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## PARAQUAT DICHLORIDE ADSORPTION FROM AQUEOUS SOLUTION USING CARBONIZED BAMBARA GROUNDNUT (*Vigna subterranean*) SHELLS

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### ABSTRACT

**Carbonized Bambara GroundNut Shell (CBGNS) was used as adsorbent for the adsorption of paraquat dichloride (PQ) from aqueous solution. The prepared adsorbent was characterized using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy methods. Several parameters that might affect the adsorption process including pH, contact time, adsorbent dosage, temperature and initial concentration were investigated and optimized using batch adsorption technique. Results of the study revealed that maximum removal efficiency (98%) was achieved using 0.05g adsorbent dosage, solution pH of 5 and 60 min of contact time. The equilibrium experimental result revealed that Langmuir model best described the adsorption process with  $R^2$  value of 0.956. The heat of adsorption process was estimated from Temkin Isotherm model to be 19.99J/mol and the mean free energy was estimated from Duninin-Radushkevich (DRK) isotherm model to be 0.289KJ/mol indicating chemisorptions process. The kinetic and thermodynamic studies revealed that the adsorption processes followed pseudo-second-order kinetics with  $R^2$  value of 0.999 and the value of  $\Delta G$  (- 27.74 kJ mol<sup>-1</sup>),  $\Delta H$  (13.145 kJ mol<sup>-1</sup>) indicate the spontaneous and endothermic nature of PQ adsorption on CBGNS. The results suggested that CBGNS had the potential to become a promising material for PQ contaminated water treatment.**

**Keywords: Adsorption, Paraquat dichloride, Carbonized Bambara Ground nut shell, Water treatment.**

### INTRODUCTION

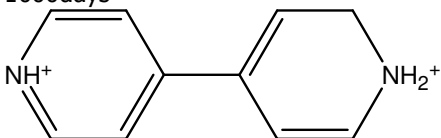
Paraquat dichloride (1, 1-dimethyl-4, 4-bipyridinium chloride) also known as Dragon (trade name) is a non selective herbicide widely used to control broad leaf weeds in field crops, orchards and non-cropped areas (Banaee *et al.*, 2013). Due to its widespread use, long-term persistence in soil, greater leaching potential and relatively high solubility in water, paraquat dichloride is frequently detected in ground, surface and drinking water (Sylvester and Ogaga, 2013). Paraquat dichloride is toxic to human health and enters the body through inhalation, ingestion and damaged skin integrity (Arivu *et al.*, 2016). According to Arivu *et al.*, (2016) a farmer died after 3 and an half hours of spraying diluted paraquat dichloride using leaking knapsack sprayer, and several others have suffered from severe acute and chronic effects result from occupational use of paraquat dichloride. Paraquat dichloride contamination of surface and subsurface water has become a serious public concern over its environmental impact. Numerous physical, chemical and biological techniques have been employed for waste water cleanup. These include; chemical (Alfano *et al.*, 2001), electrochemical (Brillas *et al.*, 2000), photochemical and photocatalytic

oxidation (Kamble *et al.*, 2004) and adsorption on granular activated carbon (Kim *et al.*, 2002). Several studies on the adsorption of herbicides on different adsorbents have been reported in literature. Ali *et al.*, (2019) investigate the sorption of carbendazim and linuron from aqueous solutions with activated carbon produced from spent coffee grounds. They found that the adsorption characteristics of these herbicides were best described by the Langmuir adsorption model. Saidat *et al.*, (2018) work on desert date shells as adsorbent for the removal of Atrazine from aqueous solution. Chemisorptions mechanism was confirmed for the adsorption of Atrazine onto desert date shell. The results of the isotherm studies revealed that the equilibrium data fitted to both Freundlich and Langmuir model. Other studies are those reported by Vijay *et al.*, (2018) (Spectral, structural and energetic study of acephate, glyphosate, monocrotophos and phorate: an experimental and computational approach), Zuhra *et al.*, (2014) (Adsorption of Selected Pesticides from Aqueous Solutions Using Cost effective Walnut Shells), Sebata *et al.*, (2013) (Adsorptive Removal of Atrazine from Aqueous Solution Using Bambara Groundnut Hulls (*Vigna Subterranean*)), Jude *et al.*, (2012) investigate

the kinetics and equilibrium isotherms of pesticides adsorption onto boiler fly ash. Chemisorptions mechanism was confirmed for the adsorption of paraquat dichloride onto boiler fly ash. The adsorption process plays an important role in determining the fate of paraquat dichloride in the environment. Despite the extensive information available on paraquat dichloride adsorption from boiler fly ash, activated carbon (Jude *et al.*, 2012), very little is known about the adsorption of paraquat dichloride onto carbonized Bambara groundnut shell. However, most of the reported studies on the adsorption of herbicides have not paid significant attention on the potential of Bambara groundnut shell as an adsorbent nor fully explored detailed mechanism for their adsorption process. Paraquat dichloride seems to have strong potentials to be adsorbed on

CBGNS because it has hetero atoms, which can act as the adsorption centre onto CBGNS. Although the uses of Bambara groundnut shells for the adsorption of paraquat dichloride has not been reported else were to the best of the knowledge of the authors, BNS is abundant in Nigeria and constitute a waste disposal problem. This material can be easily processed as a good adsorbent. Most of the reported work on the use of BGNS product is on the removal of dyes and has to do with the ability of these adsorbents in adsorbing the dyes. There are few reports on the specific mode of action of the adsorbent and the extent of adsorption: (Sebata *et al.*, 2013; Nharingo *et al.*, 2013; Akinola *et al.*, 2016). Therefore, the present study is aimed at testing the efficiency of carbonized Bambara ground nut shell for the adsorption of paraquat dichloride in aqueous solution and possibly proposed the mechanism for the adsorption process.

