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Adsorption Study of Kinetics and Equilibrium of Basic Dye on Kola Nut Pod Carbon

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Abstract

Activated carbon was produced from kola nut pod, using H_2SO_4 and CaOH as activating agents. The produced acid activated kola nut pod carbon (KPAC) and base activated kola nut pod carbon (KPBC) were respectively characterized. The effect of adsorption parameters such as pH, initial concentration, adsorbent dose and contact time, and adsorption kinetics and isotherm of basic fuchsine (BF) dye removal by KPAC and KPBC was observed in this study. Pseudo-first order model and pseudo-second order model was the selected kinetics model. Result obtained suggested that the pseudo-second order model fitted the adsorption data than the pseudo-first order model, as gathered from their regression coefficients (R^2) and rate constants (K). The adsorption mechanism determined using Weber and Morris intraparticle diffusion model, showed that the adsorption process was simultaneously controlled by film diffusion and intraparticle diffusion. Different isotherm models such as Langmuir isotherm model, Freundlich and Temkin isotherm model were used in fitting the experimental data, and the regression coefficients (R^2) of Langmuir isotherm shows that it better described the adsorption isotherm of BF dye adsorption using the produced activated carbons than the Freundlich isotherm model. Experimental result also showed that the adsorption of FB dye using KPAC and KPBC is dependent on pH, initial concentration, adsorbent dose and contact time. Comparison of the result obtained from this study with literatures showed that kola nut pod is a good precursor for producing cheap and highly efficient activated carbon.

1. INTRODUCTION

The use of dyes in manufacturing industries such as cosmetic, paper and pulp, textile, leather, food e.t.c., is a common practice in our world today. During dyeing operations, these industries are known to be discharging coloured pigments which are hazardous and environmentally unfriendly into the streams and rivers. Discharge of these coloured effluents presents a major environmental problem for developing countries because of their toxic and carcinogenic effects on living beings [1]. The presence of dye in natural water system inhibits sunlight diffusion into the water, consequently affecting the growth of bacteria and as well inhibiting the photosynthetic process of aquatic plants [2-3]. In addition, its high visibility also alters the colourless characteristic of good water. Furthermore, it is highly harmful to fish and other aquatic organism. This necessitated the removal of dyes before the discharge of effluents into surrounding water bodies.

According to available data, there are over 100,000 commercially available dyes with a production of over 7 x 10^5 metric tons per year [4]. Removal of dyes from the industrial effluents in an economic fashion remains a major problem [5]. This is as a result of the difficulty associated with treatment of effluents from dye industries especially the ones from textile industries, because of their synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to be biodegraded [4].

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Many methods which can be broadly classified into physical, chemical or biological treatment techniques have been applied in the removal of coloured matters especially dye, with different degrees of success recorded. Some of the notable methods are photodegradation, ozonation, adsorption, coagulation/flocculation, membrane separation and biodegradation [6-11]. Of these methods, adsorption is generally one of the most recognized wastewater treatment methods because it is highly efficient.

Adsorption is usually regarded to be an important separation process due to its technological, environmental and biological importance in operation. It is a separation process that favours the removal of low concentrations of pollutants from large volumes of process potable water, wastewater, and aqueous solutions. Adsorption process systems can be either of the following: liquid-gas, liquid-liquid, solid-liquid and solid-gas.

Adsorption has been successfully used in adsorbing many dyes such as malachite green, methylene blue, acid red 18, direct orange-26 dye, safranin-o, aniline blue, maxilon blue, direct yellow, brilliant green dye, ramazol brilliant blue, remazol brilliant orange 3, reactive blue and red dyes, acid orange 7, direct red-31, and direct yellow12 [12-23].

Many adsorbents have been employed in adsorption, some of which includes clay, polymers and resins, zeolites, silica gel, activated alumina and activated carbon. Activated carbon are carbons of highly micro porous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams [24].

The economic effect of commercial activated carbon is on the high side; it is costly. This has warranted the use of readily available and cheap materials that have both a high carbon and a low inorganic content, as precursors for the production of activated carbon. Agro-forestry wastes have proved to be promising raw materials for the production of activated carbons due to their availability at a low price or in exchange for nothing. Some of the agricultural by-products that have been successfully used in producing activated carbons are; cocoa shell, vitis vinafera leaf, cocos nucifera leaves, cocoa nibs, pigeon peas hulls, salacca peels, spent tea leaves, pine nut shell, and oil palm shell [25-33].

The kola nut is the fruit of the kola tree. Kola nut is a caffeine-containing nut of evergreen trees of the genus Cola, primarily the species Cola acuminata and Cola nitida [34]. Kola nuts are often used to treat whooping cough and asthma. To Western culture, it is best known as a flavouring ingredient and one of the sources of caffeine in cola and other similarly flavoured beverages, although the use of kola (or kola flavoring) in commercial cola drinks has become uncommon. Originally a tree of tropical rainforest, but can withstand a dry season in areas with a high ground water level. It may be cultivated in drier areas where ground water is available. In Nigeria, it is commonly found in southwestern states such as Ondo, Ekiti, Ogun and Osun.

The aim of this study is to produce a low-cost activated carbon from kola nut pod using two different chemical activation agents, H_2SO_4 and CaOH. The prepared activated carbons will be characterized by different surface science methods and their performance compared by testing the Basic fuchsine (BF) dye adsorption capability, kinetics and isotherm of the produced activated carbons.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbate

Fuchsine basic BF (λ_{max}= 543 nm; Molecular formula = $C_{20}H_{20}N_3 \cdot HCl$; Molar mass = 337.86 g/mol; Solubility in water = 2650 mg/L at 25°C) was purchased from a chemical store in Onitsha, Anambra, Nigeria. The dye concentration was determined through the absorbance at the characteristic wavelength using a double beams UV/Vis spectrophotometer (UV–Visible spectrophotometer, Shimadzu 1650). The absorbance and concentration of the dye solution was plotted to obtain the calibration curve of BF dye.

2.2. Preparation and characterization of Activated carbon

Kola nut pod was collected from Ifaki-Ekiti, Ido/Osi, Ekiti state, Nigeria. It was washed, dried and carbonized at 500C for 1hr. The pyrolyzed carbon was activated using the method described by Arivoli et al [35]. The carbonized kola nut pod divided into 2 separate sets. 100g of it was treated with sulphuric acid, while the other set was treated with calcium hydroxide. This was done in the ratio of 2:1 by wt. The treated carbons were placed in an oven and heated to a temperature of 200°C for a time period of 24 hours. After this, the activated carbon was washed thoroughly with distilled water, so as to neutralize the pH of the activated carbons and later dried in an oven at a temperature of 150°C for 3hrs.

