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Preparation of Activated Carbon from *Thevetia Peruviana* Leave and Seed Skin by Chemical Activation with Phosphoric Acid

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Abstract

Activated carbon was prepared from *Thevetia peruviana* leave (TPLC) and *Thevetia peruviana* seed skin (TPSC) by chemical activation with phosphoric acid. The carbons were characterized with pH of point of zero charge, iodine number, proximate analysis and concentration of surface oxygen functional groups of activated carbon. Their characteristics were compared with that of commercial activated carbon. The adsorption of methylene blue by the prepared activated carbon was analyzed by the Langmuir and Freundlich adsorption isotherms. The data for TPLC fitted well to the Freundlich adsorption isotherms while that of TPSC fitted well to Langmuir adsorption isotherm. The adsorption capacities of the carbon calculated from Langmuir isotherm were found to be 3.95 mg/g for TPLC and 4.19 mg/g for TPSC. The XRD pattern of the activated carbon is similar to that of the commercial activated carbon. Also TPSC and TPLC display ability to remove methylene blue from aqueous system and TPSC having better adsorption capacity. TPLC and TPSC showed comparable characteristic with commercial activated carbon.

Key words: Activated carbon, *Thevetia peruviana*, iodine number, pH point of zero charge, adsorption isotherm.

Introduction

Activated carbons are carbonaceous materials with highly developed internal surface area and porosity, sometimes described as solid sponges (1). It is a processed form of carbon that is extremely porous. It has long been recognized as one of the most versatile adsorbents to be used for the effective purification and removal of pollutant from both liquid and gaseous media. Commercial activated carbons are usually produced from coal which is a limited non renewable resource. The abundant availability, renewability and low cost agricultural materials make them good candidates and sources of raw materials for activated carbon production. Many researchers have shown that the use of these agricultural materials has yielded activated carbons that are economically viable and comparable to the commercial activated carbon. Sugarcane bagasse, Almond nutshells, Rice husk, Rice straw, Coconut shells Lapsi seed stone, Apricot stones, Guava seeds, Peach stones, Orange peel and Peanut shell were among the materials that have been used (2,3,4,5).

Thevetia peruviana is an ever-green ornamental dicotyledonous shrub that belongs to Apocyanaceae family(6). It is commonly found in the tropics and sub - tropics but it is native to Central and South America. It grows to about 10 -18 feet high; the leaves are spirally arranged, linear and about 13 - 15 cm in length. There are two varieties of the plant, one with yellow flowers, yellow oleander, and the other with purple flowers, nerium oleander. Both varieties flower and fruit all the year round providing a steady supply of seeds. Grown as hedges, they can produce between 400 - 800 fruits per annum depending on the rainfall pattern and plant age. The flowers are funnel-like with petals that are spirally twisted. The fruits are somewhat globular, with fleshy mesocarp and have a diameter of 4 - 5 cm. The fruits are usually green in colour and become black on ripening. Each fruit contains a nut which is longitudinally and transversely divided. The fruit contains between one to four seeds in its kernel, and the plants bears milky juice in all organs. In Nigeria, *Thevetia peruviana* has been grown for over fifty years as an ornamental plant in homes, schools and churches by missionaries and explorers(7).

The present work was undertaken produce activated carbon from *Thevetia peruviana* leaf (TPLC) and seed skin (TPSC) by chemical activation with phosphoric acid, compare the characteristics of the activated carbon produced with that of commercial activated carbon from BDH, obtain their XRD profile and compare with that of the commercial carbon, evaluate the ability of the activated carbon produced for the adsorption of methylene blue from aqueous system and model the adsorption process with Langmuir and freundlich isotherms.

Material and Methods

Preparation of activated carbon

The leaves and seed kernel of *Thevetia peruviana* were obtained from Gwagwalada area council of FCT, Nigeria. They were washed with distilled water to removed dirt and dried at 105⁰C in a Carbolite hot air oven for 24 hours. The dried samples were crushed, blended and sieved into suitable sizes. Fractions of particle size less than 300 μm were used for the production of the carbon. The crushed material was further dried at 105⁰C for 24 hours to ensure reduction of moisture in the raw materials to less than 20%. The dried samples carbonized in a box furnace that has been flushed with Nitrogen gas at 600⁰C for 30 minute. The carbonized samples were soaked in a boiling solution of 10% phosphoric acid, allowed to boil for 10 minute and then allowed to stay on the bench for 24 hours. After 24 hours, the samples were washed with distilled water to remove the residual acid and then dried at 105⁰C for 24 hours. The dried carbons were activated in the box furnace at 800⁰C for just 10 minute and allow cooling in a desiccator. After attaining the laboratory temperature, the carbons were washed thoroughly with distilled water until the pH of the filtrate is about 7.00. The carbons were dried at 105⁰C for 24 hours and stored in an air tight container for subsequent study. The activated carbon obtained from the leave, seed skin and commercial activated carbon were labeled TPLC, TPSC and CAC respectively.

