Preparation Of Phosphorized Granular Activated Carbon From Beet Molasses Using Concentrated H₃PO₄

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Abstract
In the present study, the activation features of phosphoric acid have been investigated using beet molasses as a raw material at 150°C in production of phosphorized granular activated carbon (PGAC). The quality of the prepared carbon was verified by measuring its iodine number and ability to adsorb methylene blue dye. The density, moisture content, hardness, effective size, and total ash content were also evaluated. The obtained results were compared with a carbon of a commercial grade supplied by the BDH chemical company. The comparison proved that the prepared carbon is of a good quality and comparable to the commercial one. IR analysis showed the (H₂PO₃) groups were present on the surface of prepared PGAC which enlarged the pores sizes. The PGAC was used for the sorption of MB dye from aqueous solutions at 25°C. The equilibrium sorption isotherms have been analyzed by the models Freundlich and Langmuir methods. The Freundlich isotherm had the highest correlation coefficient.

Key words: phosphorized granular activated carbon, surface area, iodine number, volume activity, molasses, sorption, equilibrium.

Introduction
Carbon has been used as an adsorbent for centuries. Early uses of carbon were reported for water filtration and for sugar solution purification. Activated carbons ability to remove a large variety of compounds from contaminated waters has led to its increased use in the last fifty years. Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. Granular activated carbon is a good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1,000 square meters. This high surface area permits the accumulation of a large number of contaminant molecules.

Activated carbon can be produced from various carbonaceous materials. The most commonly used raw materials include peat, lignite, wood and agricultural by-products and they can be manufactured by physical or chemical activation. Several studies of chemical activation have been conducted with zinc chloride, which has been found to maximize the adsorptive capacity and bulk density of activated carbons produced from lignocellulosic materials such as peach stones. However, phosphoric acid is preferred because of the problems of corrosion, inefficient chemical recovery, and environmental disadvantages associated with zinc chloride. Phosphoric acid activation has been applied to coconut shell, peach stones, coals and hardwoods and shells of nuts like almond, pecan, black walnut and macadamia nut and cotton stalks. The source of the most commonly used activated carbon in commercial practice is peat, asphalt, bituminous coals, lignite, wood, resins, used tires and coconut shell. In recent years, many different agricultural residues were used to produce activated carbon, e.g. palm stone, rice hulls, rice straw, sugarcane bagasse, pecan shells, and from natural precursors (jute and coconut fibers). On the other hand agriculture by products are lignocelluloses wastes that may offer an inexpensive additional source of activated carbons. Conversion of beet molasses by-product into carbonaceous adsorbsents that can be used in food applications such as sugar refining or wastewater treatments would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbonaceous adsorbents.

Molasses is thick syrup obtainable as sugar cane, beet, citrus or wood molasses. All contain 50–55% sugar except citrus, which contains 42%. All are low in protein but high in minerals. The common form is black treacle, a byproduct of the cane sugar industry. Used as a feed supplement to supply additional energy, because of its high carbohydrate content. Beet molasses, sugar byproduct, the brownish liquid residue left after heat crystallization of sucrose (commercial sugar) in the process of refining. Molasses contains chiefly the uncrystallizable sugars as well as some remnant sucrose.

One of the most important physical properties of activated carbon is the surface area. Activated carbons have an extensive internal pore structure that presents a high surface area available for adsorption. Because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production. Basically, there are two different processes for the preparation of activated carbon: physical and chemical activation. Physical activation consists of two steps: the carbonization of the starting material and the activation of the char by using carbon dioxide or steam. In chemical activation, both the carbonization and the activation step proceed simultaneously. Compared with the physical process, an important advantage of the chemical process is
that the yield tends to be greater since carbon burn-off is not required\textsuperscript{[13]}.

In addition, the chemical process allows us to obtain very high surface area activated carbons and takes normally place at shorter time than those used in physical activation. Thus, in the present work, we focus on the preparation of activated carbon from molasses by chemical carbonation and activation with the impregnation reagent H\textsubscript{3}PO\textsubscript{4}.

