EFFECT OF ACTIVATION PARAMETERS ON THE SURFACE AND MECHANICAL PROPERTIES OF ACTIVATED CARBON SPHERES

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ABSTRACT

Spherical activated carbon with micro porous structure has been prepared from phenolic resin spheres by carbonizing them at 850°C under the flow of nitrogen followed by activation in CO\textsubscript{2} atmosphere at different temperature for fixed duration and for different duration at fixed temperature. The effect of activation parameters such as temperature, residence time and CO\textsubscript{2} flow rate on the yield and surface properties of activated carbon spheres was studied. The effect of activation parameters on the mechanical properties of activated carbon spheres was also studied and correlated with surface properties of activated carbon spheres (ACS). The porosity of all activated samples was measured by physical adsorption of nitrogen at 77 K. The surface area was determined using multipoint BET equation and D-R method was used to determine the micro pore volume of activated carbon spheres. It was revealed from the experimental results that BET surface area and total pore volume increases with increasing residence time at constant temperature whereas mechanical strength of ACS decreases continuously on increasing residence time and activation temperature. BET surface area increases on increasing the activation temperature up to 950°C due to the creation of new micro pores and then decreases due to the widening of pores under the same experimental conditions.

KEYWORDS: Activated Carbon Sphere, Adsorption, Micro Pore Analysis & BET Surface Area

INTRODUCTION

Activated carbons have been commonly prepared from variety of carbonaceous materials such as wood, coconut shells, petroleum pitch, bituminous coal and polymers (Shrinivasakannan 2004; Wei 2003 & 2006; Lu 1992; Silvestre-Albero 2010 and Vilaplana-Ortego 2009) by carbonizing the carbonaceous material between 450°C to 850°C followed by physical activation/chemical process. Activated carbon exists in many forms i.e. powered activated carbon, granular activated carbon, palletized activated carbon, spherical activated carbon etc. Among all forms of activated carbons, spherical form i.e. activated carbon spheres (ACS) have many advantages as compared to the irregular shaped activated carbon such as the large surface area and high mechanical strength. Due to its spherical shape and rolling property, ACS can easily be filled uniformly and can be coated on the surface of any substrate to provide maximum exposure.

Babel 2006; Junbing 1999; Tang 2000; Qiong 2004; Qiao 2001 and Singh et. al. have focused their work on the synthesis of activated carbon sphere from synthetic polymers. Micro porous structure of activated carbon spheres is mainly responsible for adsorption capability of ACS against toxic gases. The micro pore structure of ACS can be controlled by controlling the activation parameters (Bing 2002; Marsh 1971 and Takshi 2003).

Apart from the activation parameters, porosity of activated carbon can also be controlled by catalytic gasification. Rodriguez-Reinoso et. al. 1991 pointed out one of the best approach to increase the meso and macro pore volume of activated carbon spheres.
In the recent years, the practice of treating the exhaust gas from combustion furnace with activated carbon has become a popular measure for preventing the public nuisance otherwise caused when exhaust gas containing oxides of sulphur and oxides of nitrogen is released into atmosphere. These particles (ACS) are useful in many applications such as ion selective resins. The carbonized microspheres of phenolic resin may be used as electrodes in Li-ion batteries. Activated carbon spheres are new generation material having a wide range of application in NBC (Neuclear, Biological and Chemical) suits, NBC Filters, NBC gloves and masks against toxic gases. Activated carbon spheres also find applications in the field of purification of chemicals and drugs, pollution control, treatment of potable water, solvent recovery and respirators meant for removal of toxic chemicals.

EXPERIMENTAL

Materials

Phenolic Resin Spheres (PRS) prepared from resole type phenolic resin by suspension polymerization technique were used as starting material for preparation of activated carbon spheres. Phenolic resin spheres were screened to a particle size of 0.43 to 0.85 mm and selected for the study.

Methods

Phenolic resin sphere of size 0.43 to 0.85 mm were subjected to carbonization at 800°C for 2 hrs soaking time in nitrogen atmosphere. The heating rate during carbonization was maintained at 1°C/min and the flow rate of nitrogen was maintained at 200 ml/min. The carbonized spheres were then activated at 925°C, 950°C, 975°C and 1000°C for different length of time. After optimization of activation temperature, carbonized sphere were activated at 950°C for 2 hrs using CO₂ as activating agent, with different gas flow rates. Carbonization and activation process were carried out using a rotary furnace having constant temperature zone of 100 mm diameter and 100 mm length.

Characterization

The pyrolysis behavior of phenolic resin spheres was determined by Thermo Gravimetric Analysis (TGA) using TG/DTA apparatus from M/s Perkin Elmer instruments. The heating rate was set at 5°C/min and flow rate of nitrogen was maintained at 200 ml/min.

Jeol make (Model-6380LA) Analytical Scanning Electron Microscope (SEM) was employed to study morphology of as such PRS, after carbonization and physical activation also.

Quantachrome make (Autosorb-1) was used to determine the porosity of all activated samples by physical adsorption of nitrogen on activated samples at 77K. Surface area and micro pore volumes of the samples were determined using BET and Dubnin-Radushevich (D-R) equations, respectively.