XRD Analysis

The structure of these activated carbons were checked and compare with that of the commercial activated by powder XRD technology with Cu α $k\beta$ radiation at room temperature using a PAN analytical high resolution X-ray diffractometer (XPRT-PRO) for $2\theta = 10^0 - 120^0$.

Determination of pH of the carbons

In order to determine pH of TPLC, TPSC and CAC ASTM standard test method⁸.1.0 g of each carbon was transferred into 100 ml distilled water taken in a beaker and kept in a magnetic stirrer for one hour. pH was then measured by pH meter. The samples were tested in duplicates.

Determination of the iodine number of carbon

Standard method reported in literatures (8,9) was used in the determination of iodine number.0.1 g of each dry activated carbon were separately taken in dried 100 ml conical and 5 ml of 5% HCl was added .The flasks were swirled until the carbon was wetted.10ml of 0.1N iodine solution was added to each flask and was shaken properly for 4 minutes. 10 ml filtrate was titrated against standard 0.1N sodium thiosulphate solution using starch as an indicator. The concentration of iodine adsorbed by activated carbon was calculated as amount of iodine adsorbed in milligrams. The iodine number was calculated using the equation below.

Iodine number = C × Conversion factor (C_f)

The conversion factor $C_f = \frac{\text{Molecular weight of Iodine} \times \text{Normality of Iodine} \times 10}{\text{weight of carbon use} \times \text{Blank reading}}$

C = Blank reading – volume of 0.1N thiosulphate used after the adsorption by activated carbon.

Determination of the ash content of carbon

ASTM standard methods (9) were used in determining the moisture content. 2.0 g each of the carbons were separately taken in dried and weighed porcelain crucibles. The crucibles were kept in a carbolite hot air oven maintained at a temperature of 105⁰C for 4 hours. The crucibles were placed in a desiccator for 1 hour and weighed. The drying, cooling and weighing were repeated to get constant weight. The percentage of moisture content was calculated as follows:

$$\text{Moisture \%} = \frac{A - B}{A} \times 100$$

Where: A = weight of dried sample, B = weight of the sample after drying at 105⁰C. The ashcontent was determined using the moisture free sample. The moisture free samples in the crucible were placed in a box furnace at 700⁰C for 6 hours. The crucible were placed in a desiccator for 1 hour and weighed. Ash content in percentage was calculated as follows:

$$\text{Ash} = \frac{D}{B} \times 100$$

Where, D = weight of residue left in gram, B = weight of dried sample in gram.

Determination of pH of point of zero charge (pH_{pzc}) carbons

pH point of zero charge of the activated carbons were determined using the method describe in the literatures (10). 1 g of each of the carbon was taken to eleven 100 ml conical flasks containing 50 ml of 0.01M NaCl, the pH of which was adjusted from 2 to 10 by addition of 0.01M HCl or NaOH. The conical flasks were sealed and placed in a shaker for 48 hours. The content of the flasks was filtered and pH was then measured by pH meter. A graph of final

pH against initial pH was plotted and the point where the curve intersects the line $pH_{\text{initial}} = pH_{\text{final}}$ was taken as the pH_{pzc} .

Determination of surface functional groups

The presence of surface functional groups in the activated carbons was quantified by Boehm titration method(10).1.0 g of activated carbons was taken in contact each with 25 ml of 0.05M NaOH, NaHCO_3 and Na_2CO_3 for acidic functional groups and 0.05 M HCl for basic groups for 24 hours. The solutions were filtered and 5 ml of the filtrate was titrated against 0.05 M HCl for acidic functional groups and against 0.05M NaOH for basic groups. The difference between the groups titrated with NaOH and NaHCO_3 was assumed to be lactones and those titrated against Na_2CO_3 was assumed to be phenol.

