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Research Article

CRYSTAL VIOLET ADSORPTION ONTO KOLANUT POD HUSK ACTIVATED CARBON; ISOTHERM, KINETIC, AND THERMODYNAMICS STUDIES

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ABSTRACT

The adsorption of crystal violet (CV) dye onto kola nut husk based activated carbon (KPAC) was carried out in this work. The effects of various reaction parameters such as contact time, initial pH, initial CV concentration, adsorbent dosage and solution temperature were investigated. The sorption of CV dye on KPAC was found to increase with increase in initial dye concentration, passed through a maximum as function of pH (at pH 8), and decreased with increase in temperature. The adsorption equilibrium data were best represented with the Langmuir model. Kinetic studies revealed that the adsorption data fit well to the pseudo-second-order model with high correlation coefficient. The apparent energy of adsorption (E) of CV using KPAC is 11.323kJmol^{-1}. The Thermodynamic properties showed that adsorption of CV onto KPAC was exothermic, spontaneous and feasible with a decrease in the degree of freedom of the adsorbed species in the temperature range 303-333K. The KPAC can be used as effective and low cost adsorbent for the removal of CV dye from aqueous solution.

Keywords: Kola nut pod husk, activated carbon, crystal violet, adsorption kinetic, isotherm, thermodynamics.

1. INTRODUCTION

Rapid industrialization and urbanization has resulted in the deterioration of water, air, and land quality [1]. Many industries discharge untreated or inadequately treated wastewater into waterways [2]. Large amount of wastewater having colour is generated by many industries like textile, leather, paper, printing, plastic and so on [3]. Dyes are difficult to treat with municipal waste treatment operations as a result of their complicated chemical structures [4].

Adsorption is the most commonly used technique for the treatment of industrial wastewaters [5]. The removal of coloured and colourless organic pollutants from industrial wastewater is considered an important application of the adsorption process using suitable adsorbent [6, 7]. It has been recognized as the most popular treatment process for the removal of dye from aqueous solution due to its simplicity, high efficiency, easy recovery and reusability of the adsorbent [8, 9].

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Activated carbon (AC) is a popular adsorbent in adsorption due to its high adsorption capacity, high surface area and microporous structure [4]. A variety of carbonaceous raw materials are used for the production of activated carbons. Physical and chemical characteristics of the raw material and the preparation methods have significant effect on the quality and properties of activated carbons [10]. Due to high carbon and low ash contents, many of agricultural by-products are appropriate for use as precursors for activated carbon production [11].

The adsorption of dyes from water and wastewaters using agro-based AC has been studied examples including, corncob and barley husk [12], cattle dung [13], Borassus bark [1] and Rice husk carbon [14].

Crystal violet is used in different production processes. For instance, it is used for dyeing papers and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers, Crystal violet can be used as a non-toxic DNA stain as an alternative to fluorescent, intercalating dyes such as ethidium bromide when conducting DNA gel electrophoresis. In medicine, crystal violet is used for marking the skin for surgery preparation and allergy testing, impetigo, used primarily before the advent of antibiotics, but still useful to persons who may be allergic to penicillin, mouth ulcer e.t.c., due to it having antibacterial, antifungal, and anthelmintic properties [15]. Regardless of this, the negative ecotoxicological effects of dyes on receiving water bodies and their bioaccumulation in wildlife makes it a necessity that dye effluent streams should be properly treated prior to discharge.

This study aims to produce, characterize, and apply activated carbon from kola nut pod husk. The effects of various parameters such as, pH, initial concentration, contact time, adsorbent dose, and temperature will be studied. In addition, kinetics study, isotherm study, and thermodynamics study will also be carried out on the adsorption of crystal violet by the produced activated carbon.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbate

In this study, Crystal violet (CV) of commercial quality (CI 42555, MF: $C_{25}H_{3}0N_{3}Cl$, MW: 408, k_{max}: 580 nm) was used. It was used without further purification. The dye was obtained from a chemical store in Onitsha, Anambra state, Nigeria. Fig. 1 shows the structural formula of Crystal violet. A stock solution of Crystal violet (CV) (1,000 mgL^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. The pH of the adsorbate was adjusted using HCL and NaOH.