Due to its well-developed pore structure, activated carbon in either powder or granules has an excellent adsorbent capacity. Depending on the nature of the raw material, on the size of the particles (granules or powder), and obviously on the chosen production process, activated carbons have different adsorption capacities. The quality of activated carbons is evaluated in terms of their physical properties of adsorption and of superficial area, using different analytical methods for liquid phase adsorption \textsuperscript{[14]}.

Phosphoric acid activation has been applied to coconut shell \textsuperscript{[15]}, peach stones \textsuperscript{[4]}, coals and hardwoods \textsuperscript{[8]}, and shells of nuts like almond, pecan, black walnut and macadamia nut \textsuperscript{[10, 9]} and cotton stalks.

Beet Molasses, which is a by-product of the manufacture of sucrose from sugar beets is the raw material in this work, it must contain not less than 48% total sugars expressed as invert and its density determined by double dilution must not be less than 79.50 Brix. IFN 4-30-289 Beet sugar molasses \textsuperscript{[16]}. Granular (20-100 mesh) activated carbons were produced by chemical activation with H\textsubscript{3}PO\textsubscript{4}. The product was characterized for its BET surface area, micropore volume, bulk density, and gravimetric/volumetric methane adsorption/storage capacities. Baksi, S. et al. \textsuperscript{[17]} carried out an investigative study on converting waste bamboo to produce usable activated carbon by impregnating with H\textsubscript{3}PO\textsubscript{4} doping agent.

Marit J. \textsuperscript{[18]} showed that the reaction of a lignocellulosic precursor with a strong chemical reagent, such as phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), at temperatures up to 350\textdegree{}C or above, can lead to the formation of a porous carbon. Depending on the reagent, its concentration, and the carbon precursor material, the carbon will possess a highly developed internal pore structure and be an effective adsorbent for molecules in the gas or liquid phase. The objectives were to improve the understanding of the relationship between activated carbon properties and the structure of the precursor, and to clarify the reaction chemistry and mechanisms.

Gonzalez-Serrano \textsuperscript{[19]} showed that activated carbons with a high BET surface area and a well-developed porosity have been prepared from pyrolysis of H\textsubscript{3}PO\textsubscript{4}-impregnated lignin precipitated from Kraft black liquors. Impregnation ratios within the range of 1-3 and activation temperatures of 623-873K have been used, giving rise to carbons with different porous and surface chemical structure. Increasing the activation temperature and the impregnation ratio leads to a widening of the porous structure with a higher relative contribution of mesoporosity.

Kim D.S. \textsuperscript{[20]}, in his study, investigated the activation features of phosphoric acid using waste peach stones as the raw material in the production of granular activated carbon. The activated carbon produced was found to be as good as that of the commercial ones. Phosphoric acid activation has been applied to coconut shell, coals, hardwoods, shells of nuts like almond, pecan, black walnut, macadamia nut, cotton stalks, and palm date pits \textsuperscript{[21]}.

The present work investigated the feasibility of producing granular activated carbon from beet molasses, by using phosphoric acid impregnated. Methylene blue dye has stable color irrespective of the pH of solution when compared with other dyes \textsuperscript{[22]}. In sorption studies, Methylene blue dye is used as a standard dye to evaluate the sorption capacity of an activated carbon and it gives the rough surface area of the mesoporous carbon.

**Experimental**

In this study, beet molasses from the refining of sugar beets was used for the preparation of activated carbon. Some specifications physical properties and chemical composition of that molasses were mentioned in Table (1) \textsuperscript{[16]}.

