Abstract—Highly porous activated carbon possessing surface oxygen- and nitrogen-containing functional groups is studied. Oil palm shell, byproduct of oil palm industry, is used as raw material. Activated carbon is prepared by pyrolysis process at 300 – 800°C using two steps process: under nitrogen and carbon dioxide. Prior pyrolysis raw material is impregnated with 85% phosphorus acid at 85°C for 24 h. The surface functional groups of the activated carbon are modified by acid and based treatments. Textural characteristics are determined by the nitrogen adsorption-desorption isotherms at 77 K. The maximum BET surface area is 1915 m²g⁻¹ consisting of micropore surface areas, 366 m²g⁻¹ and external surface areas, 1549 m²g⁻¹. The presences of Type I and IV isotherms with wide hysteresis loops indicated that the activated carbon consists of a mix micro- and mesopores. Surface oxygen- and nitrogen-containing functional groups on the surface activated carbon are determined FTIR and Boehm titration.

Keywords—Oil palm shell, Activated carbon, Micro- and mesopores, Surface oxygen- and nitrogen-containing functional group.

I. INTRODUCTION

HIGHLY porous activated carbon is effectively used as adsorbents, catalysts and catalyst supports [1]. In its application, the activated carbon should be supported by the performance of adsorptive capacity such as specific surface areas, pore volumes and pore size distributions as well as surface functional groups [2]. Basically, pore can be classified into three classes: micropores (diameter < 2 nm), mesopores (diameter 2 – 50 nm) and macropores (diameter> 50 nm) [3]. The effort to enlarged pore size distribution consisting of a mix micropores and mesopores is crucial to maximize its application in adsorption process.

Surface chemistry of the activated carbon mainly contains heteroatoms of the surface functional groups such as oxygen, nitrogen, hydrogen etc. These functional groups are strongly bonded to the edged of surface activated carbon and govern the performance on its application [4]. In its application, the heteroatoms are widely used in the catalytic reactions, chemisorption and chemical reaction processes [5]. Among the heteroatoms, the surface oxygen-containing functional groups are widely recognized for heavy metals removal in aqueous solution [6, 7].

Oil palm shell byproduct is usually burned off as solid fuel in the boiler system to produce low-energy resources and electricity or they are discarded at open are around the mills either. Actually, both activities are unfavorable to the environments [8]. However, only little information is available concerning the information of pore structure and surface chemistry of activated carbon. In order to make better understand of performance of activated carbon, it is proposed to prepare and characterize the activated carbons from oil palm shell byproduct using 85% phosphoric acid with two-step process. The pore structures were analyzed by Quantachrome Nova 2200e. Determination of surface area, pore volume and pore size distribution are carried out by the BET, t-plot and BJH method. Surface chemistry of the activated carbons was modified with steam, 10 M nitric acid and 50% urea solution. Determination of surface functional groups is carried by FTIR and Boehm titration method.

II. MATERIAL AND METHOD

A. Preparation Activated Carbon

Approximately 250 g of sample with particle size 0.5 – 1.5 mm was impregnated in 500 ml of 85% phosphoric acid. The mixture was refluxed in water bath and stirred at 85°C for 24 h. Thereafter, sample was filtered, washed with hot water and dried in oven at 120°C for 24 h. Preparation of activated carbon was carried out by two steps. In the first step, the H₃PO₃ impregnated sample was loaded into stainless steel reactor and carbonized in the graphite furnace under purified nitrogen flow of 200 cm³min⁻¹. Carbonization process was set up at different activation temperatures in the range of 300-800°C with a contact time 3 h in each of process. The yield of activated carbon was washed with hot water and added 5 M HCl solution until pH 6-7 and dried in oven at 120°C. In the second step, the dried activated carbon was carbonized according to the first procedure using carbon dioxide instead of nitrogen and contact time was set up for 1.5 h.

B. Characterization

1. Nitrogen Adsorption-Desorption isotherms

The nitrogen adsorption-desorption isotherms of the activated carbon were obtained from by pore size analyzer (Quantachrome NOVA 2200e) at temperature of 77 K. Prior

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analysis, the activated carbon was dried in oven at 120°C for 24 h and followed by degassing at 200°C for 8 h. The determination of surface areas was calculated by the BET (Brunauer–Emmett–Teller) method, the total pore volumes were measured at maximum relative pressure. The t-plot method was carried out to measure the micropore volume, micropore surface area and external surface area. The average mesopore distribution was determined by the BJH (Barret–Joyner–Halenda) method.