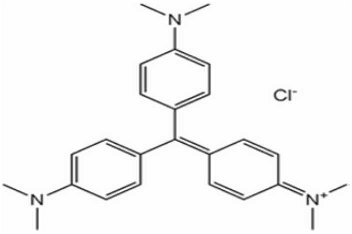

Figure 1. Structure of Crystal violet

2.2. Preparation of Adsorbents

The adsorbent precursor; raw kola nut pod husk waste was collected from Ifaki-Ekiti, Ido/Osi L.G.A, Ekiti State, Nigeria. It was washed, dried, and carbonized at 500°C for 1hr. The carbon was activated using H_2SO_4. The p roduced activated carbons was sieved with 200 mesh (75µm) size and dried at 150°C for 3 hours and kept in bottles for use. Samples of the produced activated carbon were characterized in order to determine their properties. The surface area of KPAC was analyzed using BET surface area analyzer, Micromeritics asap, USA, ASAP 2020 V3.02 G at 77K. The proximate analysis of the produced activated carbon was carried out using the method described by Bhole and Ramteke [16]:

1. Moisture content of the produced activated carbon was determined by heating 1g of activated carbon in dried, clean silica crucible in an oven at 100°C to a constant weight. The difference in weight was calculated and expressed in percentage.
2. Ash was determined by heating 1g of activated carbon in dried, silica crucible at 800°C for one hour and weighed. The difference in weight was calculated and expressed in percentage.
3. Volatile matter was determined by heating 1g of activated carbon in volatile matter crucible in absence of air at 900°C for seven minutes and weighed. The difference in weight was calculated and expressed in percentage.
4. The fixed carbon was determined by using the formula:

$$\text{Fixed carbon} = 100 - (\text{moisture content} + \text{Ash content} + \text{Volatile matter})$$

2.3. Batch adsorption studies

Equilibrium sorption experiments were conducted in which aliquots of dye solution with known concentrations (50–500 mg/L) were introduced into glass bottles (100 cm^3) containing accurately weighed amounts (1.0 g) of the absorbent. The bottles were shaken at 30°C using magnetic stirrers for a period of time (2hrs) and pH of 8 to obtain equilibrium. The adsorbent was then removed by filtration using Whatman no. 1 filter paper. The equilibrium concentrations of dyes were determined by a UV-visible spectrophotometer (Shimadzu UV 160). The amount of CV ions adsorbed by the activated carbon was taken as the difference between the initial and final ion concentration of the solutions. These were done for the acid activated carbon from kola nut pod husk (KPAC).

2.4. Kinetic Study

The adsorption kinetics of CV onto KPAC was studied at initial concentration of 50mg/L. 50mL of aqueous crystal violet solution was introduced into a 250cm^3 conical flask and mixed with 1.0g of the adsorbent. The solution was stirred continuously at 30 °C and 1 mL of solution was taken at different time intervals (0–180min). The concentration of CV was analyzed using UV-Visible spectrophotometer at wavelength 543nm and the amount of adsorption qt was calculated according to equation (1).

2.5. Isotherm study

The isotherm study was conducted by contacting 50mL of adsorbate solution of concentration 50, 100, 150, 200, 300 and 500mg/L with 1.0g of adsorbent. At the end of 60min, the reaction mixture was filtered and the filtrates analyzed for residual CV concentrations.

