CHAPTER 1
CHAPTER 1

Preparation of Activated Carbons using Agro waste material

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Activated carbon prepared from agro waste material *cicerarientinum* as effective adsorbents for removal of methylene blue from aqueous solution, communicated to Der Pharma Chemica
Preparation of Activated carbons

1.1 Introduction
Activated carbons are non-hazardous porous carbonaceous materials prepared by carbonising and activating organic substances. One of the most important features with regards to activated carbon is the porous structure which results in a high surface area. This lends to a high adsorptive capacity. This is why activated carbons have been favoured industrially as adsorbents. Activated carbons consist of hydrophobic graphene layer as well as hydrophilic surface functional groups making them beneficial for sorption and catalytic applications. Specific industrial applications include areas such as oil and natural gas, food, pharmaceuticals, water treatment, hydro metallurgy, gold recovery and carbon-in-pulp process\(^1\). Activated carbon materials are effective in removing pollutants (both gaseous and liquid). Advantage of activated carbon materials as adsorbents is that the treated effluent is of high quality, design of the process is simple, operation of the process developed or adopted is easier. In addition carbon materials are resistant to corrosive (acidic and basic) and toxic environments\(^2\).

In addition to purification of gases and liquids with high adsorption potential, activated carbon materials are also used as catalysts and catalyst supports. Carbon materials play an indispensable role in almost all electrochemical devices, to name a few, batteries\(^3\), supercapacitors\(^4\) and fuel cells\(^5\). The choice of carbon as the material is because of its unique properties of electrical conductivity and structural diversity.

Microporous carbon materials are highly disordered. In general, the structure comprises of aromatic sheets and strips. Such sheets are often bent imitating crumpled papers and wood shavings. The voids and gaps of molecular dimensions, between such aromatic sheets are regarded as micropores. Again the microporosity is dependent on the carbonprecursor as well as the method of preparation\(^6\).

On basis of X-ray analysis two types of structures have been proposed\(^7\). The first structure consists of elementary crystallites of hexagonally ordered carbon atoms, as in graphite, which are randomly oriented in the
perpendicular plane and may overlap irregularly. This was termed a "turbostratic" structure by Biscoe and Warren and is commonly assigned the dimensions of height, from 9 to 12 Å, and width, from 20 to 23 Å, although these depend greatly on the temperature of carbonisation.

The second structure is described as a disordered cross-linked space lattice of the carbon hexagons which results in their deflection from the planes of graphitic layers. The structure is stabilised by heteroatoms. Numerous investigations with X-rays revealed that both types of structure were evident in various carbon samples with more recent investigations using Raman spectroscopy also confirming the presence of two types of structures.

The average structure of a typical microporous activated carbon is shown (Fig. 1).

![Fig. 1: Structure of Activated Carbon - A schematic representation.](image)

The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As a result, cost of activated carbon is also growing depending on the application. Designing ways for the production of activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon rich and low ash precursors and sources are being explored for the production of carbon materials.

Most of the commercial activated carbons are either coal based or petroleum pitch based which are prone to exhaustion. Their global distribution is non-uniform. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. This may in
due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico-chemical properties namely, high specific surface area, micro or meso porosity or both, depending on the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition (inherent or induced presence of hetero atoms like B, N, S and P).

**Superiority of Activated Carbons**

In contrast to other support materials, such as alumina or silica, activated carbon has many advantages such as:

- Cost
- Inert nature
- Can be used in acidic or basic conditions
- Imparts selectivity to reaction
- High surface area
- Wide range of pore distribution
- Separation of catalyst is easy
- Recovery of precious metals is easy.
- Economic advantage.
- Readily available

Properties such as high surface area make carbons good adsorbents. They find application in industrial effluent treatments such as colour removal, heavy metals (Mercury, lead, arsenic, cadmium etc.) removal.

For industrial use, recovery of precious metals like platinum, palladium is important as it reduces considerable capital investment in catalyst. Various types of reactions having variety of functional groups can be carried out as the material is inert. Many stereo-selective and stereo-specific reactions are reported. High surface area allows good distribution of active phase, resulting in low loading of catalyst to carry out reactions. Indigenous raw materials can be used to manufacture the carbon saving considerable foreign exchange. There are many advantages of activated carbons. Activated carbon supports
can be used in a variety of reactions as the structure is resistant to acidic and basic media unlike silica and alumina. It is also stable at high temperatures, under inert atmospheres, even above 1000 K.

Generally, carbons are prepared as powders or granules allowing for their use in batch reactors or fixed bed reactors respectively. There are numerous reports which detail the preparation of activated carbons as monoliths suggesting a much wider range of applicability.

The hydrophobic nature of carbon is regarded as a disadvantage. Surface chemistry can be altered by activation using chemical reagents, oxidising gases or subsequent treatments increasing the hydrophilicity. Activation incorporates hetero atoms such as oxygen, nitrogen, sulphur, chlorine etc. Many properties, including surface area and porosity, structure and morphology, surface chemistry and inertness, are result of the method applied for activation. It also depends upon the raw material used.