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Values</th>
<th>Specifications</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brix</td>
<td>79.5</td>
<td>Calcium, (%)</td>
<td>0.2</td>
</tr>
<tr>
<td>Total Solids (%)</td>
<td>77.0</td>
<td>Phosphorus, (%)</td>
<td>0.03</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.41</td>
<td>Potassium, (%)</td>
<td>4.7</td>
</tr>
<tr>
<td>Total Sugars (%)</td>
<td>48.0</td>
<td>Sodium, (%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Crude Protein (%)</td>
<td>6.0</td>
<td>Chlorine, (%)</td>
<td>0.9</td>
</tr>
<tr>
<td>Nitrogen Free Extract (%)</td>
<td>62.0</td>
<td>Sulfur, (%)</td>
<td>0.5</td>
</tr>
<tr>
<td>Total Fat (%)</td>
<td>0.0</td>
<td>Energy kcal/100g kJ/100g</td>
<td>260 1100</td>
</tr>
<tr>
<td>Total Fiber (%)</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (%)</td>
<td>8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PH min</td>
<td>6.5-8.5</td>
<td>Density g/cm3</td>
<td>1.4</td>
</tr>
<tr>
<td>Moisture % by weight</td>
<td>12-17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A- Preparation and Purification of Activated Carbon:
Preparation steps of phosphorized granulated activated carbon PGAC are as followed:
(24.6 g) of beet molasses were carbonized by adding drop wise 50ml of concentrated ortho phosphoric acid with mixing and digested till all evolved gases are finished. After impregnation, the heating was carried out on hotplate at 150ºC with mixing for about (2 hr) until the foams were settled down.
The phosphorized carbon must be water washed to remove any residual phosphoric acid. This was done by washing the carbon with water many times till the washing water became neutral (pH=7). The cooled carbon was then dried in oven at (200ºC) for (2-3 hrs). The phosphorized carbon was then grinded and sieved to (20-40) mesh, (0.84-0.42 mm). Activation of phosphorized granular carbon was accomplished thermally in furnace at (500ºC) for (1 hr). The final activated carbon was cooled in a desiccator to the ambient temperature and packed in a sealed bottle.
Fig (1), Shows the flow diagram of producing PGAC from Beet Molasses.

B- Activated Carbon Properties Measurements:
1- Adsorption Properties:
1a- Determination of Carbon Activity by Iodine Adsorption Method (Iodine Number)
Iodine number (IN), is the amount (in milligrams) of iodine adsorbed from its aqueous solution by one gram of activated carbon [23]. The iodine number of PGAC was measured according to ASTM D4607-94 [23]. The iodine number of PGAC was measured according to ASTM D4607-94 [23].

1b- Methylene Blue Test for Determination of Carbon Activity (Maximum Adsorption Capacity and Specific Surface Area)
An exact weight (0.1 g) of prepared activated carbon sample was added to an aqueous solution of (20 ppm) methylene blue pigment in a conical flask. The solution was shaken by an electrical shaker for (24 hr) at a temperature of (25ºC) till adsorption of methylene blue from its aqueous solution was completed and a state of equilibrium was reached. The absorbance of the solution was determined using (CECIL-3021 Spectrophotometer) at (λ_max = 665 nm).
The final concentration of methylene blue value was calculated as the number of milligrams of methylene blue adsorbed by one gram of activated carbon using calibration curve, specially performed for this reason [24]. The adsorption of methylene blue allows the determination of the specific surface area of activated carbon directly [25].

1c- Total External Surface Area (Air-Permeability)
The total external surface area (Air-Permeability) of PGAC was measured using ASTM C204-78a [26].
2- Physical Properties:
2a- Measurement of Bulk or Apparent Density (A.D.)
The density of the prepared activated carbon was determined by weighing (10 cm³) of the carbon sample using graduated cylinder according to ASTM D2854-96 [27].
2b- Volume Activity (Volume Iodine Capacity)
Since granular activated carbons are used as adsorbers of fixed volume, apparent density (A.D.)
values can be used to calculate volume activity, which may help to determine the working capacity of an adsorber with alternative carbon loadings [28]. Volume iodine capacity can be determined by multiplying the A.D. by the weight basis activity value IN, therefore carbon which has high volume activity, might actually do more work and therefore have a longer service life than the carbon which has low volume activity and on a net cost basis, it could be the most economical one.