**Table 1** physical properties of paraquat dichloride

Active ingredient	276g/l paraquat dichloride
Chemical name	1,1-dimethyl-4,4-bipyridinium chloride
Molecular formula	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> Cl <sub>2</sub>
Molecular weight	257.16g/mol
Density	1.25
Melting point	180°C
λ <sub>max</sub>	257nm
Water solubility	Soluble
Usage	Used as contact Herbicide to control bread leaf and grassy weeds in plantation crops, fruits, orchards including non-crop land, aquatic weed control and as defoliant for cotton and hops
Adsorption coefficient	100000µg/g
Half life	1000days
Structure	

## MATERIALS AND METHODS

All the reagents and chemicals used were of analytical grade and were not subjected to any further purification. Bambara groundnut shell (*Vigna subterranean*) (BGNS) were obtained from farm in Zaki-Biam, Ukum Local Government area of Benue State, Nigeria. The herbicide used; paraquat dichloride was obtained from Yankura market, Kano, Nigeria.

### Preparation of Adsorbent

The BNS obtained, after removing the seeds from the pods, were thoroughly washed with water to remove dust and other impurities. The shells were then air-dried and oven-dried at 80 °C to constant weight in the laboratory.

The dried shells were then pulverized and sieved into fine particles as previously described by Akinola *et al.*, (2015). 100g of Bambara ground nut shell (BGNS) was carbonized in the muffle furnace at 450 °C for 1 hour. The carbon produced was washed with plenty of water and dried as described by Ash *et al.*, (2006) and was kept for further usage.

### Preparation of paraquat dichloride solution

1000mg/l of the PQ solution was prepared by mixing 3.6ml of the 276mg/l paraquat dichloride solution in 1000ml standard volumetric flask and made up to mark. Serial dilution was carried out using distilled water to give solution concentration of 10, 20, 30, 40, 50 and 60mg/l of paraquat dichloride solution.

### Characterization of the Adsorbent

#### Determination of bulk density

The bulk density of CBGNS was determined using Archimedes's principle by weighing 10cm<sup>3</sup> measuring cylinder before and after filling with the samples. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation (1) (ASTM, 2008)

$$\text{Bulk density} = \frac{W_2 - W_1}{V} \quad (1)$$

Where;  $W_1$  is weight of empty measuring cylinder,  $W_2$  is Weight of cylinder filled with sample and  $V$  is Volume.

#### Moisture Content Determination

This was done by the gravimetric method as described by AOAC, (2005) and Onwuka, (2018). 5g of CBNS was weighed and put into a weighed crucible. The crucible and its sample content were dried in the oven at 105 °C for 3 hours in the first instance. It was cooled in desiccator and reweighed. The weight was recorded while the sample was returned to the oven for further drying. Sample was heated for the second time at 105 °C for 30 min, cooled in desiccator and weighed again. The procedure was repeated several times at the same temperature for 15 min until a constant weight was obtained. The percentage moisture content of each sample was calculated from using equation (2):

$$\% \text{ moisture content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (2)$$

Where;  $W_1$  is Weight of crucible,  $W_2$  is Initial weight of crucible with sample,  $W_3$  is Final weight of crucible with sample

#### Pore (Void) Volume Determination:

In order to determine the pore volume of the CBGNS, 2.0 g of the sample was immersed in water and boiled for 15 min. After the air in the pores had been displaced, the sample was superficially dried and reweighed. The increase in weight divided by the density of water gave the pore volume (Saidat *et al.*, 2018).

### Scanning Electron Microscope (SEM)

The surface morphological change of CBGNS samples were investigated using Scanning Electron Microscope (Phenom World Eindhoven) Scanned micrographs of CBNS before and after adsorption were taken at an accelerating voltage of 15.00 kV and x500 magnification.)

### Fourier transform infrared (FT-IR) analysis

FTIR analysis of CBGNS before and after adsorption was carried out using Cary 630 Fourier Transform Infrared Spectrophotometer Agilent Technology. The resulting residue collected was dried for FTIR analysis. The analysis was done by scanning the sample through a wave number range of 650 – 4000 cm<sup>-1</sup>; 32 scans at 8cm<sup>-1</sup> resolution.

### Batch adsorption experiments

Batch experiment was carried out to determine the optimum conditions for the equilibrium adsorption of paraquat dichloride by the carbonized Bambara ground nut shells. The effect of pH on the amount of PQ removal was analyzed between the pH ranges of 3 to 9, adsorbent dosage, 0.05 to 1.2g, contact time, 20 to 120min, initial PQ concentration, 10 to 60mg/l respectively. For each parameter 10 cm<sup>3</sup> of 50 mg/l PQ solution was transferred into a stoppered conical flask containing 0.1g of CBGNS and the pH was maintained at optimized value. The mixture was agitated (150 rpm) at room temperature for 2h. After reaching adsorption equilibrium, the content was filtered through Whatmann No 1 filter paper. The filtrate was analyzed using Perkin-Elmer Uv-visible spectrophotometer at maximum absorbance wavelength of 257nm and the residual amount adsorbed was calculated from the difference between the initial and adsorbed paraquat dichloride solution. The same method was used while varying the initial concentration, the contact time and adsorbent dosage (Mitiku, 2015). Paraquat dichloride concentration retained in the adsorbent phase was calculated according to mass balance of the equation (3) (Adekola *et al.*, 2011). Paraquat dichloride uptake,  $q_e = \frac{(C_0 - C_e)V}{m}$  (3)

Where:  $C_0$  and  $C_e$  are the initial and equilibrium concentration (mg/l) respectively of paraquat dichloride solution,  $V$  is the volume of paraquat dichloride in solution (L), and  $m$  is the mass (g) of the adsorbent.