1.2 Activated Carbons from Agro waste (Lignocellulosic material)

Lignocellulosic materials have been and will be with mankind for ever and they hold a promise of renewable and inexhaustible supply of carbon materials provided suitable methods of production are developed. In addition they are more evenly distributed throughout the globe relative, to either coal or petroleum. Thus the lignocellulosic material, a regenerable natural resource, is a viable option for the generation of carbon materials.

In biological lignocellulosic material, carbohydrate (holo cellulose and cellulose) components are intimately bound to lignin. Lignin is a 3-dimensional cross linked aromatic polymer with phenyl propane units. Next to cellulose, lignin is the major constituent of plant cell wall. Lignin possesses a complicated chemical structure with both phenolic (aromatic) as well as alcoholic (aliphatic) hydroxyl groups being present in the structure. The main repeating unit of lignin is 3-(4-hydroxy phenyl) prop-2-eneol. Lignin is an aromatic amorphous biopolymer deposited as a reinforcing agent inplants offering mechanical support to the fibrous tissues of the plant. Thus, the
main function of lignin is to impart strength and rigidity to the cell wall by acting as structural matrix. The carbon precursor and the method of preparation are the determining factors of the textural and surface properties of carbon materials. Taking into considerations some specific properties like volatile matter, ash content and fixed carbon content as well as the derivable porosity, several researchers have studied the possibility of producing carbon materials from different lignocellulosic materials.

Agricultural waste materials such as fruit stones or nut shells have been explored. The choice of raw materials primarily depends upon its continuous availability. Agro waste material such as nut shells, fruit stones have been traditionally used as fodder for cattle and source of fire for cooking in villages. Medicinal use of such materials has also been explored by extraction of various components. Few of these cannot be used owing to their low nutrition value or in some cases toxicity and becomes burden for its disposal. These light materials are also expensive for transport and hence dumped. They possess good potential as raw material for preparing activated carbon.

1.2 Carbonisation
Carbonisation process is a simple pyrolysis of raw material. It yields carbon with a moderate surface area. It is the activation step, reaction of the carbon with chemical reagents or oxidising gases, which gives high surface area product. During carbonisation most of the non-carbon elements are eliminated. The freed atoms of elementary carbon are grouped into organised crystallographic formations known as elementary graphitic crystallites. These crystallites stack in an irregular manner and the space between them is filled with tarry material.

During carbonisation, firstly, physio-sorbed water molecules are removed in the temperature range of 25°C – 150°C. Such desorption of physisorbed water increases the degree of lateral order. In second stage, the structural water, involving hydrogen and hydroxyl moieties in the equatorial position, is stripped off from the cellulose in the temperature range of 150°C – 240°C due to thermal excitation. Such dehydration process is essentially intramolecular.
Major thermal degradation of cellulosic structure takes place in third stage at temperature above 240°C. Thermal scission of C-O and C-C bonds as well as dehydration takes place in third stage, in the temperature range of 240°C – 400°C, yielding tar as well as carbonaceous residue. Tar formation is supposed to be through Levoglucosan. Upon pyrolytic decomposition cellulose depolymerizes through the scission of 1, 4 glycosidic linkage. Subsequent intramolecular rearrangement of cellulosic units results in the formation of levoglucosan, which effects in the formation of tar. Even though the tarry portion is a complex mixture, the main constituent of the tar was identified to be dehydrated cellulose (mass = 144). The final breaking down of each of the cellusic ring units takes place in third stage resulting in the formation of carbon residue containing four – carbon atoms (nos. 3, 4, 5 and 6). Thus, four of the six carbon atoms in each glucose monomer are retained in the char. Such four carbon atom intermediates, a very – short lived radical species, serve as “building blocks” for the re polymerization forming carbon polymer and subsequently a graphitic structure in fourth stage, in the temperature range of 400°C – 700°C. The mechanism is presented (Fig 2).

![Fig.2: Mechanism for cellulose to aromatic carbon](image-url)
1.2.3 Activation

Activation is the reaction of activating agents with tarry material where partial burn-off of the graphitic structure produces the porous array of stacked crystallites.

The activation of carbon can be achieved in two ways:

- By carbonising the material with the addition of activating agents which influence the course of pyrolysis – Chemical activation
- By allowing the inactive carbonised product to react with suitable and usually gaseous substances – Physical activation.

1.2.3.1 Chemical Activation

Chemical activation is performed on materials such as nutshells, fruit stones and sawdust (wood). This is most likely related to the reactions that occur during the activation process. The chemical activating agent restricts the formation of tar by influencing pyrolytic processes that are taking place as the material is carbonised. Common chemical reagents used are zinc chloride, phosphoric acid and alkali-earth metal hydroxides. But the methods for large-scale production are poorly described due to the confidential character of commercial methods.