3. RESULTS AND DISCUSSION

3.1. Characterization

The properties of the produced activated carbons are shown in Table 1. Activated carbon are often priced moisture free, but if contains moisture, it should not be more than 10% because moisture reduces the adsorption capacity of an activated carbon [17-18]. From the analysis, the produced AC has favorable moisture content. Ash negatively influences the overall activity of activated carbon; it also reduces the efficiency of reactivation. The typical range of values for commercial activated carbon (CAC) is 2-10% [19], and the ash content of the produced AC falls within this range. Activated carbon having high value of fixed carbon implies that the adsorbent is having more efficiency and stability [20]. The produced AC is very rich in fixed carbon. Higher density provides greater volume activity and usually indicates better quality activated carbon [21]. The pH of the produced AC is 6.22, determined using the method described by Bansode et al [22], and the acceptable pH for most commercial activated carbon is pH6-8 [23]. From Table 1, the surface area of KPAC is 779m^2/g. The BJH adsorption and desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter is 2.228 m^2/g and 1.6877 m^2/g respectively.

Table 1. Result of physico-chemical analysis.

Parameter	**KPAC**
Moisture Content (%)	9.65
Volatile Matter (%)	1.14
Ash Content (%)	0.88
Fixed Carbon (%)	88.33
Density (g/cm^3)	0.3146
Surface area (m^2/g)	779
pH	6.22
Alkalinity (mg/L)	115

Table 2 shows the FTIR spectra of carbonized kola nut pod and the major bands. The major functional groups in it are symmetrical stretching vibration of (OH) of phenol, C=C stretching of carboxyl group, and OH stretch with wave number (cm^{-1}) 3422.34, 1617.45, and 1104.46. The FTIR (Table. 3) of KPAC shows a slight shift in the wave number of the functional groups present in the untreated kola nut pod carbon. The major difference between the untreated and the KPAC is the absence of OH stretch, and the presence of new functional groups; C–O –H stretching vibrations and physisorbed carbon dioxide on 1080.36 and 670.08 wave number bands.

Table 2. Functional groups in Untreated kola nut pod husk

Wave number (cm^{-1})	**Functional groups**
3422.34	Symmetrical stretching vibration of (OH) of phenol
1617.45	C=C stretching of carboxyl group.
1104.46	OH stretch

Table 3. Functional groups in KPAC

Wave number (cm^{-1})	**Functional groups**
3419.88	Symmetrical stretching vibration of (OH) of phenols
1618.17	C=C stretching of carboxyl group.
1080.36	C–O –H stretching vibrations
670.08	Physisorbed carbon dioxide

3.2. Effect of pH

Figure 1 shows the effect of pH for the removal of CV by KPAC. The experiments were conducted at the constant 100mg/L initial CV concentration, adsorbent dose of 1.0g/50mL, contact time of 60mins, and a temperature of 30°C. Result indicated that as the process proceeded, increase of the pH (from 2 to 10) of the adsorption system yielded greater removal by adsorption and maximum adsorption of CV took place at pH 8. However, there was not a significant change in uptake capacity from pH 8 to 10 (with variation in removal efficiency less than 1%). Lower adsorption of CV at acidic pH is probably due to the presence of excess H^+ ions competing with the CV dye for the active sites [24]. The adsorption of CV onto KPAC is affected by the characteristics of the adsorbent surface (comprised various functional groups such as carboxyl group) and the structure of CV molecule. Therefore, at various pH values, electrostatic attraction, ionic properties and structure of dye molecules, and adsorbent surface could play significant roles in the adsorption of dyes on adsorbents.

