

Adsorption of p-Phenylenediamine onto Activated Carbon Prepared from *Jatropha curcas* and *Terminalia catappa* Seed Coats

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Abstract

This research work is concerned with the applicability of sodium hydroxide-activated carbon prepared from *Jatropha curcas* seed coats and *Terminalia catappa* seed coats in the removal of p-phenylenediamine (PPD), a component of hair dye industrial effluent. The surface characteristics of the prepared activated carbons were examined using Scanning Electron Microscopy (SEM), Brunauer- Emmett-Teller (BET) surface area analysis and Fourier Transform Infrared Spectroscopy (FTIR). The influence of various factors such as initial concentration, pH, contact time, adsorbent dose and temperature were studied and the p-phenylenediamine adsorption capacity was found to be 32.4 mg/g and 45.5 mg/g for *Jatropha* activated carbon (JAC) and *Terminalia* activated carbon (TAC), respectively. The experimental data were analysed using Langmuir, Freundlich and Dubinin-Radushkevich isotherms. The data could be fitted successfully for both systems by the Langmuir and Freundlich isotherms. The data show also that the sorption process is exothermic and that it follows pseudo second order kinetics.

Keywords: Activated carbon; Adsorption; P-phenylenediamine; Kinetics; Thermodynamics.

Introduction

Para-phenylenediamine is used extensively in chemical industries as a component of hair dye and for other purposes as well. The wastes emanating from these industries are mostly discharged into the surface water body. The discharge of these coloured effluents presents a major environmental problem because of their toxic effects.^[1] Therefore, dye wastewater needs to be treated for the protection of human health and for environmental safety. Many methods such as sorption using activated carbon, chemical coagulation, ion exchange and biological treatments, have been developed for the removal of dyes from wastewater before being discharged into the environment.^[2] Among these methods, activated carbon sorption is highly cost effective and highly efficient in removing dyes and pigments as well as other organic and inorganic pollutants.^[3]

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Activated carbon can be derived from different sources and prepared in various production processes. The nature of the raw materials used, the activation process employed and the process parameters determine its physical properties and its efficiency in pollutant removal. Modification of the activation process affects the nature of the internal and external surface area as well as the pore size and pore size distribution of activated carbon.^[4-6] Hence, research is going on to prepare activated carbon of high surface activity from agricultural wastes at low cost for the removal of organic dyes.

The aim of this research is to evaluate the potential of activated carbon prepared from the seed coat of *Terminalia catappa* and *Jatropha curcas* via chemical activation in the removal of p-phenylenediamine from aqueous medium.

Materials and methods

Preparation of adsorbents

Terminalia catappa fruits were collected within the campus of University of Ilorin. The seed coats were washed, air dried and cracked. *Jatropha curcas* fruits were collected from a private estate at Oke Oyi, Kwara state, washed and air dried. Carbonization of the seed coats was carried out for 90 minutes at a temperature of 500°C. The carbonized samples were ground and sieved with mesh that allows the passage of particles < 90 µm.^[7] The prepared carbon was soaked in 0.5 M NaOH for 24 hours after which the carbon was filtered, washed to neutral pH and then air dried. The activation was completed by heating for 1 hour at a temperature of 200°C. The prepared *Jatropha curcas* seed coat activated carbon (JAC) and *Terminalia Catappa* seed coat activated carbon (TAC) were cooled and stored for use.^[8]

Characterization of the adsorbents

Proximate analysis

Moisture content: 0.20 g sample was weighed and heated in open crucibles at 105°C for 2 hrs. Heated crucibles were cooled and re-weighed.^[9]

Ash content: 0.20 g sample was weighed and heated in open crucibles at 750°C for 1.5 hr. The crucible was then cooled and re-weighed.^[9]

Bulk density: 5.00 g sample was weighed in a graduated cylinder and tapped until a constant volume is noted. The mass is determined by weighing.^[9]

Instrumental analysis

Scanning electron microscope (ASPEX 3020) was used to determine the morphological characteristics of the prepared JAC and TAC. 8400S Fourier transform infrared spectrometer was used to determine the functional groups present on JAC and TAC. An ASAP 2020 instrument was used to determine the BET specific surface area, the pore volume and diameter of JAC and TAC by nitrogen multilayer adsorption measured as a function of relative pressure.^[10]

Preparation of the adsorbate solutions

Stock solution of 500 mg/L of p-phenylenediamine in methanol was prepared and the required concentrations were prepared via serial dilution using deionised water. The concentration of PPD was monitored by means of UV-Visible spectrophotometry (Beckman Coulter DU 730) at a wavelength of 290 nm. A calibration curve with the concentration ranging from 10 to 100 mg/L was obtained.

Batch adsorption studies

The effect of initial concentration, pH, contact time, adsorbent dose and temperature on the adsorption of PPD onto JAC and TAC was investigated in batch mode aiming at evaluating their adsorption performance.^[11,12] A series of 20 ml-PPD solutions of different concentrations was prepared, their temperature was controlled at $28 \pm 2^\circ\text{C}$. To each solution, a known mass (0.020 g) of activated carbon was added and shaken in a mechanical shaker for 120 min at 200 rpm. After centrifuging for 2 min, the final PPD concentration in solution was determined by UV- Vis spectrophotometry at maximum absorbance wavelength (290 nm). The quantity adsorbed was evaluated using equation 1:

$$q_e = \frac{c_o - c_e}{m} \times V \quad \text{..... (1)}$$

where q_e is the quantity adsorbed in mg/g, c_o is the initial concentration of the adsorbing species in solution (mg L^{-1}), c_e is the concentration of the adsorbing species in solution (mg L^{-1}) at time t or after equilibrium has been established, V is the total volume of the solution used (dm^3) and m is the mass of the adsorbent used (g).^[13-15]

Adsorption isotherms

Freundlich, Langmuir and Dubinin-Radushkevich isotherms were used to study the type of interaction between the prepared activated carbons and the PPD.