Effect of activation parameters

There are various parameters which influence the properties of final material. Some of the important parameters are:

- Temperature of treatment
- Activating agent
- Concentration of activating agent
- Duration of treatment
- Sequencing of treatment
- Nature of raw material

In general, the raw material is initially impregnated with a solution of the activating agent to form slurry. Concentration of the solution and duration of time for which raw material is impregnated are both observed to influence
properties of the carbon product. This has been demonstrated for a number of different activating agents. Guo et al. revealed that longer impregnation times with phosphoric acid led to improved textural properties in the carbon product. Longer impregnation times lead to a more uniform distribution of the chemical reagent allowing for an improved development of the internal structure which would result in an increased surface area and microporous structure.

Nature of raw materials needs to be taken into consideration. Materials such as nutshells or fruit stones are denser than sawdust and are therefore, expected to require longer impregnation times. In addition, concentration of the impregnating solution will alter the textural properties of carbon product. Higher concentrations are more likely to impregnate further throughout the structure resulting in a higher surface area from more developed porosity. Do et al. have shown that for zinc chloride and potassium hydroxide, higher concentrations increase the surface area and the micropore volume which is evident in coal carbons. The increased microporosity is the result of increased elimination of volatile matter arising from the higher concentration of chemical reagent.

In the absence of any activating agent the internal pore structure is thought to shrink as a result of carbonisation but the presence of an activating agent ensures the pores are maintained firstly by creating volatile gases which help to unblock and widen existing pores but also their physical presence ensures pores cannot close. Therefore, the use of any activating agent helps to maintain porosity which is developed during carbonisation process.

**Development of Pores**

After impregnation and a series of mixing and kneading steps the material is heated in a rotary kiln in the absence of air between 400 and 1000 °C. The temperature range is broad as it is seen to alter the properties of the carbon with the effects being specific to the activating agent used.

Phosphoric acid was demonstrated to produce the highest surface area and micropore area when heated at 500 °C. Temperatures which were lower resulted in lower surface area carbons suggesting that the pore structure has
not been fully developed. At higher temperatures, the surface area and micropore volume decreased. It is possible that this has occurred as a result of shrinkage of the carbon structure leading to micropore closing. It is also possible that at high temperatures micropores get burnout. This leads to destruction of micropore walls, the formation of larger mesopores. This ultimately results in an overall decrease in surface area.

In contrast, the use of potassium hydroxide requires much higher temperatures. It is accompanied by increase in surface area and micropore area. Maximum temperature investigated was up to 800°C. It therefore appears that metal hydroxides do not react as readily with the carbon structure as classical reagents such as phosphoric acid and zinc chloride. Higher temperatures are required to initiate the elimination of volatiles and development of microporous structure.

The same pattern is evident for the carbonisation time. Longer reactions times initially improve the textural properties of the carbon as more volatile matter is removed and the pore structure is further developed. However, after prolonged carbonisation, with most reagents the surface area and porous properties decrease indicating that the pore structure is being destroyed. It is most likely that the pores are being burned out rather than shrinking because, the surface area decreases even with high concentrations of activating agents employed.

The gas flow rate is also identified as an important factor during the carbonisation. Higher flow rates increase the surface area of the carbon. This is most probably the result of higher flow rates improving the removal of volatile matter and consequently clearing the pore structure.

After carbonisation, the final step of the chemical activation process involves the extraction of the activating agent by a series of leaching and washing procedures resulting in a porous activated carbon product.

The main reaction occurring in chemical activation is that between the activating agent and the cellulose molecules of the raw material. Cellulose is composed of elongated macromolecules, up to 18000 Å, orientated in the longitudinal axis, forming agglomerates known as micelles. The oriented chains are laterally bound by bonds of different types and strengths. The
activating agent causes swelling of the cellulose during which the lateral bonds are broken whilst the macromolecules remain intact, until a colloidal state of dispersed cellulose is attained. Simultaneously, hydrolytic and oxidative reactions occur depolymerising the macromolecules as well as dehydration of cellulose resulting in the decomposition of organic substances. These dehydration reactions prevent the formation of tarry material, promoting the formation of graphitic crystallites.

1.2.3 Physical Activation

Physical activation is a two-step process consisting of a carbonisation step and an activation step. In the initial phase of carbonisation, the material (wood, coal, peat etc.) is dried at temperatures up to 170°C. Above this temperature the material begins to partially decompose with the evolution of carbon monoxide, carbon dioxide and acetic acid. At approximately 280°C considerable amount of tar, methanol and other decomposition products are formed. The carbonisation step is usually completed by heating at 400°C to 600°C. The activation process is usually performed using gaseous activating agents such as steam, carbon dioxide or air. These agents initially react with the disorganised carbon, eliminating it as gas. This leaves the surface of the elementary crystallites exposed to the action of the activating agent resulting in the burning out of some of the crystallites producing the pore structure.

As the reaction continues a simultaneous production of new pores, widening of existing pores and complete burn out of some pores occurs. The gas composition is important as the different reagents can alter the textural properties.