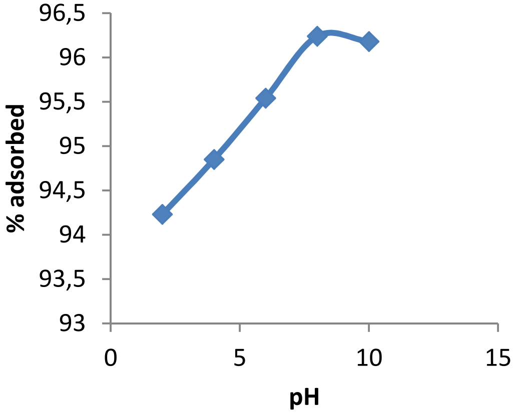

Figure 1. Effect of pH on adsorption of CV by KPAC

3.3. Effect of Initial Concentration

The effect of initial concentration of CV on the adsorption efficiency by KPAC has been systematically investigated by varying the initial concentration of CV between 50-500mg/L. The experiments were conducted at the constant pH of 8, adsorbent dose of 1.0g/50mL and contact time of 60mins. Figure 2 shows that in CV adsorption by KPAC, adsorption rate increased with increase in CV concentration. This may be as a result of an increase in the driving force of the concentration gradient [25].

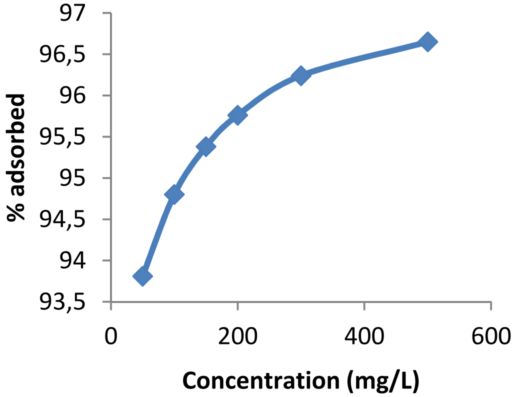

Figure 2. Effect of initial concentration on adsorption of CV by KPAC

3.4. Effect of Contact Time

The effect of contact time on the adsorption process was studied by adding 1.0g of the adsorbent to 50mL of the stock solution in different 250cm^3 flasks of pH of 8, and then agitated for a predetermined time intervals 0f 3.0-120mins. From contact time data (figure 3), it may be seen that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is attained. The fast adsorption at the initial stage may be due to the fact that a large number of surface sites are available for adsorption. Consequently, the remaining vacant surface sites are difficult to be occupied due to formation of repulsive forces between the crystal violet molecules on the solid surface and in the bulk phase [1, 26]. Additional increase of the contact time did not enhance the adsorption.

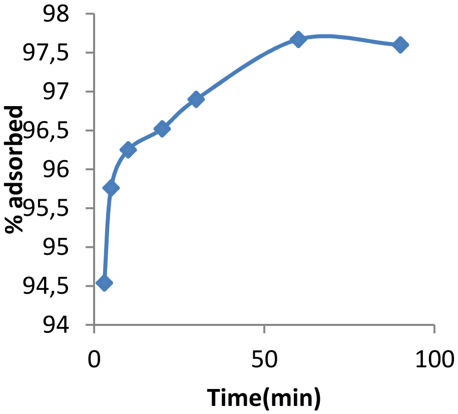

Figure 3. Effect of contact time on adsorption of CV by KPAC

3.5. Effect of adsorbent dose

Effect of adsorbent dose was studied by adding various amounts of the adsorbents (0.5, 1.0, 1.5, 2.0, and 2.5g) to 50mL of the stock solution in different 250cm^3 flasks and agitated for 60mins. The figure for the effect of adsorbent dosage on adsorption efficiency (Figure 4) shows that the process is dosage dependent. The rate of adsorption of CV with increase in adsorbent dose resulted in a decrease in adsorption efficiency. This could be as a result of overlapping or aggregation of adsorption sites which reduced the total surface area available for CV adsorption [27, 28].

3.6. Effect of temperature

The study for the effect of temperature on the removal of CV by KPAC was carried out by adding 1.0g of the adsorbent to 50mL of the stock solution in different 250cm^3 flask at different temperatures (30ºC, 40ºC, 50ºC and 60ºC) and then agitated for 60mins. The result for the adsorption of CV (figure 5) at different temperatures indicated that the adsorption capacity decreased with an increase in the temperature of the system. This can be attributed to the exothermic spontaneity of the adsorption process, and as a result of the weakening of bonds between the dye molecules and the active sites of the adsorbent at high temperatures [29, 30].

