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Adsorption Equilibrium and Kinetics of Elemental Mercury onto Coconut Pith

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ABSTRACT

The experiment to discover the ability of Coconut Pith (CP) as an elemental mercury adsorbent was carried out using a conventional flow type packed-bed adsorber with N₂ as a carrier gas, conducted at bed temperature of 50°C. The adsorbents were characterized through proximate analysis (moisture and ash content), CHNS elemental analysis, FTIR and Nitrogen Adsorption/Desorption (NAD) analysis. Adsorption results showed that the adsorption capacity increased with the increase of initial concentrations, from 0.25 to 1.04 µg g⁻¹ for 100 and 500 µg m⁻³, respectively. Meanwhile, the kinetic results showed that the Hg⁰ adsorption could be very well presented by the pseudo-second order model. Primary results suggested that the coconut pith with proper modification can be a very promising low-cost adsorbent material for Hg⁰ removal from gas streams.

Key words: Coconut, mercury, adsorbent, adsorption, kinetics

INTRODUCTION

Mercury is one of the most toxic heavy metals which can contaminate the environment and accumulate in animals and plants (Wang *et al.*, 2009; Tomczak and Kaminski, 2012). The emission of mercury by power plants is the largest source, emitted around 50 tons of mercury annually. The low concentration of mercury on the level of 1-10 ppb exists as the flue gas when coals are burned (Hsi *et al.*, 2011). This matter has become an important environmental concern because the elemental mercury and oxidized mercury (i.e., HgCl₂) are the major constituents in the combustion of flue gas. Comparing both types of mercury, gaseous elemental mercury is more difficult to be removed using the currently available mercury removal devices (i.e., electrostatic precipitators and baghouse) except for the particle bound mercury atoms. Currently, the adsorption process in solid materials (adsorbent) offers a great potential for minimizing the mercury emissions. It gives less problem of treatment and stabilization of the waste liquid streams which also will be attractive for coal combustors and hazardous/municipal waste incinerators.

Previous studies have proven that the coconut husk (fiber and pith), coconut shell and desiccated coconut are potential adsorbents for the removal of diverse heavy metal ions (Sreedhar and Anirudhan, 2000; Hasany and Ahmad, 2006; Anirudhan *et al.*, 2008; Johari *et al.*, 2013, 2014a), dyes (Hameed *et al.*, 2008; Jain and Shrivastava, 2008; Tan *et al.*, 2008a, b),

inorganic anions (Namasivayam and Sangeetha, 2004), radionuclides (Parab and Sudersanan, 2010) and miscellaneous pollutants (Igwe *et al.*, 2008) from water. However, there is a limited amount of available information in the literature related to the elemental mercury (Hg^0) removal from flue gas and natural gas streams. Hence, the use of coconut pith can be researched as a potential adsorbent for the Hg^0 adsorption and for these sorts of applications due to their abundantly low-cost of raw materials and simple preparation process. All these characteristics have lead researchers to develop high value added products (adsorbents) which are amenable to chemical modification, non-toxic, posses no waste disposal problems and contribute to the sustainability of the surrounding environment (biodegradation) (Rahman and Khan, 2007).

The use of coconut pith as a precursor for development of an elemental mercury adsorbent will be the subject of this study. Three kinetic models including pseudo-first order, pseudo-second order and Elovich equations were used to describe the adsorption process. The adsorption capacity and rate of the coconut pith adsorbent were examined by varying the initial Hg^0 concentrations.

MATERIALS AND METHODS

Materials: Coconut Pith (CP) was obtained from T&H Coconut Fiber Sdn. Bhd., Johor, Malaysia. The CP sample was washed several times using deionized water to remove dust and soluble impurities. The washed coconut pith was then oven dried at $50 \pm 1^\circ\text{C}$ for 2 days, sieved between 100-200 mesh size using standard sieves and underwent further characterization and adsorption studies. The sample was denoted as CP.

Deionized water, used to prepare all solutions, was produced using the Purite Water System (U.K) model Select Analyst HP40 which is available in the laboratory. The purified nitrogen gas (99%) was obtained from Mega Mount Industrial Gases Sdn. Bhd., Johor, Malaysia and the Dynacal permeation device (type HE-SR) was purchased from VICI Metronics Inc., U.S.A.

