

**SYNTHESIS AND CHARACTERIZATION OF LIGNOCELLULOSE WASTE CARBONS AND THEIR ADSORPTION CAPACITIES IN EMERGING POLLUTANTS****K.NIRMALA JYOTHI**

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**ABSTRACT**

This study was done in order to study if these adsorbents are really efficient in removing contaminants. The adsorbent carbon were produced from peach seeds (PSC), in a muffle and microwave oven and chemically activated with ZnCl_2 . The characterization showed that the yields of the adsorbent is similar, the pH is low, for those whose precursor was cassava and moisture and, consequently, the drying time is less than the values presented by commercial carbon. The scanning electron microscopy analysis indicated a greater porous structure in the carbon produced in muffle. The Langmuir isotherm model was better suited to the AC tested. This paper presents a study on the adsorption of methylene blue dye (MB) in aqueous solution on PSC at room temperature. Batch experiments were conducted to determine the effect of the initial concentration and time on the adsorption capacity and rate of removal. The equilibrium isotherms were analyzed based on the Langmuir and Freundlich equations using the correlation coefficient. The experimental results showed a satisfactory fit to the Langmuir isotherm. The results indicate that it is possible to use carbonaceous adsorbents produced from biomass in the treatment of industrial effluents with methylene blue dye.

Keywords: Adsorption. Peach seeds., Methylene blue adsorption, Isotherms study, surface area, kinetics.

©KY Publications**1. INTRODUCTION**

The chemical and physical characteristics of activated carbon that are directly related to performance and efficiency are mainly determined by the nature of the precursor agent. In adsorption, the choice of material becomes a determining factor for achieving high performance in the process. Activated carbon can come from different materials, as long as it has a high carbon content. In this process, several precursors can be used such as coconut shells, peat, cocoa, sewage sludge and discarded tires, olive cake, bagasse, cotton stem, pequi bark, coconut palm, coffee grounds, cashew bagasse, jute fiber, yerba mate residues, the beef cattle and moringa seeds among other materials.

According to Chandran, B. and Nigam, P., (2002)¹ a large part of the world production of activated carbon is of vegetable origin. In India, materials such as wood, bituminous and sub-bituminous carbon, animal bones and agro-industrial residues such as nuts and coconut shell are mainly used for the production of commercial activated carbon².

The carbonization process consists of the thermal treatment, also known as pyrolysis, of the precursor material normally in an inert atmosphere at a high temperature. It is a material preparation procedure, in



which volatile chemical compounds (H, N and O) and light gases (CO_2 , H_2 , CO and CH_4) are removed to the detriment of heating and decomposition of the molecules, thus forming a fixed carbon mass of primary porous structure³.

Carbonization can be carried out in conventional ovens, by conduction or convection, or in microwave ovens that use electromagnetic waves for heat transfer. Microwave heating generates less energy losses to the environment, and consequently, has greater energy savings when compared to conventional ovens.

The carbon obtained by the process of carbonization of the precursor material is fundamentally micro porous, but this porosity can be filled or partially blocked by the decomposition products. As a consequence, activation becomes necessary to unblock and increase the pores formed. After the carbonization process, the activation process occurs, which consists of submitting the carbonized material to chemical reactions in order to increase the surface area. In this process, the increase in carbon porosity will be promoted. Two different types of processes can be used for the activation of carbon: the chemical process and the physical one. Chemical activation is driven by the impregnation of a chemical dehydrating or oxidizing agent, such as Zinc Chloride (ZnCl_2), Phosphoric Acid (H_3PO_4), Potassium Hydroxide (KOH) Sulfuric Acid (H_2SO_4) among other substances on the precursor material⁴. In this process it is necessary to removal of the chemical reagent by acid extraction. It is important to emphasize the advantage of chemical activation is that it requires lower temperatures in carbonization, which are in the range of 350 to 900°C.

Physical activation involves the reaction of activated carbon with vapors and gases containing oxygen. Physical activation or gasification is a process in which the carbonized material is reacted with an oxidizing gas, usually water vapor or CO_2 or a mixture of both at temperatures in the 800 to 1000°C range. Due to the endothermic nature of the reaction, the particles must be kept in direct contact with the gases. The energy for the activation process can be supplied directly or indirectly depending on the type of oven used. In theory, physical activation results in greater pore production⁵.