2c- Hardness Number
The harder the activated carbon, the less it will crumble into fine particles during handling and use. The fine particles would then escape from the system, resulting in losses. The standard test method used for Ball-Pan Hardness of activated carbon is ASTM D3802-79 [29].

2d- Measurement of Humidity
The humidity of PGAC was measured using ASTM D2867-83 [30].

3- Determination of Total Ash Content
The inorganic material contained in activated carbon is measured as ash content, generally in the range between 2 and 10% (Yang, 2003). The total ash content of PGAC was determined using ASTM D2866-94 [31].

4- pH Value
The pH Value of activated carbon is a measure of whether it is acidic or basic. The pH value of PGAC was measured with (analysts omnimeter model OM-1B) according to ASTM D3838-83 [32].

5- Particle Size Distributions
A standard test procedure for particle size distribution (PSD) is defined in ASTM D2862 [33]. Particle size distributions are important in carbon systems because they influence handling of the activated carbon material.

6- Effective Size
The effective size is an indicator of the filtration and pressure drop performance of the carbon. The standard test method used for determination of effective size for PGAC is ASTM D2862-97 [34].

Results & discussion
Most organic materials rich in carbon that do not fuse upon carbonization can be used as raw material for the manufacture of AC [35]. During acidic carbonization, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by acidic decomposition of the starting materials (Beet Molasses). The strong chemical agent—phosphoric acid—dehydrates sugar in molasses and results in the formation of water that is removed from the raw material by moderate heat treatment. The activated carbon created by chemical activation has internal porosity developed primarily due to the action of the chemical dehydration agent. It is believed that carbonization and activation step proceeds simultaneously in chemical activation. In the manufacture of granular activated carbons, a wide variety of raw materials and widely varying quality specifications are used. While the raw material itself determines many of carbons physical properties, its adsorption capacity is dependent on the precise and carefully controlled activation process. The most popular aqueous phase carbons are Beet molasses sugar because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product [36]. Activated carbon products can be characterized by physical properties and activity properties. The most important physical properties are surface area, product density; mesh size, abrasion resistance and ash contents.

The results of the study and comparison with commercial activated carbon are shown in Table (2).
It is inferred from the results that the acid treatment of the beet molasses starting material slows down the activation rate and allows the beet molasses sample being activated to develop a larger capacity for iodine and methylene blue adsorption. It would appear that the mechanism for this increased capacity is related to an increase in activation of the inner pores accompanied by reduced surface oxidation. While it is theorized that acid treatment of the starting material may remove compounds which would catalyze or promote rapid oxidation during activation, or that the acid treatment may add or replace acid groups normally expected to slow the rate of activation.

**Total Mass Loss and Yield:** Total mass losses and yield were determined after sample processing. Total mass loss is defined in terms of the raw material mass:

\[
\text{Total Mass Loss Percent} = \frac{M_{\text{raw}} - M_{\text{processed}}}{M_{\text{raw}}} \times 100
\]

Yield is the total process yield based on raw material mass:

\[
Yield = 100 - \left( \frac{M_{\text{raw}} - M_{\text{processed}}}{M_{\text{raw}}} \right) \times 100 = 100 - \text{Total Mass Loss Percent}
\]

Yield percent in this work is 48.8% minimum, which is fair enough for Beet Molasses starting material.

**Hardness/Abrasion Number:** hardness number is a measure of activated carbon’s resistance to attrition, and it is an important indicator of activated carbon to maintain its physical integrity and withstand frictional forces imposed by backwashing etc. There are large differences in the hardness of activated carbons, depending on the raw material and activity level; also it is affected by the granulometry for granular carbon. The hardness number is a better indicator for gas phase applications. The hardness number of the prepared PGAC is good as compared with the commercial one. The mechanical strength of the activated carbon is an important factor for prevention of damaged due to regeneration, recycling etc.