The percentage of removed paraquat dichloride concentrations ( $R_{em}$  %) in solution was calculated using equation (4) (Abia and Asuquo, 2006).

$$\% \text{ Paraquat dichloride Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4)$$

## RESULTS AND DISCUSSION

### FTIR spectra Analysis

The FTIR spectra of CBGNS before adsorption on paraquat dichloride is given in figure (1a). The broad band at  $3391\text{cm}^{-1}$  is attributed to the stretching vibration of -OH group. The stretching of the -OH group bond to methyl radicals is attributed to the signal at  $2877\text{cm}^{-1}$ . Also, peaks at  $2344\text{cm}^{-1}$  and  $2110\text{cm}^{-1}$  are associated with the stretched vibration of alkynes  $\text{C}\equiv\text{C}$ , while the peak at  $1994\text{cm}^{-1}$  is ascribed to be C=O group which is affected by minor overlapping with C-C

aromatic ring stretched vibrations. The broad peak at  $1033\text{cm}^{-1}$  is associated to C-O group which confirms the lignin structure of CBNS. The peaks at  $1562\text{cm}^{-1}$  and  $1402\text{cm}^{-1}$  are associated with stretching vibrations of aromatic and C-H in alkane, while the peak at  $747\text{cm}^{-1}$  and  $870\text{cm}^{-1}$  are due to stretched vibration of C-O in aromatic, esters and ethers. Figure 1b shows FTIR spectra of CBGNS after adsorption. There was a shift and broadening of adsorption peaks after adsorption. The shift of the -OH peak from  $3391\text{cm}^{-1}$  to  $3272\text{cm}^{-1}$  shows the engagement of the -OH group in adsorption. The shift of the carbonyl group peak from  $1033\text{cm}^{-1}$  to  $1011\text{cm}^{-1}$  shows that carbonyl group participated in the adsorption of PQ. The presence of these functional groups and their enhancement in adsorption abilities of CBGNS agrees with the findings of (Sugumaran *et al.*, 2012).

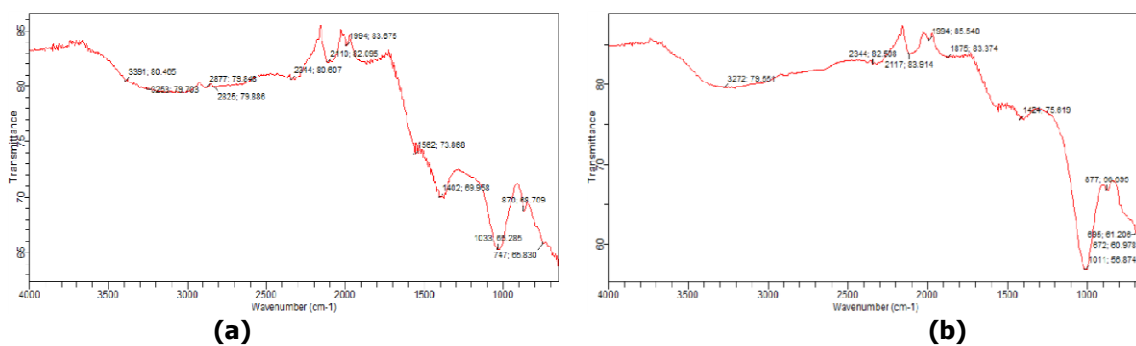


Figure (1a-b). FTIR spectrum of CBGNS before and after adsorption on PQ

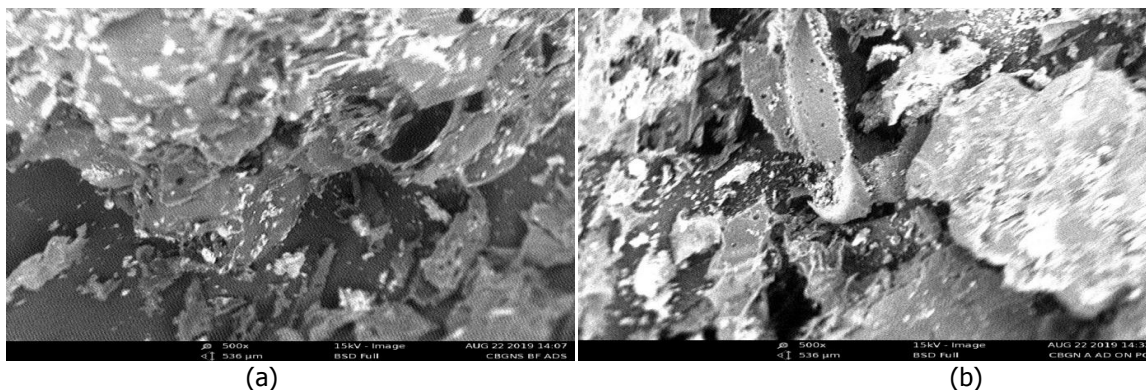


Figure (2a-b) SEM micrographs of CBGNS before and after adsorption on PQ

The SEM micrograph of the CBGNS before and after adsorption on PQ is shown in (figure 2a-b) Results showed that the surface structure of CBGNS before and after adsorption on PQ obtained are different from each other. The surface shows cracks, patches and pores after adsorption. Probably, due to the deposition of PQ by physical adsorption or progressive change in CBGNS surface mineralogy.