Mechanical strength: Mechanical strength is a most important and critical parameter for activated carbon spheres which indicate the capability to withstand the wear and tear of the adsorbent during end use applications. An apparatus for the testing of mechanical strength (crushing strength) of activated carbon spheres was fabricated as per ASTM C-695 standard. The ACS samples of average diameter 0.50 mm were selected randomly from a given batch and tested for their load resistance capacity.
RESULTS AND DISCUSSIONS

Thermal Degradation Behavior

Figure 1 shows the thermo gravimetric curve of phenolic resin spheres. The pyrolysis starts slowly at 100°C indicating the decomposition of phenolic resin spheres. A rapid weight loss occurs between 350°C to 550°C. Weight loss after 800°C is negligible indicating the end of carbonization process. The final pyrolysis yield of phenolic resin spheres up to 800°C obtained from TGA is found to be 66.7%.

![Figure 1: TGA Curve of Phenolic Resin Spheres](image)

Morphology

Figure 2(a), 2(b) & 2(c) show the SEM micrograph of as such PRS, carbonized spheres and activated carbon spheres. It is evident from SEM micrographs that size of spheres taken for the study are varying from 0.43 to 0.85 mm, besides that particles are of spherical shape with smooth surface.

![Figure 2(a)](image) ![Figure 2(b)](image) ![Figure 2(c)](image)

**Figure 2(a), 2(b) & 2(c): SEM Micrograph of as such PRS, Carbonized and Activated Spheres**

It is also clear from the SEM micrograph of phenolic resin sphere that no pore is visible after carbonization {Figure 2(b)} of phenolic resin spheres at 800°C for 2 hrs. soaking time. Probably, it is due to the tarry material produced during carbonization was deposited on the pores developed due to devolatilization, which were again reopened during activation process {Figure 2(c)}.

Carbonization and Activation Behavior

During carbonization, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of PRS and the free atoms of elementary carbon are grouped into organized crystallographic
formations. The yield after carbonization of PRS at 800°C for 2 hrs soaking time was found to be 58.5%. Thus obtained carbonized samples were activated at 925°C, 950°C, 975°C and 1000°C for different length of time. Table 1 shows the results of all activated carbon samples obtained using different set of activation conditions.

<table>
<thead>
<tr>
<th>Activation Conditions</th>
<th>Properties</th>
</tr>
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<tbody>
<tr>
<td>Temp., °C</td>
<td>Time, hrs.</td>
</tr>
<tr>
<td>925</td>
<td>3</td>
</tr>
<tr>
<td>950</td>
<td>5</td>
</tr>
<tr>
<td>975</td>
<td>2</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
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<td>975</td>
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<td>7</td>
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<td>950</td>
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<td>1000</td>
<td>2</td>
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<tr>
<td>925</td>
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</tr>
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Burn off of all activated carbon samples has been calculated on the basis of carbonized sample and yield was calculated on the basis of phenolic resin spheres. Yield of all activated carbon samples decreases as burn off increases indicating the gasification reaction of element carbon with CO\(_2\) to form carbon mono oxide.

**Nitrogen Adsorption Isotherm**

The adsorption isotherms of activated samples produced by activation at 950°C for different length of time are shown in Figure 3. In all the cases, maximum adsorption takes place in the low pressure region indicating that samples are predominantly micro porous in nature. Nitrogen adsorption in the higher-pressure region indicates the presence of mesopores.

**Figure 3: Adsorption Isotherm of Activated Carbon Spheres at 77K**

**Effect of Temperature**

To study the effect of temperature on the properties of activated carbon spheres, CO\(_2\) gas flow rate and the activation time was kept constant. The burn off increases and yield of ACS decreases on increasing temperature from
925°C to 1000°C from a value of 20.5% to 36.8% and 46.5% to 37.4%, respectively. Total pore volume of activated samples increases from a value of 0.3498 cc/g to 0.4360 cc/g on increasing the temperature from 925°C to 1000°C. It is due to the rate of reaction of element carbon with CO\(_2\) shifts towards forward direction on increasing temperature. Surface area and micro pore volume of activated samples (Fig. 4a & Fig. 4b) increase rapidly up to 950°C from 858 m\(^2\)/g to 960 m\(^2\)/g and 0.3331 cc/g to 0.3662 cc/g, respectively and then decreases slowly to a value of 941 m\(^2\)/g and 0.3524 cc/g at 1000°C, respectively. Increase in surface area and micro pore volume up to 950°C may be due to the creation of new micro pores and decrease in surface area and micro pore volume after 950°C may be due to the widening of pores. Fig. 4a & Fig.4b shows the graphical representation of effect of temperature on the properties of ACS.

