Characterization and evaluation
agricultural solid wastes as adsorbents:
A review

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ABSTRACT
At adsorption field, adsorbents characterization is very important factor that can identify the effectiveness of material as adsorbent. Scanning Electron Microscopy (SEM), Fourier Transforms Infrared Spectroscopy (FTIR), Elemental Analysis (EA) and BET-N2 adsorption/desorption are the most important analysis need to be done on the adsorbent before starting the adsorption test. These analyses help to characterize the physical and chemical surface properties of material and then its suitability as adsorbent. Furthermore these analyses play important roles in the adsorption mechanism and capacity.

Keywords: Characterization; evaluation; adsorbents; adsorption; review

1. Introduction
Characterization of physical and chemical surface properties of adsorbent has become one of the most important issues in adsorption technology because it determines its suitability for one or more of the application fields (Karakas et al., 2004). Characterization of adsorbents at adsorption fields can play an important role of adsorption process in term of adsorption capacity of adsorbents. Earlier characterization of adsorbents can predict the adsorbent efficiency. Each analysis may give single property that effect on adsorption process positively or negatively, furthermore the effect of property relate to the adsorbate type (dyes, phenols,
metals, etc). Therefore set of analysis should be done on adsorbent to characterize the physical and chemical surface properties of adsorbent. At the end of the day can be decide the effectiveness of material as adsorbent and its suitability for adsorption field.

Agricultural solid wastes have been many attempts to find inexpensive and easily available adsorbents to remove the pollutants. According to the physico-chemical characteristics and low cost of the agricultural solid wastes, they may be good potential adsorbents (Rafatullah et al., 2010). Within the last few years many ideas have been introduced in order to properly dispose of these wastes, such as intensive use as adsorbents for pollutant removal especially for dye removal where it showed high adsorption capacity (Noeline et al., 2005). Agricultural wastes are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment (Franca et al., 2009). Researchers also used carbon derived from different agricultural solid wastes to be used as adsorbents (Mahmoud et al., 2012). Different factors affect on adsorption process, such as pore structure, adsorbent properties and surface chemistry. Relation between the chemical compositions of adsorbent and elemental analysis is important. Studying the shapes of the isotherm curve and hysteresis can be used to infer distribution, shape and structure of the pores inside adsorbent differences in surface structure features of activated carbon prepared from various raw materials (Tseng, 2007). Adsorption capability of adsorbent usually related with its physical and chemical properties such as BET surface area and functional groups. The porous structure may facilitate the efficiency of dye adsorption onto the surface of the biomass.

2. Characterization

2.1 Scanning electron microscopy (SEM)

SEM analysis usually used to study the surface texture of adsorbent and to determine morphology of adsorbents surface. It produces high images of resolution and allows greater depth of focus on three dimensional solid samples.

Rebitanim et al., (2012) studied the adsorption of methylene blue dye using oil palm empty fruit bunch, and they found that The SEM image from the scanning electron micrographs shows apparent voids and large pores (Fig. 1).

Amin, (2009), studied the adsorption of direct blue-106 dye using pomegranate peel carbons. Scanning electron micrograph of activated carbon prepared from pomegranate peel. The activated carbons prepared by physical activation (PC1), treating with ZnCl₂ and H₃PO₄ (PC2) and treating with H₃NO₃ (PC3). SEM analysis showed that, activated carbons appear to have numbers of pores.

The numbers of heterogeneous pores provide high possibility for dye to be trapped and adsorbed.
Fig. 1 Scanning electron micrograph of oil palm empty fruit bunch (Rebitanim et al., 2012)

Fig. 2 Scanning electron micrograph of activated carbon prepared from pomegranate peel. (a) PC1. (b) PC2. (c) PC3 (Amin, 2009)
2.2 Fourier Transforms Infrared Spectroscopy (FTIR)

The characterization of the surface functional groups of the adsorbents is important to determine the type of functional groups in the adsorbents. The FTIR spectra are recorded in the region of 4000-400 cm\(^{-1}\). The presence, concentration of surface functional groups and chemical compositions play important roles in the adsorption mechanism and capacity (Tseng, 2007; Wu and Pendleton, 2001).

The carboxyl and hydroxyl groups are the major functional groups in the adsorption of cationic dyes. Carboxyl group bearing negative charge inhibited the adsorption of anionic dyes, while hydroxyl group is important functional group in the adsorption of anionic dyes (Gong et al., 2005).

Tan et al., (2008) used acid treated oil palm shell carbon to remove methylene blue dye. They found that the FTIR spectra were: 3572 cm\(^{-1}\) (O–H stretching vibrations in carboxylic acid), 2278 cm\(^{-1}\) (C C stretching vibrations), 1236 cm\(^{-1}\) (C–O–C stretching vibrations in ether) and 664 cm\(^{-1}\) (C–Cl stretching vibrations in chloro). Related to the presence of carboxyl and hydroxyl groups, the adsorption capacity was relatively high (303.03 mg/g).

Foo and Hameed, (2012a), studied the removal of methylene blue dye using oil palm shell activated carbon, and the FTIR results showed presence of hydroxyl groups, N–H derivatives and COOH dimmer, thus the adsorption capacity was 133.13 mg/g.