2. Surface Chemistry Modification

The highest surface area of the activated carbon was used as a model for studying their surface chemistry. Each of the activated carbon was immersed into 10 M nitric acid and 50% urea solution for 24 h. After filter, the activated carbon was carbonized at 400°C under purified nitrogen for 1 h as contact time. The result was indentified using FTIR and Boehm titration method.

III. RESULT AND DISCUSSION

A. The Nitrogen Adsorption-Desorption Isotherm

Fig. 1 shows the curves of nitrogen adsorption-desorption isotherms of the activated carbons obtained at 77 K. It was clearly shown that the curves were gradually changed with increasing the activation temperatures starting from 300 to 700°C and sharply decreasing at 800°C. The curves of adsorption isotherms sharply increase at low relative pressure and gradually increase to maximum relative pressure. These curves show a mix of the Type I and IV isotherm, characterizing the micro- and mesopores. The formation of hysteresis loops at relative pressure at higher than 0.4 indicates the essential multilayer adsorption process characterizing the mesoporous structures [9]. However, at temperature 800°C, the curve of activated carbon sharply decreased due to the effect of excessive heat energy at higher activation temperature. The overheating energy treatment has damaged pores formation followed by blocking pores. Consequently, the wall of pores is broken and blocked the entering pores. As a result, the adsorbates (nitrogen) are restrained inside the pores during the desorption process [10]. At temperature 300°C, the curve is in the lowest position indicating a poor-developed porous structure. It may be due to the insufficient heat energy treatment during the carbonization process.

B. Surface Area

Determination of surface areas were carried out by BET method at relative pressure in the range of 0.04 - 0.35. Table 1 summarizes the textural characteristics of the activated carbon obtained at different activation temperatures. It is clearly shown that the improvement of surface area is influenced by the activation temperatures. At 300°C, the surface area is low due to insufficient heat energy for pore formation. Therefore, the volatile matters of the raw materials are still blocked inside the porosity. Increasing the activation temperature to 700°C produces the highest surface area. In contrast, at 800°C, the surface area sharply decreased which may be caused by the excessive heat treatment. The walls of porosities were broken and closed the mouth of pores.

The micropore surface area and external surface area, therefore, were obtained by t-plot method. The external surface areas consist of the mesopores and macropores in the activated carbon [11]. The results showed that the higher external surface areas, the more mesopores are available in the activated carbon. The results was also confirmed with the presence of wide hysteresis lops.

![Image](image_url)

Fig. 1 Nitrogen adsorption-desorption isotherms at 77K

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>SA (m²g⁻¹)</th>
<th>t-plot</th>
<th>Micv, MSA, ExtSA (m²g⁻¹)</th>
<th>Tmes, Mesv (m³g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>695</td>
<td>0.22</td>
<td>514, 180</td>
<td>0.39, 0.17</td>
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<tr>
<td>400</td>
<td>1220</td>
<td>0.18</td>
<td>367, 853</td>
<td>1.50, 1.32</td>
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<tr>
<td>500</td>
<td>1437</td>
<td>0.14</td>
<td>295, 1142</td>
<td>2.25, 2.11</td>
</tr>
<tr>
<td>600</td>
<td>1333</td>
<td>0.13</td>
<td>256, 1077</td>
<td>1.64, 1.51</td>
</tr>
<tr>
<td>700</td>
<td>1915</td>
<td>0.17</td>
<td>366, 1549</td>
<td>1.80, 1.63</td>
</tr>
<tr>
<td>800</td>
<td>621</td>
<td>0.02</td>
<td>44, 577</td>
<td>0.64, 0.62</td>
</tr>
</tbody>
</table>

T, Temperature (°C); SA, Surface Area (m²g⁻¹); Micv, Micropore volume (cm³g⁻¹); MSA, Micro pore surface area (m²g⁻¹); ExtSA, External surface area (m²g⁻¹); Tmes, Total pore volume (cm³g⁻¹); Mesv, Mesopore volume (m³g⁻¹).

