Removal of elemental mercury by coconut pith char adsorbents

Khairiraihanna Johari\textsuperscript{a}, Norasikin Saman\textsuperscript{b}, Song Shiow Tien \textsuperscript{b}, Cheu Siew Chin\textsuperscript{b}, Helen Kong\textsuperscript{b}, Hanapi Mat\textsuperscript{b,c}\textsuperscript{*}

\textsuperscript{a}Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia.

\textsuperscript{b}Advanced Materials and Process Engineering Laboratory, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

\textsuperscript{c}Advanced Material and Separation Technologies (AMSET) Research Group, Health and Wellness Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

Abstract

Coconut pith (CP), which is abundantly available and cheap, has the potential of being used as low-cost adsorbents for elemental mercury removal. In this study, the preparation of chars was carried out through the carbonization of CP at three different environment conditions: (a) open reactor under nitrogen flow; (b) closed reactor under nitrogen environment; and (c) closed reactor under ambient environment; at the temperature of 700°C. The results show that the chemical, physical, morphological and spectral properties of the adsorbents greatly influenced by the environment of carbonization used. The highest Hg\textsubscript{o} adsorption capacity was observed for CCA700 (2395.98 P g/g), followed by CCN700 (2052.49 P g/g), and CFN700 (1416.92 P g/g). These results demonstrated that coconut pith derived chars could be potential as low-cost adsorbent alternatives for the removal of elemental mercury in gas streams.

Keywords: Coconut; char; mercury; adsorption; desorption; adsorbent.

1. Introduction

Elemental mercury is emitted from various anthropogenic sources such as coal-fired power plants, municipal incinerators, and natural gas processing [1], [2]. It has become a public concern due to its high toxicity, volatility, and bioaccumulation in the environment [3]. The existing solid materials such as activated carbon [4], [5], silica-based materials [6], [7], fly ash [8], [9] and zeolites [10], [11] have been proved as successful adsorbent for Hg\textsuperscript{o} removal by many researchers. However, there are some limitations regarding to their complex preparations, high cost and non-renewable sources. Attempts towards the new precursors, which are cheap and capable to perform high adsorption capacity, agricultural residues have been recently explored [12].

Coconut (Cocos nucifera\textsubscript{L}.), is one of the most widely planted tree species in tropical region such as Brazil, India, Philippines, Malaysia, Indonesia and some other countries. The coconut is known for its great versatility as seen in commercial and industrial uses of its parts (coconut shell, fibers, and pith). Consequently, a large amount of coconut processing wastes is becoming a problem. So far, the coconut wastes have been used for fertilizer, household, cushioning, building materials and automotive components [13], [14] or left to decompose on the fields. As another alternative, the development of high value added product from coconut wastes is essential to solve their disposal problems. Besides, it helps in improving the environment quality

\textsuperscript{*}Corresponding author. Tel.: Tel.: +607-5535590; Fax: +607-558146.

E-mail address: khairiraihanna.j@petronas.com.my
and sustainability. In recent years, the use of coconut wastes even though has been extensively studied in adsorbent preparation for specific applications [15]–[19]. However, there is no research on coconut pith except for coconut shell as elemental mercury adsorbents [20], [21]. In addition, the coconut wastes were also reported on the production of carbonaceous adsorbents for the removal of mercury [22], dye [23]–[25], arsenic [26], copper [27], and chromium [28] from water and wastewater.

With the above-mentioned facts, there has been a high increase in production and utilization of activated carbon derived from coconut, in last few decades. Due to the high cost and complex preparation, the researchers attempt to make the simple preparation for carbonaceous material, in which produced the high performance of porous carbons. In this study, carbonization is carried out by pyrolysis of precursor in an inert atmosphere to produce char. This process is clearly a desirable method that enhances the carbon content from the organic substances [29]. According to our previous study [18], the highly adsorptive porous carbon was prepared by different thermal carbonization process. It was found that with the increasing of carbonization temperatures was significantly enhanced the adsorption capacity, as well as affected the physicochemical of carbonaceous adsorbents.

In our previous works, the coconut pith has been successfully converted into char and the different thermal temperatures have been explored [18]. Thus, present investigation was conducted by using char produced at temperature of 700°C under different environmental conditions for its potential to remove elemental mercury from gas streams.