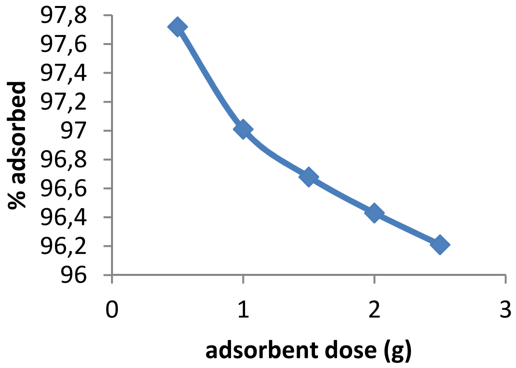

Figure 4. Effect of dosage on adsorption of CV by KPAC

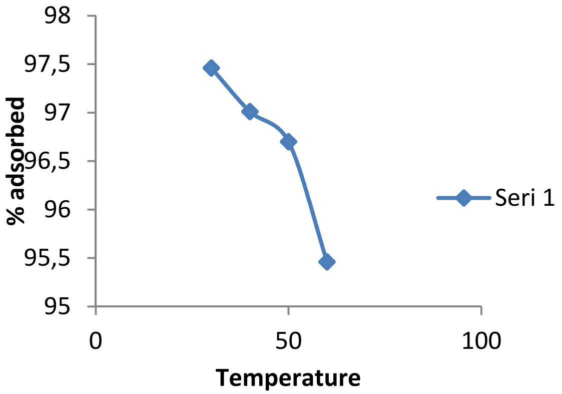

Figure 5. Effect of temperature on adsorption of CV by KPAC.

3.7. Kinetics study

In order to study the kinetics of the adsorption of crystal violet (CV) using KPAC, pseudo first order, pseudo second order, and Bhattacharya-Venkobachar equation were used. These models were comparatively studied in order to determine the one that best describe the kinetics of the adsorption under study.

The pseudo first-order kinetic equation for kinetic study is written [31] as:

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2.303 \quad (1)$$

Where q_e is the mg of dye adsorbed per mg of adsorbent material at equilibrium, q_t is the mg of dye adsorbed per mg of adsorbent material at any time t, k_1 is the pseudo first-order rate constant for the adsorption process. If the plot of log $(q_e - q_t)$ against t is linear, then the model fits the kinetic study of the adsorption system under study.

The pseudo second order adsorption kinetic rate equation as written [32] is:

$$dq_t/ dt = k_2 (q_e - q_t)^2 \quad (2)$$

on integrating, the pseudo second-order kinetic equation for kinetic study becomes:

$$t/q_t = 1/(k_2 q_e 2) + t/q_e \quad (3)$$

Where q_t is amount of adsorbate adsorbed at any time t, k_2 is the pseudo second-order constant. Like in previous models, if the plot of t/q_t against t is linear, then the model fits the kinetic study of the adsorption process.

The Bhattacharya-Venkobachar equation is written as [33]:

$$\text{Log}\,[1-(U)\,T] = (K_B/2.303)\,t \quad (4)$$

$$\text{Where } (U)\,T = (C_o - C_t)/\,Co - C_e) \quad (5)$$

Where K_B is the Bhattacharya-Venkobachar constant (l/min); C_o is the initial concentration (mg/L); C_t is the concentration at time t (mg/L) and C_e is the concentration at equilibrium (mg/L). A plot of Log [1- (U) T] versus t is expected yield a straight line, if the sorption process obeys this model. K_B can be determined from the slope. Figures 6a-6c shows the kinetic plots of the pseudo first order, pseudo second order and Bhattacharya-Venkobachar models. A comparison of the kinetic models using the linear regression coefficient (R^2) values (Table 4) shows that the pseudo second order model best describes the adsorption process (R^2 = 0.999). The experimental q_e were found to be close to the estimated one (48.091).

