Textural Characteristics of ZnCl₂-Treated Mesoporous Materials from Local Waste Products

Muhammad Abbas Ahmad Zaini Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu-Sina Institute for Scientific & Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia. Email: abbas@cheme.utm.my

Abstract

This study was aimed at characterizing the textural properties of promising mesoporous materials derived from selected local solid wastes, namely sludge of palm oil mill effluent and waste carbon powder. Zinc chloride was used in converting the precursors into mesoporous material. The textural characteristics were determined by means of surface area analyzer. Results show that the treated materials are highly mesoporous with average pore width of 7.2 and 5.1 nm for sludge and waste carbon powder, respectively. The pore volume of the derived mesoporous materials is comparable to that of the widely used mesoporous adsorbent (commercial activated carbon).

Keywords: Solid waste, adsorbent, mesoporous material, chemical activation

1. Introduction

There is an increasing concern over the presence of solid wastes in the environment. They could be originated from the domestic, agricultural and other industrial sectors. Some of which could be naturally degraded (e.g., food and plant-based wastes), while some may require special disposal methods (e.g., sludge, clinical wastes, etc.) [1].

There are several studies on the utilization of solid by-products from the industries [2-3]. In the water treatment plant for example, the solid residue namely sludge has been tested for possible applications as fertilizer [4], adsorbent [5] and concrete blend [6]. However, failure to understand the intrinsic properties of the precursor and its derived products somewhat inhibit the direction for broad applications of the solid waste [7].

Synthesis of mesoporous material has become a subject of considerable interest over the last ten years [8]. Mesoporous material is mainly used as catalyst support for accelerating a reaction, and adsorbent to capture medium molecular size pollutants, owing to its large pore volume per unit mass of the material [9-10]. However, to prepare a highly mesoporous adsorbent is a challenging task and may require large amount of chemical agent [11].

This work attempts to convert two local solid wastes, namely sludge of palm oil mill effluent and carbon powder residue into mesoporous material. It aims to offer some insight on their textural characteristics as potential alternative of mesoporous material. The findings are expected to pave the way for wide range of applications through the exploitation of solid wastes.

Manuscript History: Received 15 February, 2016, Revised 18 March, 2016, Accepted 22 March, 2016, Published 31 March, 2016

e-ISSN 2289-7771 Copyright © 2016 JASPE



2. Materials and methods

The commercial activated carbon (CAC) and zinc chloride were purchased from R&M Chemicals (UK). Sludge of palm oil mill effluent was obtained at the anaerobic pond in the palm oil milling factory, while the carbon powder was obtained from a waste tire processing factory.

The mesoporous materials were prepared by adding the precursors into a separate ZnCl₂ solution at a ratio (weight of zinc chloride-to-weight of precursor) of 1.0. The mixtures were stirred and then dried in an oven at 110°C overnight to remove the excess water. After that, the impregnated samples were carbonized in a furnace under limited air at 550°C for 1 h. The resultant materials were washed with distilled water to remove residual zinc chloride. Then they were dried and stored prior to characterization. The treated materials were designated as PS and CP for materials prepared from the sludge of palm oil mill effluent and waste carbon powder, respectively. The textural characteristics of mesoporous materials and commercial activated carbon were determined using surface area analyzer (Micrometrics ASAP2010).

3. Results and discussion

Figure 1 shows the profiles of N_2 adsorption-desorption isotherm of zinc chloride-treated materials and commercial activated carbon. In general, the commercial activated carbon has a larger pore volume than the two waste-derived materials, indicating a larger specific surface area of the former. According to the IUPAC classification, the commercial activated carbon falls under *Type I* isotherm [12]. This isotherm exhibits a convex shape with increasing relative pressure where the adsorbed volume becomes constant as the relative pressure approaching unity. It indicates a material with highly microporous (pore width is less than 2nm) textures. Both zinc chloride-treated materials display a common *Type II* with *H3* hysteresis loop of the desorption branch. The *Type II* isotherm indicates a material with mesoporous (pore width between 2 and 50 nm) or macroporous (pore width greater than 50 nm) textures, while the *H3* hysteresis loop suggests that the material possesses slit-shaped pores [12].