The produced activated carbons using sulphuric acid and calcium hydroxide were labeled as acid activated kola nut pod carbon (KPAC) and base activated kola nut pod carbon (KPBC) respectively. The method described by Bhole and Ramteke [36] was used in carrying out the proximate analysis of the produced activated carbons:

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 formular: “Fixed carbon = 100 – (moisture content + Ash content + Volatile matter)”.

2.3. Batch adsorption

Batch adsorption experiments were conducted using 250 mL glass-stopperred, Erlenmeyer flasks with 50mL of stock solution, with a concentration of 50 mg/L. 1 g of the adsorbent was added to the solution. The flasks were agitated at a constant speed of 200 rpm for 2 h in a shaker at 303 ± 1 K. Samples were withdrawn from the flasks, at preset time intervals for analyzing the residual dye concentration in the solution. The filtrate of dye in each flask was measured using UV/VIS spectrophotometer. The influence of variables such as pH (2.0–10.0), initial dye concentration (50–500 mg/L), and adsorbent dose (0.5–2.5 g) were evaluated during the present study and reported in the results and discussion part. The amounts of BF dye removed by sorbents, q_e can be calculated using the following equation: “$q_e = (C_o - C_e)V/W$”. Where C_o is the initial BF dye concentration in mg/L, C_e is equilibrium concentration of the dye ion in mg/L.V is the volume of the solution (L) and W is the mass of the adsorbent (g), each of the experiment was conducted in duplicate and the average of two values was used in the calculations.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Adsorbent

The result of the proximate analysis of KPAC as determined by Nwodika et al [37] and KPBC, studied from standard procedures, have been listed in Table 1. From the fixed carbon content of both carbons, it can be said that KPAC is richer in carbon than KPBC.

***Table 1**: Proximate analysis result for KPAC determined by Nwodika et al [37] and for KPBC*

Parameter	**KPAC**	**KPBC**
Moisture content (%)	9.66	10.83
Ash content (%)	0.88	3.95
Volatile matter (%)	1.14	1.66
Fixed carbon (%)	88.33	83.56
Surface area (m^2/g)	779	726

3.2. Effects of Process Parameters

3.2.1. Effect of pH

In adsorption, the effect of pH of the aqueous solution is very important. It has an impact on both the surface properties of an adsorbent, and the rate of adsorbate removal. The effects of initial pH on BF dye removal from aqueous solution by KPAC and KPBC were investigated by varying the pH from 2 to 10 using 0.1M HCl and 0.1M NaOH. As seen in Fig. I, adsorption efficiency was in the increase between pH of 2 and 4, and maximum efficiency was obtained at pH 4 for both adsorbents. The high percentage removal of the BF in the acidic pH range may be attributed to the electrostatic interactions between the positively charged adsorbent and the negatively charged BF dye ions [38]. As system's pH increased, adsorption efficiency decreased but started to rise again at pH of 10. A similar result was obtained by Arivoli et al [35] in the study of the effect of pH on malachite green removal by borassus bark carbon, in which case, the decrease in adsorption efficiency as pH increased was attributed to possible aggregation of the dye molecules, likely caused by attractive electrostatic interaction between the ionic groups of the monomer. This suggested that the adsorption capacity of activated carbon prepared from kola nut pod was dependent on pH. Comparing the adsorption efficiency of both activated carbons with regard to pH dependent, it is seen from the figure (Figure 1) that KPBC adsorbed more than KPAC.

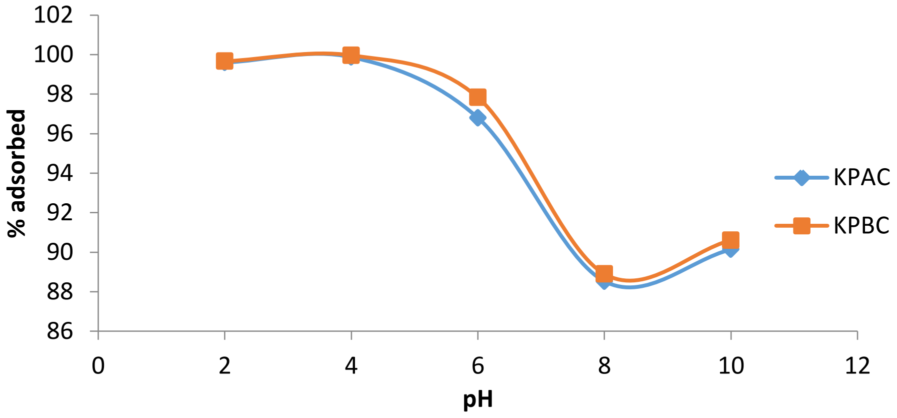


Figure 1: *Effect of pH on Basic fuchsine adsorption*

3.2.2. Effect of initial concentration on BF adsorption

KPAC and KPBC were used to adsorb BF dye of different initial concentration ranging from 50 to 500mg/L. 50mL of the stock solutions of different concentrations were prepared and 1.0g of the adsorbents was added to 250cm3flasks different concentration of stock solution. The content of each flask was agitated for 1h, filtered and analyzed. From Figure 2, it can be seen that increase in initial concentration from 50 to 500mg/L resulted in a decrease in the adsorption efficiency. This implies that dye adsorption efficiency reduced as the initial concentration of BF dye increased. The reason behind this is that at lower concentrations, there are sufficient active sites that the sorbate can easily occupy [39].

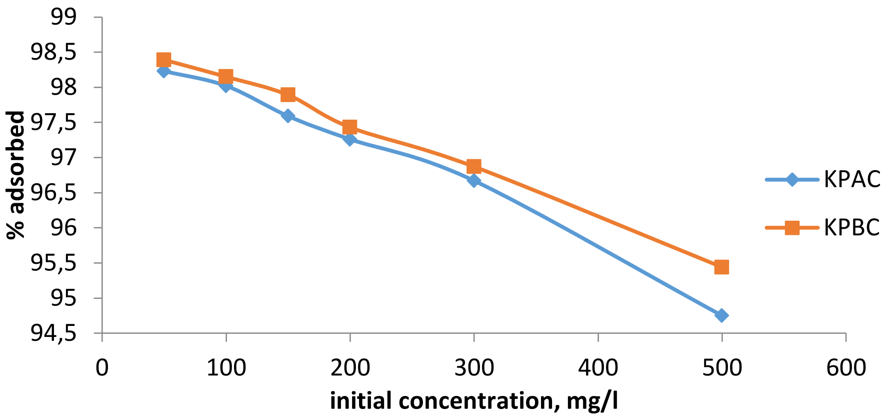


Figure 2: *Effect of initial concentration on Basic fuchsine adsorption*

3.2.3. Effect of carbon dose on BF adsorption

The adsorption of the BF dye on carbon was studied by varying the carbon dose (0.5–2.5g/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased rapidly with increases in the carbon concentration from 0.5–1.5g (Figure 3), further increase yielded no significant impact on the adsorption process for KPBC unlike KPAC where there is a slight decrease in adsorption efficiency likely as a result of aggregation resulting from high adsorbent concentration which would amount to a decrease in the adsorbent's total surface area. The increase in adsorption efficiency is attributed to increased carbon surface area and the availability of more adsorption sites [40-41]. Hence, all studies were carried out with 100 mg of adsorbent /50 ml of the varying adsorbate solutions.