Characterization: The moisture and ash content were determined by using a modified methods by ASTM E1755-01 (2007) and ASTM E1756-08 (2008), respectively, involving measurement of weight loss, followed by combustion of about 1 g of the sample in a ceramic crucible at 105 and 575°C , respectively. In order to evaluate the changes in surface physical morphology, the adsorbent sample was analyzed by using Scanning Electron Microscope (SEM) JEOL model JSM-6390LV (Japan). The surface area and pore volume of the adsorbent were determined by nitrogen adsorption/desorption method at 77 K using a surface area analyzer (NOVA-2000e; Quantachrome Corp., Boyton Beach, FL, USA). The sample was degassed for 9 h under vacuum at 393 K prior to conduct adsorption measurements. The surface area was calculated using the BET methods and pore volumes were determined using the BJH method. The different types of functional groups were identified by using Fourier Transform Infrared (FTIR) Spectroscopy (Perkin Elmer Model 2000, U.S) in the range of $4000\text{-}400\text{ cm}^{-1}$. The sample was first mixed with KBr and then pressed into pellets. The elemental compositions of samples including Carbon (C), Hydrogen (H), Nitrogen (N) and Sulfur (S) were determined through dry combustion using vario MACRO cube elemental analyzer (Elementar, Germany). All analyses were carried out in triplicate and the mean value was presented.

Experimental apparatus and procedures: A schematic diagram of the experimental setup for Hg^0 adsorption is shown in Fig. 1 which is similar to the previously employed by Granite *et al.* (2000) and Johari *et al.* (2014b) to screen sorbents for mercury captured from flue gas and

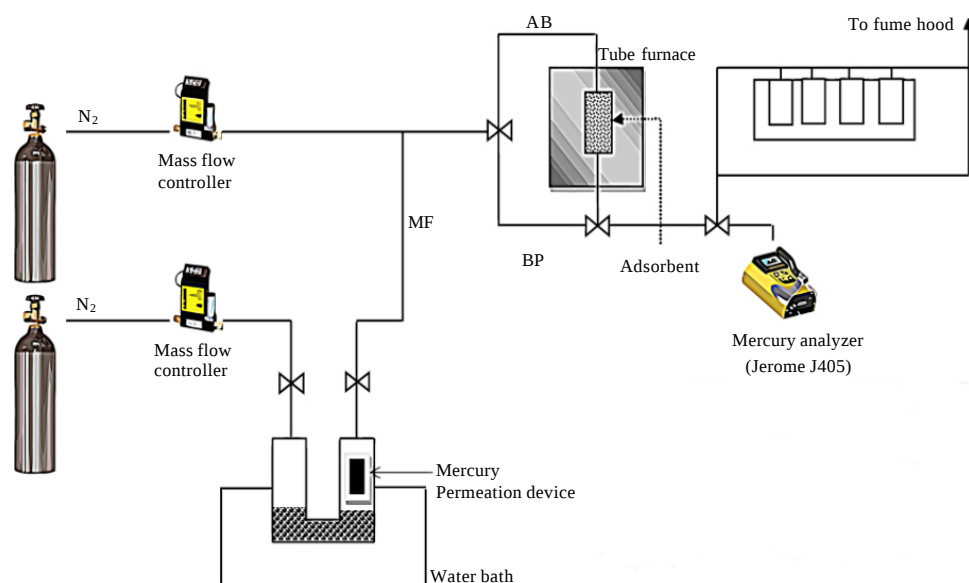


Fig. 1: A schematic diagram of experimental setup for elemental mercury adsorption study

nitrogen. The experiment was conducted using purified nitrogen (99.99%) as a carrier gas and the flow rate of the N₂ was controlled using an Aalborg mass flow controller (model GFC17). A certified Dynacal permeation tube was used as the source of Hg⁰ that has capability of producing 51 ng min⁻¹ of Hg⁰ at 45°C. The carrier gas was passed through the U-tube having mercury permeation device. The glass beads were placed in the U-tube to support permeation tube and the temperature of water-bath was maintained at 45.5±0.5°C.