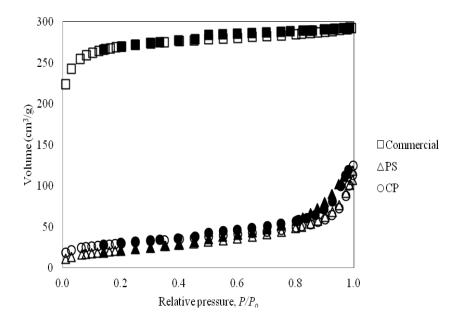


Figure 1. N₂ adsorption-desorption isotherm (filled symbols denote desorption isotherm).

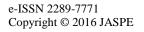


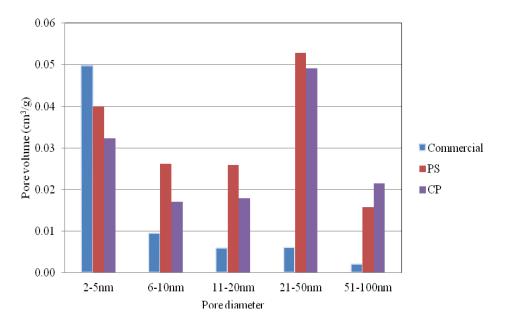


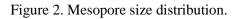
Table 1 summarizes the textural characteristics of the materials studied. The commercial activated carbon shows a nearly ten-fold higher specific surface area than the waste-derived mesoporous materials. However, the commercial activated carbon is highly microporous (76%) with the average pore width centered at 1.98 nm. On the other hand, the zinc chloride-treated waste materials are highly mesoporous. PS shows a 100% mesoporosity, while 91% mesoporosity was recorded for CP. Both waste-exploited materials possess a slightly greater mesopore volume (PS: $0.142 \text{ cm}^3/\text{g}$; CP: $0.123 \text{ cm}^3/\text{g}$) than the commercial activated carbon ($0.108 \text{ cm}^3/\text{g}$). The average pore widths of PS and CP are 7.2 and 5.1 nm, respectively, all are within the mesopore regime.

Textural properties	Commercial (CAC)	PS	СР
BET surface area (m^2/g)	911	79.4	105
Micropore area (m^2/g)	741	0	28
Total pore volume (cm ³ /g)	0.451	0.142	0.135
Micropore volume (cm ³ /g)	0.343	0	0.0121
Microporosity (%)	76.1	0	8.96
Average pore width (nm)	1.98	7.15	5.14

Table 1. Textural characteristics of commercial activated carbon and mesoporous adsorbents

Figure 2 shows the mesopore size distribution of the materials studied. At the mesopore regime, the commercial activated carbon displays a unimodal distribution with a peak centered at the pore diameter between 2 and 5 nm.





Large of the pore volume fraction is distributed at the micropore regime. Both waste-derived mesoporous materials exhibit a similar bimodal mesopore size distribution with peaks centered at 2-5 nm (PS: 23%; CP: 24%) and 21-50 nm (PS: 37%; CP: 36%). Such unique mesopore size distribution

e-ISSN 2289-7771 Copyright © 2016 JASPE



would be useful to capture medium molecular size pollutants such as dyes (methylene blue: $1.63 \text{ nm} \times 0.79 \text{ nm} \times 0.4 \text{ nm}$; orange G: $1.56 \text{ nm} \times 1.01 \text{ nm} \times 0.54 \text{ nm}$; etc.). Theoretically, these pollutants would not be able to lodge on the narrow micropore channels due to their effective molecular size larger than the pore diameter. It was also reported that the mesopore channels could enhance the affinity (attractiveness) of copper(II) to the surface of adsorbent [13].

The results demonstrate that the mesoporous material could be prepared by treating the local waste products with zinc chloride. The resultant materials are highly mesoporous, and exhibit comparable mesopore volume with the mesoporous materials found in the literature [10 and references therein]. Such textural characteristics are generally recommended for possible applications as catalyst support and adsorbent [9-10]. Nevertheless, further work would be required to evaluate the effectiveness of the waste-derived mesoporous materials for specific applications.