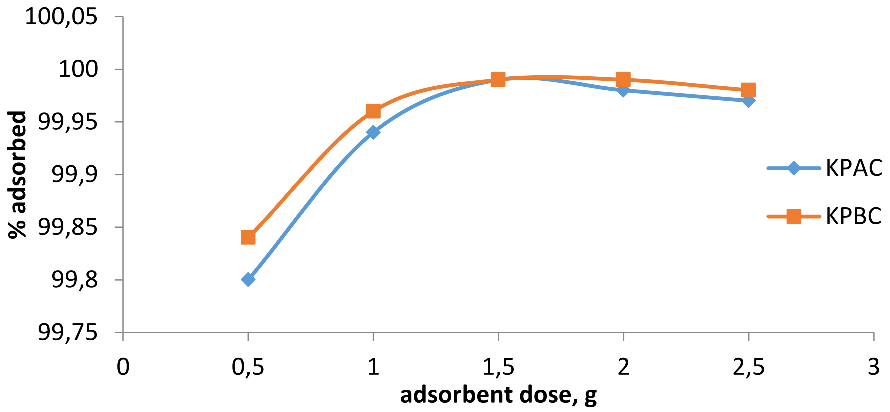


Figure 3: *Effect of adsorbent dose on Basic fuchsine adsorption*

3.2.4. Effect of contact time on BF adsorption

The effect of contact time on adsorption capacity of KPAC and KPBC for BF dye is shown in Figure 4. It is clear that the adsorption capacity of both adsorbents increased rapidly with the increase of contact time from 0 to 30 min and after 90 min, the adsorption capacity became constant, with the adsorption reaching equilibrium. As a result, 90 min was selected as the contact time for the adsorption of BF dye onto KPAC and KPBC under these particular experimental conditions. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of BF ions to the surface of adsorbent particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent [42]. Comparing the adsorption of both adsorbents showed that KPBC adsorbed more BF dye than KPAC under studied experimental conditions.

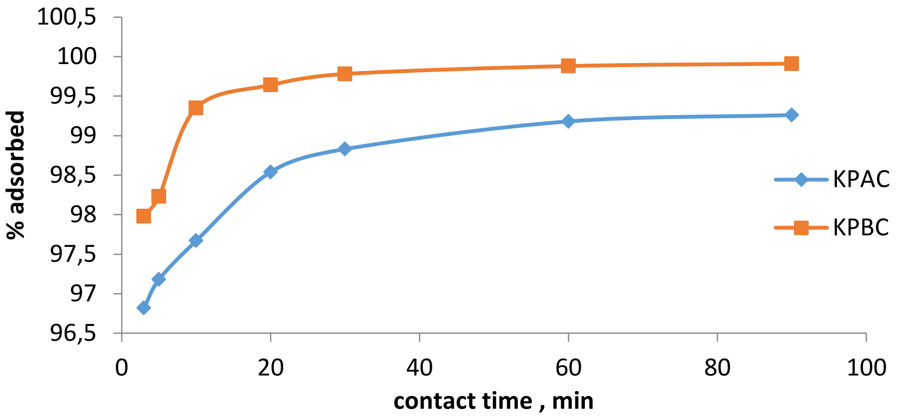


Figure 4: *Effect of contact time on Basic fuchsine adsorption*

3.3. Kinetics study

In the present research, the kinetics of adsorption of BF dye on KPAC and KPBC was studied. Two types of kinetic models, pseudo-first order [43], and pseudo-second order model [44], were employed to fit experimental data (Figure 5 and Figure 6). The straight lines plots showed a good agreement of experimental data with pseudo-first order model and pseudo-second order model. Table II listed the results of rate constant studies for both kinetic models. Comparing the R^2 values, pseudo-second-order model shows a significant agreement with adsorption mechanisms for both adsorbents in comparison to pseudo-first order model. In addition, general kinetic comparison of KPAC and KPBC shows that KPBC is favourable than KPAC. This can be gathered from their rate constants and R^2 values, both for pseudo-first order, and pseudo-second order models.

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

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2.303 \quad (3)$$

The integrated form of the pseudo second-order kinetic equation is written as:

$$t/q_t = 1/(k_2 q_e 2) + t/q_e \quad (4)$$

The rate limiting step of the adsorption process was studied using Weber and Morris intraparticle diffusion model equation:

$$q_t = k_{id} t^{1/2} + C_i \quad (5)$$

Where k_{id} is known as the intraparticle diffusion rate constant (mg/gmin$^{1/2}$), and C_i is the boundary layer's thickness. If the plot of log q_t against 0.5 log t is linear and goes through the origin, the rate-liming step is solely intraparticle diffusion. If not, then it involves both film diffusion and intraparticle diffusion.

The adsorption was controlled by both film diffusion and intraparticle diffusion at early and later stages of the adsorption respectively. This can be observed in the Weber and Morris plots of the KPAC and KPBC adsorption of basic fuchsine (Figure 7). Table 2 shows k_{id} for both plots.

