CHAPTER 2
CHAPTER 2

Characterization and Reactions of prepared Carbons

Section I
Characterization of Carbons

Section II
Reactions of Carbons

Publications:
Preparation and Characterization of activated carbons prepared from agro waste material cicerarientinum, communicated to Journal of Pharmacy Research.
Efficient route to synthesize triazoles using copper on carbon catalyst via click chemistry, communicated to Synthetic communications.
2.1 Section I

Characterization of Carbons

2.1.1 Introduction

Activated carbons prepared from agro waste material vary in their composition. It is dependent upon the raw material used, activation method employed. To make effective use of activated carbon in any application, it is important to analyse/characterize various properties of carbon. As carbon finds its major application in adsorption, analysing factors such as porosity, surface area and nature of surface functional groups is necessary. Carbon can also be used as catalyst support and in purification duties, so understanding impurities present in carbon becomes important.

It is known that carbon has surface functionalities, mainly oxygen, which improves the hydrophilicity of carbon, making it useful in applications such as catalyst support. pH of carbon determines the net charge on carbon and dictates its interaction with species being adsorbed on to its surface. Various characterization techniques, instrumental or classical, aid in proper understanding of intrinsic properties of carbon to be utilized.

Due to its high surface area and wide range of porosity, many inorganic salts can be deposited on carbon support. These form bonds with functional groups present on the surface and get fixed to carbon. Carbon provides good surface for these salts to spread up. Reactions conventionally carried out using only inorganic salts viz. oxidation, coupling, condensation and synthesis of triazoles via click chemistry, can be carried out on the salt (CuSO₄·5H₂O) deposited onto carbon support. This enables reduction in equivalents of salts required to carry out reactions.

Characterisation Techniques

Techniques such as electron microscopy, Nitrogen adsorption-desorption, FTIR and elemental analysis of by Inductively Coupled Plasma emission spectroscopy (ICP), are few of the instrumental techniques.
Laboratory methods such as pH, acid soluble matter, water soluble matter, Boehm's titrations are few of the classical tests.

2.1.1.1 Electron Microscopy

Electron Microscopy is a versatile technique used to obtain morphological information or to determine the size and shape of supported particles at a variety of magnifications. The process uses a focussed beam of electrons in the same way as an optical microscope uses light. It is the interaction between these electrons and the sample which leads to a number of detectable signals\(^1\).

Scanning electron microscopy detects the yield of either secondary or back scattered electrons as a function of the position of the primary beam, working in a similar way to a reflective light microscope and thus providing information on sample topography and morphology\(^2\). The secondary electrons have lower energies and originate from the surface of the sample with the contrast of the image arising from the orientation of the sample surface; surfaces facing the detector appear brighter\(^1\). Back scattered electrons come from deeper within the sample providing information on composition, as heavy elements scatter the beam more efficiently and thus appear brighter in the image. Schematic representation of the processes occurring in an electron microscope is presented (Fig. 2.1).

Fig. 2.1: Schematic representation of the processes occurring in an electron microscope.
The general working range for scanning electron microscopy is approximately \(10^2\) to \(10^3\) \(\mu m^2\).

2.1.1.2 Nitrogen Adsorption for Textural Analysis
Activated carbons are noted to have high surface areas and well developed porosity. These are important properties which can determine the activity of a supported catalyst. It is therefore, important to determine these properties, with the physical adsorption of nitrogen being a common method. The size of the nitrogen molecule is well documented and its extensive historical use makes it an ideal adsorbate. If the condition under which a complete adsorbed layer, averaging one molecule thick, can be established and the area covered per molecule is known, then the quantity of adsorbed nitrogen gives the total surface area of the sample.

An adsorption isotherm shows how the amount adsorbed depends upon the equilibrium pressure of the gas at a constant temperature and is quite simply a measure of the molar quantity of gas taken up at a constant temperature by an initially clean solid surface as a function of gas pressure. Convention has established that the quantity of gas is expressed as its volume at standard pressure and temperature, while the pressure is expressed as a relative pressure, which is the actual pressure divided by the vapour pressure.

2.1.1.3 Vibrational Spectroscopy
Various types of stretching and bending vibrations in molecules or in solid lattices are amplified by the absorption of photons (infrared spectroscopy) or by the scattering of photons (Raman spectroscopy). The related spectra are a plot of the intensity of absorption (IR) or scattering (Raman) as a function of the frequency \((1/\lambda)\) or wavenumber \((cm^{-1})\).

In the infrared technique the frequency of the incident radiation is varied and the quantity of radiation absorbed or transmitted by the sample is obtained. IR is an absorption spectroscopy technique.

There are particular difficulties in vibrational spectroscopy when dealing with activated carbon due to its highly absorbing nature. Thus special requirements
and modifications to a standard technique are made. One such modification is use of diffuse reflectance accessory.

**Diffuse Reflectance Infrared Fourier Transform Spectroscopy**

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) is the favoured technique for strongly scattering or absorbing particles as instead of relying on the transmission of an infrared beam, the beam is directed through a series of mirrors on to the surface of the sample. As the sample diffusely scatters the radiation it is collected in an ellipsoid mirror and directed to the amplifier via detector.

Another advantage is that the samples can be measured as loose powders, avoiding difficult and tedious wafer preparation. Schematic diagram of a DRIFTS cell is presented (Fig. 2.2).

![Schematic diagram of a DRIFTS cell.](image)

Infrared spectrum is then described using the Kubelka-Munk function (Equation 10)

\[
\frac{K}{S} = \frac{(1 - R_x)^2}{2R_x} \quad \text{(Equation 10)}
\]

where \(K\) is the absorption coefficient

\(S\) is the scattering coefficient
If the scattering coefficient does not depend on the infrared frequency the Kubelka-Munk function transforms the measured spectrum \( (R_\infty) \) into the absorption spectrum.