2.3 Elemental analysis

The analysis of the elemental constituents in materials can be done using a CHNS/O Analyzer. Measurements of elemental analysis can be employed for understanding chemical properties of activated carbon.

Dalia et al., (2011), studied the adsorption of methylene blue using acid treated kenaf fibre char. The CHNS/O results showed that the percentage of carbon, hydrogen and oxygen increased after treatment thus adsorption removal increased from 65 to 74%. Increasing of the oxygen and hydrogen content, indicate that more activated sites became available (Liu and Zhang, 2009).

Reffas et al., 2010) studied the adsorption of methylene blue using coffee grounds carbon. The characterization showed lowest content of 6% Oxygen which indicate that the surface is less acidic as a result the adsorption capacity of basic dye was high.

2.4 The BET-N\(_2\) adsorption/desorption

The shape of adsorption/desorption isotherm can provide preliminary qualitative information on the adsorption mechanism as well as on the porous structure of carbon (Chen et al., 2011).

The BET surface area can be estimated from the adsorption isotherms using BET equations within the range of P/P\(_o\), from 10\(^{-6}\) to 1. Pore size distributions of the samples can also be estimate using the BET method. Fig. 3 show the five types of isotherms. Each of these types is observed in practice but by far the most common are types I, II and IV. Type I and II of the referred IUPAC classification, are associated with a combination of microporous and
mesoporous structures (Foo and Hameed, 2011b). Type IV isotherm is a general characteristic of porous carbons that have large sized pores and represent a typical mesoporous solid (Martín et al., 1994; Xin-hui, 2011). Type I isotherms indicate that the adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Type I isotherms are observed for the adsorption of gases on microporous solids whose pore sizes are not much larger than the molecular diameter of the adsorbate. Type II isotherms do not exhibit a saturation limit. Near to the first point of inflexion of such isotherms a monolayer is completed following which adsorption occurs in successive layers. Similarly type III isotherms, show a steady increase in adsorption capacity with increasing relative pressure. Type IV isotherms are similar to type II isotherms except that adsorption terminates near to a relative pressure of unity. Type V isotherms are similar to type III isotherms at low relative pressure but then a point of inflexion is reached and a saturation limit is approached as the relative pressure is further increased (Thomas and Crittenden, 1998). According to the IUPAC definitions, adsorbent pores are classified into three groups: micropore (size <2 nm), mesopore (2–50 nm), and macropore (>50 nm). Micropores can be divided into ultramicropores (width less than 0.7 nm) and supermicropores (width from 0.7 to 2 nm) (Wei et al., 2009).

Dalia et al., 2011, characterized the treated kenaf fibre char. The BET test showed that the pores in the mesoporous range with an average pore diameter of 3 nm and the isotherm (N2 – adsorption/desorption) showed the presence of a hysteresis loop which indicated an isotherm Type IV, as a typical mesoporous solid.

Foo and Hameed, (2011b), characterized the oil palm fiber activated carbon. The BET test showed that the isotherm was between type I and II of the referred IUPAC classification, which is associated with a combination of microporous and mesoporous structures.

Table 1 listed previous studies of the adsorption of different pollutant using agricultural based adsorbents. Adsorbents that have high surface area usually give high adsorption capacity. Table 1 clarifies the relation between the adsorption capacity and the surface area of adsorbent.
Fig. 3 Types of isotherms (Thomas and Crittenden, 1998).
Table 1 Previous studies of the adsorption of different pollutant using agricultural based adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>BET surface area (m²/g)</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell activated carbon</td>
<td>Methylene blue dye</td>
<td>2825</td>
<td>916</td>
<td>Cazetta et al., (2011)</td>
</tr>
<tr>
<td>Treated wheat straw</td>
<td>Basic brown1</td>
<td>9</td>
<td>16.21</td>
<td>Batzias et al., (2009)</td>
</tr>
<tr>
<td>Activated plum kernels</td>
<td></td>
<td>1887</td>
<td>1845</td>
<td>Tseng, (2007)</td>
</tr>
<tr>
<td>Date stones char activated carbon</td>
<td>Methylene blue dye</td>
<td>856</td>
<td>316.11</td>
<td>FOO Hameed, (2011)</td>
</tr>
<tr>
<td>Empty Fruit Bunch (EFB) char</td>
<td>Methylene blue (MB) dye</td>
<td>988.23</td>
<td>55.25</td>
<td>Rebitanim et al., (2012)</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>902</td>
<td>240.6</td>
<td></td>
</tr>
<tr>
<td>Apple pulp activated carbon</td>
<td>Pb</td>
<td>1067.01</td>
<td>15.96-17.77</td>
<td>Depci, (2012)</td>
</tr>
</tbody>
</table>

3. Conclusion

This review is an attempt to highlight the important of the characterization study that can be done on material to identify the suitability of this material to be used as adsorbent. The review showed the effect of the physical and chemical properties on to adsorption capacity of adsorbent. Materials that supposed to be good adsorbents should have specific properties such as large and different pores, availability of the oxygen and hydrogen content, availability carboxyl and hydroxyl group and high BET surface area.

References