### Physical Properties of the Produced Activated Carbon

Some physical properties of the activated carbon produced are given in the Table 3. The value of the moisture content, pore volume and the bulk density of the produced activated carbon

revealed that it had good adsorptive properties. It was noticed from the properties of the carbonized carbon that, though it might not give up to 100% adsorption, it will be good for adsorption of organic substances to a very large extent (Prahas *et al.*, 2008).

**Table 3** physico-chemical properties of the CBGNS

Method	Moisture content	Density	Pore volume
CBGNS	16.8%	0.199g/cm <sup>3</sup>	1.89cm

### Effect of Various Parameters on Adsorption of Paraquat Dichloride onto CBGNS

Various parameters such as pH, contact time, initial concentration of paraquat dichloride solution, and adsorbent dosage of the solution were monitored and varied for their effects on the adsorption of paraquat dichloride from aqueous solution using the produced CBGNS.

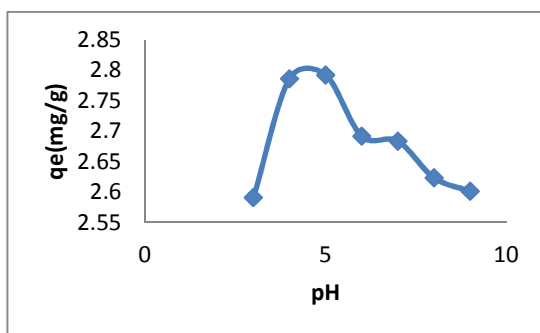
#### Effect of pH

Effect of pH was studied by varying the pH from 3 to 9 while keeping other parameters constant. Figure 4 shows plots for the variation of the amount of PQ adsorbed with pH. The plots clearly show that the amount of PQ adsorbed increases with increase in pH before decreasing. PQ removal was somewhat evidently dependent on pH with the better adsorption occurring under acidic conditions (pH 5) and decreased with increase in pH solution. This shows that the adsorbed amount of PQ decreases as pH increased from 5 to 9 due to electrostatic repulsion between adsorbent and negatively charged species in solution (Ozacar, 2006). A

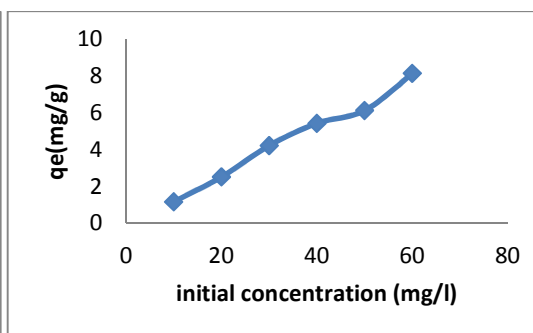
similar trend was observed in the studies of zinc (II) on magnetite, baobab (*Adansonia digitata*) and magnetite–baobab composite (Abdus-salam and Adekola, 2018).

#### Effect of initial concentration

The effect of initial PQ concentration was investigated by varying the concentration from 10 to 60mg/L. Figure 5 shows plots for the variation of the equilibrium amount of PQ adsorbed. It is evident from the plots that the amounts of PQ adsorbed by CBGNS increases with increasing concentration while the % removal of the adsorbate reduced. At low concentration, the available driving force for transfer of PQ molecules onto the adsorbent particle is low. While at high concentration, there is a corresponding increase in the driving force, thereby, enhancing the interaction between the PQ molecules in the aqueous phase and the active sites of the adsorbent. As a result of this, there was an increase in PQ uptake. Similar trends were reported by Abdus-salam and Adekola, (2018).



**Figure 4** Effect of pH on the adsorption process



**Figure 5** Effect of initial concentration

#### Effect of adsorbent dosage

Figure 6 shows a plot for the variation of equilibrium amount of PQ with adsorbent dosage. It was studied by varying amounts of adsorbent dosage from (0.05 to 1.2g) while other parameters were kept constant. Figure 6 revealed that the amount of PQ adsorbed first increased with an increase in adsorbent dosage due to increased surface area and more adsorption sites available for binding of PQ (Ahalya and Kanamadi, 2006). Maximum removal was attained at 0.05g. After 0.05g of adsorbent dosage there was no significant change in the amount of PQ removed. The decrease in adsorption per unit mass with increasing dosage of adsorbent is attributed to

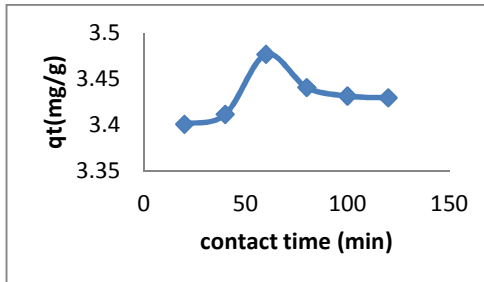
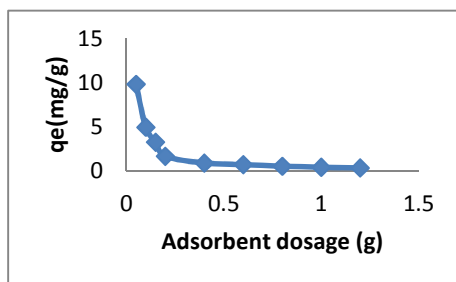
possible overlapping of adsorption sites as adsorbent dosage increases which will equally

reduce the effective adsorption sites. It was observed that as the adsorbent dosage decreased from 1.2 to 0.05g the quantity adsorbed (mg/g) decreased from 9.816 to 0.3731 mg/g. Similar trends were reported by (Yusuf *et al.*, (2009); Sebata *et al.*, 2013).