**Iodine Number:** It is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation). It is a measure of the micro pore content of the activated carbon (0 to 28 Å, or up to 2.8 nm) by adsorption of iodine from solution. It is equivalent to surface area of activated carbon between 900 m²/g and 1100 m²/g. It is the standard measure for liquid phase applications. In this investigation the iodine number is almost higher than that of the commercial activated carbon which means it has high activity. The iodine number is also a measure of the volume present in pores up to 28 Å in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing lower molecular weight substances from water. Carbons with a high iodine number are the most suitable for use as vapor phase carbons, as water molecules tend to effectively block off and isolate pore sizes less than 28 Å.

**Methylene Blue:** The methylene blue number is based on how much a sample of activated carbon can...
de-colorize a solution of this aromatic dye and is another indicator of adsorption capacity. It is a measure of mesopore structure (30–500 Å). The mesopores volume lies between the limits 0.1 to 0.5 cm³ per gram and mesopores surface areas are in the range of 20 to 100 m² per gram \[35\]. It was observed that when the equilibrium concentration of methylene blue is more than (20 ppm), there is a decrease of methylene blue adsorption in mg/g, this may be due to the desorption of the methylene blue molecules.

Methylene blue number of prepared PGAC is a little less than that of the commercial one which means a decrease in mesopore structure. The performance study with methylene blue as coloring agent gave good adsorption indices compared with the standard activated carbon sample. According to Rafie R.M. et. al. \[36\], a schematic of the interaction between the methylene blue molecule and PGAC surface is shown in Fig (4). It was assumed that there is a complete adsorption of methylene blue as a mono layer into the surface of PGAC as shown by the plateau of the adsorption isotherm.

The pore volume limits the size of the molecules that can be adsorbed while the specific surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size. The maximum adsorption capacity of adsorbent is related to its maximum internal surface area and pore volume.

**Bulk Density:**
Higher density provides greater volume activity and normally indicates better quality activated carbon. The density is very dependent on the raw material used in the production of the activated carbon. For example, wood based carbons have a lower density than coal based carbons. Here, the bulk density is greater than that of the commercial carbon; this may be due to use Beet Molasses the high molecular weight substance as the raw material. As the carbon adsorbs compounds, the density increases and therefore it is useful for determining the degree of saturation of exhausted carbons and the effectiveness of reactivation when the density goes down again. The apparent density is measured by allowing the carbon to fall into a measuring cylinder at a fixed rate from a vibrating tray to allow settling of the granules. The apparent density is useful in sizing adsorbers for gas phase applications. Raw material such as Beet Molasses was very popular for this type of AC, because their relatively high density, hardness are ideal for manufacture of hard granular AC, it may be used commercially for the production of microporous activated carbons, useful for a very wide range of applications.

**Ash Content:**
It reduces the overall activity of activated carbon, and reduces the efficiency of reactivation. The low ash content of the prepared GPAC may be due to the low concentrations of minerals and oxides present in the starting material (Beet Molasses) and acid washing was found to be useful in reducing the ash content of activated carbon.

**Particle Size Distribution:**
Generally, the rate of adsorption will increase as the particle size decreases, as the process step of diffusion to the carbon surface should be enhanced by the smaller particles. Note that another critical aspect of rate of adsorption is the pore size distribution, and development of "transport pores" within the particle that allow effective migration of contaminants to the point of adsorption. However, particle size may not be that important in all cases, as the porous nature of the carbon particles results in large surface areas in all sizes of carbon particles. Head loss through a carbon bed increases as the carbon particle size decreases and as the uniformity coefficient increases.

The surface area and porosity values are considerably high due to the phosphorus enrichment which is significant. This suggests that most of the pores are reacted with (-PO₃H₂) and enlarge their sizes but not clogged with phosphorus atom. This carbon is called phosphorized activated carbon (PAC). This would be expected to alter the adsorption properties of the carbons due to the electrostatic effects which promotes formation of hydrogen linkage.