### 2.1.1.4 Elemental Analysis

Many elements such as Ca, Mg, Fe, Si are part of the plant materials which are raw materials for making activated carbons. Carbonization process does not remove these impurities. When carbon materials are heated to more than 1000°C, organic material is burnt off leaving behind metal oxides. These elemental impurities can be analysed by dissolving them into suitable acid and then aspirating the solution in ICP against calibration with solutions of known concentration.

### 2.1.1.5 Wet techniques for Surface Analysis

Surface oxygen groups accept or donate protons from aqueous solution. As a result of this, the pH of aqueous slurry can give an overall indication of the surface groups with regards to acidic or basic nature. pH can also depend upon the activating agent used to prepare carbon and sequencing of treatment.

Various elements present in the raw material become part of the ash content. Chemical treatments in activation reduce these metals to some extent. These elements can be extracted in water giving water soluble content while few more elements can be extracted using mild acid such as dilute hydrochloric acid. This can be found out by acid soluble content.

**Boehm’s titration** - The oxygen functionality on an activated carbon surface can be quantitatively identified using acid-base titration methods. The procedure, originally devised by Boehm et al, observes that bases of different strengths can be used to differentiate between acidic oxygen containing functional groups on the carbons surface. This is based on the relative pKa values whereby sodium bicarbonate can only neutralise groups with a pKa of less than 6.37, that is, carboxyl groups; sodium carbonate can neutralise groups with pKa of less than 10.25, that is, carboxyl and lactone groups;
sodium hydroxide neutralises groups with a pKa less than 15.74, that is

carboxyl, lactone and phenol groups. Basic surface groups are neutralised
using hydrochloric acid.

2.1.2 Review of Literature

Literature review was focused on techniques used for characterization of
carbons using classical methods as well as instrumental methods. It was
observed that general stress is to find out weight loss during carbonization
and activation routines. To understand intrinsic properties of the raw material
and prepared carbon, test such as Ash content, pH of carbon slurry, water
soluble content, acid soluble content, bulk density are performed.

Development of pore structure was studied by using Nitrogen adsorption-
desorption analysis. The increment in surface area is also tracked. SEM
photographs are useful to get further insight.

Effect of activation, in terms of surface functionalities is performed which is
many times supported with FTIR and sometimes with TPD analysis.

2.1.3 Present work

Intrinsic properties of the carbon were studied by carrying out test such as
bulk density, ash content, water soluble content, acid soluble content and pH.

Inorganic material causing ash content was determined by ICP. Inorganic
material causing ash content was determined by ICP. Inorganic material causing
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ICP. Inorganic material causing ash content was determined by ICP. Inorganic
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determined by ICP. Inorganic material causing ash content was determined by

The development of pores was followed by taking SEM photographs. Surface
area and pore distribution was carried out by nitrogen adsorption-desorption
isotherms and then applying various plot methods.

Effect of activation on development of surface oxygen functionalities was
carried out by Boehm’s titration. FTIR analysis was accomplished using
defuse reflectance method. Due to strong absorbance by carbon in IR region,
it is difficult to find well defined peaks.

2.1.4 Results and Discussion

Prepared carbons are characterized by both classical and instrumental
methods. These tests are useful to understand intrinsic properties such as
composition, morphology, surface functional groups etc. of carbon. It was
observed that, preparation methods have very high influence on the properties of the prepared carbons.

2.1.4.1 pH
Carbons prepared by pure thermal treatment show basic pH (about 10). It is because of the unsaturation at the edge of graphene lattice. Increase in carbonization temperature do not have significant effect on the pH. Chemically treated carbons show pH based on the chemical reagent used as activating agent. Carbons prepared by phosphoric acid have acidic pH while those prepared by potassium hydroxide exhibit basic pH. During pre-impregnation, impregnating reagent is well spread and is effectively washed as compared to mid impregnation. This causes the pH of mid impregnated carbons to be extreme as compared to pre impregnated carbons. pH of commercial carbon is in line with pre impregnated carbon viz. PIP. pH of various carbons are tabulated (Table 1).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>pH of 10 % Slurry in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>10.58</td>
</tr>
<tr>
<td>C800</td>
<td>10.75</td>
</tr>
<tr>
<td>PIP</td>
<td>5.35</td>
</tr>
<tr>
<td>MIP</td>
<td>1.97</td>
</tr>
<tr>
<td>PIK</td>
<td>8.97</td>
</tr>
<tr>
<td>MIK</td>
<td>10.39</td>
</tr>
<tr>
<td>COM1</td>
<td>3.85</td>
</tr>
</tbody>
</table>

2.1.4.2 Water Soluble content
Water soluble content is a result of various salts present in the carbon. There is increase in water soluble content as the final temperature of carbonization is increased. This is attributed to more loss of organic matter at higher temperature while inorganic salts remain stable. Treatment of RM or intermediate carbonized material shows decrease in water soluble content of the resultant carbon as these salts are washed away along with chemical
reagents during carbon preparation. This effect is predominant in pre impregnation as compared to mid impregnation. Water soluble content of various carbons are tabulated (Table 2).

Table 2: Water soluble content of carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Water soluble content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>3.82</td>
</tr>
<tr>
<td>C800</td>
<td>6.11</td>
</tr>
<tr>
<td>PIP</td>
<td>0.89</td>
</tr>
<tr>
<td>MIP</td>
<td>7.15</td>
</tr>
<tr>
<td>PIK</td>
<td>0.93</td>
</tr>
<tr>
<td>MIK</td>
<td>5.52</td>
</tr>
<tr>
<td>COM1</td>
<td>1.65</td>
</tr>
</tbody>
</table>

2.1.4.3 Acid Soluble content

Acid soluble content is more than the water soluble content, as expected. This is because acid can dissolve few more inorganic salts than pure water. Potassium hydroxide treated carbon show more acid soluble content than phosphoric acid treated carbon because of the presence of unwashed alkali. There is difference of 5 to 7 % between only carbonized and chemically treated carbons, with only carbonized material being on higher side. This is clear cut evidence of effectiveness of chemical reagents in removing inorganic matters. Acid soluble content of various carbons are tabulated (Table 3).