2. Experimental

2.1. Materials

The raw material of coconut pith (CP) was supplied by T&H Coconut Fiber Sdn. Bhd. (Johor, Malaysia). This sample was kept in a desiccator for characterizations and further used as char precursor. The deionized water produced by the Purite Water System model Select Analyst HP40 (U.K) was used to prepare all solutions, while the double-distilled water was used for glassware washing and cleaning.

Nitrogen gas (purified, 99 %) was obtained from Mega Mount Industrial Gases Sdn. Bhd. (Johor, Malaysia). The elemental mercury vapor was generated using Metronics Dynacal permeation device (type HE-SR) purchased from VICI Metronics Inc. (USA).

2.2. Chars preparation

Coconut pith was ground and sieved into size fraction of 300-100 µm and washed for several times to remove unwanted impurities. Followed by oven-dried at 105±1 °C until consistent weight was obtained for further use.

The dry carbonization of CP sample was carried using three distinct environment procedures: (a) The feed was heated under nitrogen flow from ambient (i.e. 30 °C) to 700 °C (the product was denoted as CFN 700); (b) The nitrogen feed was purged for 30 minutes, followed by closing the valve and heating to 700 °C (the product was denoted as CCN 700); and (c) The inlet and outlet valve remain fully closed and heating to 700 °C (The product was denoted as CCA 700).

About 6g of sample were placed in the stainless steel device and heated from room temperature (30±1°C) to carbonization temperatures of 700°C, with a heating rate of 10°C/min. The sample was kept at the carbonization temperature for a retention time of 1 hour. The sample was then cooled to room temperature naturally, washed with deionized water, followed by 0.1M hydrochloric acid solution until the washing solution reached pH 7.0 to neutralize the sample surfaces. The sample was then dried in an oven at 105±1°C and stored in desiccator till further use. All produced chars were then sieved between 100-70 µm size using standard sieves and underwent further adsorption studies.

2.3. Chars characterization

The determination of moisture (M), volatile matter (VM), and ash content was conducted according to a modified ASTM method D1762-84 [30]. The changes in the surface morphology of adsorbent samples were determined by analyzing their respective SEM images, which were obtained using a scanning electron microscope (SEM) model JEOL JSM-6390LV (Japan). The surface chemistry of the adsorbent surfaces was analyzed by an FTIR (PerkinElmer Model 2000, USA). The FTIR spectra measurements were carried out over 4000-400 cm⁻¹ using the KBr method. The surface areas of samples were determined by using nitrogen adsorption/desorption method measured at 77K using a surface analyzer (NOVA-2000e; Quantachrome Corp., Boyton Beach, FL, USA). The CP or char was degassed for about 9 hours under vacuum at 393 K prior to conducting adsorption measurements. The surface area was calculated using the BET methods, and the pore volumes were taken at P/Po = 0.99.

2.4. Elemental mercury (Hg⁰) capture

The experimental setup for Hg⁰ adsorption (Fig. 1) was prepared similarly in our previous work [18]. The Hg⁰ was generated using a mercury permeation device (VICI Metronics Inc., USA) loaded in a U-tube, supported with glass beads, and maintained at 45.5±0.5 °C placed in a water bath in which it generated 51 ng/min of Hg⁰. Purified nitrogen (99.9999%) was used as a carrier...
gas at 50 mL/min, yielding a constant Hg\(^{0}\) concentration of 200±20 µg/m\(^3\). The flow rate of nitrogen gas was controlled using a calibrated Aalborg mass flow controller (model GFC17).

![Fig. 1. A schematic diagram of experimental setup for mercury vapor adsorption study.](image)

The system was equipped with a 3-way valve that allowed bypass (BP) and adsorbent-bed (AB) streams. The stainless steel cell (Thermo Scientific), of 4.6 mm inner diameter and 50 mm length, was placed in a vertical tubular furnace equipped with a temperature controller. The amount of Hg\(^{0}\) in the BP and AB streams was determined using a mercury analyzer (JEROME, Arizona Instrument LLC, USA). The Hg\(^{0}\) adsorption capacity of the adsorbents was calculated using a mass balance based on the initial mercury concentration obtained from the BP stream. Excess Hg\(^{0}\) was trapped in an impinger Teflon column, containing a mixture of activated carbon and elemental sulfur, controlled by using a three-way valve. For safety reasons, the exit line was connected to a fume hood.