Freundlich isotherm

This isotherm is an empirical equation and can be employed to describe heterogeneous systems.

$$q_e = K_f c_e^{1/n} \quad \text{..... (2)}$$

where q_e is the amount of substance adsorbed at equilibrium in (mg/g), c_e is the equilibrium adsorbate concentration in the fluid (mg/L), $1/n$ is a heterogeneity factor less than 1 if the adsorption process is favourable, K_f is the Freundlich constant which is a measure of adsorption capacity (mg/g). K_f can also be defined as the adsorption or distribution coefficient and represents the quantity adsorbed for a unit equilibrium concentration.^[16] The linearized form of Freundlich model is given by the equation 3:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad \text{..... (3)}$$

A plot of $\log q_e$ against $\log c_e$ gives a straight line with $1/n$ as slope and $\log K_f$ as intercept.^[17]

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where maximum adsorption at the surface is achieved.^[18] The linear form of Langmuir isotherm model given by the equation 4 and the separation factor by equation 5:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} c_e \quad \dots (4)$$

$$R_L = \frac{1}{1 + K_L c_o} \quad \dots (5)$$

where c_e is the equilibrium concentration of the adsorbate (mg/L), q_e the amount adsorbed per unit mass of adsorbent (mg/g), K_L is the Langmuir adsorption constant and $q_{\max}$ is the maximum adsorption capacity (mg /g). R_L is a dimensionless constant referred to as separation factor or equilibrium parameter. If $RL > 1$, the adsorption is unfavourable, $RL = 1$ it is linear, $0 < RL < 1$ the adsorption is favourable and if $RL = 0$, the adsorption is irreversible.

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D-R) isotherm is an empirical equation where the adsorption is characterized by multi-layer condensation involving van der Waals forces and is suitable for physisorption.^[19] The expression for the linear form of the D-R isotherm is given by equation 6:

$$\ln q_e = \ln q_d - \beta \varepsilon^2 \quad \dots (6)$$

where q_d is the D-R constant which refers to maximum adsorption capacity (mg/g), β (mol^2/J^2) is a constant related to free energy and ε is the Polanyi potential which is defined in equation 7 as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \quad \dots (7)$$

where R is the general gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the absolute temperature. The constant β gives the mean free energy E (equation 8):

$$E = \frac{1}{\sqrt{2\beta}} \quad \dots (8)$$

E values between 1–16 kJ/mol indicate physical adsorption while values above 16 kJ/mol indicate chemisorptions.^[20]

Adsorption kinetics

Studying the adsorption kinetics is important for determining the adsorption efficiency and its potential applications.^[21] Three kinetic models, pseudo first-order, pseudo second-order and Elovich equation, were used to examine the experimental data.

Pseudo first order

The pseudo-first order equation was successfully applied to describe the rate of adsorption from the liquid phase.^[22] The integrated form is given by equation 9:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{..... (9)}$$

where q_e and q_t are the amounts of adsorbed (mg g^{-1}) at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the rate constant of the pseudo first-order adsorption process.

Pseudo second order

The integrated form of pseudo second order model is given by equation 10:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{..... (10)}$$

where q_e is the amount adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at time t (mg/g) and k_2 is the rate constant for pseudo second order adsorption (g/mg.min). Thus, a plot t/q_t versus t should give a linear relationship with a slope of $1/q_e$ and an intercept of $k_2 q_e^2$.^[22]

Elovich model

The Elovich or Roginsky – Zeldovich equation is generally expressed as follows:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad \text{..... (11)}$$

where q_t is the amount adsorbed in mg/g at time t , α is the initial rate of sorption in $\text{mg.g}^{-1}\text{min}^{-1}$ and β is the desorption constant in g/mg .

To simplify the Elovich equation, Chien and Clayton assumed that $\alpha \beta \gg 1$, and on applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, integration yields equation 12 and the constants α and β can be obtained from the slope and intercept of the linear plot of q_t versus $\ln t$.^[23]

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad \text{..... (12)}$$

Intra-particle diffusion model

The adsorbate transport from solution to the surface of the adsorbent particles may occur in several steps. The overall rate of adsorption may be controlled either by one or more steps which include, for example, film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or by a combination of more than one of these steps.^[23] In batch mode with rapid stirring, there is also the possibility that the transport of adsorbate molecules from solution into the pores of the adsorbent is the rate controlling step. This possibility was tested in terms of a graphical relationship between the amount of dye adsorbed and the square root of time for different initial dye concentrations.

$$q_t = k_{diff} t^{1/2} + C \quad \text{.....(13)}$$

The initial portion of the plot could be related to mass transfer and the linear part is due to intra-particle diffusion. The features of the plots of q_t (mg/g) vs $t^{1/2}$ ($\text{min}^{1/2}$) characterize the different steps of adsorption process.^[22] The value of rate constant for intra-particle diffusion, k_{diff} ($\text{mg/g min}^{1/2}$), for different initial dye concentrations for all adsorbents was determined from the slopes of the linear portions of the respective plots.

Adsorption thermodynamics

The adsorption of PPD onto the adsorbents was investigated as a function of temperature. The value of thermodynamics parameters ΔG° , ΔH° and ΔS° were calculated to determine the spontaneity and feasibility of the adsorbent-adsorbate interaction. The following thermodynamics relations (equations 14 and 15) were used to determine the thermodynamics parameter

$$\Delta G^\circ = -RT \ln K \quad \text{..... (14)}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} \quad \text{..... (15)}$$

K is the equilibrium constant which was determined by plotting q_e/c_e against c_e and then dividing the intercept by q_{max} . T is the temperature in Kelvin and R is the general gas constant. A plot of $\ln K$ against $1/T$ should be linear and ΔH° and ΔS° can be determined from the slope and the intercept, respectively.

