# Activated Carbons Prepared from Biomass Solid Waste and their Applications for Gaseous Pollutant Removal

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**Abstract:** Activated carbons were prepared from abundantly-available biomass solid wastes, *e.g.*, oil-palm shell, pistachio-nut shell, and bamboo, by thermal or chemical activation method. Characterizations were carried out by an accelerated surface area and porosimeter and a Fourier transform infrared spectrometer. Dynamic adsorption of pollutant gases ($SO_2$, $NH_3$, or $H_2S$) was conducted to test the adsorptive capacities. Static adsorption was carried out to verify the occurrence of chemisorption and/or oxidation of gases. It was found that impregnation with different agents had significant effects on the surface functional groups of the activated carbons, which were closely related to the adsorptive capacity of the activated carbons. Besides physisorption, $NH_3$ or $H_2S$ could be adsorbed onto active adsorption sites provided by oxygen functional groups *via* hydrogen bonding. $H_2S$ might be also oxidized, resulting in elemental sulphur attached onto the surface of the activated carbon.

**Key words:** activated carbon; biomass solid wastes; sulphur dioxide; ammonia; hydrogen sulphide

## 1 Introduction

Activated carbons are widely used as adsorbents for the removal or reduction of pollutants from the exhaust gases of industrial sources such as power stations, kilns, smelters, and acid production plants. A large number of biomass solid wastes, such as oil-palm shell, pistachio-nut shell, and bamboo have been successfully converted into activated carbons by carbonization, followed by either physical or chemical activation[1]. Chemical activation may generate a secondary environmental pollution due to the use of some chemicals (*e.g.* zinc chloride $ZnCl_2$, potassium hydroxide KOH, phosphoric acid $H_3PO_4$ or sulfuric acid $H_2SO_4$) as activating agents[2]. The physical process usually involves two stages, *i.e.* carbonization and activation. In the first stage, the starting materials are carbonized at a moderate temperature (700 to 800°C) to remove the volatile matters and produce chars with rudimentary pore structures. Subsequently, in the second stage, the resulting chars are subjected to a partial gasification at a higher temperature (usually 900°C) with oxidizing gases, such as steam, carbon dioxide, air or a mixture of these, to produce final products with well-developed and accessible internal porosities. The adsorptive capacity of the activated carbon, which is related to its internal surface area, pore structure and pore size distribution, is largely determined by the nature of the starting material and the history of preparation[3].

## 2 Experimental

### 2.1 Adsorbent preparation

Biomass solid wastes (oil-palm shell, pistachio-nut shell, or bamboo) were dried, crushed and sieved to a particle size fraction of 1.0–2.0 mm. 10 g of this processed starting material was impregnated with 200 ml of $H_2SO_4$ or KOH at room temperature for 24 h and then dried overnight. The mixture was activated in a stainless-steel reactor under a stream of nitrogen gas. The reactor was heated in a vertical tube furnace from room temperature to a pre-set temperature (*e.g.* 900°C) for 0.5 to 2 h. After cooling to room temperature, the resulting products were taken out and leached with distilled water. In the comparative study, the preparation of activated carbons by thermal activation with carbon dioxide gas was also investigated.

### 2.2 Characterizations

Textural characteristics of samples were determined by $N_2$ adsorption at -196°C with an accelerated surface area and porosimeter (ASAP-2000, Micromeritics). The specific surface area was calculated from the isotherms by the Brunauer-Emmett-Teller (BET) equation. The Dubinin–Radushkevich (DR) equation was used to calculate the micropore volume from the adsorption data[4]. For general surface functional groups, the samples were studied by a Fourier transform infrared spectrometer (FTIR-2000, Perkin Elmer). By comparing to the standard frequency patterns, various characteristic chemical bonds (or stretchings) were determined, from which certain surface functional groups were derived.

### 2.3 Adsorption test

Dynamic adsorption of pollutant gases (*e.g.* $SO_2$, $NH_3$, or $H_2S$) was conducted in a copper column (10.0 mm i.d. and 20 cm long) filled with pre-dried activated carbons, which were retained on a metal mesh at the bottom of the column. The column was operated in the up-flow mode. Adsorbates from a gas cylinder were introduced to the inlet of the adsorption column at a certain volumetric flow rate. The time-dependent concentration at the exit of the column was continually monitored by a gas detector. The column was operated until saturation.

Static adsorption was carried out in a thermogravimetric analyzer (TGA-50, Shimadzu). Adsorbates were introduced into the analyzer chamber, where a platinum pan with the adsorbent was suspended. At room temperature, the subsequent sample weight gain due to the amount of gas adsorbed onto the adsorbent was recorded. After adsorption, desorption tests using He gas flushing through the analyzer chamber at the same temperature of adsorption and a higher temperature of 200$^o$C were conducted to verify the occurrence of chemisorption.