The activation process aims to remove the organic compounds present, such as tar, creosote and naphtha, in addition to other residues that may clog the pores⁶. In this context, the activation stage leads to the formation of free sites, with a high adsorption capacity.

2.0 Material and Methods

Obtaining the precursor material: In the production of activated carbon, peach seed precursor material was used as it is a common agricultural residue in the Guntur region.

Preparation of raw material: Initially, the peach seeds were washed and exposed to the sun to lose moisture and prevent the spread of fungi. The lumps were then ground and passed through the sieving process with a magnetic separator using a sieve in the mesh 75 micron size range.

The study was carried out in triplicate and the samples were first submitted to the impregnation process, where the material remained in dynamic contact with the chemical agent for later carbonization. The samples were weighed before and after carbonization, to verify the process yield.

Carbonization process: The carbonization process was carried out in porcelain crucibles, in muffle furnace oven, with different temperature and time ranges being applied in the carbonization process. Thus, temperatures of 500°C, 700°C and 900°C and times of 10, 15 and 20 minutes were used to study the effect of carbonization under the activated carbon adsorption efficiency.

Activation process: To activate the material, 10 g of fresh material were separated and placed in dynamic contact on a Prolab 752A magnetic stirrer at room temperature for 24 hours, with 10 g of Zinc Chloride dissolved in 30 ml of distilled water, ensuring a ratio of 1: 1 (ZnCl_2 / material).

The chemical treatment samples were washed, first, with a 2.5% HCl solution, for total elimination of zinc ions and unblocking of the pores. Subsequently, the samples were washed with distilled water until the pH



of the washing water was equal to the initial pH of the water and then the material was dried in an oven at 110°C for 1 hour.

The procedures for washing the residue, chemical activation and carbonization were established based on the study with a difference in the concentrations and times employed.

2.1 Characterization of materials

Surface area (BET) and porosity analysis: The adsorption and desorption isotherms of N₂ were carried out at 77 K in an Autosorb-1 equipment, Quantachrome. The sample was previously treated at 250°C for 12 h. The pore size distribution was calculated from the N₂ adsorption isotherm using the BJH method. The specific surface area was calculated using the BET equation in the low pressure region ($p/p_0 = 0.200$).

Elementary analysis (CHN) and ash content: The samples were analysed for C, H, N levels in a Perkin Elmer PE 2400 device. The oxygen content was obtained by difference. The ash content was determined by weighing 1 g of material in a previously tarred porcelain crucible; then, the materials were placed in a muffle and heated to 550°C, where they were kept until the complete calcination of the carbon.

Scanning electron microscopy: The morphology of the materials was obtained by scanning electron microscopy (SEM), using a Leo Evo 40XVP device, using a voltage of 25 kV. The sample was placed on the surface of the aluminium support with double-sided carbon tape and covered with a thin layer of gold on an evaporator.

Infrared spectroscopy: The materials were analyzed by spectroscopy in the infrared region with Fourier transform (FTIR), in a Digilab Excalibur device, series FTS 3000 with a spectral range of 400 to 4000 cm⁻¹ and resolution of 4 cm⁻¹. The samples were prepared in the form of a KBr tablet (2 kBar for 2 min).

Adsorption kinetics: The adsorption kinetics was investigated at room temperature (25 ± 1 °C) and pH 5.4. Samples of 10 mg of charcoal were added to containers containing 10 mL of 50 mg/L solution of the dye Methylene Blue. Aliquots of the supernatant were removed at predetermined intervals and the concentration of the adsorbent determined by UV-Visible spectrophotometry (Biosystems, model SP-2000 UV).

2.2 Adsorption isotherms

To obtain the adsorption isotherms, 10 mg of the adsorbent materials were placed in contact with 10 mL of solutions of different concentrations ranging from 10 to 1000 mg/L and kept under stirring for 24 h at room temperature (30±1°C) and pH 5.4. Then, the material was centrifuged and the remaining concentration was monitored by UV-Visible (SP-2000) at the appropriate wavelength for MB.

The amount of material adsorbed per unit mass of adsorbent (mg/g) was calculated using Equation 1.

$$q_{eq} = \frac{(C_o - C_{eq})V}{m} \quad Eq..1$$

where Co (mg/L) and C_{eq} (mg/L) represent the initial and equilibrium concentrations, respectively, V (L) the volume of adsorbate in (g) the mass of the adsorbent material. The isotherms were adjusted to the Langmuir and Freundlich isotherm models. Commercial carbon (Dynamic) was used as a reference.