C. Pore Volume And Pore Size Distribution

The t-plot method was used to calculate micropore volume of activated carbons. The total of pore volumes was obtained at relative pressure 0.99. The differences of total pore volumes and micropore volumes could be assigned to the present mesopore volumes of the activated carbon. As results shown in Table 1, mesopore volume is much higher than micropore volume which indicated that the activated carbons have predominantly mesoporous structures.

Pore size distributions of the activated carbon prepared by phosphoric were determined by the BJH method. Fig. 2 shows the BJH plots of pore diameter ranging from 1 to 100 nm. As seen in the figure, most of pore diameters are concentrated between 2 – 50 nm indicating the present mesopores [12]. It can be assumed that preparation of activated carbon by phosphoric acid provided wide pores consisting of predominantly mesoporous activated carbon.
D. The Surface Chemistry of Activated Carbon

The activated carbon prepared at 700°C possessing the highest surface area was selected for study of their surface functional groups. Prior analysis, the surface functional groups of the activated carbon were decomposed during pyrolysis process over a wide range of activation temperatures.

The treatments of the activated carbon using steam, nitric acid and urea have increased the intensity of the FT-IR spectra of activated carbon. The bands 3414 cm\(^{-1}\) are assigned to O – H stretching vibration in hydroxyl groups for steam and nitric acid treatments, but it is also strongly associated with N-H stretching vibration in amine groups for urea treatment. The weak bands between 2912 and 2848 cm\(^{-1}\) observed at the carbon dioxide and nitric acid were attributed to asymmetric and symmetric C–H stretching vibration in aliphatic groups and showed a good overlap with the N-H stretching vibration of amine, for urea treatment. A new band at 1708 cm\(^{-1}\) from the nitric acid is assigned to C=O stretching vibration in ketones, aldehydes or carboxylic groups [13]. A strong band at 1635 cm\(^{-1}\) which was obtained under urea treatment could be assigned to C=O stretching vibration and strongly associated with C=N stretching vibration in pyridine and amide structures. A band at 1562 cm\(^{-1}\) on the nitrogen, carbon dioxide, nitric acid and steam is assigned to C=C stretching vibration in aromatic rings, and C=N stretching vibration which is due to the urea treatment. A band at 1385 cm\(^{-1}\) was only obtained under urea treatment and it can be attributed to the plane N-H bending vibration [14, 15]. A band at 1098 cm\(^{-1}\) is attributed to C-O stretching vibration in hydroxyl and phenol groups. Combination of bands at 1798 and 1098 cm\(^{-1}\) suggested that it is predominantly carboxylic groups. However, this band may overlap with the presence of a phosphate ester groups which is attributed to hydrogen-bonded P=O in phosphate ester, to O-C bond in P-O-C (aromatic) linkage and to P=OOH [16]. For urea treatment, a band at 1098 cm\(^{-1}\) is attributed to N-O stretching vibration. A band at 647 cm\(^{-1}\) is assigned to N-H stretching vibration in cyclic amide groups. By comparing the FT-IR spectra, the surface modification for activated carbons under steam and nitric acid provided more surface oxygen containing functional groups as acidic surface functional groups. Conversely, the nitrogen surface functional groups were observed at activated carbon prepared by urea modification.

E. Boehm Titration

The activated carbon prepared at 700°C was used as reference for surface functional modification. Table 2 shows that the reference activated carbons (PC) have 0.03 and 0.05 meq g\(^{-1}\) for carboxylic and phenolic groups, respectively. However, after treating with nitric acid (PN), the results show an increasing number of carboxylic, lactonic and phenolic groups. It indicated that introducing nitric acid to the reference has extended the number of oxygen functional groups such as O – H, C = O, and C-OH [Huanga et al. 2009]. This result is also relevance with the FTIR spectra of the activated carbon under nitric acid. In contrast, the activated carbon treated with urea (PU) show a decreasing the number of acid groups, with the exception carboxylic groups. The decreasing of total acid group on the activated carbon treated with urea may be caused by the present surface nitrogen-containing functional groups as basic groups.

IV. Conclusion

Oil palm shell byproduct is a good raw material for preparation of highly porous activated carbons using phosphoric acid as activating agent. The maximum BET surface area is 1915 cm\(^2\) g\(^{-1}\) at 700°C. Pore size distributions of the activated carbon are predominantly mesoporous structures. Modification of the activated carbon with steam and nitric acid provided more surface oxygen-containing surface functional groups as acidic groups.
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