## 3 Results and Discussion

### 3.1 Adsorption of sulphur dioxide

Figure 1 shows the amounts of $SO_2$ adsorbed by the oil-palm shell activated carbons impregnated with 10% KOH and 30% $H_3PO_4$. Activated carbon impregnated with 30% $H_3PO_4$ had larger BET and micropore surface areas than that with 10% KOH. For a fixed $SO_2$ concentration of 2000 ppm and adsorption temperatures of 25 and 50$^o$C, the amount of $SO_2$ adsorbed by the sample pre-treated with 10% KOH was obviously larger than the one pre-treated with 30% $H_3PO_4$. This suggested that the adsorptive capacity of the chemically activated carbon was not only proportional to their surface areas, but also dependent on the impregnating agent used or the surface chemistry of the activated carbon.

The spectrum of the sample pre-treated with 30% $H_3PO_4$ solution displayed the following bands: 3608 cm$^{-1}$, free O–H stretches; 1725 cm$^{-1}$, C=O stretch in ketones; 1642 cm$^{-1}$, C=O stretch in acids; 1506 cm$^{-1}$, C=C stretch in aromatic rings; and 1219 cm$^{-1}$, C–OH stretch in alcohols. The main surface organic functional groups present were presumed to be phenols and carboxylic acids, typical acidic functional groups. These acidic functional groups are favorable for adsorbing alkaline gases but not acidic gases such as $SO_2$.

On the other hand, the spectrum of the sample impregnated with 10% KOH displayed the different bands: 1754 cm$^{-1}$, C=O stretch in ketones; 1503 cm$^{-1}$, C=C stretch in aromatic rings; 1251 cm$^{-1}$, C–O stretches; and 814/695 cm$^{-1}$, C–H out-of-plane bending in benzene derivatives. These bands were presumed to be alkaline groups of pyrones (cyclic ketone) and other keto-derivatives of pyran[5]. These functional groups contributed to the adsorption of $SO_2$ gas onto the activated carbons impregnated with KOH.

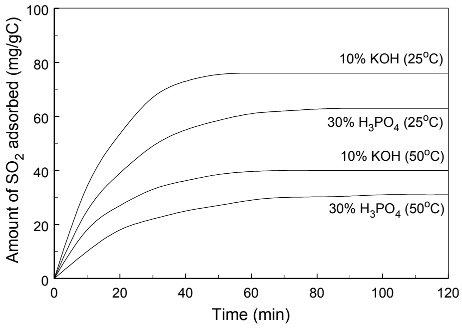

**Figure 1. Effect of impregnation on the amount of $SO_2$ adsorbed**

### 3.2 Adsorption of ammonia

The amount of ammonia ($NH_3$) adsorbed at 50$^o$C onto the palm-shell activated carbons prepared by thermal and chemical activation versus BET surface area is plotted in Figure 2.

For the palm-shell activated carbons prepared by $CO_2$ thermal activation, the amount of $NH_3$ adsorbed increases with increasing BET surface area. A linear relationship between the surface area and the adsorptive capacity is obtained. However, for the activated carbons prepared by $H_2SO_4$ activation, the data are dispersed, suggesting that the adsorptive capacity is not solely a function of the BET surface area. Similar observation was also reported by Lee and Reucroft[6] when they studied the adsorption of $NH_3$ onto the wood-base activated carbons prepared by phosphoric acid ($H_3PO_4$). Figure 3 shows the amount of $NH_3$ adsorbed onto these two samples at different temperatures. For the activated carbon prepared by thermal activation, the adsorptive capacity decreased with increasing adsorption temperature, which is a typical physisorption phenomenon due to the interaction of *van de Waals* forces between the adsorbate and the adsorbent. $NH_3$ adsorption onto the $H_2SO_4$-impregnated activated carbon shows a different trend. At a low temperature range, the adsorptive capacity decreased with increasing adsorption temperature, which suggests that physisorption be predominant. The decreases in adsorptive capacity were due to the partial desorption. On the other hand, adsorptive amount increased as the temperature further increasing from 60 to

80°C. This may be due to the occurrence of chemisorption. Finally, as the adsorption temperature further increases up to 100°C, the amount adsorbed decreases due to the exothermic nature of the adsorption processes.

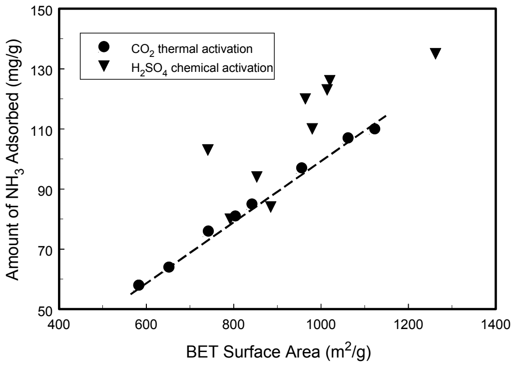

**Figure 2. Amount of $NH_3$ adsorbed onto the activated carbons**

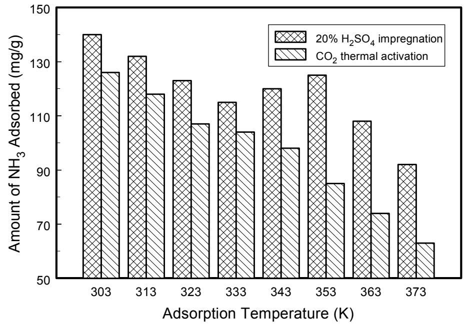

**Figure 3. Amount of $NH_3$ adsorbed at various temperatures**

During $NH_3$ adsorption, besides physisorption onto the pore surface due to *van de Waals* forces, chemisorption by forming hydrogen bonding also occurred such that:

$$[\ C_nH_xO_{y+3}\ ] + NH_3 \rightarrow [\ NH_3 \cdots O_{y+3}C_nH_x\ ] \qquad (1)$$