A blank test performed prior to the adsorption experiment indicated no Hg\(^{0}\) adsorption. About 50 mg of adsorbent with particle sizes of 100-70 µm was packed into the stainless steel cell and placed in the temperature controlled vertical tube furnace. In a typical experiment, the Hg\(^{0}\) flowrate of 50 mL/min was used. Adsorbed moisture was removed from the adsorbent bed prior to the experiment by purging the adsorbent bed with the pure nitrogen gas by opening the NF valve, closing MF valve and switching the 3-way valve to the AB stream position, while heating the adsorbent bed to a temperature of 105°C. This purging process was carried out overnight. The adsorption experiment was started by initially determining the steady state Hg\(^{0}\) concentration. This was done by closing the NF valve, opening the MF valve and switching the 3-way valve to the AB stream position and recording the outlet (downstream) Hg\(^{0}\) concentration until it reached a steady state, which would then be taken as the initial Hg\(^{0}\) concentration. After reaching the steady state Hg\(^{0}\) concentration, the 3-way valve was switched into the adsorbent bed (AB) stream position and the outlet (or downstream) Hg\(^{0}\) concentration was recorded at selected time intervals. This process was allowed to proceed until the Hg\(^{0}\) concentration reached about 99.99% exhaustion.

During the adsorption experiments, the outlet Hg\(^{0}\) concentrations were measured over time. The Hg\(^{0}\) adsorption results were plotted in a dimensionless adsorption breakthrough curve, in which the normalized concentration term defined as the ratio of outlet Hg\(^{0}\) concentration at time, \(t = t\) (C) to outlet Hg\(^{0}\) concentration at time, \(t = 0\) (C\(_0\)) given by C/C\(_0\), was plotted as a function of time. The outlet Hg\(^{0}\) concentration at time, \(t = 0\) is equal to the initial Hg\(^{0}\) concentration (C\(_0\)) or the bypassed Hg\(^{0}\) concentration (C\(_{BP}\)). The Hg\(^{0}\) adsorption capacity at any time \(t\), \(q_t\) (ng/g) was calculated by using Eq. 1. The integration term was evaluated by calculating the area above the curve.

\[
q_t = \frac{V(C_0 - C_t)}{m} - \int_{t}^{t} \frac{C_0 - C_t}{\Delta t} dt
\]

where \(V\) is the volumetric flow rate of N\(_2\) gas (L/min), C\(_0\) and C\(_t\) are the outlet Hg\(^{0}\) concentrations (µg/m\(^3\)) at time \(t = 0\) (min) and \(t = t\) (min), respectively. The mercury adsorption capacity at saturation, \(q_e\) is referred to as the Hg\(^{0}\) adsorption capacity, \(q_t\) at time \(t\) of the saturation (\(t_s\)).

3. Results and Discussion

3.1. Char characterization

Table 1 show details on the yield of chars, as well as approximate analysis (moisture, volatile matter, and ash content) produced under different environment conditions. The results indicate that there are no significantly changed on the yield of the three chars, in which CCA700 yielded only about 6-9% higher than CFN700 and CCN700. As reported by Masek et al. [31], the decrease in yield of biochar is due to the none severe pyrolysis conditions that enhance the biomass decomposition. The results indicated that there are no drastic changes on the surface of the chars at different environment conditions.

The surface morphologies of chars are shown in Fig. 2. It was observed that the surfaces of chars are in flake-like form. However, some differences can be highlighted such as CCA700 showed a smooth surface and the numerous particles can be found in the surface of CFN700 and CCN700. The surface morphology also showed that there were the pores over the surface.
forming a pore structure of CCA700 adsorbent. On the other hand, both adsorbents (CFN7000 and CCN700) resulted in closing pores in which the surfaces more solidified areas in appearances.