Table 3: Acid soluble content of carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Acid soluble content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>9.27</td>
</tr>
<tr>
<td>C800</td>
<td>14.24</td>
</tr>
<tr>
<td>PIP</td>
<td>2.33</td>
</tr>
<tr>
<td>MIP</td>
<td>7.84</td>
</tr>
<tr>
<td>PIK</td>
<td>4.53</td>
</tr>
<tr>
<td>MIK</td>
<td>12.94</td>
</tr>
<tr>
<td>COM1</td>
<td>3.61</td>
</tr>
</tbody>
</table>
2.1.4.4 Bulk density

Bulk density (BD) of all the carbons is in the range of 0.33 to 0.44 g/cc. Commercial carbon has the lowest BD of 0.27 g/cc. Presence of inorganic salts in the carbon increase the bulk density as the salts are heavier than carbon. Lower BD of commercial carbon indicates presence of lower amount of inorganic impurities which is evident by lower ash content. Bulk densities of various carbons are tabulated (Table 4).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Bulk density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>0.36</td>
</tr>
<tr>
<td>C800</td>
<td>0.44</td>
</tr>
<tr>
<td>PIP</td>
<td>0.33</td>
</tr>
<tr>
<td>MIP</td>
<td>0.37</td>
</tr>
<tr>
<td>PIK</td>
<td>0.35</td>
</tr>
<tr>
<td>MIK</td>
<td>0.40</td>
</tr>
<tr>
<td>COM1</td>
<td>0.26</td>
</tr>
</tbody>
</table>

2.1.4.5 Ash content

Agro waste materials used for preparing carbon are of natural origin. Inorganic salts present in RM along with residual salts after chemical treatment cause ash content of the carbon. Increase in ash content along with increase in preparation temperature is line with the loss of organic matter with increasing temperature. Great decrease in ash content from "only carbonized" to "chemically treated" carbon is in line with the observations in water soluble, acid soluble contents. Chemical reagents aid in getting rid of inorganic matter present in the raw material or intermediate carbonized material. Some increase in ash content in mid impregnated carbons over pre impregnated carbon is indication of residual salts on the surface after treatment. This is also evident in the difference in pH of prepared carbons using same activating agent. It may also indicate inefficient removal of inorganic content present in
the raw material as it may get fixed in the carbon structure as oxide during carbonization. Ash content of the commercial carbon is close to PIP. Ash contents of various carbons are tabulated (Table 4).

### Table 4: Ash content of carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>14.56</td>
</tr>
<tr>
<td>C800</td>
<td>15.96</td>
</tr>
<tr>
<td>PIP</td>
<td>5.83</td>
</tr>
<tr>
<td>MIP</td>
<td>13.63</td>
</tr>
<tr>
<td>PIK</td>
<td>6.17</td>
</tr>
<tr>
<td>MIK</td>
<td>15.46</td>
</tr>
<tr>
<td>COM1</td>
<td>3.61</td>
</tr>
</tbody>
</table>

#### 2.1.4.6 Inorganic matter

Elements such as Ca, Fe, K, Na, Mg, Si and S are found quantitatively when analysed on ICP OES. These salts are typically found in soil and are integral part of vegetation. Results are summarized (Table 5).

### Table 5: Inorganic matter

<table>
<thead>
<tr>
<th>Elements</th>
<th>C600</th>
<th>C800</th>
<th>PIP</th>
<th>MIP</th>
<th>PIK</th>
<th>MIK</th>
<th>COM1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (ppm)</td>
<td>7388</td>
<td>8094</td>
<td>3876</td>
<td>3969</td>
<td>7548</td>
<td>10110</td>
<td>2458</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>1506</td>
<td>2096</td>
<td>1433</td>
<td>2111</td>
<td>1590</td>
<td>2605</td>
<td>1289</td>
</tr>
<tr>
<td>K (ppm)</td>
<td>46486</td>
<td>48750</td>
<td>3997</td>
<td>8381</td>
<td>15613</td>
<td>50228</td>
<td>1459</td>
</tr>
<tr>
<td>Na (ppm)</td>
<td>10371</td>
<td>9941</td>
<td>2136</td>
<td>2278</td>
<td>4658</td>
<td>5851</td>
<td>1475</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>5395</td>
<td>5726</td>
<td>1672</td>
<td>2993</td>
<td>3298</td>
<td>7087</td>
<td>1479</td>
</tr>
<tr>
<td>Si (ppm)</td>
<td>2050</td>
<td>2371</td>
<td>733</td>
<td>1527</td>
<td>789</td>
<td>1862</td>
<td>766</td>
</tr>
<tr>
<td>S(ppm)</td>
<td>4715</td>
<td>5298</td>
<td>765</td>
<td>771</td>
<td>899</td>
<td>2767</td>
<td>830</td>
</tr>
</tbody>
</table>

#### 2.1.4.7 Boehm’s titrations

Carboxylic groups are absent on all the carbons except in PIP& MIP. This can be attributed to the high temperature of carbonization (800 °C) employed.
Carboxylic groups are unstable at higher temperatures and are evolved as carbon dioxide. There is overall increase in oxygen functionalities in chemically activated carbons as compared to only carbonized material. Pre-impregnated carbons have more amount of lactone groups as compared to corresponding mid-impregnated carbons suggesting that impregnation of RM is more effective to create these groups than impregnation of partially carbonized material. Highly stable phenolic and carbonyl oxygen groups are present in higher amounts in mid-impregnated carbons compared to their pre-impregnated counterparts. This could be due to stability of these groups at higher temperatures. In general all carbons contain carbonyl groups in higher proportion. Presence and distribution of oxygen functional groups is given (Table 6, Graph 2).