Methylene blue adsorption

Methylene blue adsorption tests were conducted by mixing 0.3 g of each, prepared activated carbon and commercial activated carbon separately with 50 ml of 5, 10, 15, 20, 25 and 30 mgL^{-1} methylene blue solutions. After shaking for 24 hours, the suspensions were filtered and methylene blue residual concentration was measured at 665 nm using an UV /Vis spectrophotometer (CECIL-7500). Linear Beer-Lambert relationship was used for the determination of residual concentration.

Result and Discussion

The activated carbon

The activated carbons were prepared by chemical activation using phosphoric acid as the activating agent. Phosphoric acid was selected because of its wide use as an activating agent and it yields the best adsorption results among acid activating agents and the time taken for the process is lesser than those of physical activation methods. It has been reported that the yield of carbon in chemical activation is usually higher than those in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of other volatile products. On carbonization, the impregnated chemicals dehydrate the raw materials, which results in changing and aromatization of the carbon skeleton leading to the creation of a porous structure (10).

XRD profile of the carbons

Figure 1 to 3 shows the XRD profile for the commercial activated carbon (CAC), Thevetia peruviana leaf activated carbon (TPLC) and Thevetia peruviana seed skin activated carbon (TPSC) respectively.

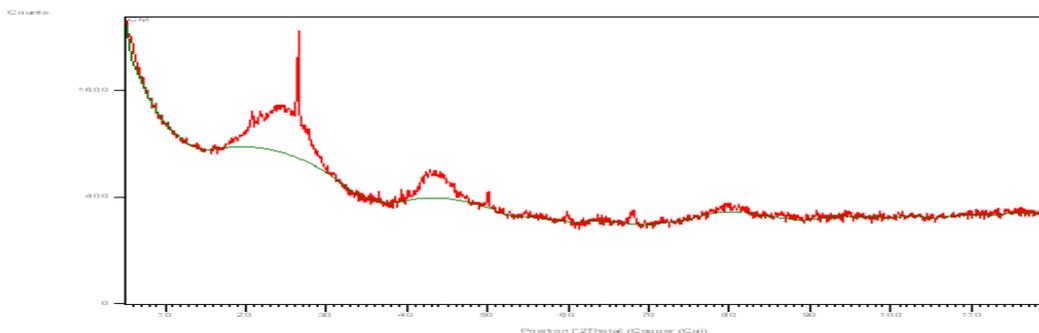


Figure.1. X-ray diffractogram of commercial activated carbon (CAC) from BDH

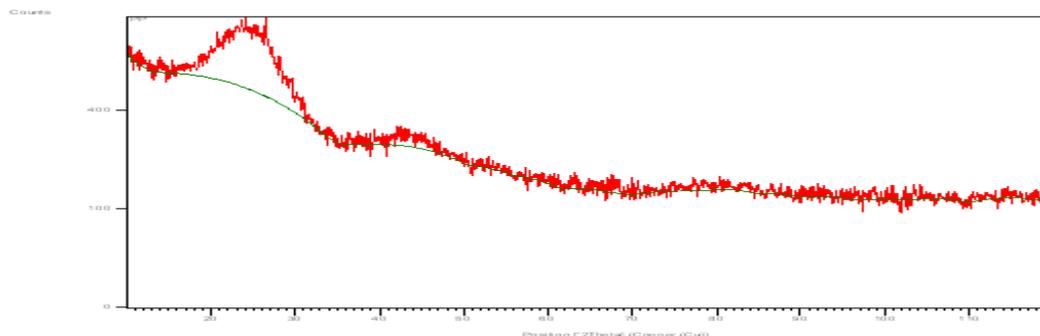


Figure.2. X-ray diffractogram of Thevetia peruviana leaf activated carbon (TPLC)