**Effect of contact time**

On the other hand, variation of the amount of PQ adsorbed with time is shown in Figure 7, from the plots, it is evident that the rate increased quickly with time, and then reached

equilibrium. The contact time to reach equilibrium was 60 min. At this time, removal efficiency reached was 69.5%. This can be explained due to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are not easy to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar findings were reported by (Naghizadeh *et al.*, 2011).



**Fig. 6 Effect of adsorbent dosage on the adsorption process Fig. 7 Effect of contact time on the adsorption process**

**Adsorption isotherm**

Curve fittings to identify best isotherms, for the adsorption of PQ on CBNS was fitted in Langmuir, Freundlich, Temkin and Dubunin-Radushkevich isotherms.

**Langmuir adsorption isotherm**

The Langmuir adsorption equation can be written as,

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (5)$$

Where;  $C_e$  is the equilibrium concentration of adsorbate (mg/L),  $q_e$  is the amount of PQ adsorbed per gram of the adsorbent at equilibrium (mg/g),  $Q_o$  is maximum monolayer coverage capacity (mg/g),  $K_L$  is Langmuir isotherm constant (L/mg). The values of  $q_{max}$  and  $K_L$  were computed from the slope and intercept of the Langmuir plot of  $\frac{1}{q_e}$  versus

$\frac{1}{C_e}$  (Langmuir *et al.*, 1918). The values of  $Q_o$  and  $K_L$  were calculated from slope and intercepts of the plots and listed in Table 4. The value was used to conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of adsorbate in plane of the adsorbent surface. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogenous distribution of active sites on the adsorbent since If  $n$  lies between one and ten, this indicates a favorable adsorption process (Goldberg, 2005). From the data in table 4, that value of  $1/n = 0.880$  while  $n=1.128$  indicating that the adsorption of PQ onto CBGNS is favourable and the  $R^2$  value is 0.928.

the Langmuir equation assumes that the surface is homogenous. The separation factor  $R_L$  for the isotherm can be used to predict the shape and the favourability condition of the adsorption process. The result of the separation factor ( $R_L$ ) presented in Table 4 from this research work showed that the values are within the range ( $0 < R_L < 1$ ) which indicates that the adsorption of PQ onto CBGNS is favourable.

**Freundlich adsorption isotherm**

Freundlich adsorption isotherm, can be expressed as,

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

Where;  $K_f$  is Freundlich isotherm constant (mg/g),  $n$  is adsorption intensity,  $C_e$  is the equilibrium concentration of adsorbate (mg/L),  $Q_e$  is the amount of PQ adsorbed per gram of the adsorbent at equilibrium (mg/g). The constant  $K_f$  is an approximate indicator of adsorption capacity, while  $1/n$  is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002). If  $n = 1$  then the partition between the two phases are independent of the concentration. If value of  $1/n$  is below one it indicates a normal adsorption. On the other hand,  $1/n$  being above one indicates cooperative adsorption (Mohan and Karthikeyan, 1997).

**Temkin adsorption isotherm**

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Temkin and Tyzhey, 1940; Aharoni and Ungarish, 1977). As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity adsorbed  $q_e$  against  $\ln C_e$  and the constants were determined from the slope and intercept. The model is given by the following equation (7)

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b}\right) \ln C_e \quad (7)$$

Where;  $A_T$  is Temkin isotherm equilibrium binding constant (L/g),  $b_T$  is Temkin isotherm constant

$R$  is universal gas constant (8.314J/mol/K),  $T$  is Temperature at 298K,  $B$  is Constant related to heat of adsorption (J/mol). From the Temkin

plots the following values were evaluated:  $A_T = 0.304$  L/g,  $B=19.99$ J/mol and the  $R^2=0.912$ .

**Dubinin-Radushkevich adsorption isotherm (DRK)**

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Gunay et al., 2007; Dabrowski, 2012). It can be expressed as;

$$\ln q_e = \ln (q_s) - (k_{ad} \epsilon^2) \quad (8)$$

Where  $q_e$ ,  $K_{ad}$ ,  $\epsilon$  are  $q_e$  = amount of adsorbate in the adsorbent at equilibrium (mg/g),  $q_s$  is theoretical isotherm saturation capacity (mg/g),  $K_{ad}$  = Dubinin–Radushkevich isotherm constant (mol<sup>2</sup>/kJ<sup>2</sup>) and  $\epsilon$  = Dubinin–Radushkevich isotherm constant

From the linear plot of DRK model,  $q_s$  was determined to 34.23mg/g, the mean free energy,  $E= 0.289$ KJ/mol and the  $R^2= 0.912$  the same to that of Temkin. The  $R^2$  value of the Langmuir model is greater than the  $R^2$  values of other models for PQ adsorption onto CBGNS indicating chemisorptions process.

