PREPARATION AND CHARACTERIZATION OF HIGH SURFACE AREA ACTIVATED CARBONS FROM PALM SHELLS SUITABLE FOR ADSORPTION OF HIGHER MOLECULAR WEIGHT COMPOUNDS

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Introduction

Utilization of biomass for production of porous carbons is well established industrially, as the demand is abundant due to varied industrial application. Activated carbons with highly developed surface area are widely used in a variety of industries for applications which include separation/purification of liquids and gases, removal of toxic substances, as catalysts and catalyst support [1, 2]. Activated carbons have been traditionally produced by the partial gasification of the char either with steam or CO_2 or a combination of both. Usually the physical activation is a two-step process which involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, or their mixtures. In chemical activation process the precursors are impregnated with dehydrating chemicals such as H_3PO_4, $ZnCl_2$, K_2CO_3, NaOH or KOH and carbonized at desired conditions in a single step. Chemical activation offers several advantages which include single step activation, low activation temperatures, low activation time, higher yields and better porous structure.

A detailed summarization of the number of studies pertaining to preparation of activated carbon using palm shells utilizing physical, chemical and combination of physical and chemical activation methods as well as the properties of the resulting PSAC has been due to Srinivasakannan et al [3]. It can be observed that majority of the work reports only about the pore characteristics without mentioning the corresponding yield. Among the reported literature the yield of activated carbon using physical activation methods is found to be less than 17%, with the activation temperatures around 900°C. While the combination of physical/chemical activation methods reports yield less than 30% with the activation temperatures of around 800°C, with an exception of $ZnCl_2/CO_2$ activation resulting in a yield of 37%. Among the chemical activation methods the K_2CO_3 activation produced a very low yield of 19%, while the phosphoric acid activation at 500°C resulted in a yield of 40%, which is significantly higher than the other activation methods and activating agents. It can be observed that the yield of activated carbon varied widely depending upon the processing methods. Induced by the result due to Guo and Lua [4], and the advantages of phosphoric based activation methods due to Srinivasakannan and Bakar [5] the present study attempts to explore further into the low temperature activation using phosphoric acid for conversion of palm shells in to activated carbon. The choice of low activation temperature and time is aimed at improving the process economics is also induced by the recent report due to Gratuito et al. [6].

Experimental

The palm shells are water washed to remove dirt and fibers. The cleaned shells are dried at 105°C in a hot air oven until it is completely dry, which are then crushed, sieved to obtain particle with size range 1-2 mm and stored in airtight containers for further experimentation. The experimental samples are prepared by mixing 20 grams of pre-dried palm shells with phosphoric acid based on impregnation ratio between 0.5 and 3. The impregnation ratio is defined as the ratio of weight of 100% phosphoric acid utilized for impregnation to the weight of the dry palm shells. A 65% phosphoric acid is utilized for soaking so as to promote the adsorption of reagents into the sample. The phosphoric acid soaked sample is left overnight in ambient environment and the excess water was evaporated in oven (100°C) to ensure complete absorbance of the phosphoric acid on to the palm shell powder. The acid soaked samples are semi-carbonized in a hot air oven at a preset furnace temperature of 170°C for 1h. The semi-carbonized material is activated in a muffle furnace for desirable activation condition at 425°C and 30 min. All activations are carried out by exposing the samples directly to 425°C without the flow of inert gas. After activation, the activated carbon is immediately quenched in distilled water before being manually grinded to fine powder. The samples are subsequently washed repetitively with distilled water to remove residual acid. The completeness of washing process is confirmed with the conductivity of wash liquor less than 50μS, using conductivity meter.

The activated carbon is characterized, for yield and iodine adsorption capacity and pore characteristics for the selected sample. Yield is defined as the ratio of weight activated carbon produced to the dry weight of precursor. Iodine number is defined as milligrams of iodine adsorbed by a gram of carbon, using the procedure as stated in ASTM [D4607-94(2006)]. Pore structure of the selected sample is characterized by nitrogen adsorption at 77K with an accelerated surface area porosimetry system (Autosorb-1-C, Quantachrome).

Results and Discussion

Figure 1 shows the effect of impregnation ratio on the yield of activated carbon while Figure 2 shows the effect of impregnation ratio on the iodine adsorption capacity of the activated carbon. An increase in the impregnation ratio do not show any tangible effect on the yield of activated carbon and the yield is found to be approximately around 50% for all the impregnation ratios. This indicates that the impregnation ratio do not alter the kinetics of the reaction between the carbon and the phosphoric acid. Similar study due to Guo and Lua [4] reported a decrease of yield with increase in activation temperature, while the effect of impregnation ratio was not

reported.