Carbon dioxide has been identified as favouring the formation of mesopores while activation with steam results in more microporous carbons. This is the result of the molecular size of the two gases. The larger dimension of carbon dioxide restricts its accessibility to the microporous regions. It also experiences slower diffusion throughout the pore structure than steam and therefore does not react so readily with the internal structure wherein the majority of micropores exist.
In the reaction of a gaseous activating agent, complex surface compounds are temporarily formed on active sites, edge, corner and defect sites. On their decomposition the oxidised carbon is removed from the surface as carbon monoxide and carbon dioxide, resulting in the exposure of new saturated carbon atoms on the surface. The reaction with steam or carbon dioxide is endothermic and therefore requires temperatures ranging from 750 °C up to 1100 °C.

A long reaction time would result in further reaction between the gaseous reagent and the pore edges, decreasing the surface area and pore volume. At lower temperatures longer reactions times produced high surface area carbons with well-developed porosity.

The exact nature of the reaction is poorly understood owing to numerous experimental difficulties including the variation of the raw materials, the catalytic effect of inorganic impurities and complications arising from secondary reactions. However, this proposed scheme for the reaction of steam and carbon is considered to be the most probable:

\[
\begin{align*}
C + H_2O & \rightarrow C(H_2O) \\
C(H_2O) & \rightarrow H_2 + C(O) \\
C(O) & \rightarrow CO
\end{align*}
\]

In the initial step, the steam is adsorbed on to the active sites of the carbon. Dissociative chemisorption of the water then forms adsorbed hydrogen and hydroxide which proceeds to the formation of adsorbed oxygen and hydrogen gas. The adsorbed oxygen then reacts to form carbon monoxide, removing the primary layer of carbon leaving further sites exposed for reaction.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation whereby carbon dioxide and hydrogen formation are catalysed by the carbon surface.

1.3 Dye Adsorption

One of the prominent applications of activated carbon is effluent treatment. Dyes and gases are common pollutants. Dyes are the most visible pollutants in waste water generated by various industries. Dyes consume dissolved
oxygen in water and pose great threat to aquatic organisms. Now a days, selective adsorption of these dyes by activated carbon has proven to be effective solution in environment management. Varieties of other adsorbing materials are also employed.

1.3.1 Adsorption

Adsorption is a surface phenomenon. Surface chemistry is a subject that is important in a range of technologies. Surface chemistry deals with chemical processes at the interface between two phases and the special properties of the colloidal systems. The Langmuir adsorption equation is used to model monolayer adsorption where all surface adsorption sites have the same affinity for the adsorbing species. The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. Adsorption can be defined as the change in concentration at the interfacial layer between two phases of a system.

**Adsorbent**

The solid surface onto which adsorption can occur. / The substance which adsorbs another substance is called an adsorbent.

**Adsorbate**

The general term for the atomic or molecular species which are adsorbed (or capable of being adsorbed) onto the substrate / the substance which is being adsorbed is called an adsorbate.

**Coverage**

It is a measure of the extent of adsorption of a species onto a surface. Usually denoted by the lower case Greek “theta”.

Adsorption is expected when two heterogeneous phases are brought in contact with each other. Hence there are three cases of adsorption and these are mentioned.

- Gas-solid - Adsorption of sulphur dioxide gas on charcoal.
- Liquid-solid – Adsorption of acetic acid on charcoal.
Gas – liquid – Adsorption of oxygen gas on mercury.

There are two principal modes of adsorption of molecules on surfaces:

- Physical adsorption (Physisorption)
- Chemical adsorption (Chemisorption)

Physisorption is a process whereby a molecule adheres to a surface without the formation of a chemical bond, usually by Van der Walls forces or electrostatic attraction. It occurs at low temperature. Heat of adsorption is of the order of $<10 \text{ k Cal mole}^{-1}$ of adsorbent. There is a formation of multi molecular layer. For example gases like hydrogen, nitrogen and carbon dioxide get adsorbed on charcoal.

Chemisorption is a process whereby a molecule adheres to a surface through the formation of a chemical bond. The forces involved in chemisorption are strong and highly specific in nature.

1.3.1 The factors affecting the process of adsorption

- Nature of adsorbent
- Concentration
- Temperature

The relationship between the amount of a substance adsorbed per unit mass of adsorbent and the equilibrium pressure or concentration at any constant temperature is called an adsorption isotherm. The important adsorption isotherms which are used to describe the process of adsorption are Freundlich and Langmuir isotherms.

Following applications are based on adsorption principle:

- Catalysis
- Production of high vacuum
- Chromatography
- Adsorption indicators
- Determination of surface area by BET method
- Purification of water
1.3.2 Carbon as Adsorber

Activated carbon is a material which consists of hydrophobic as well as hydrophilic surface functional groups which make them beneficial for adsorption. The choice of carbon as adsorbent material is because of its unique properties of electrical conductivity and structural diversity. The demand for activated carbon is increasing in pollution control. As a result, the cost of activated carbon is also growing depending on the applications.