The IR spectrum of the prepared PGAC was recorded in the range 4000 to 450 cm⁻¹ as given in Fig 2. Due to low temperature carbonization of the beet molasses, some functional groups may be present on the surface of the carbon. Some fundamental IR absorption frequencies of phosphorized activated carbon are given in Table (3) and it’s IR chart is given in Fig (2). These observations are consistent with the suggested schematic of the interaction occurred between methylene blue molecule and PGAC surface (C-PO₃H₂) which is shown in Fig (3). Infrared investigations showed that carbons activated with phosphoric acid may be regarded as prospective cation exchangers for the removal of heavy metals from water solutions.

The acidic properties of synthetic phosphoric acid activated carbons may be related to phosphorus-containing compounds formed during carbonization. It should be stressed that the acidic character of synthetic chemically activated carbons cannot be ascribed to an excess of phosphoric acid remaining in pores after carbonization, because the carbons were extensively washed with water until a neutral pH was attained.
Table (3): Some fundamental IR absorption frequencies of phosphorized activated carbon.

<table>
<thead>
<tr>
<th>No.</th>
<th>Band position cm⁻¹</th>
<th>Possible assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1130</td>
<td>C-P Stretching, small, sharp and doublet due to the P groups (-H₂PO₃) bonded to activated carbon</td>
</tr>
<tr>
<td>2</td>
<td>950</td>
<td>P=O Stretching</td>
</tr>
<tr>
<td>3</td>
<td>770</td>
<td>P-O-P Asymmetric stretching</td>
</tr>
<tr>
<td>4</td>
<td>930</td>
<td>P-OH Bending, small and sharp</td>
</tr>
<tr>
<td>5</td>
<td>740</td>
<td>P-P Stretching</td>
</tr>
<tr>
<td>6</td>
<td>2780</td>
<td>C=H Stretching, multiplet, sharp and medium</td>
</tr>
<tr>
<td>7</td>
<td>2760</td>
<td>C=H Stretching, singlet, small and sharp</td>
</tr>
<tr>
<td>8</td>
<td>2890</td>
<td>O-H Stretching, multiplet and strong, bonded</td>
</tr>
</tbody>
</table>

Typically, such a treatment lasted for (0.5 – 1 hr). Also, oxygen-containing surface groups of acid character (carboxylic, phenolic and lactonic) should not be ruled out as possible contributors to the cation-exchange properties of synthetic phosphoric acid activated carbons. Although the most acidic oxygen-containing groups are known to begin to decompose at temperatures above (250°C) and thus would not withstand carbonization at (500°C), some acidic groups might be formed as a result of oxidation induced by self-heating and/or subsequent hydrolysis after the cooled samples were exposed to air. Infrared spectroscopy provides information on the chemical structure of the adsorbent material [7].

Fig (3): Schematic model of methylene blue and phosphorized granular activated carbon.
The IR spectra show absorption band at (2890 cm\(^{-1}\)) which assigned to the stretching mode of hydroxyl groups and adsorbed water. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds. The IR spectrum shows absorption bands due to aliphatic (2760 cm\(^{-1}\)) and aromatic structures (2780 cm\(^{-1}\)). The absorption peak at (1130 cm\(^{-1}\)) reported the appearance of C-P bonds in carbon obtained from activation by phosphoric acid, this peak was assigned to phosphates. P-OH bending, P-O asymmetric stretching, and P=O stretching were shown in phosphate-carbon complexes\(^{[37]}\).

From Table (2), it was shown that the volume activity of the prepared PGAC is higher than that of the commercial activated carbon, which indicates that the commercial AC actually do more work and therefore have a longer service life than prepared PGAC of an equal volume.