4. Conclusion

Highly mesoporous materials were prepared from the local waste products, namely sludge of palm oil mill effluent and waste carbon powder. Both treated materials possess average pore width within the lower limit of mesopore regime, and having the mesopore volume comparable with commercial activated carbon and other mesoporous materials. The study offers some insight on the possibility of converting the solid wastes into mesoporous materials for potential utilization as adsorbent and catalyst support. Yet, further investigation would be recommended to establish the effectiveness of the derived mesoporous materials for specific applications.

Acknowledgements

This work was supported by Universiti Teknologi Malaysia and Malaysia Ministry of Higher Education through Flagship Grant #03G07.

References

- [1] Manaf, L.A., Samah, M.A.A., and Zukki, N.I.M. (2009). Municipal solid waste management in Malaysia: Practices and challenges. *Waste Management*, *29*, 2902-2906.
- [2] Ng, W.P.Q., Lam, H.L., Ng, F.Y., Kamal, M., and Lim, J.H.E. (2012). Waste-to-wealth: green potential from palm biomass in Malaysia. *Journal of Cleaner Production*, *34*, 57-65.
- [3] Mumtaz, T., Yahaya, N.A., Abd-Aziz, S., Rahman, N.A.A., Yee, P.L., Shirai, Y., and Hassan M.A. (2010). Turning waste to wealth-biodegradable plastics polyhydroxyalkanoates from palm oil mill effluent: A Malaysian perspective. *Journal of Cleaner Production*, *18*, 1393-1402.
- [4] Nogueira, T.A.R., Franco, A., He, Z., Braga, V.S., Firme, L.P., and Abreu-Junior, C.H. (2013). Shortterm usage of sewage sludge as organic fertilizer to sugarcane in a tropical soil bears little threat of heavy metal contamination. *Journal of Environmental Management*, *114*, 168-177.
- [5] Smith, K.M., Fowler, G.D., Pullket, S.,and Graham, N.J.D. (2009). Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications. *Water Research*, *43*, 2569-2594.
- [6] Yague, A., Valls, S., Vazquez, E., & Albareda, F. (2005). Durability of concrete with addition of dry sludge from waste water treatment plants. *Cement and Concrete Research*, *35*, 1064-1073.
- [7] Kumar, S., Bhattacharyya, J.K., Vaidya, A.N., Chakrabarti, T., Devotta, S., and Akolkar, A.B. (2009). Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: An insight. *Waste Management*, 29, 883-895.
- [8] Kumar, P., and Guliants, V.V. (2010). Periodic mesoporous organic–inorganic hybrid materials: Applications in membrane separations and adsorption. *Microporous and Mesoporous Materials*, 132, 1-14.

e-ISSN 2289-7771 Copyright © 2016 JASPE



- [9] Hamoudi, S. Saad, R. and Belkacemi, K. (2007). Adsorptive removal of phosphate and nitrate anions from aqueous solutions using ammonium-functionalized mesoporous silica. *Industrial & Engineering Chemistry Research.*, *46*, 8806-8812.
- [10] Shen, Y., Zhao, P. and Shao, Q. (2014). Porous silica and carbon derived materials from rice husk pyrolysis char. *Microporous and Mesoporous Materials*, *188*, 46-76.
- [11] Zaini, M.A.A., Okayama, R. and Machida, M. (2009). Adsorption of aqueous metal ions on cattlemanure-compost based activated carbons. *Journal of Hazardous Materials*, *170*, 1119-1124.
- [12] Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., and Siemieniewska, T. (1985). Reporting physisorption data for gasrsolid systems with special reference to the determination of surface area and porosity. *Pure & Applied Chemistry*, *57*, 603-619.
- [13] Zaini, M.A.A., Che-Yunus, M.A., Mohd.-Setapar, S.H., Amano, Y. and Machida, M. (2013). Effect of heat treatment on copper removal onto manure-compost-activated carbons. *Desalination and Water Treatment*, *51*, 5608-5616.

Authors



Muhammad Abbas Ahmad Zaini

Muhammad Abbas Ahmad Zaini obtained a PhD in Applied Chemistry from Chiba University Japan in 2010, and currently serves as a senior lecturer at the Department of Chemical Engineering, Universiti Teknologi Malaysia (UTM). His research interests include (microwave-assisted) preparation and characterization of activated carbons/adsorbents for dyes, heavy metals and oil removal from water.