Need for alternate sources

Most of the commercial activated carbons are either coal based which are prone to exhaustion, non-renewable and relatively expensive. Their global distribution is non-uniform. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. This may in due course result in insufficiency of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely, high specific surface area, micro or meso porosity or both, depending upon the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition.

1.3.2 Dyes as Water pollutants

Dyes are used as colouring matter by various industries. Unspent colouring materials are discharged into the aquatic environment and therefore are considered to be one of the important visible pollutants of industrial wastewater. Dyes are highly coloured compounds which are non-biodegradable. These dyes persist in water, which retards photosynthetic activity, inhibit growth of aquatic biota and decrease recreation value of stream.

Methylene blue is an important basic dye used for printing calico, dyeing cotton and leather. It is not strongly hazardous but has various harmful effects, such as eye burns, irritation to the gastrointestinal tract and...
causing various skin diseases. Therefore, it is necessary to remove methylene blue from waste water.

The reports revealed that the removal of dye can be achieved by chemical coagulation, ozonation, membrane filtration, ion-exchange, precipitation and adsorption. Among these, adsorption is the most effective and economical method. Activated carbon has been the most effective adsorbent for the removal of various pollutants from waste water. This is due to its highly porous nature, large surface area to volume ratio and presence of surface functional groups. The high cost of activated carbon however, restricts its application in developing countries including India. This has promoted growing research interest into the production of low-cost alternatives to activated carbon. Above mentioned techniques/supports are costly and involves use of chemicals. Activated carbon offers simple way of treatment for adsorption. Dye adsorption capacity of particular carbon can be good indication of its textural properties, surface area. Carbon showing good capacities can further be considered as support material for catalyst.

1.4 Review of literature

Literature review focused on preparation of activated carbon from various resources used worldwide. Focus was put upon the use of agro waste materials as raw material. Various activation methodologies were studied. Considering the hardware limitations, stress was given to chemical activation routes. Phosphoric acid and potassium hydroxide treatments were found to be of choice by various workers.

Dye adsorption is an important application for activated carbon, in effluent treatments. Literature survey revealed that, activated carbons have good capacity for adsorption of various dyes. Effect of various parameters on adsorption, were reviewed.

1.4.1 Carbon preparation

Numerous reports are available in literature, which details the preparation of activated carbons as powders, granules, cloths and fibres. Use of
locally available material is predominant\textsuperscript{39-44}. Recent advances have made use of other waste materials including newspapers\textsuperscript{45} and tyres\textsuperscript{45-46}. Reports revealed that, various chemical reagents, such as zinc chloride\textsuperscript{42}, phosphoric acid \textsuperscript{1,43} and alkali-earth metal hydroxides\textsuperscript{39,44,47} have been used for activation.

\subsection*{1.4.2 Adsorption study}

Adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon is a form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area. This results in producing reasonably cheap and excellent adsorbent \textsuperscript{48-50}. There is a multitude of industrial applications of activated carbon. Pollution control and wastewater treatment are growing areas of use to combat environmental pollution\textsuperscript{48-50}. Some agro waste materials which have been used as adsorbent for dye sorption from wastewater are listed (Table 1).

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
\textbf{Adsorbent(s)} & \textbf{Dye(s)} & \textbf{References} \\
\hline
Jackfruit peel & Methylene blue & 51 \\
Jackfruit leaf & Methylene blue & 30 \\
Cotton fibre & Methylene blue & 52 \\
Sugarcane bagasse & Methyl red & 53 \\
Rice husk, groundnut shell, coconutsheil, Bamboo dust & Methylene blue & 54 \\
Indian Rose Wood Sawdust & Methylene blue & 55 \\
Oil palm trunk fibre & Malachite green & 56 \\
Yellow passion fruit peel & Methylene blue & 57 \\
Rice husk & Malachite green & 58 \\
Banana pith & Congored, Rhodamine-B, Procion orange & 59-63 \\
Guava leaf powder & Methylene blue & 64 \\
Groundnut shell & Malachite green & 65 \\
Rice husk & Methylene blue & 66 \\
\hline
\end{tabular}
\caption{Agro waste materials used in Dye adsorption}
\end{table}
1.5 Present work

1.5.1 Carbon preparation

*Cicerarietinum* stalk was chosen to be the raw material for preparation of activated carbon based on its good adsorption properties demonstrated by earlier workers. It is agro waste material with no commercial value.

The chemical activation methods were chosen because of simplicity of operation and limitation of hardware setup that is typically required in physical activation.

Choice of activation methods was based on the literature study. Aim was to get mesoporous carbon which is believed to be good support for preparation of heterogeneous catalyst.

Further activation was carried out using two activating agents viz. phosphoric acid, potassium hydroxide. Chemical activation involves impregnation of raw material (RM) or intermediate charred material by chemical agents. Sequencing of impregnation has profound effect on the properties of activated carbon. Two impregnation routines viz. pre-impregnation and mid-impregnation were employed.

Commercial carbon (phosphoric acid treated) was taken for comparative study. Six carbon materials were prepared by combination of activating agents, temperatures and sequencing of treatments. Details are mentioned (Table 2).