The elemental mercury adsorption rig was equipped with 3-way valves that allowed having a bypass (BP) stream and an Adsorbent-Bed (AB) stream. A stainless cell (BETASIL Silica-100, Thermo Scientific) which had a 4.6 mm inner diameter and a 50 mm length, was placed in a vertical tubular furnace equipped with a temperature controller for controlling the furnace temperature as required. About 50 mg of the chosen adsorbent was packed into the stainless steel cell. The amount of Hg⁰ in the BP and AB streams was determined using mercury analyzer (JEROME, Arizona Instrument LLC). The concentration of the mercury adsorbed by the adsorbent was calculated using mass balance based on the initial mercury concentration obtained from the BP stream. The experimental rig also had a series of impinger glass column, containing a mix of activated carbon and elemental sulfur to trap the excessive Hg⁰, controlled by using a three-way valve. For safety reasons, the exit line was connected to a fume hood.

Typical tests were carried out by purging N₂ through the AB stream to remove adsorbed moistures from the adsorbent, by heating it overnight at a temperature of 50°C. The nitrogen was then fed into the U-tube having mercury permeation tube (mercury feed (MF) stream) and to the BP stream until the measured mercury concentration gave a steady state concentration. This mercury concentration was used as an initial mercury concentration in the MF stream. After the steady state concentration had been achieved, the MF stream was switched to AB stream and the downstream (outlet) elemental mercury concentration was determined, again using the mercury

analyzer at selected time intervals. The experiment was conducted until the mercury analyzer reached about 100% exhaustion. The Hg⁰ adsorption experiment was carried at bed temperatures of 50°C. In practice, the bed temperature is commonly used in a number of gas processing plants, for instances, 61°C at Salam gas plant (Aly *et al.*, 2008), 18°C at PTT GSP-5 gas plant, Rayong, Thailand and 30-40°C at Enterprise Meeker, Colorado (Eckersley, 2010). The adsorption data presented were based on a single run experiment except for those with significant deviation from the overall trend were repeatedly run to ensure the reproducibility of the data.

During the adsorption experiments, the outlet concentrations of mercury were measured over time. The mercury adsorption results were plotted in a dimensionless adsorption breakthrough curve, in which the normalized concentration term defined as the ratio of outlet concentration at time, $t = t$ (C) to outlet concentration at time, $t = 0$ (C₀) given by C/C_0 , was plotted as a function of time. The outlet Hg⁰ concentration at time, $t = 0$ is equal to initial Hg⁰ concentration, C₀ or the bypassed Hg⁰ concentration at the by-pass stream, C_{BP}. The mercury adsorption capacity was calculated by integrating the area above the curve using Eq. 1:

$$Q = \dot{V} C_0 \int_0^t \left(\frac{C_t}{C_0} \right) dt \quad (1)$$

where, Q is the total amount of adsorbed mercury (ng), $\dot{V}$ is the volumetric flow rate of N₂ gas (L min⁻¹), C₀ and C_t are outlet Hg⁰ concentrations (μg m⁻³) at time $t = 0$ (min) and $t = t$ (min), respectively. The quantity of mercury adsorbed per unit mass was calculated by using Eq. 2:

$$q = \frac{\dot{V} C_0 \int_0^t \left(\frac{C_t}{C_0} \right) dt}{m} \quad (2)$$

where, q is the mercury adsorption capacity (ng g⁻¹) at time (t) and m is the mass of the adsorbent used (g).

RESULTS AND DISCUSSION

Adsorbent characterizations: The measured surface area, pore volume and pore diameter of CP were 1.67 m² g⁻¹, 8.38×10⁻³ cm³ g⁻¹ and 222.04 nm, respectively. The CHNS analysis results indicated that the percentage of carbon was the highest (45.86%), followed by hydrogen (5.16%), nitrogen (3.84%) and sulfur (0.19%). The FTIR analysis of CP adsorbent in the range of 4000-400 cm⁻¹ is presented in Fig. 2. The functional groups, C-O, C = O, C-H and O-H were the main characteristics attributed to the presence of cellulose, hemicelluloses and lignin and thus being the main characteristics of the natural fibers (Sreenivasan *et al.*, 1996; Sreekala *et al.*, 1997; Rout *et al.*, 2001). The strong and broad band between 3252 and 3440 cm⁻¹ corresponded to the stretching vibrations of the hydroxyl (-OH) and amine (N-H) groups. The bands at ~2900 and ~1716 cm⁻¹ represented the C-H stretching from the CH₂ group and the C = O stretching from lignin and hemicellulose, respectively. The peak at ~1630 cm⁻¹ was attributed to the O-H bending assigned to the C-O-H bending while the peak at ~1024 cm⁻¹ was indicative of C-O stretching.