The kinetics result is similar to that obtained by Rais Ahmad [34] and Depci et al [35], in the adsorption of crystal violet using coniferous pinus bark powder (CPBP) and activated carbon obtained from Golbasi lignite, in which pseudo-secondorder kinetic model best described the adsorption kinetics.

Table 4. Kinetic parameters of KPAC

Parameter	**KPAC**
Pseudo first order model	
$K_1(min^{-1})$	0.072
q(mg/g)	14.147
R^2	0.989
Pseudo second order model	
K_2(g/mg/min)	0.191
q(mg/g)	48.091
R^2	0.999
Bhattacharya-Venkobachar model	
$K_B(min^{-1})$	-0.030
R^2	0.337

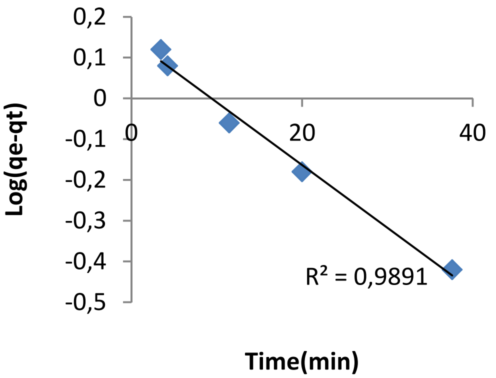

Figure 6a. Pseudo first order kinetic plot of CV adsorption by KPAC.

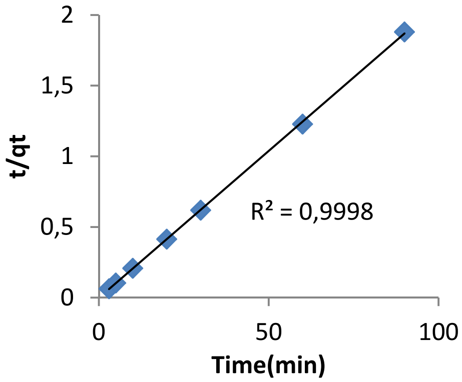

Figure 6b. Pseudo second order kinetic plot of CV adsorption by KPAC

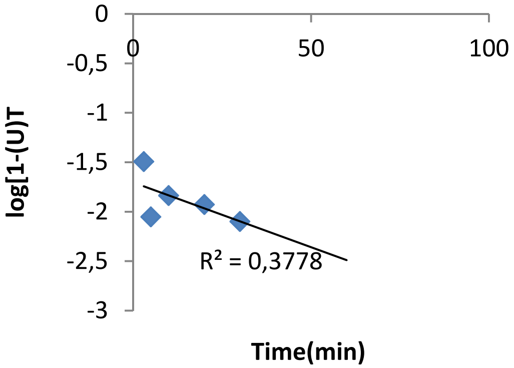

Figure 6c. Bhattacharya -Venkobachar kinetic plot of CV adsorption by KPAC.

3.8. Sorption isotherms

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and that remaining in solution at fixed temperature at equilibrium [36]. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation [37, 38]. These two isotherms and the Dubinin-Radushkevich isotherm model were employed to assess the different isotherms and their ability to correlate the experimental data.

The linearized Freundlich equation is given as:

$$\log Qe = \log K_F + 1/n \log Ce \quad (6)$$

Where, Ce is the equilibrium liquid phase ion concentration (mg/L) and Qe is the equilibrium solid phase ion concentration (mg/g). In addition, K_F and n are the Freundlich empirical constants.

The Langmuir isotherm can be represented by the following equation [39]:

$$1/Q_e = 1/Q_m b \; 1/C_e + 1/Q_m \quad (7)$$

Where C_e is the equilibrium concentration (mg/L), Qe is the amount of adsorbate adsorbed at equilibrium (mg/g). Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption respectively [39].