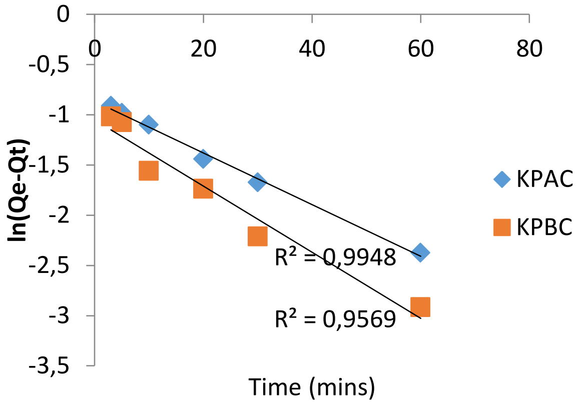
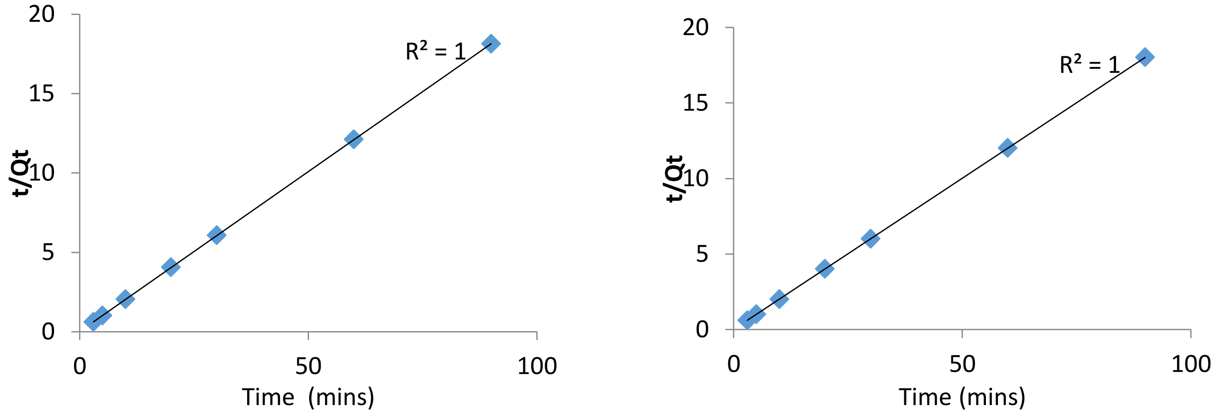
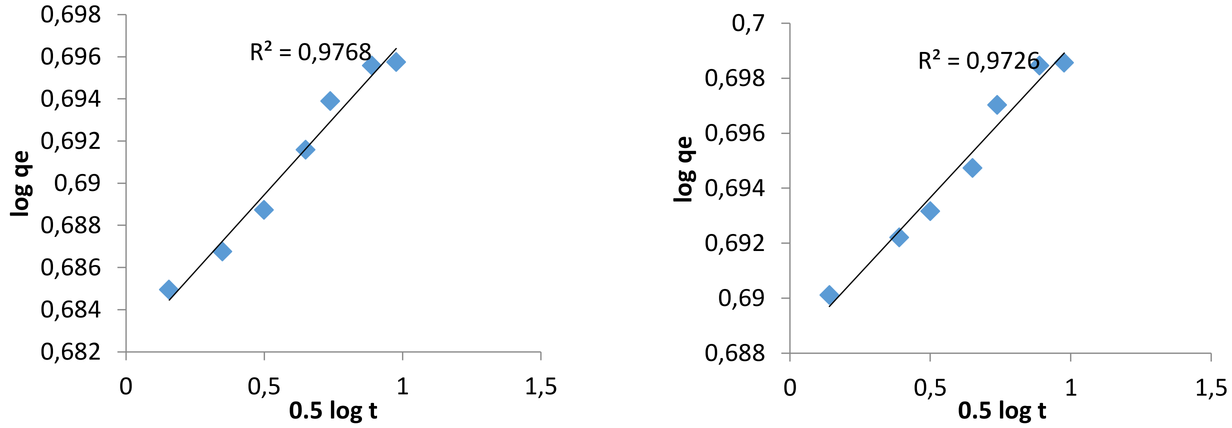


Figure 5: *Pseudo-first order kinetic of KPAC and KPBC for adsorption of Basic fuchsine*



(a) KPAC ***(b) KPBC***

Figure 6: *Pseudo-second order kinetic of (a) KPAC and (b) KPBC for adsorption of BF*



(a) KPAC ***(b) KPBC***

Figure 7: *Intraparticle diffusion of (a) KPAC and (b) KPBC for adsorption of BF*

Table 2: *Kinetic parameters of KPAC and KPBC*

Parameter	**KPAC**	**KPBC**
Pseudo first order model		
$K_1(min^{-1})$	0.132	0.146

q(mg/g)	4.947	4.992
R^2	0.994	0.956
Pseudo second order model		
K_2(g/mg/min)	1.452	2.724
q(mg/g)	4.970	5.000
R^2	1.000	1.000
Intraparticle diffusion model		
K_{id} (mg/gmin-^{1})	0.015	0.011
R^2	0.976	0.972

3.4. Isotherm study

The isotherm of the adsorption was fitted with two isotherm models; Langmuir model and Freundlich model. Langmuir isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and is presented by the equation [45]:

$$Q_e = Q_e=\underline{Q_mK_aC_e}/1 + K_aC_e \qquad (6)$$

$$1/Q_e = (1/K_aQ_m)1/C_e + 1/Q_m \qquad (7)$$

where Q_e (mg of adsorbate per g of adsorbent) is the adsorption density at the equilibrium solute concentration C_e. C_e is the equilibrium concentration of adsorbate in solution (mg/L). Q_m (mg of solute adsorbed per g of adsorbent) is the maximum adsorption capacity corresponding to complete monolayer coverage. K_a is the Langmuir constant related to energy of the adsorption (L of adsorbate per mg of adsorbent).

Freundlich isotherm is an empirical equation employed to describe the heterogeneous system. The linear form of the equation is given below [46]:

$$\text{Log}q_e = \log K_f + 1/n \log C_e. \qquad (8)$$

where q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium, where K_f and $1/n$ are empirical constants dependent on the nature of sorbent and sorbate and the temperature. Both of these values (K_f and 1/n) are important in selecting an adsorbent as a separating medium, in which K_f (mg/g) is the over-all adsorption capacity (q_e at C_e = 1mg/L or log C_e = 0) and $1/n$ is the heterogeneity factor. The heterogeneity factor 1/n indicates the strength of bond energy between sorbate and sorbent. A plot of log q_e against log C_e yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

From the figures (Figure 8 and Figure 9) of the isotherm plots of the adsorption of BF dye using the produced activated carbons, it can be seen that Langmuir isotherm model better described the adsorption isotherm of KPAC and KPBC than the Freundlich isotherm model, as can be reached from the value of their regression coefficients (R^2). In like manner, the regression coefficients (R^2) of both adsorbent for Langmuir isotherm model and Freundlich isotherm model also suggest that KPBC is a better adsorbent of the two, for the removal of BF dye from aqueous solution.

According to Abdel-Ghani et al [47], the Temkin isotherm model can be applied in this form:

$$X = a + b \ln C \qquad (9)$$

Where C is the concentration of adsorbate in solution at equilibrium (mg/L), while X is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). In addition, a and b are constants related to adsorption capacity and intensity of adsorption respectively. If the plot of ln C against X is linear for an adsorption system, it implies that Temkin isotherm can be used to describe it. From Figure 10, the adsorption of BF using KPAC and KPBC can be described using this model. The regression coefficient and Temkin parameters are expressed in Table 3.