Result and discussion

Characterization of the adsorbent

Proximate analysis

Table 1 shows the results of the proximate analysis of JAC and TAC. The lower ash content reveals that both JAC and TAC could be used for adsorption ($n=3$, $0 \leq \%E \leq 0.88$).

Table 1: Proximate analysis of adsorbents, isotherms fitting parameters, kinetic and thermodynamic parameters of adsorption of PPD onto JAC and TAC.

Parameters		Values (JAC)	Values (TAC)
Proximate			
% Moisture Content		34	31.05
% Ash content		9.9	8.01
Bulk density (gcm ⁻³)		1.33	2.00
Isotherms			
Langmuir	q _{max} (mg/g)	31.35	51.02
	R _L	1.5x10 ⁻³	0.107
	R ²	0.9976	0.9556
Freundlich	K _f (mg/g)	1.297	0.891
	n	1.01	0.831
	R ²	0.969	0.9645
Dubinin-Radushkevich	β (mol ² /J ²)	6 x10 ⁻⁶	7x10 ⁻⁶
	E (Jmol ⁻¹)	288.7	267.3
	R ²	0.7769	0.7796
Kinetics Model			
Pseudo-first order	k ₁ (min ⁻¹)	0.0138	0.0307
	R ²	0.9847	0.9647
Pseudo-second order	k ₂ (gmg ⁻¹ min ⁻¹)	0.0125	1.52x10 ⁻³
	R ²	0.9985	0.9862
Elovich	α	2.73x10 ⁻³	18.18
	β	0.452	0.101
	R ²	0.9867	0.9654
Thermodynamics			
ΔH (kJmol ⁻¹)		-61.7	-31.1
ΔS (Jmol ⁻¹ K ⁻¹)		-201	-97

Surface morphology

The micrographs of prepared JAC and TAC are presented in figure 1a & 1b, respectively. Figure 1 reveals the morphological characteristics of the surface of the prepared activated carbon showing structures having cavities, pores and rough surfaces. The surface is pitted and fragmented due to carbonization and activation using the chemical method.^[24, 25]

Surface area and pore characteristics

The results of the N₂ adsorption-desorption experiments show the BET surface area, pore volume and pore size of JAC to be 50.29 m²/g, 0.0265 cm³/g and 21.1 Å, respectively, while those for TAC were found to be 75.70 m²/g, 0.0476 cm³/g and 25.1 Å, respectively. These values indicate that the surface of JAC and TAC is dominated by mesopores which are in general favoured in adsorption applications.^[26]

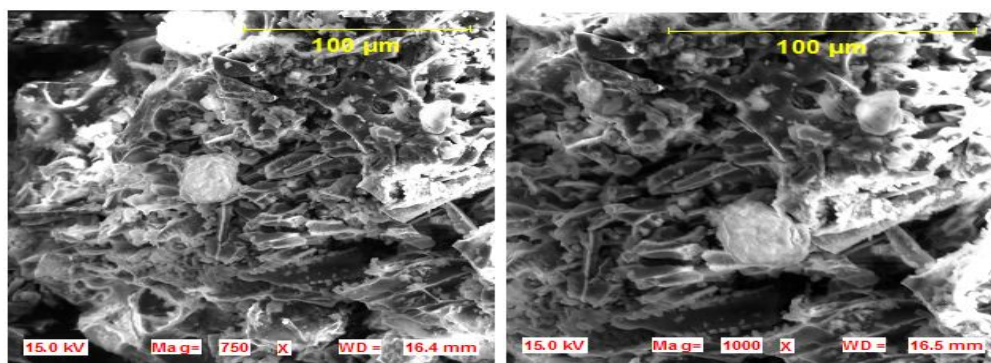


Figure 1a: SEM micrograph of JAC (left: mag=750; right: mag=1000)

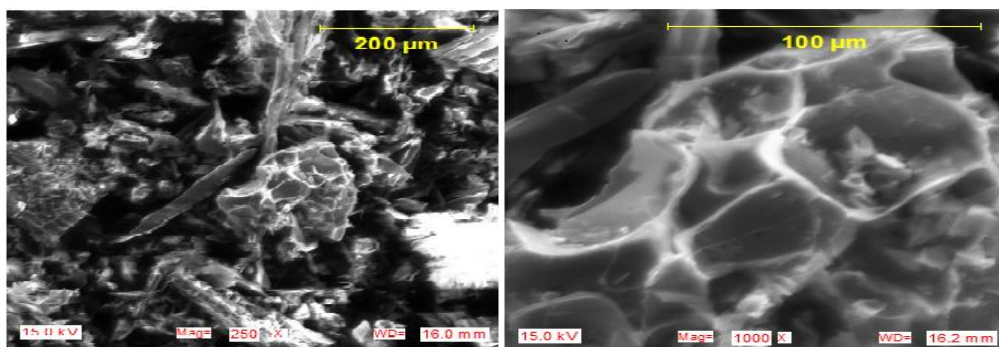


Figure 1b: SEM micrograph of TAC (left: mag=250; right: mag=1000)

Functional groups

The most prominent bands at $\sim 1570\text{ cm}^{-1}$ and 1370 cm^{-1} in the FTIR spectra of JAC and TAC (figure 2a & b) can be attributed to graphitic structures that are expected to dominate activated carbons. The broad band above 3400 cm^{-1} is assigned to the OH stretching frequency in adsorbed water but also to surface OH groups as expected for phenols, lactones and carboxylic acid groups known to exist at the surface of activated carbon. The OH bending mode is usually observed around 1600 cm^{-1} and apparently contributes to the broadening of the graphitic band. The band at $\sim 1200\text{ cm}^{-1}$ can be attributed to the C-O stretching mode confirming the existence of oxygenated functional groups at the adsorbent surface.^[27-29]

PPD adsorption

Effect of initial concentration

Figure 3a shows that amount adsorbed on JAC and TAC increases, as expected, with increased initial concentration of PPD until saturation is reached.^[30] It can also be seen that the adsorption capacity of TAC is higher than that of JAC.

