA) using a 5°–80° 2θ scale with a step size of 0.02°. The surface morphology of the composite was characterised using a scanning electron microscope (SEM, Quanta- FEG-250). Thermogravimetric analysis (TGA) of the samples were done from room temperature to 700 °C in a Discovery TGA (USA) thermal analyser at a heating rate of 10 °C/min under nitrogen atmosphere with a flowrate of 10 mL/min. DSC analysis was carried out on a Discovery DSC (TA instruments) for temperature ranging from −30 to 200 °C at a ramp rate of 10 °C/min under nitrogen atmosphere. T_g was analysed on the second cycle of the thermogram. The true density of the samples was analysed using an Ultra Pycnometer 1000 by Quantachrome Instruments.

2.4. Mercury adsorption tests

The mercury adsorption tests were conducted according to the previously reported method [14]. In brief, 50 mg of samples with an average size of 5 mm, obtained as described in Section 2.2, were packed in a glass tube as shown in Fig. S2 and placed inside a tubular reactor having a diameter of 2.54 cm and a length of 10 cm. The reactor was kept in a water bath to maintain a constant adsorption temperature (40 or 60 °C). The source of the mercury vapour was a mercury permeation device (VICI Metronics Inc., Santa Clara, CA), which generated a constant inlet concentration by varying the nitrogen flow rate and permeation device temperature. The mercury carried into the tubular reactor by nitrogen adsorbs and the capacity of the adsorbent was measured by an automatic mercury analyser (DMA-80, manufactured by Milestone Switzerland). A schematic of the experimental setup is shown in Fig. 1.

2.5. Thermal conductivity measurement

Thermal conductivity tests were performed at different temperatures by an LFA 457 Micro Flash (Netzsch). Circular disc-shaped porous