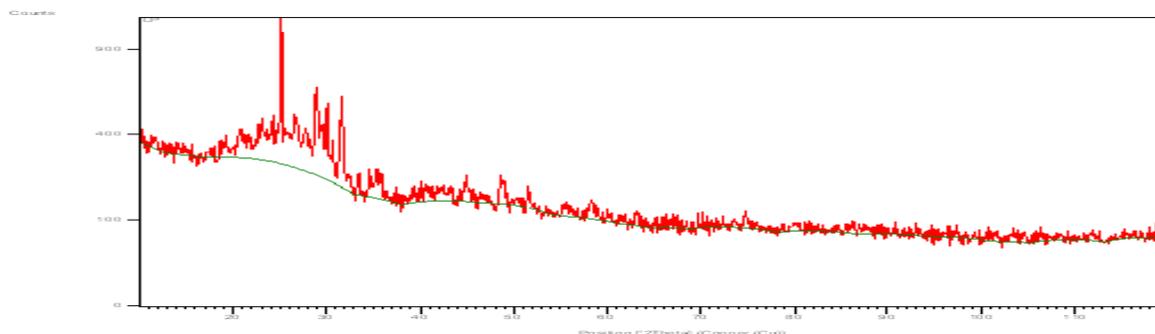


Figure.3. X-ray diffractogram of Thevetia peruviana seed skin activated carbon (TPSC)

The peak intensity evolution of the three carbon shows high intensity at position $[^{02}Th]$ range of 25.12 to 26.55. This peak correspond to peak (hk) and (002) peak type which is a characteristic for raw activated carbon (11). Comparing the sharpness and the intensity of the peak, it was observe that the commercial activated carbon (CAC) has a better peak followed by Thevetia peruviana seed skin activated carbon (TPSC).

Characterization of the activated carbon

Table 1 show the result of the characterization of the TPLC, TPSC and CAC. The moisture and ash content of the TPLC and TPSC are more than that of CAC. The ash content of TPSC is comparably low to that of TPLC. This indicates that the Thevetia peruviana seed kernel is a better raw material for the preparation of activated carbons compare to the leave. Ash content reduces adsorptive power of activated carbons and the efficiency of reactivation. A small increase in ash content causes a decrease in adsorptive properties of activated carbon. So lower the ash content better the activated carbon for use in adsorption process(12). Therefore, the activated carbon prepared from the seed kernel can be used as a potential adsorbent in place of commercial activated carbon.

Table 1 Physicochemical analysis of phosphoric acid activated *Thevetia peruviana* leaf and seed skin carbon (TPLC and TPSC) and commercial activated carbon (CAC)

Property	TPLC	TPKC	CAC
pH	6.43	6.53	6.8
Moisture (%)	4.31	10.24	5.09
Ash (%)	45.21	15.35	4.78
Iodine number(mg/g)	435.65	511.84	804.28
pHpzc	4.95	5.66	6.79
Carboxylic (meq g-1)	0.035	0.033	0.045
Lactonic (meq g-1)	0.017	0.045	0.018
Phenolic (meq g-1)	0.017	0.036	0.015
Basic site (meq g-1)	0.032	0.034	0.036

The pH of TPLC, TPSC and CAC was found to be 6.43and 6.53 and respectively. A carbon of pH 6-8 is acceptable for most application such as for sugar decolorization, water treatment (12) etc. pH is affected not only by the reaction of carbon dioxide but also by organic and inorganic solutes present in water. Any alteration in water pH is accomplished by the change in other physicochemical parameters (13). The pHpzc of an adsorbent indicates the net surface charge on the surface of the carbon in solution. If the pH of the solution in which the carbon is being used is less than the pHpzc of the carbon, the carbon surface will have net positive charge as a result be a surface on which anion may be adsorbed. On the other hand, if the solution pH is greater than that of pHpzc of activated carbons, the surface of the carbons will bear negatively charged and cations may be adsorbed on the surface. The pHpzc of TPLC, TPSC and CAC were found to be 4.95, 5.66 and 6.79 respectively.

Figure 1 shows the curve for determination of pHpzc for TPSC. The adsorption of aqueous iodine is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm (14). The iodine number is defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration. It is an indication of the adsorption capacity in microspores; therefore it is often employed to examine the adsorption capacity of the activated carbons by researchers. It is accepted as the most fundamental parameter used to characterize activated carbon performance. It gives the measure of activity level (higher number indicates higher degree of activation). Table 1 show the iodine number of TPLC, TPSC and CAC. The iodine number is greater in CAC compare to TPSC and TPLC. This shows that CAC has greater surface area and available microspores for adsorption of iodine molecule on the surface than the TPSC and TPLC. CAC is actually expensive for the adsorption process.