Effect of pH

The effect of pH on the adsorption of PPD onto JAC and TAC was investigated (Figure 3b). The adsorption of PPD under these conditions decreases significantly as the pH increases from 2 to 4. However, at pH=2, the adsorption capacity was high probably due to the electrostatic attraction between the adsorbent surface and the lone

pair electrons on the amino groups of PPD. At higher pH values, there is a decrease in the adsorption capacity due to the electrostatic repulsive force existing between PPD molecules and the surface of the adsorbent.^[14,31,32]

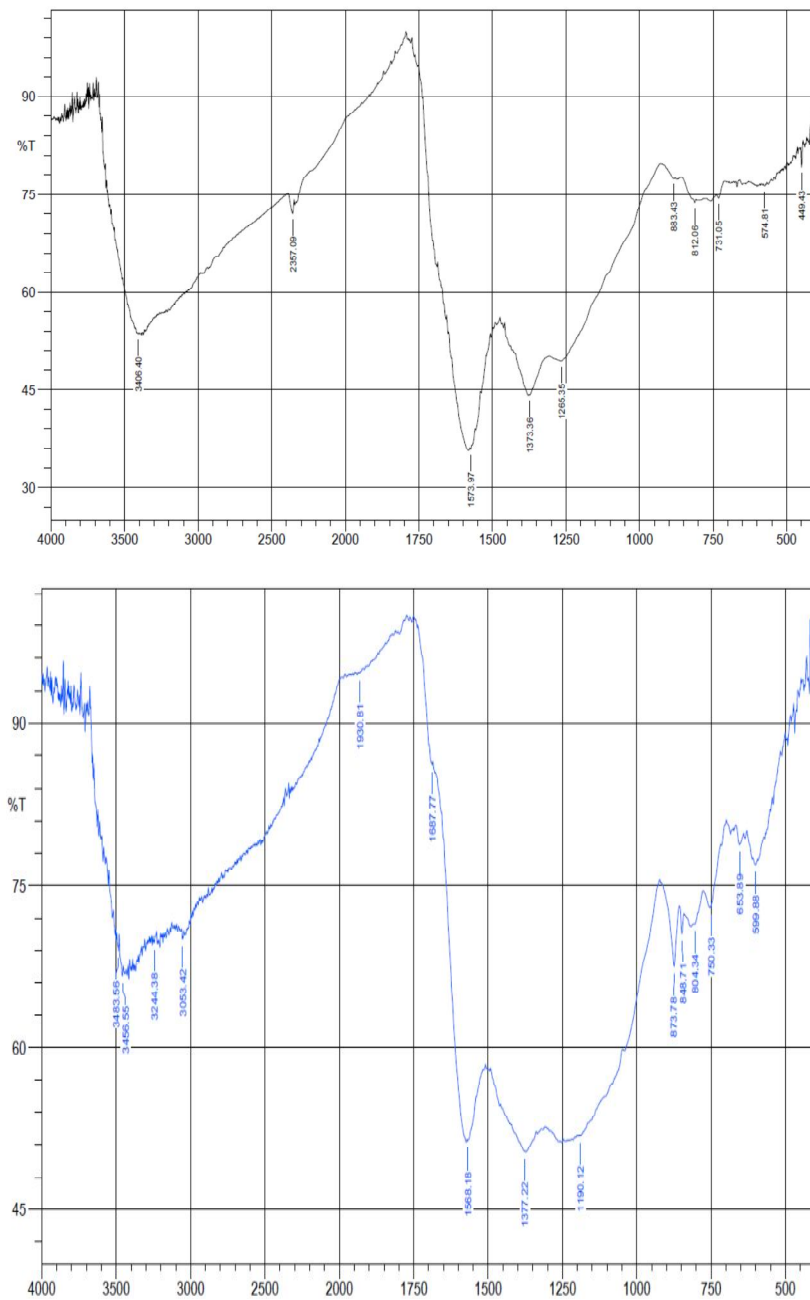


Figure 2: FTIR Spectra of a) JAC (upper) and b) TAC (lower).

Effect of contact time

Figure 3c shows the progress of PPD adsorption as a function of contact time. In the first 5 minutes of contact, there was a rapid uptake of PPD. The quantity adsorbed increases thereafter until equilibrium was reached and no change in the quantity adsorbed can be seen beyond this point.^[30, 33]

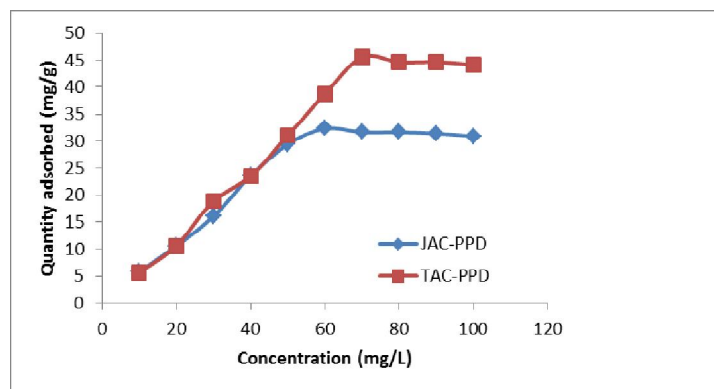


Figure 3a: Effect of concentration (Conditions: pH=6.8, adsorbent dose=0.020 g, $t=28\pm 2^{\circ}\text{C}$, agitation time=120 min, agitation speed=200 rpm, $n=3$, $0 \leq \%E \leq 0.92$).