3.0 Results and Discussion

3.1 Surface area (BET): The N₂ adsorption / desorption isotherm (Figure 1a) indicated high adsorption at low N₂ pressures, showing the formation of micropores. The surface area determined by the BET method was 516 m²/g. The analysis of the distribution of the pore volume as a function of the diameter (Figure1b) indicated that the PSC is mainly composed of micropores with a diameter of 1.1 to 1.7 nm.

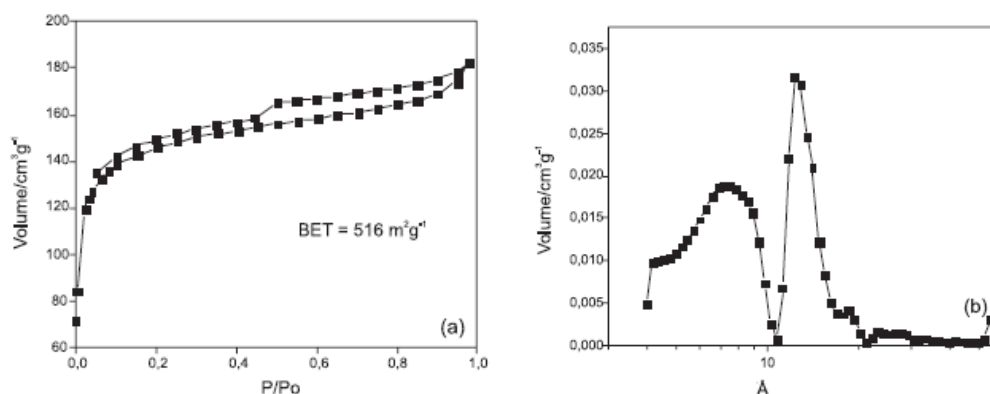


Figure 1: N₂ adsorption / desorption isotherm at 77 K for PSC (a) distribution of pore volume to PSC (b)

3.2 Infrared spectroscopy: Comparing the FTIR spectra of the parchment and the PSC (Figure 2a and b , respectively) it is possible to observe the decrease in the band intensity by approximately 3400 cm^{-1} , characteristic of vibrational stretching of -OH groups that, after the formation of the PSC pass to be, if present, preferably at the edges of the graphical layers. 14 The disappearance of the band in approximately 2929 cm^{-1} , attributed to the symmetrical and asymmetric vibrational stretches of >CH groups, shows the occurrence of parchment pyrolysis.

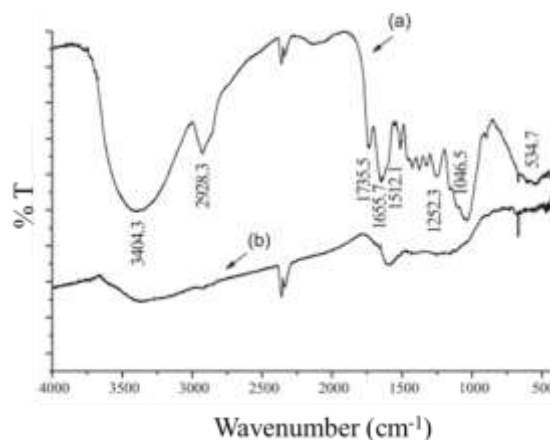


Figure 2: FTIR spectra of seeds (a) and activated carbon of PSC (b)

3.3 Elemental analysis (CHN): The starting material has a low ash content (4.33%), which is a positive factor for the production of activated carbon (Table 1), since the mineral matter causes a dielectric effect on the adsorption process, preferably adsorbing water due to hydrophilic character.

Table 1. Elementary analysis and ash content of precursor and activated carbon prepared by activation with ZnCl₂

Material	C (%)	H (%)	N (%)	O* (%)	C/H	Ashes (%)
Raw Peach	38.7	5.4	1.6	50.4	7.17	4.33
PSC	66.98	3.53	1.9	27.59	18.9	20

However, after pyrolysis and activation there is a high ash content (20%) which can negatively influence the adsorption capacity of the materials? The increase in ash content may be related to the activation method and the fact that the inorganic compounds present in the starting material are retained (occluded or bound to the carbonaceous material) after the pyrolysis process, and are not leached in the washing process. The significant



increase in the C / H ratio and the decrease in the oxygen content in the pyrolysis and activation processes are good indicators of the great extent of the carbonization process. This process occurs with the release of volatile compounds rich in oxygen and hydrogen. The increase in the C / H ratio indicates an increase in the degree of aromaticity after the material activation process.

