



Alginate-pyrolyzed porous carbon as efficient gas phase elemental mercury scavenger



Anjali Achazhiyath Edathil, Fawzi Banat*, K. Suresh Kumar Reddy, C. Srinivasakannan, Ahmed Shoaibi

Department of Chemical Engineering, Khalifa University of Science and Technology (KU), Abu Dhabi, United Arab Emirates

ARTICLE INFO

Keywords:

Alginate biomass
Pyrolysis
Porous carbon
Elemental mercury
Adsorption
Langmuir model

ABSTRACT

The present research work demonstrates the potential of porous carbon (PC) fabricated through facile one-step method from calcium alginate biomass as a low cost and efficient scavenger for gas phase elemental mercury (Hg^0) from natural gas. Performance of the prepared PC at different temperatures (500, 700 and 900 °C) using fixed-bed setup mimicking the plant conditions revealed that PC-900 demonstrated to be a promising adsorbent for removing Hg^0 . The excellent sorption performance of PC-900 could be attributed to its BET surface area and large pore volume which rendered easy sorption of Hg^0 into the porous network. The equilibrium adsorption results further confirmed that sorption capacity decreased from 1236 to 1089 $\mu\text{g/g}$ with increase in temperature from 30 to 50 °C, indicating exothermic nature of adsorption. The sorption isotherms well fitted the Langmuir model, with maximum adsorption capacity of 1236 $\mu\text{g/g}$ at 30 °C. A comparison of the sorption capability of bio-derived PC-900 with sulfur impregnated carbon (SIC) at 50 °C affirmed that the uptake capacity of PC-900 (1089.6 $\mu\text{g/g}$) was much higher than SIC (887.2 $\mu\text{g/g}$). These results reveal the promising solutions offered by alginate pyrolyzed PC for scavenging Hg^0 from natural gas, by not only reducing the environmental problems associated with gaseous mercury emissions but also by making the process more economical.

1. Introduction

Mercury is one of the most dangerous heavy metals on earth. Its presence in the environment has become an issue worldwide owing to its volatility, persistence and bioaccumulation in the ecosystem and has been classified as a hazardous air pollutant (HAP) as per the recommendations of the Clean Air Act (CAA) of 1990 (Pavlish et al., 2004). The air pollutant emission inventory confirms that mercury emissions are mainly in the form of elemental (Hg^0), oxidized (HgCl_2 or HgO), and particulate ($\text{Hg}(\text{p})$) (Kumar Reddy et al., 2016). After coal fired power plants, the natural gas processing industry is reported, depending on the type of gas reservoir, to be a major anthropogenic source of mercury emissions, especially in the form of Hg^0 with concentrations as high as 4400 $\mu\text{g}/\text{m}^3$ (Abbott and Oppenshaw, 2002). Even when present in small concentrations at the natural gas wellhead, Hg^0 can cause (i) severe and catastrophic damage to the brazed aluminum heat exchangers and other equipment's of cryogenic, petrochemical, and liquefied natural gas (LNG) plants through liquid metal embrittlement or amalgam corrosion, (ii) dramatically shorten the life of precious downstream metal catalyst such as platinum or palladium and (iii) cause difficulty in the disposal of mercury-contaminated equipment. Moreover, Hg^0 is

highly volatile, toxic, chemically inert and has a lifetime of 6–12 months in atmosphere. Hence, considerable release of emissions to the environment and constant exposure of workers to high level of mercury during maintenance operations may pose serious threat to the ecosystem making it a global environmental pollutant. Consequently, the rapid progress in the development and exploration of oil and gas fields for obtaining mercury free hydrocarbons owing to its high impact on the operation of gas processing industries along with associated health, safety and environmental (HSE) issues has necessitated the need for exerting stringent regulations on mercury emissions. Various programs such as the United Nations Environment Program (UNEP) of 2002 and Minamata Convention on mercury (2013) were initiated with the aim of enforcing strict measures to protect the ecosystem from the long-term harm caused by the anthropogenic mercury emission (Chemicals and Chemicals, 2002; Kessler, 2013). As a result, considerable efforts were paved for finding and developing suitable separation technologies to remove Hg^0 from the natural gas stream, thereby meeting the requirements of the international and regional regulatory standards (Lee and Lee, 2012; Zhao et al., 2015).