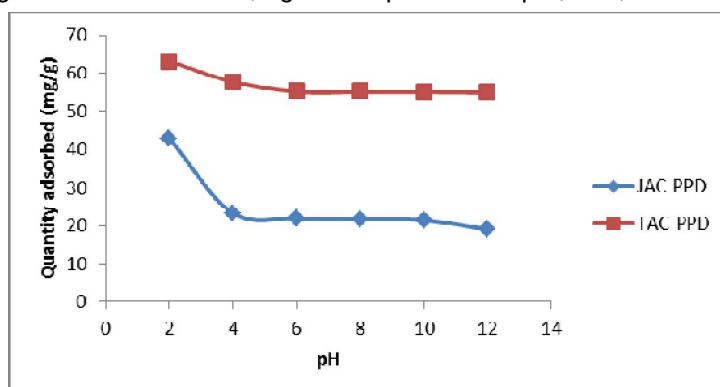


Figure 3b: Effect of pH (Conditions: concentration=60 mg/L, adsorbent dose=0.020 g, $t=28\pm 2^{\circ}\text{C}$, agitation time=120 min, agitation speed=200 rpm, $n=3$,).

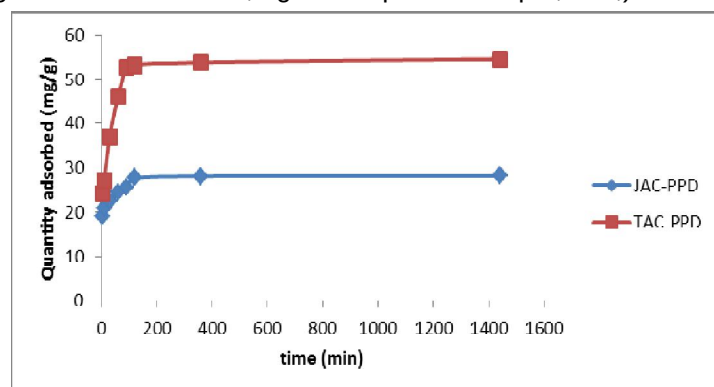


Figure 3c: Effect of contact time (Conditions: $[\text{PPD}]_0=60$ mg/L, $t=28\pm 2^{\circ}\text{C}$, adsorbent dose=0.020 g, agitation time=120 min, agitation speed=200 rpm, $n=3$, $0 \leq \%E \leq 0.87$).

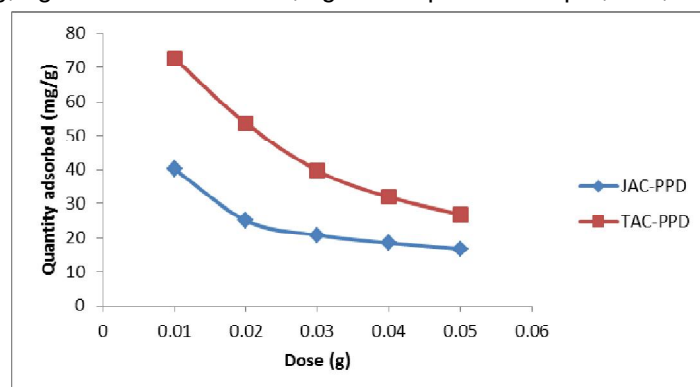


Figure 3d: Effect of adsorbent dose (Conditions: concentration=60 mg/L, pH=6, $t=28\pm 2^{\circ}\text{C}$, agitation time=120 min, agitation speed=200 rpm, $n=3$, $0 \leq \%E \leq 0.03$).

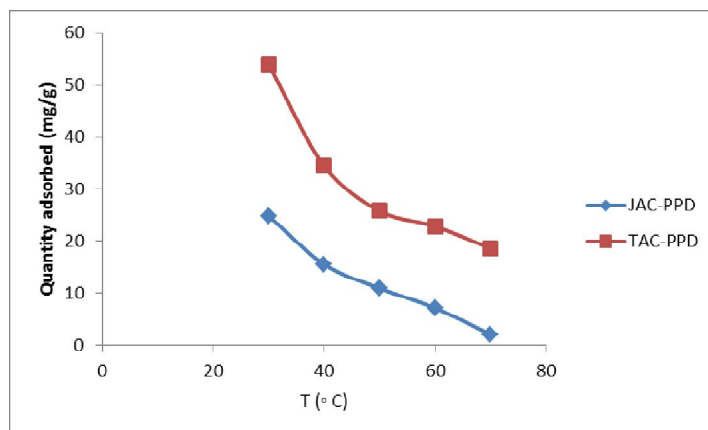


Figure 3e: Effect of Temperature (Conditions: $c=60$ mg/L, $pH=6$, adsorbent dose=0.020 g, agitation time=120 min, agitation speed=200 rpm, $n=3$, $0 \leq \%E \leq 0.06$).

Effect of adsorbent dose

The influence of adsorbent dose of JAC and TAC on the adsorption of PPD is presented in Figure 3d. The amount adsorbed decreases with increased adsorbent dose which is behaviour typical in adsorption processes and reflects the fact that by increasing the dose of adsorbent, PPD molecules become distributed over a larger amount of adsorbent, the share per gram will thus decrease.^[34,35]

Effect of temperature

The effect of temperature on the adsorption of PPD onto JAC and TAC is presented in Figure 3e. The amount adsorbed on JAC and TAC was found to decrease with the increase in the system temperature. This observation suggests that the force binding the PPD molecule to the surface of activated carbon is being weakened as the temperature of the medium increases.^[36,37,38]

Adsorption isotherms

Freundlich, Langmuir and D-R plots are presented in Figure 4 for the adsorption of PPD on JAC and TAC. Based on the values of correlation coefficient of the various isotherms, it can be concluded that both Langmuir and Freundlich models fit the data well. Although Freundlich isotherm assumes heterogeneity of the adsorption sites, the fact that both Langmuir and Freundlich isotherm describe the adsorption data well indicates that surface heterogeneity is of minor role. However, the experimental data do not fit well into the D-R isotherm.