Effect of Soaking Time

To study the effect of soaking time on the surface properties of activated carbon spheres, the gas flow rate and activation temperature during activation process were kept constant. It has been observed that the Yield of ACS decreases and the total pore volume increases from 41.5% to 15.9% and 0.4093 cc/g to 1.159 cc/g on increasing the activation time from 3 hrs. to 12 hrs., respectively. This is due to the continuous increase in porosity with respect to time. The surface area and micro pore volume also increases continuously from a value of 960 m\(^2\)/g to 2092 m\(^2\)/g and 0.3662 cc/g to 0.7221 cc/g, respectively on increasing soaking time due to the creation of new micro pores (Figure 5(a) & Figure 5(b)).
**Effect of Gas Flow Rate**

To study the effect of CO\textsubscript{2} gas flow rate during activation process on the micro porosity of activated carbon sphere, the activation time and temperature were kept constant. Fig. 6a & Fig. 6b shows the graphical representation of samples activated at 950°C for 2 hrs soaking time at different gas flow rate. It has been observed that the yield of ACS decreases and total pore volume increases slowly from 49.3% to 45.2% and 0.1925 cc/g to 0.3273 cc/g on increasing the gas flow rate from 100 ml/min to 500 ml/min, respectively. BET Surface area and micro pore volume also increase very slowly from a value of 447 m\textsuperscript{2}/g to 738 m\textsuperscript{2}/g and 0.1753 cc/g to 0.2878 cc/g, respectively on increasing the flow rate from 100 ml/min to 500 ml/min. The slow change in surface properties may be due to the excess amount of CO\textsubscript{2} remains un-reacted during activation process.

**Figure 6(a)**

**Figure 6(b)**

Figure 6(a) & 6(b): Effect of Flow Rate on the Properties of Activated Carbon Spheres

**Effect of Surface Properties on Mechanical Strength**

Crushing strength of activated carbon spheres is strongly dependent on the surface properties of. An adverse effect was observed on the crushing strength of activated carbon spheres on increasing activation temperature, activation time and the flow of activating gas. The crushing strength of activated carbon spheres decreases sharply as surface area, burn off, total pore volume and micropore volume increases. A graphical representation of crushing strength of ACS with respect to surface properties has been shown in Figure 7(a) & Figure 7(b).

**Figure 7(a)**

**Figure 7(b)**

Figure 7(a) & 7(b): Effect of Surface Properties on the Crushing Strength of Activated Carbon Spheres
Effect of Activation Parameters on the Surface and Mechanical Properties of Activated Carbon Spheres

DR Micropore Analysis

The microporosity of activated carbon spheres activated at 950°C for different length of time have been determined by DR equation given below:

\[
\log W = \log W_0 - m[\log(KP_0/P)]^2
\]

where, \( W \) represents the weight adsorbed at relative pressure \( P/P_0 \), \( W_0 \) is the total weight adsorbed in micropores, \( m \) is the slope of straight line and

\[
K = (Pc/P_0)(T/Tc)^2,
\]

where, critical pressure of adsorbate (mm Hg), \( P_0 \) is the saturated vapor pressure of adsorbate (mm Hg), \( T \) is the adsorption temperature (K) and \( T_c \) is the critical temperature of adsorbate (K).

![Figure 8: DR plot of Carbon Spheres Activated for different Length of Time](image)

Linearity of the DR plot between \( \log W \) versus \( \log^2(P/P_0) \) over a wide range of relative pressure \( P/P_0 \) shown in Fig.7 indicates narrow micropores are presents in all the samples of activated carbon spheres.

CONCLUSIONS

This study has demonstrated that activated carbon spheres with high surface area and high pore volume can be prepared from commercially available phenolic resin by controlling the activation conditions. BET surface area and micro pore volume of activated samples increase rapidly up to 950°C from 858 m²/g to 960 m²/g and 0.3331 cc/g to 0.3662 cc/g, respectively and then decreases slowly to a value of 941 m²/g and 0.3524 cc/g at 1000°C, respectively. Therefore, from this study, it was found that the optimum temperature for activation of phenolic resin spheres was 950°C. Activation of phenolic resin spheres at 950°C for 12 hrs soaking time found to have a surface area 2092 m²/g and total pore volume 1.159 cc/g. Total pore volume of activated samples increases from a value of 0.3498 cc/g to 0.436 cc/g on increasing the temperature from 925°C to 1000°C. Percent micro pore fraction of ACS increases when activation of PRS was carried out at relatively lower than the optimum temperature whereas it decreases when activation was carried out at relatively higher than the optimum temperature.

The BET surface area, micro pore volume and total pore volume increase from a value of 960 m²/g to 2092 m²/g, 0.3662 cc/g to 0.7221 cc/g and 0.4093 cc/g to 1.159 cc/g respectively on increasing soaking time from 3 hrs. to 12 hrs. Small variation in the surface properties of activated carbon spheres was observed with changing the gas flow rate during
activation process. Surface area and micro pore volume increase very slowly from a value of 300 m\(^2\)/g to 392 m\(^2\)/g and 0.1198 cc/g to 0.1583 cc/g respectively on increasing the gas flow rate from 80 ml/min to 800 ml/min.

The crushing strength of activated carbon spheres decreases sharply as surface area, burn off, total pore volume and micropore volume increases. The crushing was found to be greater than 2 kg/sphere at the surface area below 738 m\(^2\)/g. The crushing was found to be 0.953 kg/sphere at the highest surface area of 2092 m\(^2\)/g.

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