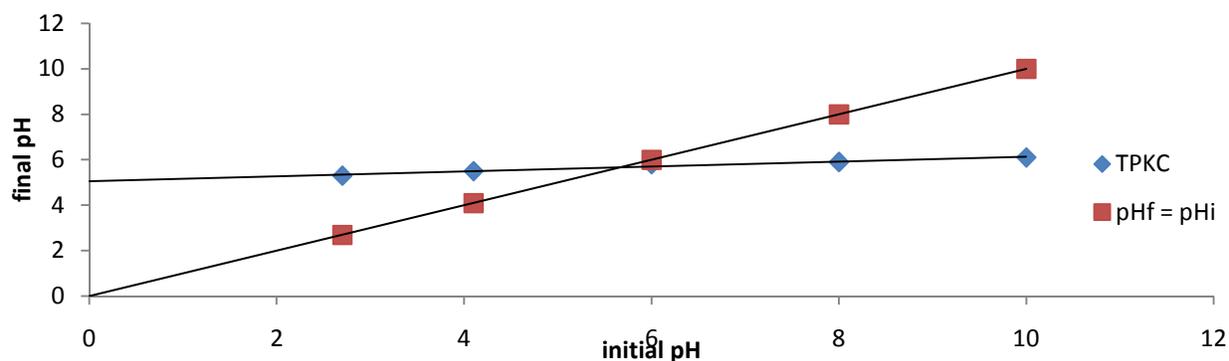


Figure1. Graph of final pH against initial pH for determination on pHpzc for TPKC

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 surface of carbon surface overcome the attractive forces of the liquid (15). Thevetia peruviana seed kernel is inexpensive readily available material, the activated carbon obtained from it in this study TPSC has iodine number of about 511 and therefore it can be a candidate for production of activated carbon for adsorption processes. TPLC has iodine number of about 435. The quantification of surface functional groups of activated carbons was determined by Boehm titration. The method based on that the weakest base NaHCO_3 neutralizes only the strongest acidic functional groups which are carboxylic acid groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups(16,17,18). The strongest base NaOH neutralizes carboxylic, lactonic and phenolic groups. On the basis of amount of acid and bases consumed the different kinds of functional groups can be quantitatively calculated. The presence of basic groups in activated carbons was determined by titration with HCl . Carboxylic groups were therefore quantified by direct titration with NaHCO_3 . The difference between the groups titrated with Na_2CO_3 and those titrated with NaHCO_3 was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na_2CO_3 was assumed to be phenol. Basic sites were determined by titration with HCl . Neutralisation points were known using methyl red indicator.

Adsorption isotherm

The adsorption isotherm gives information on how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process attains an equilibrium state. The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is known as adsorption isotherm (19). Langmuir and Freundlich adsorption isotherm models are employed in this study to describe the experimental adsorption isotherm(20). The applicability of the isotherm equations was compared by judging with the coefficients of determination R^2 . Langmuir adsorption is based on the fact that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can be represented by:

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0}$$

Where q_e is the amount of methylene blue adsorbed (mg/g) and C_e is the equilibrium concentration of methylene blue in the bulk solution (mg/L) while Q^0 is the langmuir monolayer adsorption capacity (mg/g) and $b(\text{L}/\text{mg})$ is the Langmuir constant(21,22). Langmuir constant and adsorption capacity for the adsorption of methylene blue from aqueous system by TPLC and TPSC were determined from the slope and intercept of the plot C_e/q_e versus C_e (Figure 2) and are presented in table 2.

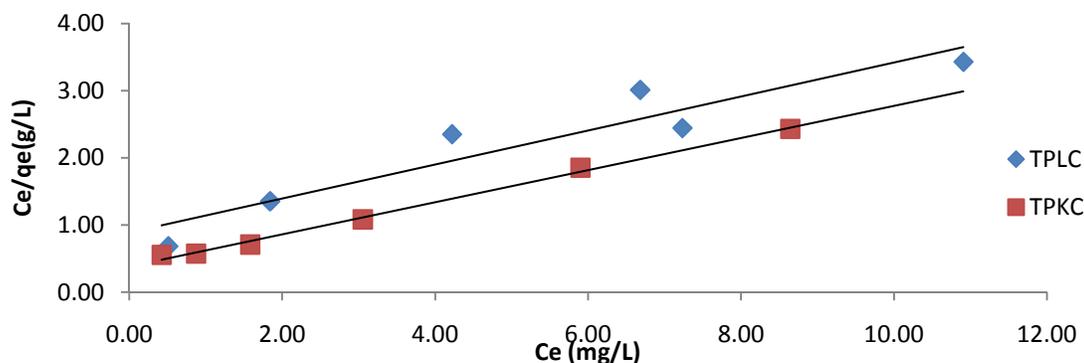


Figure.2. Langmuir Isotherm for the adsorption of methylene blue by TPLC and TPSC