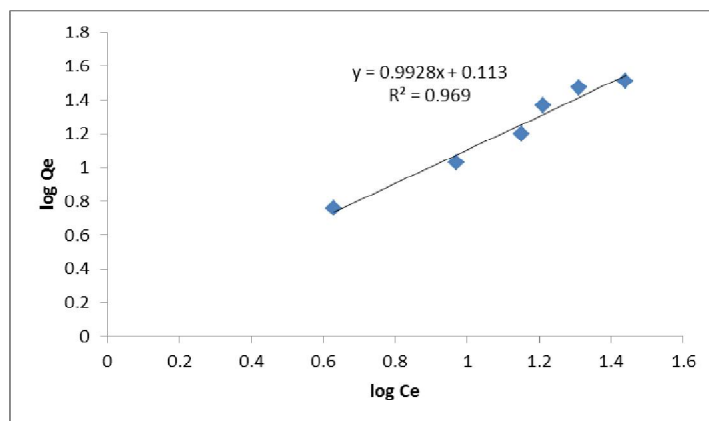


Figure 4a: Freundlich plot for PPD adsorption on JAC.

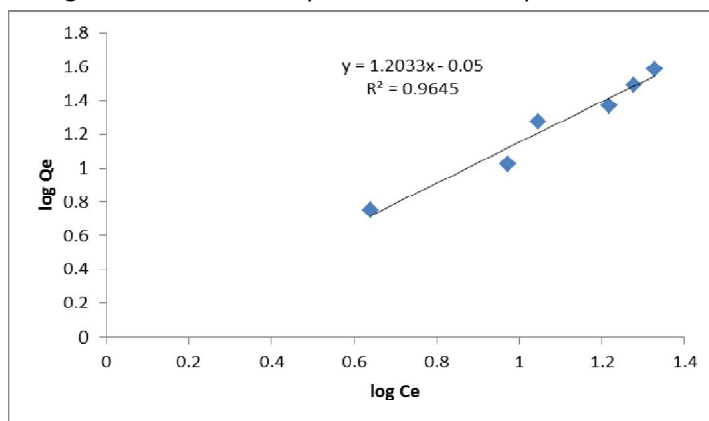


Figure 4b: Freundlich plot for PPD adsorption on TAC.

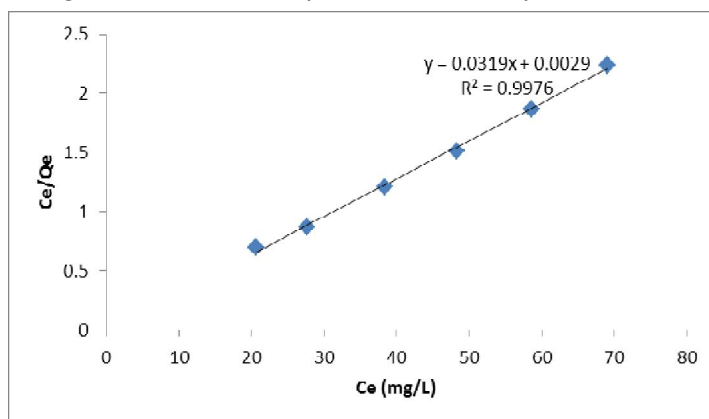


Figure 4c: Langmuir plot for PPD adsorption on JAC.

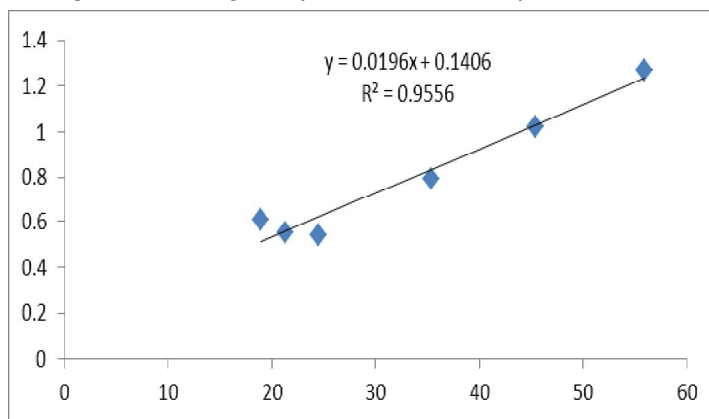


Figure 4d: Langmuir plot for PPD adsorption on TAC.

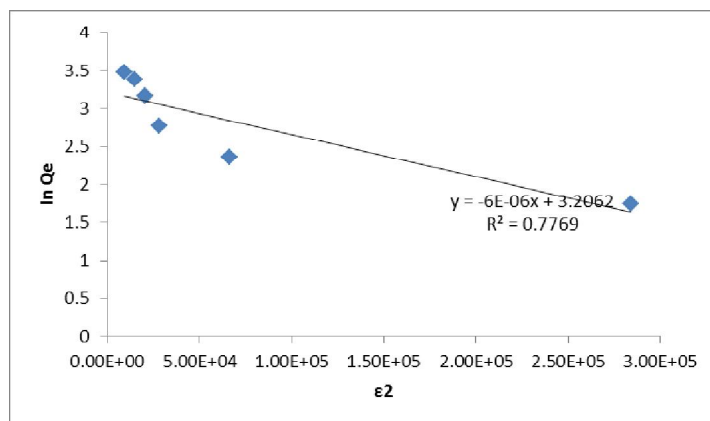


Figure 4e: D-R plot for PPD adsorption on JAC.