**Table 4** Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of paraquat dichloride onto CBGNS

Isotherm Parameters		Numerical values	
<b>Langmuir</b>	$Q_0$ (mg/g)		55.55
			$2.4 \times 10^{-2}$
	$K_L$ (L/mg)	$R_L$	0.49
		$R^2$	0.956
<b>Freundlich</b>	$1/n$		0.880
	$n$		1.128
			1.380
	$K_f$ (mg/l)	$R^2$	0.928
<b>Temkin</b>			0.304
$A_T$ (l/mg)		$b_T$	123.9
		$B$	19.99
		$R^2$	0.912
<b>Dubini-Raduskevich</b>	$q_s$ (mg/g)		34.23
			$6 \times 10^{-6}$
	$K_{ad}$ (mol <sup>2</sup> /K <sup>2</sup> )		0.289
	$E$ (KJ/mol)	$R^2$	0.912

**Kinetic study**

The study of adsorption kinetic describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Effects of adsorption kinetics on PQ were studied by varying the contact time as 5, 10, 15, 20, 30, 40, 50, 60, 80, 100 and 120min. by keeping all other parameters (pH=5, adsorbent dosage 0.05g, initial PQ concentration= 60mg/l) at optimized values. The kinetics of PQ adsorption onto CBGNS were analysed using pseudo first-order (Lagergren, 1898), pseudo second-order (Ho *et al.*, 2000), Elovich model (Guo *et al.*, 2010) and intra particle diffusion (Weber and Morris, 1963) kinetic models. The conformity between experimental data and the model predicted values were expressed by the correlation coefficients ( $R^2$ , values close or equal to 1). A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of PQ adsorption. Linear forms of pseudo first and

second order kinetics are given in equation (9) and (10).

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} (t) \quad (10)$$

From equation (9), a plot of  $\log(q_e - q_t)$  versus  $t$ , pseudo first- order kinetics is obeyed. Also from equation (10), plots of  $(t/q_t)$  vs  $t$  is linear for data obeying a pseudo second order kinetics. Kinetic data obtained from slopes and intercepts of the plots are presented in Table 5. The results contain evidences on the existent of significant differences between calculated and experimental equilibrium amount of PQ that are adsorbed on CBGNS surface. However, these values are in better agreement with the pseudo second-order kinetics than for the pseudo first-order and Elovich model. Calculated values of  $R^2$  also confirm that the adsorption of PQ favours pseudo second-order kinetics better than pseudo first-order and Elovich kinetics.

**Table 5** Kinetic parameters for the adsorption of PQ onto CBGNS

Kinetic model				
Pseudo first-order	$q_e(\text{mg/g})_{\text{cal}}$ 0.487	$q_e(\text{mg/g})_{\text{Exp}}$ 10.91	$K_1$ 0.035	$R^2$ 0.795
Pseudo-second order	$q_e(\text{mg/g})_{\text{cal}}$ 10.75	$Q_e(\text{mg/g})_{\text{EXP}}$ 10.91	$K_2$ 0.0169	$R^2$ 0.999
Elovich	$a$ $2.1 \times 10^{27}$	$\beta$ 6.369		$R^2$ 0.589
Intra particle diffusion	$K_3(\text{mg}/(\text{g.mi})n^{1/2})$ 10.75	$C(\text{mg/g})$ 108.9		$R^2$ 0.602

**Elovich Equation**

The Elovich kinetic model is described by the following relation (Guo *et al.*, 2010).

$$qt = 1/\beta \ln(a\beta) + (1/\beta) \ln t \quad (11)$$

This model gives useful information on the extent of both surface activity and activation energy for chemisorptions process. The parameters ( $a$ ) and ( $\beta$ ) can be calculated from the slope and intercept of the linear plot of  $qt$  versus  $\ln(t)$ . The obtained  $R^2$  value of this model (Table 5) is 0.589. The deviation from linearity reflects that this model suggested by Elovich does not fit kinetic data.

**Intraparticle Diffusion Equation**

Possibility of involvement of intra particle diffusion model as the sole mechanism was investigated according to Weber– Moris Eq. (11) (Weber and Morris, 1963):

$$qe = C + k_{\text{int}} t^{1/2} \quad (12)$$

Where the constant  $k_{\text{int}}(\text{mg/g min}^{0.5})$  is the intra particle diffusion rate and  $C$  is the boundary. The thermodynamic constants such as changes in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy

layer thickness. If the rate-limiting step is only due to the intra particle diffusion, then  $qt$  versus  $t^{1/2}$  will be linear and the plot passes through the origin. Otherwise, some other mechanisms along with the intra particle diffusion mechanism is also involved. Table 5 shows that the intra particle diffusion model is not applicable for PQ removal by CBNS. Since the plots of  $qt$  versus  $t^{1/2}$  do not pass through origin with zero intercept, it can be concluded that the intra particle diffusion is not the rate-determining step of the adsorption mechanism.

**Thermodynamic study**

Thermodynamic parameters give advantageous information about the adsorption nature of this work. The effect of temperature on the adsorption of PQ onto CBGNS were studied by varying the temperature from 303 to 333k while keeping all other parameters (pH=5, adsorbent dosage 0.05g, initial PQ concentration=60mg/l,  $t=60\text{min}$ ) at optimized values. ( $\Delta S^\circ$ ) give useful view about the feasibility and the spontaneous nature of the adsorption



process and generally can be obtained from equation (13)

$$\Delta G^\circ = -RT \ln K_c \quad (13)$$

$$\ln K_c = -\Delta G^\circ/RT = -(\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (14)$$

Where  $R$  is the gas constant (8.314 J/molK),  $T$  is the absolute temperature (K), and  $K_c$  is the thermodynamic equilibrium constant and can be obtained from the relation (Calvete *et al.*, 2010):

$$K_c = C_a/C_e \quad (15)$$

Where  $C_a$  is mg of PQ adsorbed per liter and  $C_e$  is the equilibrium PQ concentration of solution (mg/L). Both  $\Delta H^\circ$  and  $\Delta G^\circ$  can be obtained from the slope and intercept of van't Hoff plot of  $\ln K_c$  versus  $1/T$ . The data are tabulated in Table 6. As can be seen on the Table 6, the positive value of  $\Delta H^\circ$  indicates that the adsorption of the

PQ onto CBGNS is an endothermic reaction, and the adsorption occurs easily at higher temperature. The negative  $\Delta S^\circ$  indicate decreased randomness at the solid-liquid interface during adsorption of PQ (Guang *et al.*, 2009). The negative values of  $\Delta G^\circ$  show the adsorption is thermodynamically feasible and spontaneous. Also, the  $\Delta G^\circ$  value increase as the temperature is being increased from 303 to 333 K. The magnitude of  $\Delta H^\circ$  describes the type of adsorption, where the heat of Physical adsorption falls within the range of 2.1–20.9 kJ/mol, while chemisorptions generally falls into a higher range of 80–200 kJ/mol (Abdelkreem and Husein, 2012). This suggests that the adsorption of the PQ on the CBGNS is physisorption.