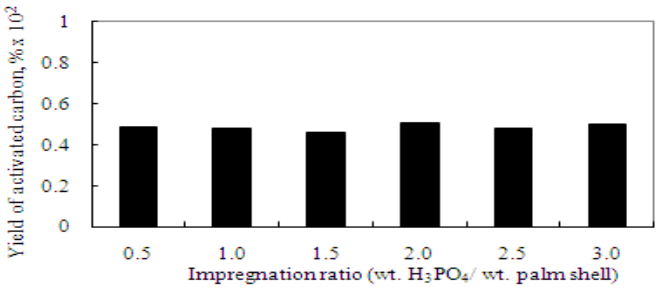
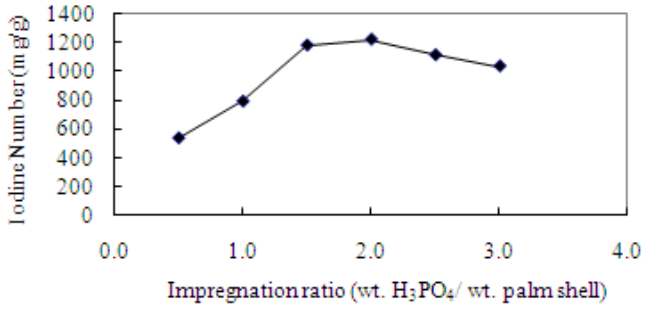
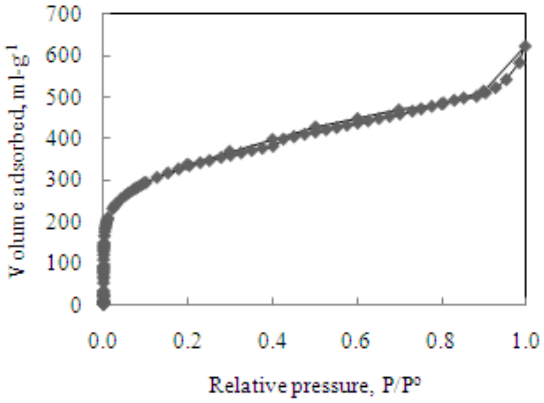


Figure 2 shows an increase in iodine number with increase in the impregnation ratio, with the highest iodine number of 1210 mg/g corresponding to an optimum impregnation ratio of 2.



As the objective of present study is to evidence the ability of the phosphoric acid activation process to produce high yielding activated carbon with good textural characteristics, the BET surface area analysis of the sample corresponding to an impregnation ratio of 3 with an iodine number of 1035 mg/g was performed using a BET surface area analyzer. This sample was chosen as the relation between surface area and the iodine number is well established up to an iodine number of 1000mg/g. The BET surface area corresponding to the iodine number of 1035mg/g is estimated to be 1109m^2/g, with the pore volume is 0.903cm^3/g. Although the pore volume is significantly higher than that reported in literature, the surface area is comparable to the literature values owing to the high pore diameter. The average pore diameter is estimated to be 3.2 nm with the contribution of micropore volume being 50%. Figure 3 shows the nitrogen adsorption capacity of activated carbon with respect to the nitrogen relative pressure (P/Po). The sharp rise in the amount of nitrogen adsorbed at low relative pressures well indicates the amount of micro pores available with the activated carbon. The pore volume continued to progressively increase with increase in the relative pressure with a shape rise at high relative pressure. The progressive rise in pore volume indicates the availability of mesopores and the process of multilayer filling of the pores. The isotherm exhibits a pattern of type II isotherm, under the IUPAC classification of isotherms, based on the progressive increase in the adsorption capacity beyond the relative pressure of 0.1. The sharp rise beyond a relative pressure of 0.9 and formation of hysteresis loop, while desorbing indicate a type IV isotherm. This type of isotherm is a general characteristic of porous carbons that have large sized pores. The pore size distribution shown in figure 4 substantiates the amount of pores in the mesoporous range, with the average pore diameter estimated to be 3.2nm. The pore size distribution shows a twin peak in the micropore region, contributing nearly to the 50% of total pore volume.



Conclusions

The yield of activated carbon has not been found effected by the impregnation ratio at an activation temperature of 425°C and 30 minutes of activation time, while the the textural characteristic is found to improve with increase in the impregnation ratio up to 2.0, characterized by the iodine number of 1210 mg/g. The yield of activated carbon has been found to be around 50%, while the BET surface area of the activated corresponding to an iodine number of 1035 mg/g is estimated to be 1109m^2/g, with a pore volume of 0.903 cm^3/g, and an average pore diameter of 3.2 nm. The adsorption isotherm of the activated carbon indicate multilayer filling, characteristic of activated carbon with significant mesopores.

References

[1] Ribeiro AM, Loureiro JM, Simulation of toxic gases and vapours removal by activated carbon filters, Chemical Engineering Science 2002; 57:1621-1626.

[2] Fuente AM, Pulgar G, González F, Pesquera C, Activated carbon supported Pt catalysts: effect of support texture and metal precursor on activity of acetone hydrogenation. J. Applied Catalysis A: General 2001; 208: 35-46.

[3] Lim WC, Srinivasakannan C, N. Balasubramanian, Activation of palm shells by phosphoric acid impregnation for high yielding activated carbon. J. Analytical and Applied Pyrolysis, 2010; (in Press).

[4] Guo J, Lua AC, Textural and chemical properties of adsorbent prepared from palm shell by phosphoric acid activation. Materials Chemistry and Physics 2003; 80:114-119.

[5] Srinivasakannan C, Abu Bakar MZ,, Production of activated carbon from rubber wood sawdust. Biomass Energy 2004; 27: 89-96.

[6] Gratuito MKB, Panyathanmaporn T, Chumnanklang RA, Sirinuntawittaya N, Dutta A, Production of activated carbon from coconut shell: Optimization using response surface methodology, Bioresource Technology. 2008; 99:4887-4895.