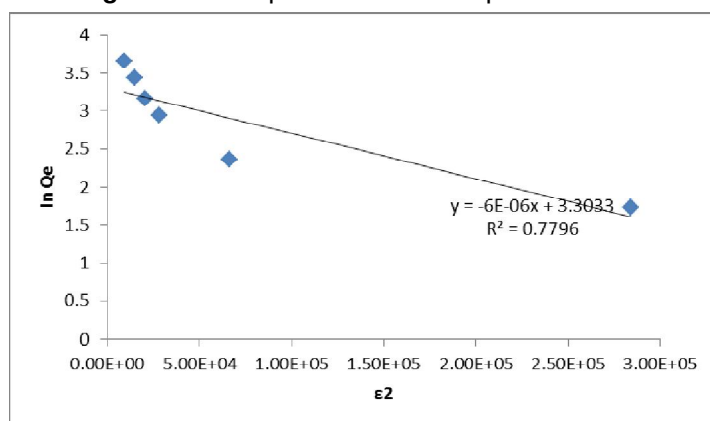


Figure 4f: D-R plot for PPD adsorption on TAC.

Adsorption kinetics

The pseudo first order, pseudo second order and Elovich plots for the adsorption of PPD onto JAC and TAC are presented in figure 5. The observed correlation coefficients, R^2 , are summarized in the Table 1 and they suggest that pseudo second order kinetics fitted best the sorption data.^[30,38]

Thermodynamics of adsorption

The thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) can be obtained from the temperature dependence of adsorption by plotting the logarithm of the equilibrium adsorption constant K versus $1/T$ (Figure 6). The values of ΔH° (determined from the slope) and ΔS° (calculated from the intercept) are presented in Table 1. The negative value of ΔH° indicates of the exothermic nature of the process. The negative value of ΔS° suggests a decreased randomness at the solid-solute adsorption systems. This indicates that the gain of entropy caused by water molecules displaced was less than that lost by the PPD molecules.^[39,40]

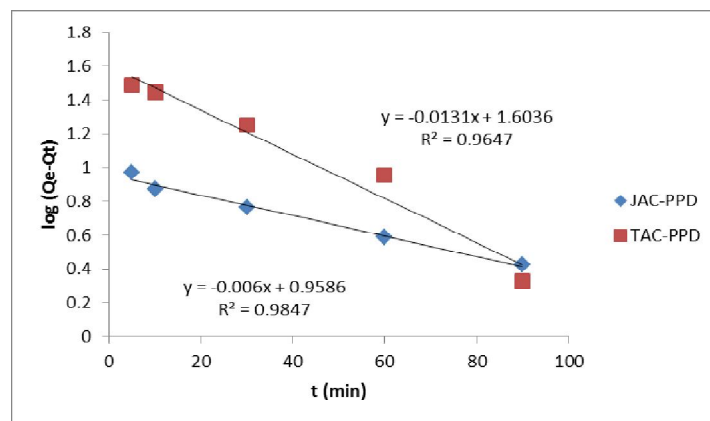


Figure 5a: Pseudo first order plots for the adsorption PPD onto JAC and TAC.

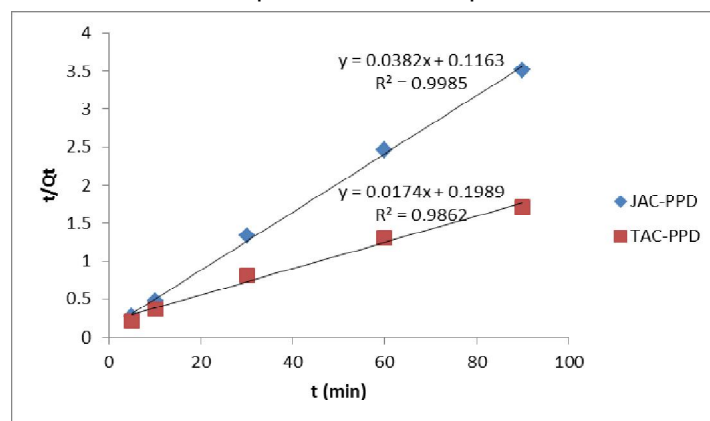


Figure 5b: Pseudo second order plots for the adsorption of PPD onto JAC and TAC.

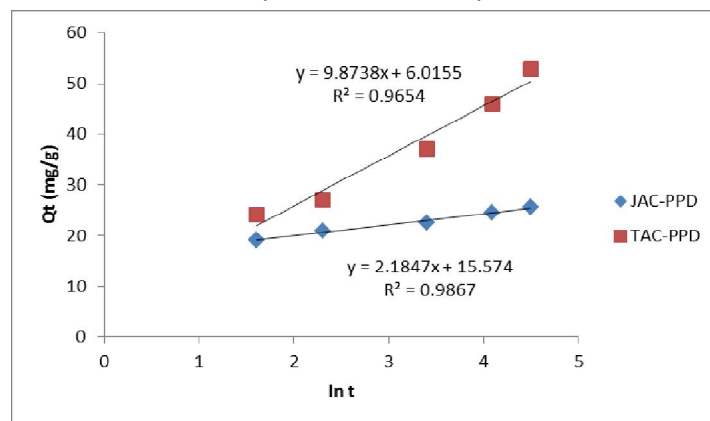


Figure 5c: The Elovich plots for the adsorption of PPD onto JAC and TAC.