Table 6 Thermodynamic parameters for the adsorption of PQ on CBNS

T(K)	Q <sub>e</sub> (mg/l)	% Rem	ΔG°(KJ/mol)	ΔH°(KJ/mol)	ΔS°(J/mol.k)
303	37.51	62.51	-1287.28	13.145	-47.59
313	39.98	66.63	-1800.78		
323	41.17	68.61	-2100.01		
333	43.89	73.15	-2774.09		

## CONCLUSION

CBGNS were used for the removal of paraquat dichloride from aqueous solution using batch adsorption method. The experimental result revealed that the removal of PQ was dependent on pH, initial concentration and contact time. The rate of adsorption is always high at the beginning of each experiment. In addition, the higher the initial PQ concentration, the higher the amount of PQ adsorbed. Chemisorptions mechanism favors the adsorption of PQ on CBGNS as the adsorption characteristic was found to follow the pseudo second-order kinetics model and Langmuir adsorption isotherm model

with  $R^2$ -value 0.999 and 0.956 respectively. Thermodynamic studies showed that the adsorption processes were endothermic and mostly spontaneous Therefore; CBGNS can be used as adsorbents for the removal of PQ and structurally related herbicides from waste water and industrial effluents.

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## REFERENCES

- Abdelkreem, M., and Husein, D.Z. (2012). Removal of strontium from aqueous solutions by adsorption onto orange peel: Isotherms, kinetics, and thermodynamic studies. *EJER* **1**, 42–61.
- Abdus-Salam, N., and Adekola, S. K. (2018). Adsorption studies of zinc (II) on magnetite, baobab (*Adansonia digitata*) and magnetite–baobab composite *Applied Water Science*, 28-222. <https://doi.org/10.1007/s13201-018-0867-7>
- Abia, A. A., and Asuquo, E. D. (2006). Lead (II) and Nickel (I) adsorption kinetics from aqueous metal solutions using chemically modified and unmodified agricultural adsorbents. *Afr J Biotechnol*, 5(16):1475–1482
- Adekola F.A., and Abdus-Salam N., Abdul-Rauf L. B. (2011). Removal of arsenic from aqueous solution by synthetic hematite. *J Chem Soc Niger*, 36(2):52–58
- Ahalya, N., T.V. Ramachandra, T. V., and Kanamadi, R. D. (2006). "Removal of hexavalent chromium using coffee husk", *Bioresources technology*, 2, 85-105.
- Aharoni, C., and Ungarish, M. (1977). Kinetics of activated chemisorption. Part 2. Theoretical models, *J. Chem. Soc. Faraday Trans.* 73, 456–464.
- Akinola, L.K., Ibrahim, A., and Chadi, A.S. (2016). Kinetic and Equilibrium Studies of Congo Red Adsorption on Adsorbent