Among various treatment technologies available to remove mercury, adsorption is the most preferred treatment method, owing to its

* Corresponding author.

E-mail addresses: fbanat@pi.ac.ae, fawzibanat@gmail.com (F. Banat).

easy design, cost effectiveness, efficiency and freedom from any associated secondary contamination (Yang et al., 2007; Xu et al., 2018). Installing a mercury removal unit with an appropriate adsorbent is to date the most well-established and tested technology, as experimentally obtained sorption isotherms along with the associated kinetics data facilitates having a better understanding of the design of a robust adsorption column that has extended life and high mercury scavenging capacity. As a result of the magnitude of its impact in solving one of the major challenges faced by the natural gas processing industry, widespread interest has been generated by researchers in developing effective and economical adsorbent based mercury control technologies.

Numerous results are reported in the literature on using porous activated carbon as sorbent material for oxidizing Hg^0 (Diamantopoulou et al., 2010; Granite et al., 2000; Tan et al., 2012; Scala et al., 2011; Prabhu et al., 2012). The high surface area, pore volume and wide pore size distribution enable easy accessibility of the carbon-oxygen groups (lactone, carbonyl or carboxyl) present on the surface of the activated carbon to act as surface-active moiety for the adsorption and oxidation of elemental mercury. These characteristics, on which the adsorptive capacity depends, are further defined by the nature of the starting material and process used for preparation. Therefore, tremendous interest has been created by researchers to modify the surface chemistry of the activated carbon using sulfur, metal sulfides, halides or thiols with aim of enhancing the mercury adsorption capacity through chemisorption (Rashid et al., 2013; Vidic and Siler, 2001; Mei et al., 2007; Liu et al., 2000; Tan et al., 2011a; Shen et al., 2010; Lee et al., 2004; Sugier and Villa, 1978). However, exorbitant cost associated with the additional surface modifications performed on activated carbon limits the practical utilization of these adsorbents for industrial purposes. Therefore, the search for developing low cost porous carbon based materials with well-built pore structures, extraordinary surface area, better surface properties and superior mercury adsorptive ability as sorbents from low-cost precursors has been gaining substantial attention (Han et al., 2016; Tong et al., 2017).

In recent years, various researchers have directed their investigation on utilizing bio-based materials such as bamboo (Johari et al., 2015), rice/barley/sunflower husk (Hsi et al., 2011; Fuente-Cuesta et al., 2012), coconut husk/pith (Johari et al., 2015), poultry litter (Fuente-Cuesta et al., 2012) and pistachio shell (Hsi et al., 2002) as an economical and potential adsorbent source for removing elemental mercury from gas streams. The low-cost, wide availability and low environmental impact of these bio-based materials make these waste materials very attractive for producing value added products such as adsorbents through facile and inexpensive preparation procedures (Gupta et al., 2015; Ahmaruzzaman and Gupta, 2011). Alginate biomass, a readily available natural polysaccharide extracted from brown algae (Phaeophyceae) is one such renewable source which possesses these favorable characteristics and can be processed into bio-char by pyrolysis (Edathil et al., 2017). Unlike other bio-based materials, alginate possess large number of carboxylic groups in each of the polymer's monomeric units and hence the so-obtained bio-char holds an abundant porous structure, large surface area and suitable surface chemistry with extremely active carbon-oxygen functional groups ($-\text{O}$ donor binding groups) which can act as a good sequestering agent for mercury. This information has encouraged us to explore the practicality of using porous carbonaceous adsorbents derived from calcium alginate biomass materials as potential candidates for scavenging gaseous mercury.