The Dubinin-Radushkevich (D-R) isotherm model is expressed in linear form as [48]:

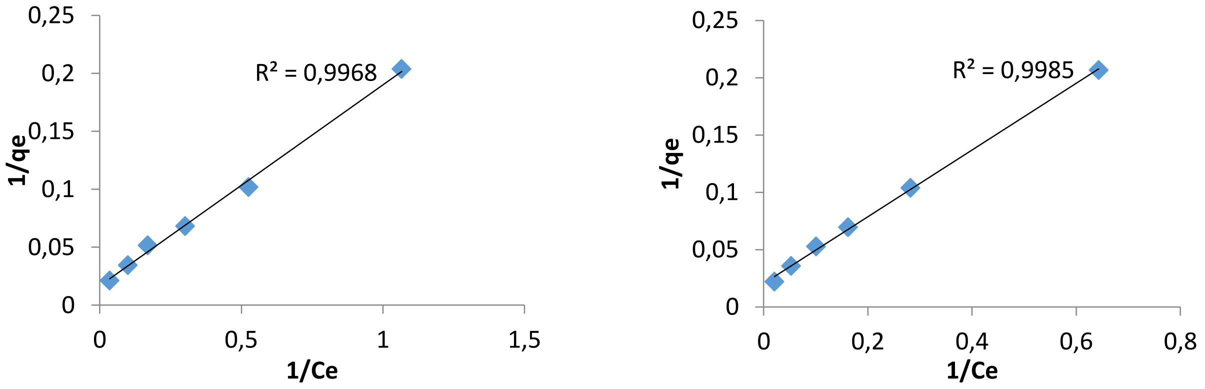
$$\ln q_e = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \qquad (10)$$

A plot of ln q_e against RT ln (1 + 1/C_e) if linear, shows that this model described the adsorption isotherm suitably. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relation given below [49].

$$E= {}^{1}/\sqrt{2}\, B_D \qquad (11)$$

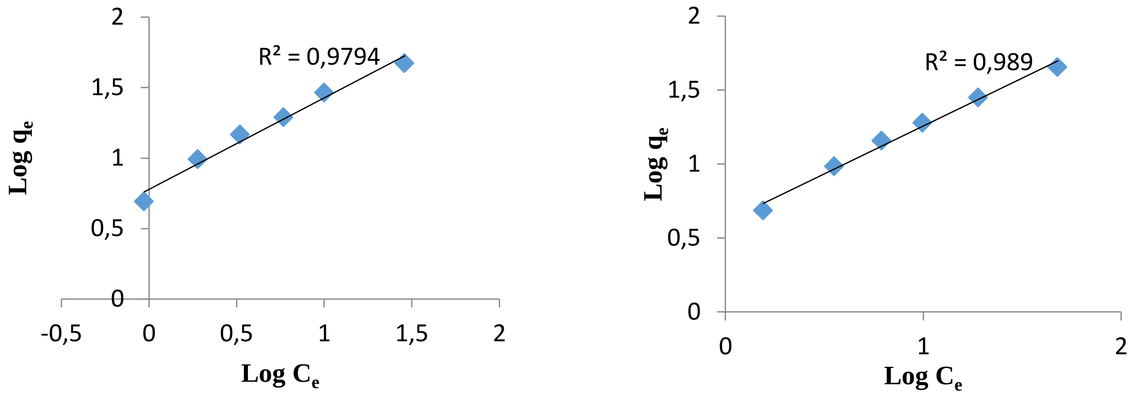
In D-R isotherm, if E<8kJmol^{-1}, physisorption dominates the sorption mechanism. If E is between 8 and 16kJmol^{-1}, ion-exchange is the dominant factor. If E >16kJmol^{-1}, sorption is dominated by particle diffusion [50].

The mean adsorption energy (E) calculated from the Dubinin-Radushkevich (D-R) isotherm provides important information about the physical and chemical properties of the adsorption of any adsorption process [50-51]. From Table 3, the value of E for the adsorption of BF using KPAC and KPBF are greater than 16 kJmol^{-1}(E>16kJmol^{-1}) this suggests that the adsorption process is dominated by particle diffusion [51].



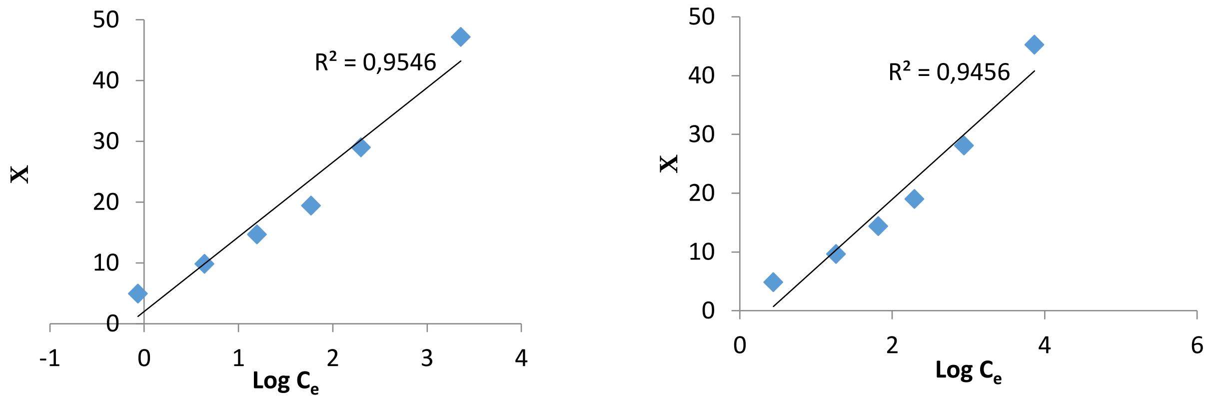
(a) KPAC ***(b) KPBC***

Figure 8: *Langmuir isotherm plot of (a) KPAC and (b) KPBC for adsorption of BF*



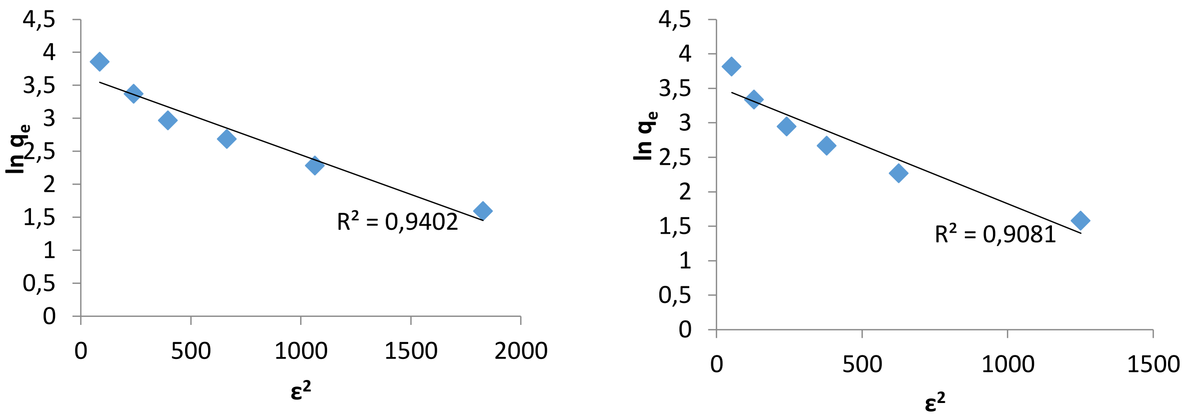
(a) KPAC ***(b) KPBC***

Figure 9: *Freundlich isotherm plot of (a) KPAC and (b) KPBC for adsorption of BF*