**Table 6: Oxygen functional groups distribution**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>mM of carboxylic group</th>
<th>mM of Lactone group</th>
<th>mM of Phenolic group</th>
<th>mM of Carbonyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>0.00</td>
<td>0.08</td>
<td>1.08</td>
<td>1.55</td>
</tr>
<tr>
<td>C800</td>
<td>0.00</td>
<td>0.43</td>
<td>1.05</td>
<td>1.38</td>
</tr>
<tr>
<td>PIP</td>
<td>0.02</td>
<td>0.18</td>
<td>0.90</td>
<td>2.00</td>
</tr>
<tr>
<td>MIP</td>
<td>0.48</td>
<td>0.07</td>
<td>1.18</td>
<td>2.45</td>
</tr>
<tr>
<td>PIK</td>
<td>0.00</td>
<td>0.31</td>
<td>1.15</td>
<td>1.68</td>
</tr>
<tr>
<td>MIK</td>
<td>0.00</td>
<td>0.00</td>
<td>1.53</td>
<td>1.78</td>
</tr>
<tr>
<td>COM1</td>
<td>0.00</td>
<td>0.20</td>
<td>0.99</td>
<td>2.08</td>
</tr>
</tbody>
</table>

**Graph 2: Oxygen functional groups distribution**
2.1.4.8 FTIR

C600 – C600 carbon shows C-H stretching at 3032 cm\(^{-1}\) and 2969 cm\(^{-1}\). Peak at 1691 cm\(^{-1}\) indicates presence of conjugated carbonyl group. Olefinic C=C is indicated by 1642 cm\(^{-1}\). Peaks at 1561 cm\(^{-1}\), 1552 cm\(^{-1}\) and 1495 cm\(^{-1}\) show the presence of aromatic compounds. Presence of ester is shown by peaks at 1253 cm\(^{-1}\) of ester acyl carbon and ethereal C-O stretching in ester peaks at 1191 cm\(^{-1}\), 1136 cm\(^{-1}\) and 1088 cm\(^{-1}\)(Fig 2.3).

C800 – C800 shows peaks similar to C600 carbon. C-H stretching peak is at 3122 cm\(^{-1}\). Peak at 1784 cm\(^{-1}\) is indicative carbonyl group in lactone. Presence of lactone group is further confirmed by ester C-O stretching frequencies at 1267 cm\(^{-1}\), 1167 cm\(^{-1}\) and 1106 cm\(^{-1}\). Sharp and strong peaks at 985 cm\(^{-1}\) and 895 cm\(^{-1}\) indicate presence of terminal olefins. Generation of terminal olefins can be due to high temperature employed to prepare this carbon. Peak at 1377 cm\(^{-1}\) indicates the presence of methyl group (Fig 2.4).

PIP – Treatment of raw material followed by carbonization generates phenolic groups. Phenolic –OH group is indicated by peaks at 3380 cm\(^{-1}\), 3305 cm\(^{-1}\). Peak at 1771 cm\(^{-1}\) is indicative of carbonyl group of six membered lactone. Ester carbonyl is also indicated by peak at 1724 cm\(^{-1}\). Olefinic C=C is indicated by peak at 1650 cm\(^{-1}\). Sharp and strong peak at 1197 cm\(^{-1}\) shows presence of Phosphorus. Peaks of C-O stretching at 1061 cm\(^{-1}\) and 1059 cm\(^{-1}\) further confirm the presence of lactone. Peaks at 1563 cm\(^{-1}\), 1506 cm\(^{-1}\) and 1454 cm\(^{-1}\) indicate aromatic groups (Fig 2.5).

MIP – MIP carbon also shows presence of phenolic O-H at 3424 cm\(^{-1}\). Peak at 1094 indicates presence of Phosphorus. Peaks at 2850 cm\(^{-1}\), 2822 cm\(^{-1}\) indicate C-H stretching. Olefinic C=C is indicated by peak at 1656 cm\(^{-1}\). Ether C-O stretching is shown by peak at 1028 cm\(^{-1}\). Presence of peaks at 1529 cm\(^{-1}\) and 1459 cm\(^{-1}\) indicate aromatics (Fig 2.6).

PIK – Peak at 3050 cm\(^{-1}\) indicates C-H stretching frequency. Peaks at 1487 cm\(^{-1}\) and 1431 cm\(^{-1}\) show presence of aromatics. Peak at 1695 cm\(^{-1}\) indicates carbonyl group. Peaks at 1209 cm\(^{-1}\), 1037 cm\(^{-1}\) show presence of acyl C-O in ester (Fig 2.7).
MIK – MIK carbon shows presence of free hydroxyl groups at 3524 cm\(^{-1}\). Associate hydroxyl groups are also indicated by peaks at 3305 cm\(^{-1}\) and 3214 cm\(^{-1}\). Peaks at 3015 cm\(^{-1}\), 2951 cm\(^{-1}\) and 2891 cm\(^{-1}\) are of C-H stretching. Peak at 2715 cm\(^{-1}\) indicated carbonyl group. Peaks at 1779 cm\(^{-1}\), 1729 cm\(^{-1}\) and 1697 cm\(^{-1}\) indicate carboxylic groups of lactone, ester and conjugated ketone respectively. Olefin C=C is indicated by peak at 1646 cm\(^{-1}\). Aromatic groups are indicated by peaks at 1445 cm\(^{-1}\) and 1495 cm\(^{-1}\). Presence of ester is further confirmed by C-O stretching frequency peaks at 1215 cm\(^{-1}\), 1139 cm\(^{-1}\) and 1070 cm\(^{-1}\)(Fig 2.8).