3.4 Scanning electron microscopy: The morphology of PSC was studied by scanning electron microscopy (SEM), as shown in Figure 3.

SEM analysis of the precursor showed a material with a fibrous structure (Figure 2S , Supplementary Material). After the pyrolysis and activation process, a modification of the precursor structure is observed, with the formation of pores in the form of uniform craters (hive type). The SEM analysis by backscattered electrons does not show the presence of aggregates containing heavy nuclei. This result is an indication that the metal oxides formed must be evenly distributed in the material.

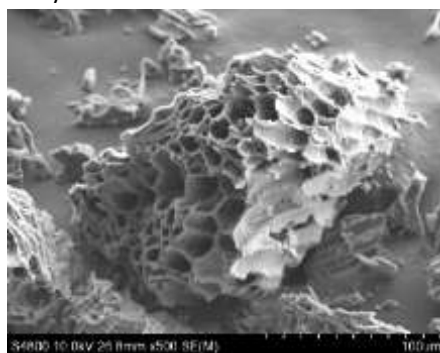


Figure 3: SEM image of prepared activated carbon

3. 6 Effect of dye concentration

For a strict adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial dye concentration. The adsorption capacity of oxidized carbon adsorbent was systematically studied by varying the initial concentration of dye solution between 10 to 100 mg/L and at optimized condition 3.5 to 4.5 g of dose, 35 to 45 min contact time. The effect of initial concentration of dye solution on the extent of removal of dye in terms of amount of the dye adsorbed on the activated carbon material is given in Figure 3.1. The amount adsorbed exponentially increases while the percentage removal exponentially decreases with the increase in initial concentration of the dyes. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of dye.

The results (figure 4) indicate that in the case of MB removal, the percent removal decreases from 99.90 to 84.62 % while the amount adsorbed increases from 2.8543 to 24.1714 mg/g. From the results it was concluded that MB is effectively removed from aq.media.

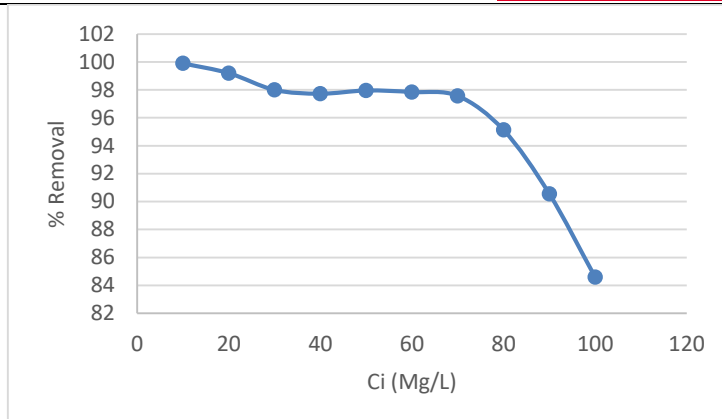


Figure 4: The plot showing the relationship between percent removal of dye by adsorption with prepared carbon.

3.6.1 Adsorption isotherm study: When an affinity is established between activated carbon and MB, the latter is attracted to the solid, through different mechanisms, until an equilibrium is reached between the two. This equilibrium is described by mathematical models, better known as adsorption isotherms, which relates the amount of MB removed and that which remains in solution when equilibrium is reached, at a constant temperature⁷. Several equilibrium models have been developed to fit the experimental data to the adsorption isotherms. The Freundlich and Langmuir models are the most widely used and have been applied in the present work.