<table>
<thead>
<tr>
<th>Carbon Nomenclature</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>C600</td>
<td>RM carbonised to 600°C</td>
</tr>
<tr>
<td>C800</td>
<td>RM carbonised to 800°C</td>
</tr>
<tr>
<td>PIP</td>
<td>Pre-impregnated with H$_3$PO$_4$</td>
</tr>
<tr>
<td>MIP</td>
<td>Mid-impregnated with H$_3$PO$_4$</td>
</tr>
<tr>
<td>PIK</td>
<td>Pre-impregnated with KOH</td>
</tr>
<tr>
<td>MIK</td>
<td>Mid-impregnated with KOH</td>
</tr>
<tr>
<td>COM1</td>
<td>Commercial carbon</td>
</tr>
</tbody>
</table>
1.5.2 Dye Adsorption

The aim of the dye adsorption study was to determine the optimum conditions for the removal of a cationic dye that is methylene blue. In this study, only carbonized material C800, phosphoric acid treated carbon MIP, potassium hydroxide treated carbon MIK and commercial carbon COM1 were tested at various experimental conditions. The aim was to study adsorption capacity of the prepared carbons and then compare it with commercial carbon. Applicability of Langmuir and Freundlich isotherms was checked to deduce mechanism of adsorption. This study is found to be useful when designing hardware setup for effluent treatment plants. Adsorption isotherm parameters obtained from different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate.

1.6 Results and Discussion

1.6.1 Carbon Preparation

Proportionate loss in weight is observed in the material during carbonization process. Loss up to 60% is observed when the material was treated to 600 °C and it is 70% at 800 °C. Loss in weight is attributed to removal of Lignocellulosic material, heteroatoms such as hydrogen, nitrogen which are easily removed as gases.

In case of PIP and PIK carbons, loss in weight is close to 59%. This slight decrease in weight loss may be due to adsorption of activating agents by RM which are not evolved as gases during carbonization.

In case of MIP, there is gain of 1% in carbonized material after impregnation. It is maintained when material is further carbonized at 500 °C. In case of MIK carbon there is loss of 5% in weight after impregnation as the second carbonization is at 800 °C. Weight loss during carbon preparation is shown (Graph 1).
1.6.2 Dye Adsorption

Effect of adsorbent dose

Sorbent dosage is an important parameter which affects the removal efficiency of a sorbent at given initial concentration of the sorbate. The adsorption of MB using various prepared carbons viz. C800, MIP, MIK and commercial carbon COM1 at different dosages viz. 10 to 250 mg, has been studied, keeping other parameters viz. contact time (30 minutes), temperature constant. The percentage removal of MB at different dosages of carbons is presented (Graph 2).

All the prepared carbons show similar trend. Percentage adsorption goes on increasing with increasing amount of adsorbent dosage. Commercial carbon is superior to prepared carbons. There is clear cut distinction at lower loading of carbon. This is due to high surface area of commercial carbon as compared to prepared carbons. Amongst the prepared carbon, MIP has shown better performance as compared to MIK and C800. This can be due to its acidic pH. At higher concentration of adsorbents, the difference in percentage adsorption between adsorbents is negligible.
Graph 2: Effect of adsorbent dose on the % removal of MB

Similar observations are found in adsorption capacity graph (Graph 3). There is distinction at the lower adsorbent dosage while at higher dosage the values converge.

Graph 3: Effect of adsorbent dose on the adsorption capacity
Applicability of adsorption isotherms

Freundlich Isotherm

The equilibrium data is subjected to Freundlich model. The values of $K_F$ and $1/n$ are obtained from the intercept and slope of the Freundlich plot, $\log q_e$ vs. $\log C_e$ (Graph 4 (a), (b), (c)) and are the measures of sorption capacity and intensity of sorption respectively. The values of $K_F$ is found to be 0.04 mg/g, 0.05 mg/g and 0.08 mg/g for MIP, MIK and C800 respectively. This indicates a fairly good adsorption capacity. The value of $1/n$ is found to be 0.3262, 0.5793 and 0.702 for MIP, MIK and C800 respectively. The value of $1/n$ is in between 0 and 1 indicating that the dye is favorably adsorbed on adsorbent. The smaller value of $1/n$ indicates formation of relatively stronger bonds between adsorbent and adsorbate. The value of correlation coefficient, $R^2$, is 0.63, 0.84 and 0.95 for MIP, MIK and C800 respectively, indicates that the Freundlich isotherm provides fairly good linearity for MIK and C800 carbon.