(a) KPAC ***(b) KPBC***

Figure 10: *Temkin plot of (a) KPAC and (b) KPBC for adsorption of BF*



(a) KPAC ***(b) KPBC***

Figure 11: *D-R isotherm plot of (a) KPAC and (b) KPBC for adsorption of BF*

Table 3: *Isotherm parameters of KPAC and KPBC*

Parameter	**KPAC**	**KPBC**
Langmuir model coefficients		
Qm(Mg/g)	5.769	3.436
K_a(L/mg)	10.417	14.286

R_L	0.0020	0.0014
R^2	0.996	0.998
Freundlich model coefficients		
K_F(Mg/g)	4.459	4.424
1/n	0.779	0.611
R^2	0.979	0.989
Temkin model coefficients		
a	12.273	11.698
b	1.991	-4.426
R^2	0.954	0.945
D-R model coefficients		
B_D(mol^2kJ^{-2})	-0.0012	-0.0017
q_D(Mg/g)	1.2940	1.2600
E($kJmol^{-1}$)	20.412	17.150
R^2	0.940	0.908

3.5. Thermodynamic study

Van’t Hoff equation [52] was used in studying the thermodynamic of the adsorption of basic fuchsine (BF) using KPAC and KPBC:

$$\log K_c = -\Delta H/2.303RT + \Delta S/2.303R \tag{12}$$

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:

$$\Delta G = -RT \ln K_c \tag{13}$$

R is the ideal gas constant. The slope and intercept of the plot of log K_c against 1/T gives the values of ΔH and ΔS respectively.

Based on the thermodynamic studies, the negative values obtained for the enthalpy (ΔH) and free energy (ΔG), as shown in Table 4, reflects the exothermic, and feasibility and spontaneous nature of sorption respectively [52-53]. This could be a resultant of weakened 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 show a decrease in the degree of freedom of the adsorbed species. These negative values of the entropy also indicate favourable adsorption. The entropy $\Delta S < -10$J/mol generally imply an associative mechanism [52]. For both activated carbons, the negative entropy values suggest dye sorption to be of an associative mechanism.

Table 4: *Thermodynamic parameters KPAC and KPBC*

Parameter		**Activated carbon**	
	Temperature	**KPAC**	**KPBC**
ΔG° (kJ/mol)	30ºC	-8.758	-9.780
	40ºC	-8.019	-8.343
	50ºC	-8.219	-8.408
	60ºC	-7.953	-7.895
ΔH(kJ/mol)		-46.85	-81.32
ΔS(J/mol/K)		-22.78	-57.09

3.6. Comparison with Literatures

The result of this study was compared to those obtained from other studies on the adsorption of basic fuchsine, using other adsorbents. Emphasis was placed on best fitting kinetic and isotherm model of those studies, in addition to the thermodynamics (if studied). Generally, the kinetic of the literatures considered, favoured the pseudo-second order kinetic model. Best fitted isotherm model varied with respect to adsorbent, likewise the thermodynamics study outcome. The adsorption efficiency of KNA and KNB (99. 4% and 99.7% respectively), is of the same range with modified aromatic polyurethane foam material which has a maximum adsorption efficiency of 99.5% [54], and a more than that of Euryale ferox Salisbury which is 97.4% [55]. Table V presents the summary of this comparison.

Table 5: *Summary of literature comparison*

Adsorbent	**Best fitted kinetic model**	**Best fitted isotherm model**	**Thermodynamics comment**	**Source**
Modified aromatic poyurethane foam	Pseudo-second order	Langmuir	Spontaneous, endothermic	[54]
Euryale ferox salisbury	Pseudo-second order	Langmuir	Spontaneous, endothermic	[55]
Loess based copolymer	Pseudo-second order	Freundlich		[56]
Jackfruit waste activated carbon	Pseudo-second order	Langmuir		[57]
Leather activated carbon	Pseudo-second order	Freundlich	Spontaneous, exothermic	[58]
Biosorbents	Pseudo-second order	Langmuir	Spontaneous, endothermic	[59]
Carboxylated-functionalized cellulose nanocrystal	Pseudo-second order	Langmuir	Spontaneous, exothermic	[60]
Kola nut pod activated carbon	Pseudo-second order	Langmuir	Spontaneous, exothermic	Present study

4. CONCLUSION

In conclusion to this research, the result presented clearly suggests that the produced activated carbon; KPAC and KPBC can be efficiently used for the removal of Basic fuchsine dye. KPBC proved to be more efficient than KPAC for the adsorption of Fuchsine basic dye. At room temperature, an amount of 1g of KPAC and KPBC could remove over 95% of Fuchsine basic from an aqueous solution of 50mg/L, with solution pH of 4, at a stirring speed of 200rpm for a contact time of 90 minutes. The adsorption data was tested with pseudo-first order and pseudo-second order kinetic models and it was observed that though both models fitted the adsorption data, pseudo-second order model better fitted the experimental data. The Langmuir isotherm model fitted the adsorption data better than the Freundlich isotherm model for both KPAC and KPBC. The use of activated carbon from kola nut pod for dye removal from industrial effluents is economically feasible and environmentally friendly.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

[1] Unal, G., Gulce O. and Gizem, C.G., "Removal of methylene blue from aqueous solution by activated carbon prepared from Pea shells (PislumSativam)", *Journal of Chemistry*, 3, Article ID614083, 9 pages, (2013).

[2] Ayanda, O.S., Adeyi, O., Durojaiye, B. and Olafisoye, O., “Adsorption kinetics and intra-particulate diffusivities of congo red onto kola nut pod carbon”, *Pol. J. Environ. Stud.,* 21(5): 1147–1152, (2012).

[3] Oladayo, A., Olushola, S.A., Godwin, O.O. and Olamide, G., “Adsorption kinetics and intra-particulate diffusivity of Aniline blue dye onto activated plantain peels carbon”, *Chemical Science Transactions,* 2(1): 294–300, (2012).