The Dubinin-Radushkevich isotherm model is represented by the equation (8):

$$q_e = q_D \exp(-K_D \varepsilon^2) \quad (8)$$

Where, K_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface [40]. The linear form of equation (8) is given as:

$$\ln q_e = \ln q_D - 2K_D \varepsilon \quad (9)$$

If a plot of ln q_e against ε^2 yields straight line, it indicates a good fit of the isotherm to the experimental data. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relation given below [40]:

$$E=1\sqrt{}2K_D \quad (10)$$

The Langmuir isotherm represents the equilibrium distribution of adsorbate ions between the solid and liquid phases. The linear plot of $1/Q_e$ versus $1/C_e$ suggests the applicability of the Langmuir isotherm (Figure 7a). The R^2 value (0.992) of the Langmiur model gave a better fit to the sorption process when compared to the other isotherms tested. The values of the Langmiur constants are shown in Table 5. Q_m and b, the Langmuir constants relates to adsorption efficiency and energy of adsorption respectively [39].

The use of the Freundlich isotherm equation model to analyze the equilibrium isotherms of CV ions gave linear plot, Figure 7b for KPAC. The linear regression equations and the regression co-efficient (R^2) are shown in Table 5. The regression coefficient (R^2) of KPAC is 0.984, for 75 µm particle size. Generally, this model gave very good fit to the experimental data.

The Freundlich empirical constants, K_F and n are also shown in Table 5. The values of K_F and n determine the steepness and curvature of the isotherm [41]. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background [33]. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice verse [42]. From Table 5, it can be observed that 1/n is more than unity. This indicates that significant adsorption takes place at higher concentrations. In addition, higher K_F value indicates greater adsorption intensity of an adsorbent.

The Dubinin-Radushkevich isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The R^2 values obtained from the linear plots of this isotherm for CV sorption using KPAC is 0.925. This means that this model can suitably describe the sorption. If E >16kJmol^{-1}, sorption is dominated by particle diffusion [43]. From Table 5, the value of E for the adsorption of CV using KPAC is 11.323 kJmol^{-1}. This indicates that the sorption is not dominated by particle diffusion.

From literatures, similar result was obtained in recent studies by Malarvizhi and Ho [44] and Wang et al. [45] on the adsorption of CV. They found that the equilibrium adsorption data obtained from their batch adsorption experiments for the adsorption of CV on different adsorbents were well described by the Langmuir model.

Table 5. Isotherm regression parameters for Crystal violet (CV).

Parameter	**KPAC**
Langmuir	
Q_m(mg/g)	1.371
K_a(L/mg)	-26.316
R_L	-0.0008
R^2	0.992
Freundlich	
K_F(mg/g)	22.628
1/n	1.356
R^2	0.984
Dubinin-Radushkevich	
K_D(mol^2kJ^{-2})	-0.0039
q_D(mg/g)	1.4177
E($kJmol^{-1}$)	11.323
R^2	0.925