![Graph 4 (a)](image)

$y = 0.3262x + 0.0335$
$R^2 = 0.6394$

![Graph 4 (b)](image)

$y = 0.5793x + 0.0481$
$R^2 = 0.8426$
Graph 4 (a), (b), (c): Freundlich isotherm for adsorption

**Langmuir Isotherm**

The equilibrium data is further analyzed using linearized form of Langmuir isotherm. The linear plot of Ce/qe vs. Ce, is obtained (Graph 5 (a), (b), (c)), from which the Langmuir constants, Q^0\textsuperscript{-}-maximum adsorption capacity (mg/g) and b - binding energy are determined from the slope and intercept of the plot respectively. Langmuir constant b, which is 0.6084, 0.1135 and 0.6729 for carbons MIP, MIK and C800 respectively, is between 0 and 1 and high value of correlation coefficient, R^2, viz. 0.9793, 0.9655 and 0.9173 for MIP, MIK and C800 respectively, indicates Langmuir isotherm model is suitable for experimental data.
Graph 5(a), (b), (c): Langmuir Isotherm for adsorption

1.7 Conclusions

1.7.1 Carbon Preparation

Proportionate loss in weight is observed in the material during carbonization process. Higher the carbonization temperature more is the weight loss. Activating agents used are effectively removed by washing. After carbonization, only small amount remains in the final product. Removal is more effective in pre-impregnated carbons as compared to mid-impregnated carbons. This is also evident in the ash content of these carbons and extreme pH shown by mid impregnated carbons.
1.7.2 Dye Adsorption

There is distinction between the adsorption capacities of prepared carbons against commercial carbon at lower dosages. At higher loading values match with commercial carbon. MIP carbon is superior in terms of both, adsorption capacity and percentage adsorption, than MIK and MIP. This is because of the acidic pH of MIP carbon, while MIK and commercial carbons show basic pH as dye retards material with basic pH.

Langmuir isotherm is more favourable for all three prepared carbons viz. MIK, MIP and C800 than Freundlich isotherm.

1.8 Experimental

1.8.1 Carbon Preparation

RM was washed with ample amount of DM water to get rid of soil and other foreign particles. It was dried in bright sunlight for 15 days. Stalks were cut to 3-4 cm length. Material was carbonized and treated as is.

Carbons were prepared by only carbonization, pre-impregnation of RM and by mid-impregnation of partially carbonized material. Phosphoric acid and potassium hydroxide were used as activating agents.

In pre-impregnation, RM was soaked in 10 % (w/v) of respective activating agent for 4 hrs at 80°C on magnetic stirrer with heating arrangement. Further it was cooled to room temperature, supernatant solution was decanted.

Material was washed to neutral pH by multiple washings and decantation with DM water. Then, material was dried in oven at 120°C for 8 hrs. Dried material was further used for carbonization.

In phosphoric acid treated material, final temperature for carbonization was 500°C, while for potassium hydroxide treated material, it was 800°C.

In mid-impregnation, raw material was first carbonized at 600°C under flow of nitrogen. Temperature was increased from room temperature to 600°C at rate of 200°C/hr. Carbonized material was soaked in 10 % (w/v) of respective activating agent for 4 hrs at 80°C on magnetic stirrer with heating arrangement.
Further it was cooled to room temperature and supernatant solution was decanted. Material was washed to neutral pH by multiple washings and decantation with DM water. Then, material was dried in oven at 120°C for eight hrs. This was taken for further thermal treatment.

In case of phosphoric acid treatment, the final carbonization temperature after impregnation was maintained as 500 °C for two hours.

With potassium hydroxide, the final carbonization temperature after impregnation was maintained as 800 °C for two hours.

After completion of thermal treatment, material was powdered in mixer grinder and further sieved through 63 micron mesh. As same mesh size carbon particles were employed to carry out further experiments. Oversize material was blended two times more till material passed through 63 mesh.

Prepared carbons were stored in self-sealing polythene liners to prevent ingress of moisture.

Preparation methods which were carried out are summarized (Table 3).

### Table 3: Various methods for preparation of activated carbons

<table>
<thead>
<tr>
<th>RM</th>
<th>Thermal treatment</th>
<th>Activating agent</th>
<th>Activation routine</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cicerarieti num Sticks</td>
<td>RT - 200 °C/hr- 500 °C - maintained for 2 hr</td>
<td>Phosphoric Acid</td>
<td>Pre impregnation</td>
<td>PIP</td>
</tr>
<tr>
<td></td>
<td>RT - 200 °C/hr- 500 °C - maintained for 2 hr</td>
<td>Phosphoric Acid</td>
<td>Mid impregnation</td>
<td>MIP</td>
</tr>
<tr>
<td></td>
<td>RT - 200 °C/hr- 800 °C - maintained for 2 hr</td>
<td>KOH</td>
<td>Pre impregnation</td>
<td>PIK</td>
</tr>
<tr>
<td></td>
<td>RT - 200 °C/hr- 800 °C - maintained for 2 hr</td>
<td>KOH</td>
<td>Mid impregnation</td>
<td>MIK</td>
</tr>
<tr>
<td></td>
<td>RT - 200 °C/hr - 600 °C</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RT - 200 °C/hr - 800 °C</td>
<td>-</td>
<td>-</td>
<td>C 600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C 800</td>
</tr>
</tbody>
</table>
1.8.2 Dye Adsorption

Preparation of solutions

Methylene Blue (MB) (3, 9-bisdimethylaminophenazo thionium chloride), a cationic dye (molecular formula C$_{18}$H$_{18}$N$_{3}$SCl.3H$_{2}$O, molecular weight 373.90 g mol$^{-1}$, with C.I.Number 52015) was chosen as the sorbent. The chemical structure of methylene blue is as shown (Fig.3).