[4] Robinson, T., Mcmullan, G., Marchant, R. and Nigam, P., “Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternatives”, *Bioresour. Technol.,* 77: 247–255, (2001).

[5] Figueiredo, J.L., Sousa, P.S., Orge, C.A., Pereira, M.F.R. and Orfao, J.J.M., “Adsorption of dyes on carbon xerogels and templated carbon influence of surface chemistry”, *Adsorption,* 17(3): 431–441, (2000).

[6] Wahi, R.K., Yu, W.W., Liu, Y., Mejia, M.L., Falkner, J.C., Nolte, W. and Colvin, V.L., “Photodegradation of congo red catalized by nanosized TiO2”, *J. Mol. Catal. A – Chem,* 242: 48–56, (2005).

[7] Khadhraoui, M., Trabelsi, H., Ksibi, M., Bouguerra, S. and Elleuch, B., “Decoloration and detoxification of a congo red solution by means of ozone treatment for a possible water reuse”, *J. Hazard Mater,* 161: 974–981, (2009).

[8] Banat, F. and Al-Bastaki, N., “Treating dye wastewater by an integrated process of adsorption using activated carbon and ultrafiltration”, *Desalination,* 170: 69–75, (2004).

[9] Golob, V., Vinder, A. and Simonic, M., “Efficiency of coagulation/ flocculation method for the treatment of dye bath effluents”, *Dyes and Pigments,* 67(2): 93–97, (2005).

[10]Mo, J.H., Lee, Y.H., Kim, J., Jeong, J.Y. and Jegal, J., “Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse”, *Dyes and Pigments,* 76(2): 429–434, (2008).

[11]Gopinath, K.P., Murugesan, S., Abraham, J. and Muthukumar, K., “Bacillus sp. mutant for improved biodegradation of congo red: random mutagenesis approach”, *Bioresource Technol.,* 100(4): 6295–6300, (2009).

[12]Jedynak, K., and Repelewicz, M., “Adsorption of methylene blue and malachite green on micro-mesoporous carbon materials”, *Adsorption science and technology,* 35: 499–506, (2017).

[13]Ahmad, M.A. and Rahman, N.K., “Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon”, *Chemical Engineering Journal,* 170: 154–161, (2011).

[14]Khaled, A., El Nemr, A., Ei-Sikaily, A. and Abdelwahab, A., “Treatment of artificial textile dye effluent containing direct yellow 12 by orange peel carbon”, *Desalination,* 238: 210–232, (2009).

[15]Naraghi, B., Zabihi, F., Narooie, M. R., Saedi, M., and Biglari N., “Removal of acid orange 7 dye from aqueous solution by adsorption onto Kenya tea pulps; granulated shape”, *Electron physician,* 9: 4312–4321, (2017).

[16]Safa, Y. and Bhatti, H.N., “Kinetics and thermodynamics modeling for the removal of direct red-31, and direct orange-26 dyes from aqueous solutions by rice husk”, *Desalination,* 272: 313–322, (2011).

[17]Sahu, M. K., and Patel, R. K., “Removal of safranin-o dye from aqueous solution using modified red mud: kinetic and equilibrium studies”, *RSC Advances*, 5: 78491–78501, (2015).

[18]Mafra, M. R., Marshi-Mafra, L., Zuim, D. R., Vasquez, E. C., and Ferreira, M. A., “Adsorption of ramazol brilliant blue on an orange peel adsorbent”, *Brazilian Journal of Chemical Engineering,* 30: 657–665, (2013).

[19]Zazouli, M. A., and Moradi, E., “Adsorption of acid red 18 dye using sargassum glaucesceus from aqueous solution”, *Iranian journal of health sciences*, 3: 7–13, 2015.

[20]Armagan, B., and Toprak, F. “Optimum isotherm parameters for reactive azo dye on pistachio nut shells: Comparison of linear and nonlinear methods”, *Pol. J. Environ. Stud.,* 22(4): 1007–1011, (2013).

[21]Rehman, M.S., Munir, M., Ashfaq, M., Rashid, N., Nazar, M.F., Danish, M. and Han, J., “Adsorption of brilliant green dye from aqueous solution onto red clay”, *Chem. Eng. J.,* 228: 54–62, (2013).

[22]Abbas, H. S., Waleed, M. A., Tariq J., and Dhafar F. A., “Single and binary adsorption of reactive blue and red dyes onto activated carbon”, Interational J Eng Innov and Res., 3: 642 – 649, (2014).

[23]Aljeboree, A.M., Alshirifi, A.N. and Alkaim, A.F., “Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon”, *Arabian Journal of Chemistry,* http://dx.doi.org/10.1016/j.arabjc.2014.01.020, (2014).

[24]Sudhanshu, K., Bharat, S. and Singh, K.S., “Comparative study on removal of fluoride from groundwater by natural and modified bagasse carbon of sugarcane”, *International Research Journal of Pure & Applied Chemistry,* 8(3): 147–156, (2015).

[25]Theivarasu, C. and Mylsamy, S., “Equilibrium and Kinetic adsorption studies of Rhodamine-B from aqueous solutions using cocoa (Theobroma cacao) shell as a new adsorbent”, *IJEST,* 2:6284-6292 (2010).

[26]Fagbeyigbo, B. O., Opeolu, B. O., Fatoki, O. S., Akenga, T. A., and Olatunji, O. S., “Removal of PFOA and PFOS from aqueous solution using activated carbon produced from vitis vinafera leaf litter”, *Environ Sci. Pollut. Res. Int.*, 24: 13107–13120, (2017).

[27]Jadhav, A., and Moharaj, G., “Synthesis of activated carbon from cocos nucifera leaves agrowaste by chemical activation method”, *Scientific – Technical J. Chem. and Chem. Technol.*, 10: 201–208, (2016).

[28]Khairuladli, N., Fisal, A., Mohd Sukri, H., Khairumisa, N., and Ahmad, M. A., “Adsorption of chemically prepared cocoa nibs based activated carbon onto methylene blue: equilibrium and kinetic studies”, *Int. J. Pet. Resour.,* 1:15–18, (2017).

[29]Venkata Ramana, D. K., and Min.K., “Activated carbon produced from pigeon peas hulls waste as lowcost agro-waste adsorbent for Cu (II) and Cd (II) removal”, *Desalination and Water Treatment,* 57: 6967–6980, (2016).

[30]Arenst, A. A., Vincent and Aditya, P., “Activated carbons from KOH-activation of salacca peels as low cost potential adsorbents for dye removal”, *Adv. Mater. Lett.,* 7: 226–229, (2016).

[31]Akar, E., Altinisik, A., and Seki, Y., “Using of activated carbon produced from spent tea leaves for the removal of malachite green from aqueous solutions”, *Ecol Eng.,* 52:19–27, (2013).