Moisture and ash content were determined using proximate chemical analysis of biomass according to ASTM E1755-01 (2007) and ASTM E1756-08 (2008), respectively. The moisture

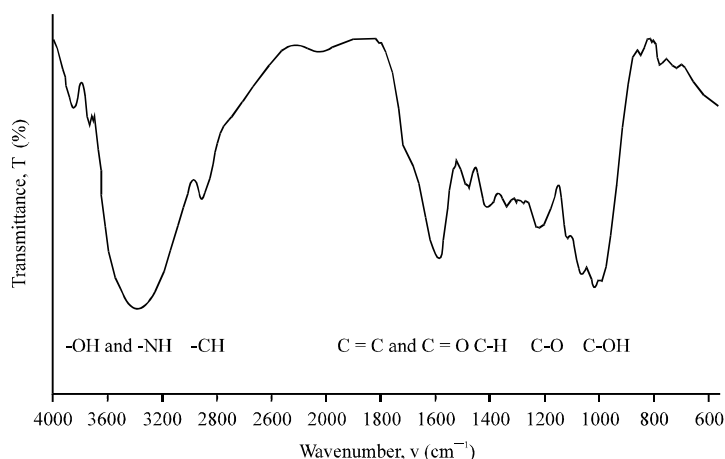


Fig. 2: FTIR spectrum of CP adsorbent

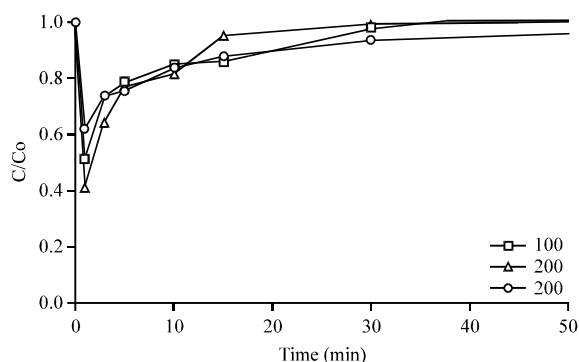


Fig. 3: Effect of initial Hg⁰ concentrations ($\mu\text{g m}^{-3}$) on breakthrough curves of CP adsorbent

content of CP adsorbent obtained was about 12.04% which was consistent within the range as stated in previous literatures which had reported values of 8-15% (Bismarck *et al.*, 2001; Bilba *et al.*, 2007; Asasutjarit *et al.*, 2007). The ash content obtained was about 3.16%. As reported by Israel *et al.* (2011), the low ash content suggests that the coir pith might contain low extractives with little or no waxes and resin, when compared with other non-woody lignocellulosic materials.

Adsorption equilibrium: The typical adsorption breakthrough curves of CP adsorbent are shown in Fig. 3 which show the relation between the normalized mercury concentration (C/C_0) versus adsorption time, t . The approximate exhaustion time, t (min) was set at $C/C_0 = 0.99$. In order to test the practical application of the material, the Hg⁰ adsorption using CP at different initial Hg⁰ concentrations were investigated. The results indicate that the increase of the initial concentration from 100 to 500 $\mu\text{g m}^{-3}$ caused the increase of Hg⁰ adsorption capacity from 0.25 to 1.04 $\mu\text{g g}^{-1}$ and the total mercury exhaustion time increased from 30 to 90 min. A similar result was reported by Skodras *et al.* (2008), where the mercury adsorption capacity increased almost linearly with the increase in influent mercury concentration. This suggests that under the experimental conditions, the mercury adsorption tends to occur in Henry's law region and higher mercury concentration will provide a higher driving force to facilitate mercury uptake (Skodras *et al.*, 2008).