The objective of this study was to synthesize and characterize new bio-derived porous carbon (PC) materials using calcium alginate as carbon precursor at pyrolysis temperatures ranging between 500 and 900 °C and assess the possibility of using these materials as a potential sequestering agents for capturing elemental mercury (Hg^0) from a simulated gas stream in a laboratory scale fixed-bed tubular reactor, mimicking the plant conditions. The bio-derived porous carbon obtained from calcium alginate was prepared and used for the first time to scavenge elemental mercury from gaseous streams. Efforts were made

in identifying the influence of adsorption temperature and initial Hg^0 concentration on the Hg^0 uptake capacity for gaining a better understanding of the sorption characteristics exhibited by the porous carbon materials. The effects of various chemical/physical properties such as carbon pore structure, surface area, pore size distribution and surface chemistry on the mercury adsorptive ability were investigated by XRD, BET and SEM-EDX analysis. The mechanism responsible for capture of Hg^0 were elucidated by correlating the Hg^0 removal results from the packed-bed testing with sorbent's physio-chemical properties. In addition, an attempt was made to compare the Hg^0 sorption characteristics of the developed bio-derived porous carbon with sulfur impregnated carbons (SIC).

2. Experimental section

2.1. Materials

All the chemicals used were of reagent grade and used without any further modification. The precursor used to prepare the bio-derived carbon was alginic acid calcium salt from brown algae and was purchased from Sigma Aldrich (USA). Deionized water was used for washing the synthesized carbon particles to remove any impurities and oven-dried at 60 °C overnight.

2.2. Preparation of bio-derived porous carbon

Bio-derived porous carbon particles were prepared by the direct carbonization of calcium alginate biomass under nitrogen atmosphere. Briefly, calcium alginate was placed in a ceramic crucible, and the furnace temperature was programmed as follows: (a) from room temperature to 200 °C in 20 min, (b) held at 200 °C for 2 h, (c) ramped to desired pyrolysis temperature of 500, 700 and 900 °C and (d) held for 1 h at the pyrolysis temperature (to ensure complete graphitization). After cooling down naturally to room temperature, the so-obtained carbon samples, denoted as PC - 500, 700 and 900 depending on the temperature used for pyrolysis were collected, washed, dried and stored for further use and characterizations.

2.3. Characterization

The crystallographic nature of the PC samples was recorded by collecting X-ray diffraction (XRD) patterns using X'Pert PRO Powder Diffractometer ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) using a 2θ scale of 20–70° with a step size of 0.02° and scan rate of 2° min^{-1} . The Brunauer-Emmett-Teller (BET) specific surface area, pore volume and pore size distribution of the prepared PC were determined by using N_2 adsorption and desorption isotherm models at 77 K on a Autosorb-1, Quanta chrome analyzer. The specific surface area and pore volume were calculated based on BET method, whereas the pore size distribution was calculated by fitting the adsorption data of the isotherms using Barrett-Joyner-Halenda (BJH) method. All the sorbent samples were degassed at 573 K prior for 15 h prior to the BET measurements. The morphology, structure and elemental composition of the prepared samples were characterized using FEG Quant 250 Scanning Electron Microscopy (SEM) equipped with EDX analyzer (Oxford-EDX, UK).

2.4. Gas phase mercury adsorption test

The removal capacity of the developed porous carbon for elemental mercury was investigated by using a flow-type packed bed reactor under atmospheric pressure according to the earlier reported method (Kumar Reddy et al., 2016). Fig. 1 shows the schematic of the experimental set up used for conducting mercury sorption tests. In a typical experiment, 100 mg of carbon samples were packed inside the quartz tubular reactor having a length and diameter of 10 and 0.254 cm, respectively. The reactor was then jacketed with a circulation bath to

Download English Version:

<https://daneshyari.com/en/article/8127958>

Download Persian Version:

<https://daneshyari.com/article/8127958>

[Daneshyari.com](https://daneshyari.com)