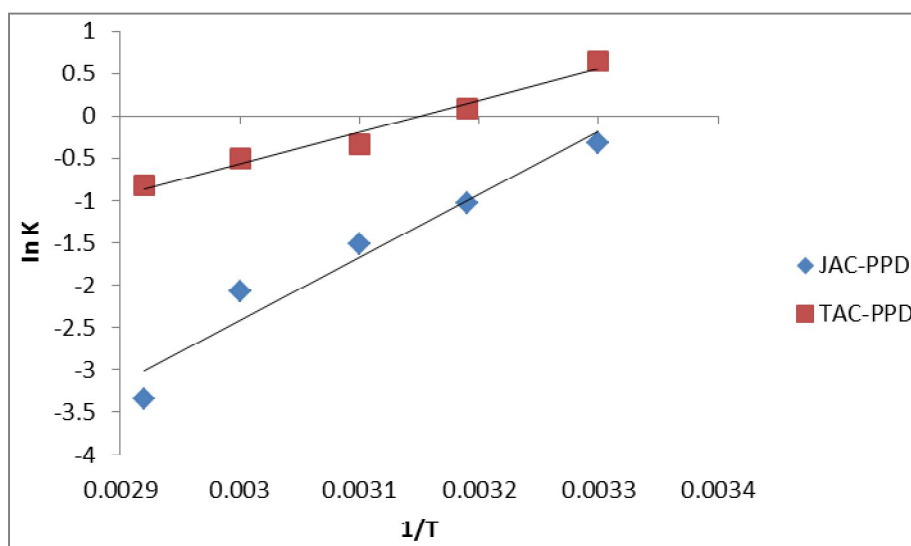


Figure 6: Vant Hoff's plots for the adsorption of PPD onto JAC and TAC.

Intra-particle diffusion model

To check the possibility that the transport of adsorbate molecules from solution into the pores of the adsorbent is the rate determining step, the amount of dye adsorbed, q_t (mg/g), was plotted, following the Intra-particle diffusion model, versus the square root of time, $t^{1/2}$ ($\text{min}^{1/2}$) according to equation 13 (Figure 7). The initial portion of the plot is related to mass transfer to the adsorbent surface and the next part is due to intra-particle diffusion.^[37] The value of the corresponding rate constants, k_{id} ($\text{mg/g min}^{1/2}$), was determine from the respective plots.

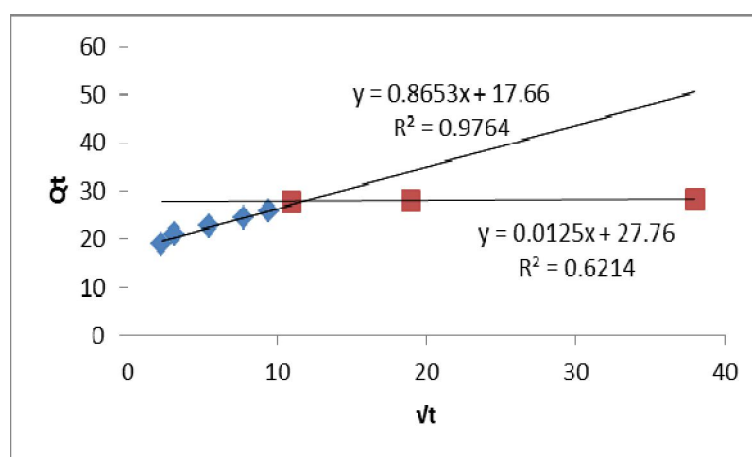


Figure 7a: Intra-particle diffusion model for PPD adsorption on JAC.

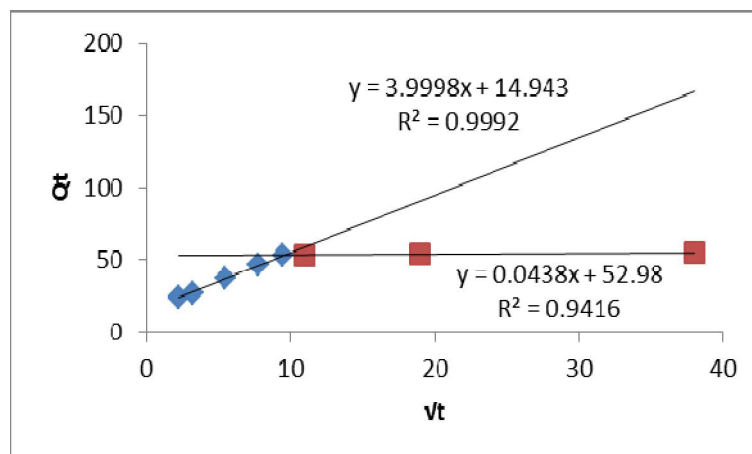


Figure7b: Intra-particle diffusion model for PPD adsorption on TAC.

Figures 7a and 7b present plots of q_t (mg/g) versus $\sqrt{t}$ for the adsorption of PPD onto JAC and TAC, respectively. The plots present multi-step plots of the experimental data. The plots obtained indicate that intra-particle diffusion is involved in the adsorption process. The values of C (see Table 2) give an idea about the thickness of the boundary layer, as larger C values suggest greater boundary layer effect. The deviation of straight lines from the origin signifies the difference between the rate of mass transfer in the initial and final stages of adsorption, as it also suggests that the pore diffusion was not the sole rate-controlling step. It seems that surface diffusion is involved to a larger extent in the adsorption process than intra-particle diffusion.^[40]

Table 2: Intra-particle diffusion parameters of PPD adsorption onto JAC and TAC.

parameters	JAC	TAC
$K_{id,1}$ (mgg ⁻¹ min ^{-1/2})	0.8653	3.9998
$K_{id,2}$ (mgg ⁻¹ min ^{-1/2})	0.0125	0.0438
C_1 (mg/g)	17.66	14.943
C_2 (mg/g)	27.76	52.98
R^2_1	0.9764	0.9992
R^2_2	0.6214	0.9416

Conclusions

Activated carbon prepared from *Jatropha Curcas* seed coat (JAC) and *Terminalia Cattapa* seed coat (TAC) were found to be effective as adsorbent in removing p-phenylenediamine (PPD) from aqueous medium but the extent of their effectiveness depends on the surface characteristics and process conditions. The quantity adsorbed was found to depend on the initial concentration of the dye, pH, contact time, adsorbent dose and temperature.

The adsorption of PPD on prepared JAC and TAC could be modelled successfully by the Langmuir and Freundlich isotherms. The adsorption kinetics was

best fitted by pseudo second order model. The heat of adsorption (ΔH^0) was determined and found to be negative indicating an exothermic process.

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