COM1 – Commercial carbon sowed peaks at 3025 cm\(^{-1}\), 2882 cm\(^{-1}\) indicative of C-H stretching. Peak at 1680 cm\(^{-1}\) indicates conjugated carbonyl while peak at 1611 cm\(^{-1}\) indicates conjugated olefin. Aromatic region is indicated by peak at 1560 cm\(^{-1}\) and 1516 cm\(^{-1}\). Esters are notified by acyl C-O stretching frequencies at 1304 cm\(^{-1}\), 1215 cm\(^{-1}\) and 1078 cm\(^{-1}\)(Fig 2.9).

2.1.4.9 Scanning Electron Microscopy (SEM)

SEM images show well developed pores in phosphoric acid pre-impregnated carbon PIP. Only carbonized material viz. C800 do not show any pores while mid impregnated carbon MIP shows development of pores to lesser extent. The cylindrical shape of the material is maintained irrespective of the treatment. SEM image of commercial carbon COM1 do not show any porosity. Base structure of the COM1 is totally different than any of the prepared activated carbons. Porosity development is observed to lesser extent in PIK and MIK carbons. Images are shown (Fig. 2.10-2.15).

Fig. 2.10: C800

Fig. 2.11: PIP
2.1.4.10 Surface Area, Pore size, Distribution

Activated carbons are known to have high surface areas as a result of well-developed porosity, the majority of which is said to fall into the microporous region and cannot be identified using microscopy\textsuperscript{14}.

In order to assess the surface area and porosity of each of the different activated carbon samples, nitrogen adsorption isotherms are obtained. Surface area and porosity data are then obtained by applying equations such as the Brunauer Emmett and Teller (BET) equation\textsuperscript{15} or the Kelvin equation\textsuperscript{4} to the isotherm data. However, information about the nature of the sample
with regards to the mesoporosity, microporosity and pore shape can be obtained from the isotherm plot.

From the adsorption isotherms, plots of the pore size distribution can be obtained. It is well established that the pore space of a mesoporous solid fills up with condensed adsorbate below the saturated vapour pressure of the adsorptive. When combined with a correlating function that relates the pore size to critical condensation pressure, the mesopore size distribution can be characterised. The most commonly used correlating function is the Kelvin equation (equation 7). In Barrett, Joyner and Halenda plots (BJH plots) the Kelvin equation is used to calculate the volume and area at each value of relative pressure, corresponding to a pore diameter providing a pore size distribution. The BJH plots obtained for each of activated carbon samples differ and provide a pore size distribution highlighting at which diameters the pore volume is concentrated.

Fig. 2.16: Adsorption Desorption Isotherm COM1
Fig. 2.17: Pore size distribution first derivative curve COM1

The adsorption isotherms obtained for commercial catalyst COM1 (Fig. 2.16) appear to exhibit predominantly type IV character, based on the Brunauer, Deming, Deming and Teller (BDDT) classification. Type IV isotherms, indicative of mesoporous materials, are characterised by an initial steep incline, followed by a period of gradual increase and a further steep incline at high relative pressures. The initial incline indicates that high energy sites are adsorbing the gas. These sites may be defects on the carbon surface but may also be present as mesopores. The pore size distribution (Fig. 2.17) indicates significant amounts of mesopores are present.

In case of only carbonized material C800, adsorption-desorption isotherm is of Type I (Fig. 2.18). Adsorption and desorption branches remain nearly horizontal over a wide range of relative pressures, which is the characteristic behaviour of micro porous materials. This is also well supported by pore distribution (Fig. 2.19)
Fig. 2.18: Adsorption Desorption Isotherm C800

Fig. 2.19: Pore size distribution first derivative curve C800
2.1.5 Conclusions

There is a profound effect of preparation and activation methods on the carbon. Activating agents develop more porosity into end product as compared to only carbonized materials. Between pre impregnation and mid impregnation, pre impregnation is more effective in generating pores. Activating agents also help in removing inorganic matter in the carbon. Acids are more effective activating agents than bases. All the prepared carbons show significantly lower surface area as compared to commercial carbon. With activation there is improvement in surface area. Activation also creates surface oxygen functionalities. Mid impregnated carbons have more number of surface oxygen groups as compared to corresponding pre impregnated material. Washing off of activating agents is difficult in case of mid impregnation as compared to pre impregnation. Activating with phosphoric acid generates lactone functionalities while potassium hydroxide treated material generates phenolic bodies as evident from IR graphs.

2.1.7 Materials and Methods

pH of the carbon was measured on digital pH meter. It was calibrated using three buffer solutions, before analysing samples. The IR graphs were recorded on Shimadzu FTIR using diffuse reflectance accessory. Inorganic content was measured on Varian ICP OES by aspirating acid dissolved ash sample against the calibration using standard solution. Yttrium was used as internal standard to overcome density differences in the aspirating solutions.

2.1.7 Experimental

Both classical and instrumental methods are employed for characterization of prepared carbons. pH, acid soluble content, water soluble content, bulk density were carried out in laboratory by simple classical methods of analysis. Instruments such as SEM, FTIR, Surface area analyser and ICP were used to characterize carbons for morphology, surface functionalities, pore size and their distribution and inorganic contents respectively.
2.1.7.1 pH

pH of carbons was measured by preparing 10 % (w/v) slurry in DM water. The slurry was kept under circulation for 15 min so as to achieve equilibrium.