Freundlich's isotherm: In 1906, Freundlich studied the adsorption of a solute on activated carbon and found an exponential relationship between the amount of solute adsorbed and the equilibrium concentration, which is expressed by the following equation⁸

The linearized Freundlich adsorption isotherm, which is of the form

$$\log(q_e) = \log K_f + (1/n) \log C_e$$

Where, K_f and $1/n$ are the Freundlich constants, q_e is the amount of dye adsorbed per unit weight of the adsorbent (in mg/g), and if $1/n < 1$ bond energies increases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$, all surface sites are equivalent, related to sorption capacity and sorption intensity respectively. In the present adsorption study these $1/n$ values are 0.31 and 0.2831 for MB removal. The results indicate $1/n < 1$ i.e bond energies increases with surface density. C_e is the equilibrium concentration of dye (in mg/L). The isotherms exhibited the Freundlich behaviour, R^2 0.97 and 0.98 for two dyes, which indicates a heterogeneous surface binding. Linear plots of $\log(C_e)$ Vs $\log(q_e)$ at different dye concentrations are applied to confirm the applicability of Freundlich isotherm model for the removal of dye is shown in Figure 5.

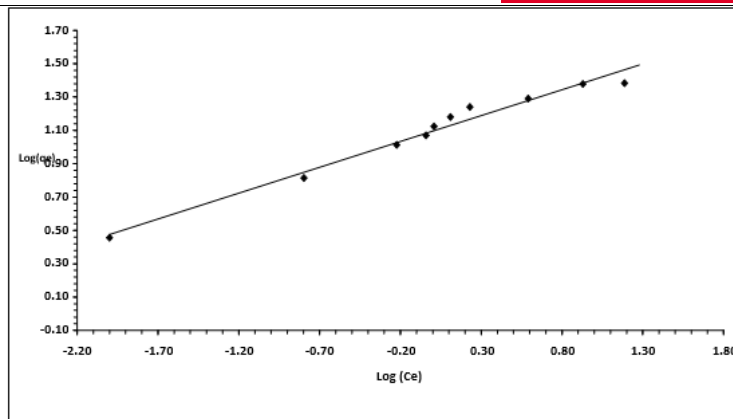


Figure 5: Freundlich isotherm for the removal of MB by adsorption with prepared carbon

Langmuir isotherm⁹: The Langmuir adsorption isotherm has been successfully applied to many adsorption processes and it has been used here to explain the sorption of cationic dye onto carbon. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as (g);

$$C_e/q_e = (1/Q_0b) + C_e/Q_0$$

where q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L), Q_0 and b are the Langmuir constants related to capacity and energy of adsorption, respectively. When C_e is plotted against C_e/q_e , a straight line with slope $1/ba$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 6. The Langmuir constants 'b' and 'Q₀' are calculated from the slope and intercept with Y-axis. The observed linear relationships as evidenced by r-value close to unity (0.99) confirm that adsorption isotherm is applicable and from the R^2 values Langmuir isotherm is more fitted than Freundlich isotherm.

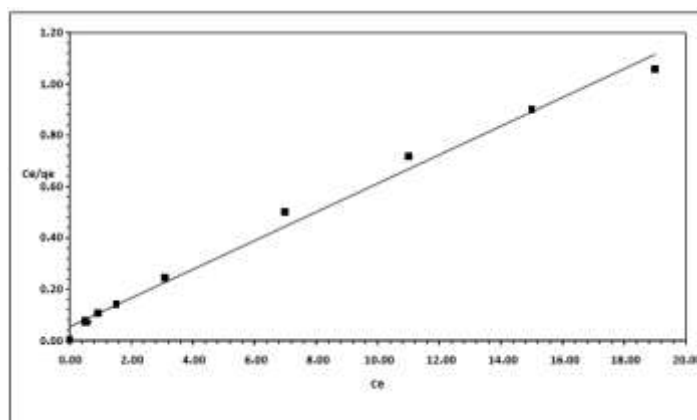


Figure 6: Langmuir isotherm for the removal of MB by adsorption with prepared carbon

3.7 Contact Time Study: The kinetic curves of activated carbon PSC are shown in Figure 7. The extent of methylene blue dye removal by activated carbon increased with the increased of contact time. The removal



percentage of dye by activated carbon PSC was found to be rapid at the initial period of contact time and then became slower with the increase of contact time. This is due to the strong attractive forces between the dye molecules and the activated carbon. The rate of adsorption varied among the different activated carbon samples. The kinetic curves of activated carbons followed power equation with very good correlation coefficient with the range of 0.91 to 0.99. The adsorption kinetic curves show that after a minute of contact time percentage of dye removed varied from 24% to 34%.