Table 1: Comparison of Hg⁰ adsorption capacity with published data

Adsorbent types	Adsorption temperature (°C)	Initial Hg ⁰ concentration	Adsorption capacity (µg g ⁻¹)	References
CP	50	200 µg m ⁻³	0.73	Present study
CP-CHAR	20	200 µg m ⁻³	3142.57	Johari <i>et al.</i> (2015)
Rice husk	150	*10-15 µg Nm ⁻³	161.20	Hsi <i>et al.</i> (2011)
RH-650S	150	*10-15 µg Nm ⁻³	344.30	Hsi <i>et al.</i> (2011)

*Temperature and pressure (0°C or 15°C and 1 bar)

Table 2: Kinetic model constants and R² values of CP adsorbent at various initial concentrations

Kinetic models	Linearized equation	Concentration (µg m ⁻³)		
		100	200	500
Pseudo-first order	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	$q_{e,theory} = 0.260$ $k_1 = 0.100$ $R^2 = 0.930$	$q_{e,theory} = 0.59$ $k_1 = 0.12$ $R^2 = 0.98$	$q_{e,theory} = 1.00$ $k_1 = 0.21$ $R^2 = 0.95$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$q_{e,theory} = 0.290$ $k_2 = 0.581$ $R^2 = 0.930$	$q_{e,theory} = 0.95$ $k_2 = 0.15$ $R^2 = 0.99$	$q_{e,theory} = 1.06$ $k_2 = 1.02$ $R^2 = 0.99$
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	$\alpha = 0.180$ $\beta = 26.320$ $R^2 = 0.930$	$\alpha = 0.32$ $\beta = 5.03$ $R^2 = 0.98$	$\alpha = 0.56$ $\beta = 5.05$ $R^2 = 0.99$

The low Hg⁰ adsorption capacity presented might be well explained by the characteristics of CP adsorbent which had low surface area and did not contain specific active sites for Hg⁰ bondings. However, oxygen groups such as carbonyl and carboxyl groups on the biomass surfaces might act as adsorption sites for Hg⁰ adsorption. Table 1 shows the results of Hg⁰ adsorption capacity by raw and modified agricultural wastes adsorbents. It was observed that proper modifications of agricultural wastes such as coconut pith resulted in higher elemental mercury adsorption capacity. In addition, these results indicate that the coconut pith has specifically proven as a potential precursor for elemental mercury adsorbents.

Adsorption kinetics: In order to investigate the effect of initial concentration on mercury adsorption rate, kinetic models are commonly used, by employing the data derived from the experiments. The increase of initial concentration caused a decrease in the kinetic constant k_2 , indicating that lower initial concentration provided faster adsorption kinetic and smaller breakthrough times. The modeling kinetic constants and R² values using pseudo-first order, pseudo-second order and Elovich equations are presented in Table 2.

It was observed that over the entire adsorption period, the pseudo-second order kinetic model gave the best fitting model, compared to the pseudo-first order and Elovich equation models. The calculated q_e values from the pseudo-second order kinetic model, agreed well with the experimental q_e values. In addition, the results show an excellent agreement between the experimental data and theoretical adsorption curves using non-linear regression calculated from pseudo-second order as illustrated in Fig. 4. This indicates that Hg⁰ adsorption onto CP followed the pseudo-second order kinetic model for all initial concentrations and hence suggests that chemisorption might have controlled the entire range of the adsorption process. Such results were consistent with the findings by Skodras *et al.* (2008) and Hsi *et al.* (2011) which reported that the adsorption system is better

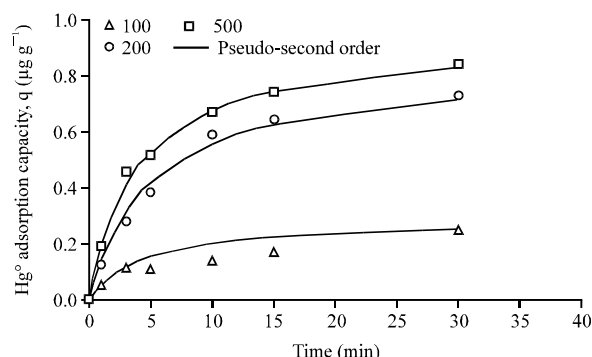


Fig. 4: Kinetic model analysis of Hg° adsorption for various initial mercury concentrations ($\mu\text{g m}^{-3}$)

described by using the pseudo-second order kinetic model, indicating that the chemisorption of Hg° on the adsorbents was in a bimolecular reaction form.

CONCLUSION

Elemental mercury adsorption behavior was studied on coconut pith via a packed-bed adsorber system. The results show that the adsorption capacity increased with the increase of initial Hg° concentration and the experimental data could be very well presented by using a pseudo-second order model. These adsorption results suggested that the coconut pith adsorbent with proper modification can be a very promising adsorbent material for Hg° removal process from gas streams which is an on-going research in our laboratory.

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