2.1.7.2 Water Soluble content

Carbon (2 g) was slurried with 25 ml of DM water. The slurry was heated to 80 °C and temperature was maintained for 15 min. Slurry was filtered through Whatman no 1 filter paper and filtrate was collected in previously dried and weighed 50 ml beaker. The beaker was kept on hotplate with moderate heat and liquid was slowly evaporated to dryness. It was further dried in an oven at 120 °C for 2 hrs, to get constant weight.

2.1.7.3 Acid Soluble content

Carbon (2 g) was slurried with 25 ml of 10 % hydrochloric acid solution. The slurry was heated to 80 °C and temperature was maintained for 15 min. Slurry was filtered through Whatman no 1 filter paper and filtrate was collected in previously dried and weighed 50 ml beaker. The beaker was kept on hotplate with moderate heat and liquid was slowly evaporated to dryness. It was further dried in an oven at 120 °C for 2 hrs, to get constant weight.

2.1.7.4 Bulk density

Bulk density is an indirect measure of fineness and compaction of prepared carbons. Carbon (2 g) was taken into 10 ml glass cylinder. The cylinder was covered and tapped for 100 times on soft surface. It was then allowed to settle for 10 minutes before taking reading.

2.1.7.5 Ash content

Ash content is a result of inorganic matter present in the carbon. These salts are stable at high temperatures while organic matter gets burnt out. Carbon (1 g) was taken into previously dried and weighed 50 ml silica crucible. It was placed in muffle furnace and heated to 600 °C at rate of 100 °C / hr.
Temperature was maintained for 5 hrs. Crucible was then taken out of the furnace and cooled to RT in desiccator to get constant weight.

2.1.7.6 Inorganic matter
The ash was further dissolved in 50 ml aqua regia. The solution was diluted to 100 ml with DM water. 1 ml of 100 ppm of Yttrium solution was added before making up the volume. Yttrium is used as internal standard. The solution was analysed for impurities on ICP OES

2.1.7.7 Boehm’s titrations
Carbon (0.2 g) of was slurried in 20 ml solution of 0.05 M solutions of NaHCO₃, Na₂CO₃, NaOH and NaOEt in 50 ml conical flask each. The flasks were kept in water bath at RT for 24 hrs with intermittent shaking. The slurry was filtered through Whatman no 1 filter paper. 10 ml of the filtrate was titrated against std 0.05 M HCl solution.

2.1.7.8 FTIR
The IR spectra were recorded on Shimadzu FT-IR 1600 instrument using diffuse reflectance accessory. Sample was ground with KBR for dilution.

2.1.7.9 Scanning Electron Microscopy (SEM)
The scanning electron microscope used to obtain images of each of the activated carbon samples was a Jeol JSM-5200 microscope. About 1 mg of catalyst sample was sonicated in 10 ml of iso propyl alcohol (IPA) for about 10 to 20 minutes. It was further diluted and is allowed to settle. Upper clear liquid was taken for analysis. 1-2 drops of the diluted sample was put onto silicon wafer and was allowed to dry at RT. This sample is used for analysis.

2.1.7.10 Surface Area, Pore size and distribution
Nitrogen adsorption isotherms were determined at 77 K via the standard static volume method. Samples were degassed at 90 °C for 1 hr and 300 °C for 3 hrs under flowing nitrogen prior to analysis to ensure a clean surface, capable
of adsorption. The static volume method measures adsorption using mass balance equations, appropriate gas equations of state and measured pressures\textsuperscript{4}. Nitrogen gas enters the sample tube in incremental doses of known volume. The sample attracts this gas and retains at its surface a percentage of the total admitted to the tube. The gas adsorbed is unable to exert a pressure but molecules which remain in the gas phase, that is, which are not adsorbed, express themselves as a gas and hence, exert a pressure. As more doses are added the amount of nitrogen adsorbed increases as does the overall pressure. Since the gas adsorbed on the sample cannot be determined directly, it has to be calculated as the difference between the total amount dosed and the gas remaining in the free space after some portion has been adsorbed.

This process is allowed to reach equilibrium before calculation. The calculation requires that the free space volume be known and thus it is established prior to analysis using helium gas. The pressure is measured and the volume adsorbed recorded as the data point.

In order to plot the relative pressure the saturation pressure must be calculated at each point, as it varies with temperature and so small changes to the cryogenic temperature will alter its value.

A small capillary tube placed near the sample holder in the cryogenic bath is charged with gas until saturation occurs and the pressure is measured automatically.

Data points are collected from 0 up to 0.995 relative pressure comprising the adsorption branch of the isotherm. The desorption branch is measured as a result of systematically reducing the pressure, which results in the desorption of adsorbed molecules. The changing quantity of gas on the solid at each decreasing equilibrium pressure is then quantified and plotted as with the adsorption data points. The complete plot is denoted as the adsorption-desorption isotherm.

Analysis of the shape of the isotherms yields information about the surface and internal pore characteristics of the material. However specific values require model calculations. Surface area calculations are made using the Brunauer-Emmett-Teller (BET) and Langmuir equations.
The Langmuir equation is based on the assumption that gases form only one molecular monolayer on a solid and is represented by equation (Equation 1)

\[ \frac{P}{V_a} = \frac{1}{V_m b} + \frac{P}{V_m} \]  

(Equation 1)

where \(V_a\) is the volume adsorbed

\(V_m\) is the quantity of gas in a monolayer

If the equation applies, a plot of \(P/V_a\) against \(P\) results in a straight line. In cases of nitrogen adsorption at 77 K the straight line plot only occurs over limited regions due to the energetically heterogeneous surface of the carbon sample. From the straight line, values of \(b\) and \(V_m\) can be evaluated from the slope and intercept of the line respectively. The surface area is then calculated from the equation (Equation 2)

\[ S_a = \frac{V_m \sigma N_A}{m V_o} \]  

(Equation 2)

where \(\sigma\) is the cross-sectional area of nitrogen (16.2 Å)