[32]Chu, X., Zhao, L., Sun, Y., Xie, H., and Xi, C., “Preparation and application of high surface area activated carbon based on pine nut shell”, *Journal of Nanoengineering and Nanomanufacturing,* 4: 336–340, (2014).

[33]Hamad, B. K., Noor, A. M., and Rahim, A. A., “Removal of 4-chloro-2-methoxyphenol from aqueous solution by adsorption to oil palm shell activated carbon activated with K_2CO_3”, *J. Phys. Sci.,* 22: 39–55, (2011).

[34]Burdock, G.A., Carabin, G.I.G. and Crincoli, C.M., “Safety assessment of kola nut extract as a food ingredient”, *Food and Chemical Toxicology,* 47(8): 1725–1732, (2009).

[35]Arivoli, S., Hema, M. and Prasath, P.M.D., “Adsorption of malachite green onto carbon produced from borassus bark”, *The Arabian Journal for Science and Engineering,* 34(2A): 31–42, (2009).

[36]Bhole, V. and Ramteke, D.S., “Preferential adsorption of heavy metals on activated carbon”, *Bangladesh Journal of Sci. and Industrial Research,* 46(2): 211–218, (2011).

[37]Nwodika, C., and Onukwuli, O. D., “Crystal violet adsorption onto kola nut pod husk activated carbon; isotherm, kinetic, and thermodynamics studies”, Sigma. J. Eng. Nat. Sci., 35: 411-426, (2017).

[38]Idris, M. N., Ahmad, Z. A., and Ahmad, M. A., “Adsorption equilibrium of malachite green dye onto rubber seed coat based activated carbon”, *International Journal of Basic and Applied Science, IJBAS-IJENS.* 11: 38–43, (2011).

[39]Mane, P. C., Bhosle, A. B., Deshmukh, P.D. and Jangam, C.M., “Chromium adsorption on activated carbon derived from tendu (*diospyros melanoxylon*) leaf refuse: Influence of metal/carbon ratio, time and pH”, *Advances in Applied Science Research,* 1(3): 212–221, (2010).

[40]Mall , I.D., Srivastava, V.C., Agarwal, N.K. and Mishra, I.M., “Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon kinetic study and equilibrium isotherm analysis”, *Colloids and surfaces,* 264: 17–28, (2005).

[41]Rahman, I. A., Saad, B., Shaidan, S., and Sya Rizal, E. S., “Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical thermal process”, *Bioresour. Technol.,* 96: 1578–1583, (2005).

[42]El-Wakil, A.M., Abou El-Maaty, W.M., Awad, F.S. and Oudah, A.A., "Solid phase extraction and determination of cationic azo dye from aqueous solution using dried papyrus plant", *International Journal of Science and Research (IJSR),* 4(2): 2045–2052, (2015).

[43]Lagergren, S., "About the theory of so-called adsorption of soluble substances", *Kungliga Suensk Vetenskapsakademiens Handlingar,* 241: 1–39, (1898).

[44]Ho, Y. S., and Mckay, G., "Pseudo-second order model for sorption processes", *Process Biochemistry,* 34: 451–465, (1999).

[45]Langmuir, I., "Adsorption of gases on plain surfaces of glass mica Platinum", *J. Am. Chem. Soc,* 40: 1361–1403, (1918).

[46]Freundlich, H. and Heller, W., "The adsorption of cis- and transazobenzene", *J. Am. Chem. Soc,* 61: 2228–2230, (1939).

[47]Abdel-Ghani N. T.; Hefny M.; & El-Chaghaby, G. A. F., "Removal of lead from aqueous solution using low cost abundantly available adsorbent", *Int. J. Environ. Sci. Tech,* 4: 67–73, (2007).

[48]Igwe, J. C., and Abia A. A., "Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from wastewater using unmodified and EDTA-modified maize husk", *Electronic Journal of Biotechnology,* 10: 1–15, (2007).

[49]Horsfall, M. Jnr., Spiff; A.I., and Abia, A.A., "Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (manihot sculenta cranz) waste biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution", *Bulletin of the Korean Chemical Society*, 25: 969–976, (2004).

[50]Bering, B. P., Dubinin, M. M., and Serpinsky, V.V., "Thermodynamics of adsorption in micropores", *J. Colloid Interf. Sci.,* 38: 184–194, (1972).

[51]Argun. M. E., Dursun, S., Ozmedir, C., and Karatas M., "Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetic", *J. Hazard. Mater.,* 141: 77–85, (2007).

[52]Abdul, G., "Removal of lead (II) Ions from aqueous solution under different physicochemical conditions using various sorbents." *The Arabian Journal for Science and Engineering*, 33: 55–61, (2008).

[53]Al-Othman, Z. A., Hashem, A., and Habila, M. A., "Kinetics, equilibrium, and thermodynamics studies of Ca(II) adsorption by modified agricultural waste", *Molecules,* 16: 10443–10456, (2011).

[54]Qin, J., Qiu, F., "Removal of basic fuchsine from aqueous solution using graphite oxide modified aromatic polyurethane foam material", *Toxicology and Environmental Chemistry*, 96: 849–860, (2014).

[55]Kalita, S., Pathak, M., Devi, G., Sarma, H. P., Bhattacharyya, K. G., Sarma, A., and Devi, A., "Utilization of euryale ferox salisbury seed shell for removal of basic fuchsin dye from water: equilibrium and kinetics investigation", *RSC Adv.*, 7: 27248–27259, (2017).

[56]Wang, L., He, W. J., Feng He, Y., Li, H., and Wang, R. M., "Loess Based Copolymer Composite for Removing Basic Fuchsine, *Key Engineering Materials*, 633: 165–168, (2014).

[57]Nagalakshmi, T. V., Emmanuel, K. A., Sureshbabu, C., Nagaraju, K., and Rao, K. S., "Adsorption of basic textile dye from aqueous solution by prepared activated carbon", *J. Applicable Chemistry,* 5: 452–465, (2016).

[58]Kong, J. J., Huang, L., Yue, Q., and Gao, B., "Preparation of activated carbon derived from leather waste by H_3PO_4 activation and its application for basic fuchsine adsorption", *Desalination and Water Treatment,* 52: 2440–2449, (2014).

[59]Patil, S., Patil, J., and Patel, N., "Comparative Study of Kinetics of Removal of Fuchsin Basic from Aqueous Solutions Using Biosorbents", *Journal of Environmental Science, Toxicology and Food Technology,* 9: 8–20, (2015).

[60]Qiao, H., Zhou, Y., Yu, F., Wang, E., Min, Y., Huang, Q., Pang, L., and Ma, T., "Effective removal of cationic dyes using carboxylate-functionalized cellulose nanocrystals", *Chemosphere,* 141: 297–303, (2015).