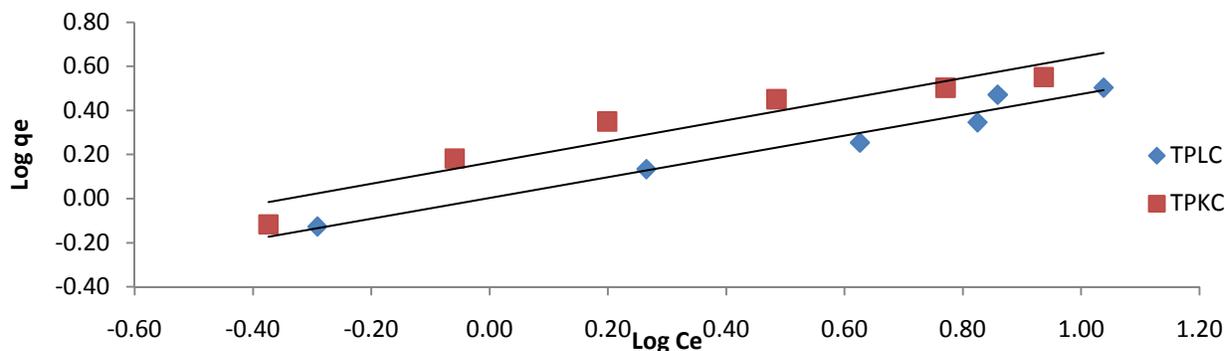
Table 2 Langmuir and Freundlich constants for methylene blue adsorption onto TPLC and TPSC

Adsorbent	Langmuir			Freundlich		
	Q ⁰ (mg/g)	b(L/mg)	R ²	K(mg/g)	n	R
TPLC	3.59	0.31	0.9701	1.01	2.38	0.8903
TPSC	4.19	0.61	0.9956	1.46	2.08	0.9098

Freundlich isotherm is an empirical equation describing the heterogeneous adsorption and assumes that different sites with several adsorption energies are involved. The linear form of the Freundlich equation is shown below:

$$\text{Log } q_e = \text{Log } K + \frac{1}{n} \text{Log } C_e$$

Where K and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. From the slope and intercept of straight portion of the linear plot obtained by plotting log q_e versus log C_e (Figure 3) the values of Freundlich parameters are calculated and presented in Table 2.

**Figure.3. Freundlich Isotherm for the adsorption of methylene blue by TPLC and TPSC**

As presented in Table 2 the activated carbon from the seed skin of *Thevetia peruviana* (TPSC) has better adsorption capacity for methylene blue than the carbon obtained from the leave (TPLC). It has been reported in the literature that if the coefficient of determination R² is greater than 0.5 it is an indication of good fit (23). Therefore, the methylene blue adsorption data gave a good fit for both the Langmuir and Freundlich isotherm. However, comparing the R² value in Table 2, it was observed that the Langmuir model provide a better fit for the adsorption process. This will support the theory that the number of active sites on the carbon surface is limited and methylene blue forms a monolayer on the surface. The values of the Freundlich exponent 'n' obtained in this study are greater than 1 for both TPLC and TPSC, this indicate favourable adsorption of the methylene blue by the adsorbent (24,25,26). Similar result has been reported in literatures (10).

Conclusion

Activated carbon was prepared from *Thevetia peruviana* leaf and seed skin seed by chemical activation with phosphoric acid. Different parameters like iodine number, methylene blue adsorption, ash content, moisture content, pH_{pzc}, surface functional groups have been determined to find the quality of the activated carbon and compare with that of the commercial activated carbon. The experimental data of methylene blue adsorption is good in agreement with Langmuir adsorption model and has shown to a better fitting to the experimental data. The monolayer adsorption capacity calculated from Langmuir model is 3.95 mg/g for TPLC and 4.19 mg/g for TPSC. The activated carbon is found to be comparable to the commercial activated carbon. The activated carbon prepared from *Thevetia peruviana* leaf and seed skin seed can be used as an adsorbent.

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