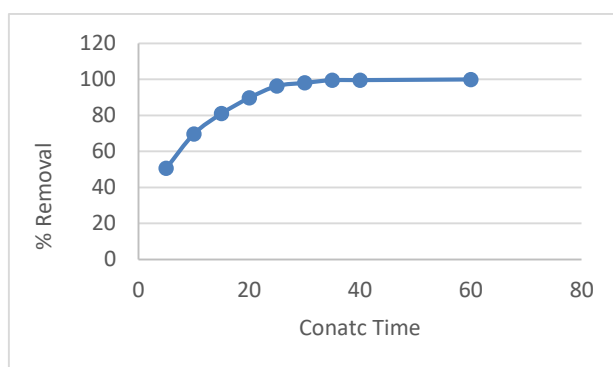


Figure 7: Plot showing the relation between agitation time and the percent removal of MB by adsorption with prepared carbon.

3.7.1 Kinetic adsorption models: The transient behavior of the methylene blue adsorption process by the adsorbents was analyzed using the pseudo-second order model (Figure 8) and the intraparticle diffusion model (Figure 9). The validity of these models can be assessed by the linear graphs of each equation: t/q_t vs t for the pseudo-second order model eq_t vs $t^{1/2}$ for intraparticle diffusion. The kinetic parameters of the methylene blue adsorption process on PSC was obtained by linear regressions of the graphs of each model. The quantitative assessment of the models was performed by comparing the correlation coefficients. The results showed that the adsorption process adjusted better to the pseudo-second order mechanism for adsorption process and, consequently, in the speed control an activated adsorption mechanism or chemisorption must be involved. The linearity observed in all graphs q vs $t^{0.5}$, as well as the deviation of the lines from the origin pointed to the presence of intraparticle diffusion as a non-determining step in the speed of the adsorption process of the methylene blue / PSC system. Similar results were obtained with the kinetic studies of the methylene blue adsorption process on coal ash zeolites sampled in Australia.

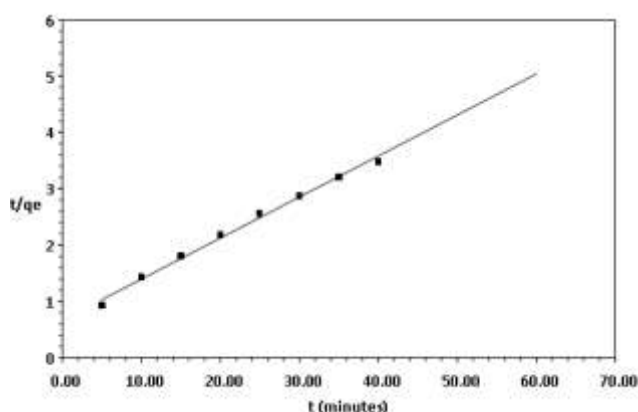


Figure 8: Pseudo second order plots for the decoloration with PSC

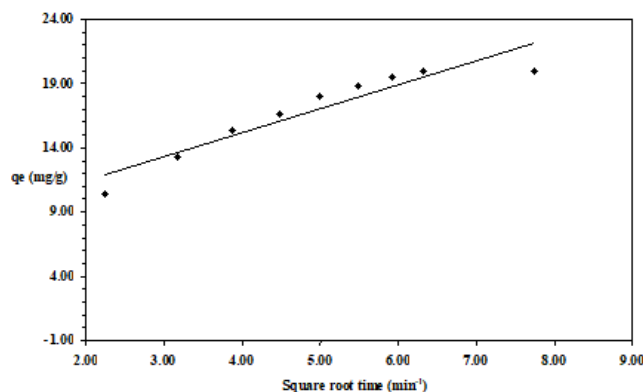


Figure 9:: Plot to evaluate intraparticle diffusion coefficient K_p for the sorption of MB on PSC

CONCLUSION

The PSC defect proved to be a good precursor for the production of activated carbon. The charcoal obtained from the coffee PSC defect had a small surface area when compared to those described in the literature, but it had a maximum adsorption capacity for dyes, comparable to that of commercial activated carbon. The fact that PSC has a higher maximum adsorption capacity for the methylene blue dye compared to the adsorption of the reactive red textile dye may be related to the charges presented by the surface of the adsorbents and the ability of the molecules to access the pores of the adsorbent material. The results show that the AC produced from a PSC defect proved to be potential adsorbents for contaminants in the aqueous medium, and can be used as an alternative source for the production of low-cost adsorbent materials.

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