Hydrogen atoms in $NH_3$ could strongly interact with oxygen in form of hydroxyl (H–O) and carbonyl (C=O) groups due to the high electrostatic attraction. Their hydrogen bonding (N–H···O) energy has been reported to be as much as 3 kcal/mol. $NH_3$ can therefore preferably adsorb onto active adsorption sites provided by oxygen functional groups *via* hydrogen boding besides on pure carbon sites.

### 3.3 Adsorption of hydrogen sulphide

Hydrogen sulphide ($H_2S$) breakthrough curves for activated carbons prepared from palm-shell by different activation methods and a commercial coconut-based activated carbon are shown in Figure 4.

In a fixed bed for adsorption, the part that displays a gradient in adsorbate concentration from zero to equilibrium is called the mass transfer zone (MTZ). This is the active part of the bed where adsorption actually takes place. As the saturated part of the bed increases, the MTZ travels downstream and eventually exits the bed[7].

Compared to the palm-shell activated carbon by thermal activation and coconut-shell activated carbon, the activated carbons prepared by KOH and $H_2SO_4$ activation had better dynamic adsorption performances due to longer breakthrough times, prolonged exhaustion times, and relatively short MTZs. Therefore, the corresponding adsorption capacities were also larger. This suggests that the palm-shell activated carbons prepared by chemical activation are more capable for $H_2S$ adsorption.

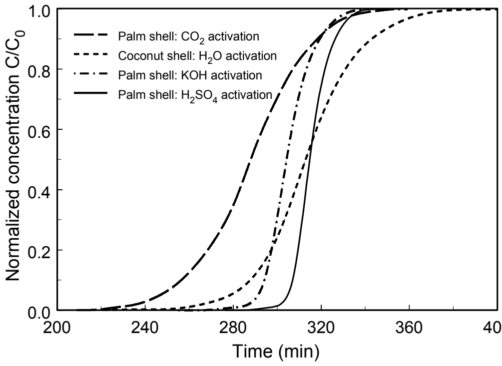

**Figure 4. $H_2S$ breakthrough curves for activated carbons**

For $H_2S$ adsorption, besides physisorption onto the pore surface due to *van de Waals* forces, chemisorption by forming hydrogen bonding also occurred such that:

$$[\ C_nH_xO_{y+3}\ ] + H_2S \rightarrow [\ C_nH_xO_{y+3} \cdots H_2S\ ] \qquad (2)$$

Hydrogen atom in $H_2S$ could strongly interact with oxygen in form of hydroxyl (H–O) and carbonyl (C=O) groups due to the high electrostatic attraction. $H_2S$ can therefore preferably adsorb onto active adsorption sites provided by oxygen functional groups *via* hydrogen bonds besides on carbon sites. In addition, due to the functional groups, $H_2S$ was easily oxidized as follows:

$$[\ C_nH_xO_{y+3}\ ] + H_2S \rightarrow [\ C_nH_xO_{y+2}\ ] + S_{\text{(element)}} + H_2O \qquad (3)$$

This may explain why there were still some residual weights on the carbon surface when desorption was carried out at up to 200°C. Some irreversible chemical reactions ($H_2S$ oxidization) occurred and indecomposable products (elemental sulphur) attached to the sample[8].

## 4 Conclusions

1） Comparing the activated carbon pre-treated with 30% $H_3PO_4$ with the sample pre-impregnated with 10% KOH, the former with larger BET and micropore surface areas had a lower adsorptive capacity for $SO_2$ than the latter. Impregnation with different agents had significant effects on their surface functional groups, which were closely related to the adsorptive capacity.

2） Adsorption tests showed that the amounts of $NH_3$ adsorbed onto the chemically activated carbons, unlike those prepared by $CO_2$ thermal activation, were not solely a function of the specific surface areas. $NH_3$ could therefore adsorb onto active adsorption sites provided by oxygen functional groups *via* hydrogen boding.

3） Besides physisorption, some $H_2S$ adsorbed by chemisorption via hydrogen bonding occurred. There were still some residual weights on the carbon surface when desorption was carried out at up to $200^oC$ since $H_2S$ oxidization resulted in indecomposable products of elemental sulphur attached to the activated carbon.

## Acknowledgements

The financial supports from Key Laboratory for Green Chemical Process of Ministry of Education Open Grant (GCP200803) and the Program for New Century Excellent Talents in University (NCET-05-0681) Ministry of Education, are highly appreciated.

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