\(N_A\) is Avagadros number

\(m\) is the mass of sample

The BET equation incorporated the concept of multilayer adsorption to the Langmuir theory and is thus said to be favoured for materials that contain pores larger than micropores, that is, pores greater than 2 nm in diameter. The fundamental assumption is that the forces active in the condensation of gases are also responsible for the binding energy in multilayer adsorption. By equating the rate of condensation of gas molecules on to an already adsorbed layer to the rate of evaporation from that layer and summing it for infinite layers the following expression is obtained (Equation 3)
\[
\frac{P}{V_a(P_o - P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \left( \frac{P}{P_o} \right) \tag{Equation 3}
\]

where \(P_o\) is the saturation pressure

Other terms are as previously defined

The term \(C\) is a constant which in the simplest terms can be defined by the relationship (Equation 4)

\[
C \propto \exp \frac{q_l - q_i}{RT} \tag{Equation 4}
\]

where \(q_i\) is the heat of adsorption

\(q_l\) is the heat of liquefaction

As with the Langmuir theory, a BET plot of \(P/V_a(P_o - P)\) against \(P/P_o\) should give a straight line with a \(1/V_mC\) intercept and a slope of \((C-1)/V_mC\). The surface area can then be calculated using equation 2.

Calculation of the pore structure, area and volume, required the use of the t-plot method for microporosity and the BJH plot method for mesoporosity. The t-plot method sees the adsorbed volume plotted against the thickness of the adsorbed layer. The thickness is determined at any point on the isotherm by multiplying the fraction of monolayer capacity, \(V_a/V_m\), at that point by the thickness of the monolayer. If the thickness of a nitrogen monolayer is taken to be 3.54 Å, the thickness of any adsorbed layer is (Equation 5)

\[
t = 3.54 \left( \frac{V_a}{V_m} \right) \tag{Equation 5}
\]

For any value of thickness there is some value of \(V_a\) for both the test material and a standard non-porous material. For the purpose of calculating t-values for each of the carbon samples a standard carbon black t-value was calculated using the Harkins & Jura equation (Equation 6)
where 13.99 is the slope of the standard plot
0.034 is the intercept of the standard plot

Once the \( t \) versus \( V_g \) data are plotted a straight line is fitted to the data. The gradient of this line provides the micropore surface area whilst the total micropore volume is calculated from the intercept.

In order to calculate the mesoporous properties, BJH plots are used. This procedure for calculating pore size distributions, using the Kelvin equation, involves an imaginary emptying of condensed adsorptive in the pores, in a step-wise manner, as the relative pressure is decreased. The pores are said to be theoretically full at a relative pressure of 0.995. The isotherm is then seen as a series of downward steps with the amount of adsorptive lost in each step representing the core volume of pores emptied in that step. The thickness of the adsorbed layer remaining is calculated from equation 6.

Using the Kelvin equation (equation 7), replacing \( r_m \) with \( (r-t) \), a value for \( r \) can be established (Equation 7)

\[
\ln\left( \frac{P^*}{P_o} \right) = -\left( \frac{2\gamma v \cos \theta}{RT r_m} \right)
\]  
(Equation 7)

where \( P^* \) is the critical condensation pressure
\( \gamma \) is the liquid surface tension

At this point a cylindrical pore model is assumed and the value of \( r_m \) and the volume of pores of size \( r_m \) are substituted in to the general equation (Equation 8)

\[
\text{volume} = \pi r^2 L
\]
(Equation 8)

From the value of \( L \) the area can then be calculated using the general equation (Equation 9)
area = 2πL \quad \text{(Equation 9)}

This process is repeated for each downward step of pressure on the isotherm giving a total mesopore volume, a total mesopore area and a pore size distribution as a BJH plot. From this an average pore diameter is calculated.
Spectral data

Fig. 2.3: FTIR scan for C600

Fig. 2.4: FTIR scan for C800
Fig. 2.5: FTIR scan for PIP

Fig. 2.6: FTIR scan for MIP
Fig. 2.7: FTIR scan for PIK

Fig. 2.8: FTIR scan for MIK
Fig. 2.9: FTIR scan for COM1
2.2 Section II
Reactions of Carbons

2.2.1 Introduction

Oxidation reactions - Synthesis of Triazoles via Click Chemistry

Click chemistry is a term applied to chemical synthesis tailored to generate substances quickly and reliably by joining small units together. Click chemistry is not a single specific reaction, but describes a way of generating products that follows examples in nature, which also generates substances by joining small modular units. The term was coined by K. Barry Sharpless in 1998, and was first fully described by Sharpless, Hartmuth Kolb, and M.G. Finn\textsuperscript{17-19}. One of the most popular reactions within the Click chemistry concept is the azide alkyne Huisgen cycloaddition using a Copper (Cu) catalyst at room temperature\textsuperscript{19, 21}. The copper-catalyzed reaction was later expanded by Yamamoto and coworkers using a bimetallic catalyst so that 1,4,5-substituted triazoles could be obtained from seemingly internal alkynes.

2.2.2 Review of Literature

Click chemistry concept was developed in parallel with the interest within the pharmaceutical, materials, and other industries in capabilities for generating large libraries of compounds for screening in discovery research. Several types of reaction have been identified that fulfil these criteria, thermodynamically-favoured reactions that lead specifically to one product, such as nucleophilic ring opening reactions of epoxides and aziridines, non-aldol type carbonyl reactions, such as formation of hydrazones and heterocycles, additions to carbon-carbon multiple bonds, such as oxidative formation of epoxides and Michael Additions, and cyclo addition reactions. Huisgen 1,3-Dipolar Cyclo-addition of alkynes to azides requires elevated temperatures and often produces mixtures of the two region isomers when using asymmetric alkynes. A copper-catalyzed variant that follows a different mechanism can be conducted under aqueous conditions, even at room
2.2.3 Present work

Reactions for the synthesis of triazoles have been carried out by using 2 eq. of an alkyne/allene, copper sulfate and sodium ascorbate. In situ reduction of copper(II) salts such as CuSO₄·5H₂O with sodium ascorbate in aqueous alcoholic solvents allows the formation of 1,4-triazoles at room temperature in high yield with less than 2 mol % catalyst loading. Primary, secondary, and tertiary substituted azides as well as aromatic azides can be synthesized. Numerous terminal acetylene components participate in the transformation and the reaction is compatible with various functional groups such as esters, acids, alkenes, alcohols, and amines.