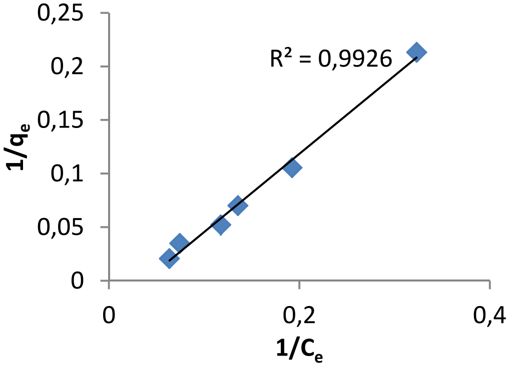

Figure 7a. Langmuir Isotherm plot of CV adsorption by KPAC

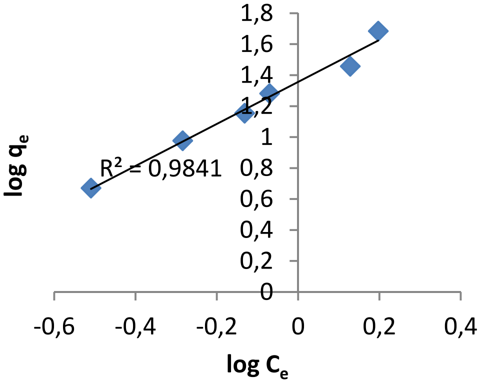

Figure 7b. Freundlich Isotherm plot of CV adsorption by KPAC

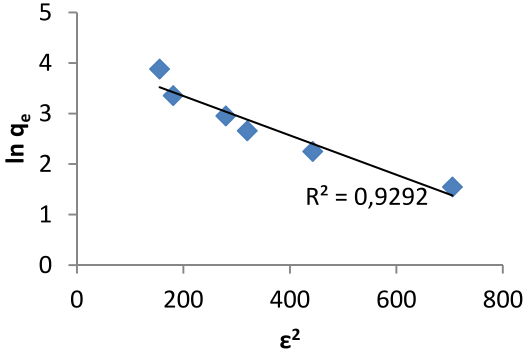

Figure 7c. Dubinin-Radushkevich Isotherm plot of CV adsorption by KPAC

3.8. Thermodynamics study

The changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for an adsorption process can be obtained using the following equations [46]:

$$\log K_c = -\Delta H/2.303RT + \Delta S/2.303R \text{ (linearized Van't Hoff equation)} \qquad (11)$$

Where K_c = F/1+F. where F is the fraction sorbed at equilibrium. T is absolute temperature (K).

The free energy of adsorption ΔG was calculated using the equation [47]:

$$\Delta G = -RT \ln K_c \qquad (12)$$

R is known as the ideal gas constant. The values of ΔH and ΔS can be obtained from the slope and intercept of the plot of log K_c against 1/T respectively.

Based on the thermodynamic studies, the negative values obtained for the enthalpy and free energy reflects the exothermic, and feasibility and spontaneous nature of sorption, respectively [46]. This could be attributed to the weakening of adsorptive forces between the active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of the adsorbed phase. The negative values of ΔS from Table 6 show a decrease in the degree of freedom of the adsorbed species. The negative value of the entropy also indicates favourable adsorption. The entropy ΔS > -10J/mol generally imply a dissociative mechanism [46].

Table 6. Thermodynamics parameters of adsorption of CV by KPAC

Parameter		**KPAC**
ΔG°	30°C	9.183
(kJ/mol)	40°C	-8.526
	50°C	-9.074
	60°C	-8.430
ΔH(kJ/mol)		-43.35
ΔS(J/mol/K)		-17.17

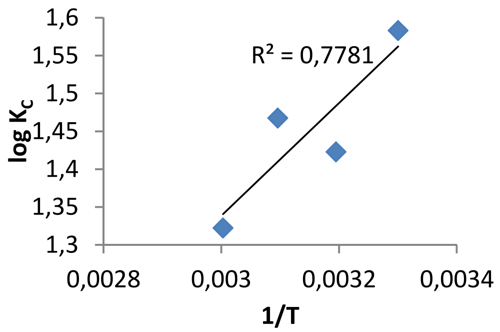

Figure 8. Thermodynamics plot of CV adsorption by KPAC.

4. CONCLUSION

The present study focused on adsorption of CV from aqueous solution using KPAC as a low cost adsorbent. The conclusions drawn from the study are:

1. Kola nut pod husk which is an environmental pollutant have been found to be good activated carbon precursor to adsorb dyes and achieve a cleaner environment.
2. The kinetic data fits very well with the pseudo-second order equation.
3. The experimental data were analyzed using Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. The Langmuir model provides the best correlation of the experimental equilibrium data.
4. The energy of adsorption of CV using the KPAC indicates that it is a physiosorption.
5. The negative values of the thermodynamics parameters evaluated shows that the adsorption process is exothermic in nature.

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