Table 1 show that the CCA700 performed larger surface area and porosity compared to other chars. Among all the environment of carbonization tested, it can be inferred that ambient with closed reactor is effective. Thus, it can be concluded that these method performed well and should be considered, due to its easy preparation method and lower price compared with nitrogen. FTIR spectra of CFN700, CCN700 and CCA700 (Fig. 3) in the range of wavenumber 4000-370 cm⁻¹ are described as follows. The bands at 3000 cm⁻¹ are correspond with –OH vibrations in hydroxyl groups, that might involved in hydrogen bonds, and probably with participation of water adsorbed by carbon samples. Comparing to the previous studies [18], [32], the raw coconut pith performed a strong and broad band between 3252 and 3440 cm⁻¹, however, the results obtained show the stretching band of hydrogen-bonded hydroxyl groups were reduced and diminished. This might be due to the higher mass loss during thermal carbonization process. The peaks around 1600-1400 cm⁻¹ could be the presence of C=C or C=O stretching and the spectrum in the region of 1200-1000 cm⁻¹ is attributed C-O or C-OH stretching vibration of functional groups such as alcohols, ethers, carboxylic and ester. In addition, there is also an extra peaks appear around 800 cm⁻¹ which may be related to C=C and C-H in aromatic rings.

Table 1: Carbonization yields and properties of chars.

<table>
<thead>
<tr>
<th></th>
<th>CFN700</th>
<th>CCN700</th>
<th>CCA700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yields (wt.%, dry basis)</td>
<td>28.42±1.48</td>
<td>29.49±1.54</td>
<td>31.41±1.86</td>
</tr>
<tr>
<td>Moisture (wt.%, dry basis)</td>
<td>8.28±4</td>
<td>4.547±7</td>
<td>5.09±3</td>
</tr>
<tr>
<td>Volatile matter (wt.%, dry basis)</td>
<td>23.101</td>
<td>22.451±7</td>
<td>13.49±6</td>
</tr>
<tr>
<td>Ash (wt.%, dry basis)</td>
<td>67.29±4</td>
<td>73.29±7</td>
<td>81.279±2</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>102.70±4</td>
<td>88.51±4</td>
<td>315.063±3</td>
</tr>
<tr>
<td>Pore volume (cm³/g) x10⁻³</td>
<td>56.13±4</td>
<td>48.94±4</td>
<td>149.7±3</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>2.186±4</td>
<td>2.212±4</td>
<td>1.901±3</td>
</tr>
</tbody>
</table>

Fig. 3. FTIR spectra of chars produced under different environment conditions

3.2. Elemental mercury (Hg⁰) adsorption capacity

A comparison of breakthrough curves for the three different environments of chars is presented in Fig. 4. The breakthrough time measured for the three chars were longer (> 7 days), especially CCA700 (~ 10 days), indicating better retention of Hg⁰ adsorption toward adsorbent. In addition, the results obtained indicate that adsorption capacity of CCA700 is higher than that the two other chars (CFN700 and CCN700), however, both chars are still maintain with a better adsorption capacity. The order in terms of adsorption capacity for chars is CCA700> CCN700> CFN700. This is probably due to the physical effect of CCA700, which performed significantly difference on the textural properties of the adsorbent. Given the higher BET surface area, volumes
of different pores, a more effective Hg° adsorption onto the CCA700 was observed (Table 1). This is comparable with the adsorption performance of adsorbents reported by several literatures [33]–[35]. The adsorbent possessed a highly developed micropore volume and BET surface area, in which enhanced the Hg° adsorption capacity. In contrast, several literatures reported that the surface area of the adsorbent used did not appear to have a major impact on the elemental mercury adsorption [12], [36]–[38].

![Fig. 4. The breakthrough adsorption curves of char adsorbents prepared at different environment conditions. Experimental conditions: Inlet mercury concentration [Hg°] = 200 μg/m³; bed temperature = 50±1°C; N₂ flow rate = 50 mL/min; and mass of adsorbent = 50 mg.](image)

4. Conclusion

In this study the properties of chars are significantly influenced by the environment conditions of carbonization process. Large BET surface area, pore volume, with higher of carbon content were performed by char produced in closed reactor with ambient environment at temperature of 700°C. The Hg° adsorption performance of chars showed that clear dependence on the environment conditions of carbonization process with closed-ambient environment performing the best. Based on char adsorbent requirements of low cost raw material, high adsorption capacity, hence, it can be concluded that chars produced at temperature of 700°C with closed-ambient environment (CCA7000), is the best adsorbent among the other two chars (CFN700 and CCN700) tested study.

Acknowledgements

The financial supports from the Ministry of Higher Education (MOHE), Malaysia for the MyBrain15 scholarship and the Ministry of Agriculture (MOA), Malaysia for the eScience Fund (Project No. 05-01-06-SF 1006/79410) are gratefully acknowledged.

References