The pH of the carbon was found to be 5 due to the existence of the functional groups like phenolic, carboxylic, sulfuric and phosphoric acid group\(^{[38]}\).

**Sorption Isotherm Models:**
The distribution of dye molecules between the sorbent and the dye solution is an important factor to establish the sorption capacity of PGAC. Sorption isotherms are the equilibrium relation between the concentration of the adsorbate in the solid phase and in the liquid phase at constant temperature. The sorption isotherm of the MB dye on PGAC at 25ºC is represented in Fig (4). The sorption was found to be dependent on initial MB dye concentration.

\[
y = 3.9412e^{0.1331x} \\
R^2 = 0.9986
\]

![Fig (4): Fitted isotherm model for PGAC-MB system.](image)

The experimental equilibrium sorption data were analyzed using the well known models viz., Freundlich and Langmuir. The Langmuir isotherm takes an assumption that the sorption occurs at specific homogeneous sites within the sorbent\(^{[39]}\), and the equation is:

\[
q_s = \frac{q_m K_s C }{1 + K_C C} \quad (1)
\]

The Freundlich isotherm is an empirical equation\(^{[40]}\) employed to describe the heterogeneous system. The equation is given below:

\[
q_s = K F C_s^{1/\nu} \quad (2)
\]

Fig (5a), illustrate the Freundlich isotherm model fitting on the equilibrium sorption data and Fig (5b) represent fitting sorption data with Langmuir model shows strong affinity between PGAC and MB dye.

![Fig (5): The plot of the sorption of methylene blue dye on Phosphorized Granular Activated Carbon (PGAC) produced from Beet Molasses: a) Freundlich b) Langmuir isotherm at 25 ºC.](image)
Binding parameters of MB dye sorption onto PGAC calculated from intercepts and slopes of these plots are presented in Table (4), together with the correlation coefficients ($R^2$) as a goodness of fit criterion.

### Table (4): Parameters for the fitted isotherm models for the PGAC-MB system at pH = 7 and at 25 ºC.

<table>
<thead>
<tr>
<th>Model</th>
<th>$q_m$ (mg/g)</th>
<th>$K_L$ (L/mg)</th>
<th>$b$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>60.61</td>
<td>0.0217</td>
<td></td>
<td>0.9953</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td></td>
<td></td>
<td>$1/n$</td>
<td>0.56</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$n$</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_F$ (L/g)</td>
<td>25.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r$</td>
<td>0.9965</td>
</tr>
</tbody>
</table>

The values in Table (4) show that the experimental data were more suitable to the Freundlich model than to the Langmuir.

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تحضير كاربون منشط حبيبي مفسفر من مولاس البنجر باستخدام حامض الفسفوريك المركز
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المنخص
تم في هذه الدراسة تحري ميزات استعمال حامض الفسفوريك المركز لتحضير كاربون منشط حبيبي عند درجة 150°م مولاً من مولاس البنجر كمادة لأولية. نوعية وجودة الكاربون المفسفر اختُبرت بواسطة قياس العدد البولي وقابلية إمتاز صبغة المثيلين الزرقاء. تم أيضاً حساب الكثافة، محتملي الرطوبة، الصلاحيات الحجم المؤثر، ومحتوى الرماد الكلي. نتائج التحكمات المستحيلة للكربون المفسفر تمت مقارنتها مع مثيلاتها من المواصفات الكارية، المتبعة وناتجة عن اختبارات الأشعة تحت الحمراء اثبت وجود مجموعة (H3PO4) على سطح الكربون المفسفر المحضر التي تزيد حجم فجوات الكربون. وذلك تمت دراسة الامتزاز الأوزومي لمحصول صبغة المثيلين الزرقاء عند درجة 25°م و تم إجراء تحمل توان الامتزاز الأوزومي بطريقة فريدانش ولذلك يعتبر وجد معالفة فريدانش لامتزاز الأوزومي تمكناً أعلى معامل ارتباط ولمللائمة للنظام العملي إلى حد كبير.