In order to attain more atom economy and lower amount of hazardous solvents and other chemicals, the reaction is tried with copper nitrate on carbon. Reaction can be carried out at much lower equivalent of reagents and catalysts because of the spreading of copper salt on to the carbon surface. Reaction scheme adopted for the work is shown (Fig. 2.20).

![Reaction scheme for synthesis of triazoles](image)

Fig. 2.20: Reaction scheme for synthesis of triazoles

2.2.4 Results and Discussion

Various solvent systems are used to find out most suitable system. When 10 % cu-on-carbon is used, quantitative yields of product are observed. Dioxane, very common aprotic dipolar solvent, indicates zero dipole moment. Similarly, THF, aprotic dipolar shows dipole moment of 1.7 which is close to methanol 1.69. The substrate is semipolar which dissolves in the above solvents to
similar extent and product is formed in nearly similar percentage. However, the solubility of substrate is significant in dioxane-water (3:1) system which has maximum yield. Water being protic polar, substrate has less solubility. So, yield of the product is less.

With increasing amount of Cu-on-Carbon, there is gradual increase in yield in dioxane, dioxane-water, methanol and water while yield in THF remains same. The results are shown (Table 7).

**Table 7:** Isolated yields of adduct using varying amount of Cu-On-Carbon

<table>
<thead>
<tr>
<th>Amount of Cu on carbon (mg)</th>
<th>Dioxane</th>
<th>Dioxane: water 3:1</th>
<th>Methanol</th>
<th>THF</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>89</td>
<td>92</td>
<td>88</td>
<td>88</td>
<td>76</td>
</tr>
<tr>
<td>20</td>
<td>90</td>
<td>93</td>
<td>89</td>
<td>88</td>
<td>79</td>
</tr>
<tr>
<td>30</td>
<td>91</td>
<td>93</td>
<td>91</td>
<td>88</td>
<td>79</td>
</tr>
</tbody>
</table>

From Table 7, it is evident that the reaction worked very well with mixture of dioxane and water (3:1) as a solvent. Low yields in water as a solvent indicates that an aprotic polar solvent is necessary for dissolution. It also confirms that the output of the reaction increases with increase in amount of Copper-on-carbon. Thus the optimum conditions for the reaction would be the use of dioxane:water (3:1) as a solvent and 30 mg. of copper-on-carbon as a catalyst. Reaction yields using various prepared carbons.

There is no vast difference in the yields with respect to change in carbon. Yields with commercial carbon are on slightly higher side as compared to prepared carbons. Results are presented (Table 8).

**Table 8:** Reaction yields using various carbons

<table>
<thead>
<tr>
<th>Carbon used for Cu-On-Carbon</th>
<th>% Yield (Isolated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C600</td>
<td>93</td>
</tr>
<tr>
<td>C800</td>
<td>92</td>
</tr>
<tr>
<td>MIP</td>
<td>93</td>
</tr>
<tr>
<td>COM1</td>
<td>94</td>
</tr>
</tbody>
</table>
The triazole product is characterized using spectral techniques. LC-MS (Fig. 2.21) exhibits a molecular ion peak at m/z 268 [M+1]^+. ^1H-NMR spectrum (Fig. ) illustrates a down field singlet at δ 8.24 for olefinic proton of triazolene ring, H4, (s, 1H). Another downfield aromatic proton, H2, appeared at δ 8.22 as merged doublet of doublet (m, 1H) due to presence of fluorine atom at its ortho position. Other seven aromatic protons viz. H1, H3, H6, H7, H8, H9 and H10 appear as cluster between δ7.00 to δ 7.58. A strong singlet is seen at δ 5.7 (s, 2H) is assigned for methylene proton, H5 attached to benzene and triazole nitrogen atom. A sharp singlet is noted at δ 1.6 for methyl protons (s, 3H)

![Chemical Structure](image)

### 2.2.5 Conclusions

Increasing amount of catalyst (Copper-on-Carbon) increases the yield of reaction. Very minute change in yields even when there is great increase in surface area and other properties, going from C600 to C0M1 carbon, indicate that the Cu salt does not penetrate the pores of the carbon and is deposited only on the surface. Surface active groups help in stabilizing the salt on its surface. The amount required for carrying out reaction using Copper-on-Carbon as compared to only Copper salt underlines the importance of carbon to increase the available surface for reaction.

### 2.2.7 Materials and Methods

Benzyl triazide and 2-methyl-3-fluorophenyl acetylene were sourced from Alpha Aiser. All the solvents used were of AR grade. Demineralized water was used as solvent.
Copper nitrate was deposited on the carbon slurry, stirred for 2 hr. The slurry was filtered and then kept for drying in oven at 100 °C.

2.2.7 Experimental
Reactions were carried out using 100 mg of azide, 1.1 equivalent of alkyne and varying amount of Copper-On-Carbon. The mixture was stirred for 24 hrs at room temperature. It was filtered and filtrate was dried over anhydrous sodium sulphate, purified on column chromatography (as and when required) and the product was isolated.
Spectral Data

Fig. 2.21: Mass Spectrogram of triazole product

Fig. 2.22: NMR of triazole product
References