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
(\text{H}_3\text{C})_2\text{N} \\
\text{N(CH}_3)_2
\end{array}
\quad + \quad \begin{array}{c}
\text{Cl}^{-}
\end{array}
\]

Fig. 3: Structure of methylene blue

The stock solution of methylene blue was prepared (1000 mg/l) in distilled water. Systronic colorimeter 112 was used to measure absorbance of sample solution, before and after adsorption.

Optimization of process variables

Batch mode adsorption studies were carried out to study the effects of variables such as

- Adsorbent dose
- Initial concentration of the sorbate

Adsorption process had been optimized with respect to each of these process parameters by varying the parameter-under-consideration and keeping other parameters at a constant value. Effect of each parameter mentioned above was studied and accordingly optimum value of each parameter for maximum removal of adsorbate was determined.

Adsorption experiments were performed using varying amounts (10 mg to 250 mg) of carbons. To each of the weighed material 25 ml of dye (MB) solution of 10 mg/l concentration ($C_0$) was added. The flasks were stirred on a magnetic stirrer for a period of 30 minute at room temperature and then filtered. The amount of dye adsorbed was calculated for all the carbons from the
differences in the initial concentration (\(C_0\)) and equilibrium concentration (\(C_e\)) by measuring absorbance on colorimeter at 615 nm filter.

**Adsorption isotherms**
To study applicability of Langmuir and Freundlich isotherms, desired concentrations of methylene blue (10 mg/l to 30 mg/l) were prepared from stock solution. 25 ml of each of the solution was charged in conical flask. Each carbon (0.2 g) was added to the flask. The solutions were stirred at 200 rpm for 30 min at room temperature. They were filtered through Whatman filter no 42. The absorbance was measured on colorimeter at 615 nm before and after adsorption to evaluate the initial concentration (\(C_0\)) and equilibrium concentration (\(C_e\)) of methylene blue.
All the experiments were carried out in triplicate and mean value of all the three were used.

**Mathematical equations and model**
Freundlich and Langmuir adsorption isotherms are applied in this study.

**Freundlich Isotherm Model**
Freundlich equation describes heterogeneous surface energy term. It explains the adsorption intensity of the adsorbate on the adsorbent surface and is expressed as,
\[
q_e = K_F C_e^{1/n} \quad \text{(Equation 1)}
\]

The linearized Freundlich isotherm\(^{67}\) is represented as,
\[
\log q_e = \log K_F + (1/n) \log C_e \quad \text{(Equation 2)}
\]

Where, \(K_F\) (mg/g) and 1/n are Freundlich constants including all factors affecting the adsorption capacity and favourability of adsorption.

The plots of \(\log q_e\) vs. \(\log C_e\) are used to determine the values of \(K_F\) and 1/n from the intercept and slope.
The Freundlich parameter 1/n relates to the surface heterogeneity. When 0 < 1/n < 1, the adsorption is favourable; 1/n = 1, the adsorption is homogeneous and there is no interaction between the adsorbed species; 1/n > 1, the adsorption is unfavorable.

**Langmuir Isotherm Model**

The Langmuir isotherm has been the most widely used adsorption isotherm. It determines the maximum capacity of adsorbent. The Langmuir isotherm theory is based on the assumption that:

- Adsorption takes place at specific homogeneous sites within the adsorbent,
- There is negligible interaction among adsorbed ions,
- Adsorbent surface is saturated after adsorption,
- All sites are energetically equivalent.

The unmodified Langmuir equation is defined as:

\[ q_e = \frac{Q^0 b C_e}{1 + b C_e} \]  
(Equation 3)

Where,

- \( Q^0 \) = Langmuir constant related to maximum adsorption capacity (mg/g)
- \( b \) = Langmuir constant related to binding energy of the adsorption system (L mg\(^{-1}\))

The Langmuir equation is used in the linearized form in order to evaluate adsorption capacity and Langmuir constant as,

\[ \frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \]  
(Equation 4)

The plot, of \( C_e/q_e \) vs. \( C_e \) was used to determine the values of \( Q^0 \) and \( b \) from the slope and intercept respectively.

The Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (Halls Separation Factor) \( R_L \), which is defined as:

\[ R_L = \frac{1}{(1 + b C_0)} \]  
(Equation 5)
Where,

$C_0$ is the maximum initial sorbate concentration (mg L$^{-1}$). McKay et al.$^{71}$, have shown that the value of parameter $R_L$ indicates the type of isotherm as,

<table>
<thead>
<tr>
<th>Value of $R_L$</th>
<th>Type of isotherm</th>
<th>Value of $R_L$</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable</td>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
<td>$R_L &lt; 0$</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
References