- from Bambara Groundnut Hulls Al-Hikmah, *Journal of Pure & Applied Sciences*, 2016, 2(2), 79-88.
- Alfano, O.M., R.J. Brandi and Cassano, A. E. (2001). Degradation kinetics of 2,4-D in water employing hydrogen peroxide and UV radiation. *Chem. Eng. Journal*, 82(1-3), 209-218.
- Ali, H., Mladenka, N., & Mihajlović, I. (2018). Sorption of carbendazim and linuron from aqueous solutions with activated carbon produced from spent coffee grounds: Equilibrium, kinetic and thermodynamic approach, *Journal of Environmental Science and Health, Part B*, DOI: 10.1080/03601234.2018.1550307
- AOAC *Official Methods of Analysis*. AOAC International Washington D.C 17th Edn, 2005, pp. 1456-1500.
- Arivu, I., and Muniyan, M., Muuthulingam, M., Parthiban, P., Ambedkar, G., Kamalanth, S. (2016). "Toxicity of paraquat on freshwater fingerlings of Labeo rohita (Hamilton)". *International Journal of Scientific and Engineering Research*, 7(10), 1965-1971.
- Ash, B., Satapathy, D., Mukherjee, P. S., Nanda, B., Gumaste, J. L., and Mishra, B. K. (2006). Characterization and application of activated carbon prepared from coir pith, *J.Sci.Ind.Res.* 65,1008-1012.
- ASTM, Standards, ASTM International, West Conshohocken, Method D6751-08; Alcoholysis for Biodiesel Fuel Production and Application of the Reaction to Oil Processing. *Journal of Molecular Catalysis B: Enzymatic*, 76, 133-142.
- Banaee, M., Davodi, M.H., and Zoheiri, F. (2013). "Histopathological changes induced by paraquat on some tissues of gourami fish (*Trichogaster trichopterus*)". *Open Veterinary Journal*, 3(1), 36-42.
- Brillas, E., J.C. Calpe and J. Casado. (2000). Mineralization of 2, 4-D by advanced electrochemical oxidation processes. *Water Resources journal*, 34(8), 2253-2262.
- Dabrowski, A. (2001). Adsorption—from theory to practice, *Adv. Colloid Interface Sci.*93, 135-224. Department of Chemical Technology Midlands State University Gweru, Zimbabwe. *International Journal of Engineering Research & Technology*, 2(5), 2278-0181.
- Goldberg, S. (2005). Equations and Models Describing Adsorption Processes in Soils". *Soil Science Society of America*, 677 S. Segoe Road, Madison, WI 53711, USA. *Chemical Processes in Soils. SSSA Book Series*, no. 8.
- Guang-Cai C., Xiao-Quan S., Yi-Quan Z., Xiu-e S., Hong-Lin H., Shahamat, U. K. (2009). Adsorption kinetics, isotherms and thermodynamics of atrazine on surfaceoxidized multiwalled carbon nanotubes *Journal of Hazardous Materials* (169):912-918 doi:10.1016/j.jhazmat.2009.04.034.
- Gunay, A., Arslankaya, E., and Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, *J.Hazard. Mater.* 146, 362-371.
- Guo, S., Liang, X., Feng, N., Tian, Q. (2010). Isotherms, kinetics and thermodynamic studies of adsorption of Cu<sup>2+</sup> from aqueous solutions by Mg<sup>2+</sup>/K<sup>+</sup> type orange peel adsorbents. *J. Hazard. Material.* 174, 756-762.
- Hoys, M. G., Wase, D., and Foster, C. (2000). Study of the sorption of divalent metal ions on to peat *Adsorp. Sci. Technol*, 18, 639-650. <https://doi.org/10.1007/s13201-018-0867-7>.
- Jude C., Igwe, Felix C., Nwadike, Augustine, A. A. (2012). Kinetics and equilibrium isotherms of pesticides adsorption onto boiler fly ash. *Terrestrial and aquatic environmental toxicology, global science books*, 6(1), 21-29.
- Kamble, S.P., Sarkar, S.B., Sawant, J.A. (2004). Mouljin and V.G. Pangarkar, Photocatalytic continuous operation. *Ind. Eng. Chem. Res.*, 43(26), 8178-8187.
- Kim, S.J., T.Y. Kim, S.J., Kim and Cho, S. Y. (2002). Adsorption equilibrium characteristics of degradation of 2, 4-dichlorophenoxyacetic acid using concentrated solar radiation: batch and dichlorophenoxyacetic acid and 2, 4 dinitrophenol on granular activated carbons. *Korean J. Chem.Eng.*, 19(6), 967-977.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* 24, 1-39.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum". *J. Am. Chem. Soc.* 40, 1362-1403.
- Mitiku, A. C. (2015). Removal of 2, 4-D, Atrazine and major metabolites of atrazine from aqueous solution by Fe-Zr-Mn nano

- composite. Msc dissertation. Haramaya University.
- Mohan, S., and Karthikeyan. J. (1997). Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal", *Environ. Pollut.* 97, 183-187
- Naghizadeh, A., Nasser, S., and Nazmara, S. (2011). Removal of Trichloroethylene from water by adsorption on to Multiwall Carbon Nanotubes. *Iran Journal of Environmental Health Science Engineering*, 8(4): 317-24.
- Nharingo, T., Muzondo, N.M., Madungwe, E., Chigondo, F., Guyo, U., and Nyamunda, B. (2013). Isotherm Study of the Biosorption of Cu (II) from Aqueous Solution by *Vigna subterranea* (L.) Verdc Hull. *International Journal of Scientific and Technology Research*, 2(4), pp. 199 – 206.
- Onwuka, G. I. (2018). *Food Analysis and Instrumentation: Theory and Practice*. 2nd Ed. Naphtali Prints, Lagos, pp. 179-228.
- Ozacar, M. (2006). Contact time optimization of two-stage batch absorber design using second- order kinetic model for the adsorption of phosphate onto alunite. *Journal of Hazardous Materials*, 137: 218–225.
- Prahas, D., Kartika, Y., Indraswati, N., and Ismadji, S. (2008). Activated carbon from jackfruit peel waste by H<sub>3</sub>PO<sub>4</sub> chemical activation: pore structure and surface chemistry characterization, *Chemical Engineering Journal*, 140, 32–42.
- Saidat, O., Giwa, Job, S., Moses, Abel, A., Adeyi, and Abdulwahab, G. (2018). Adsorption of Atrazine from Aqueous Solution Using Desert Date Seed Shell Activated Carbon. *ABUAD Journal of Engineering Research and Development*, 1(3), 317-325.
- Sebata, E., M., Moyo, U., Guyo, N. P., Ngano, B. C., Nyamunda, F., Chigondo, V., Chitsa, M. S. (2013). Adsorptive Removal of Atrazine from Aqueous Solution Using Bambara Groundnut Hulls. *International Journal of Engineering Research & Technology*, 2(5), 312 – 321.
- Sugumaran, P., V. Priya, V. S., Ravichandran, P., and Seshadri, S. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and *Delonix regia* Fruit Pod. *Journal of Sustainable Energy & Environment* 3, 125-132
- Sylvester, C. I., and Ogaga, A.A. (2018). Acute Toxicity of Paraquat Dichloride Based Herbicide against *Heterobranchus bidorsalis* Fingerlings, *EC Agriculture* 4(2): 128-132.
- Tempkin, M., I. Pyzhev, V. (1940). Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phys. Chim. USSR* 12 (1940), 327–356.
- Vijay, K., Simranjeet, S., Rohit, S., Niraj, U., Joginder, S., Pramila, P., Ravindra, S., Bhavana, S., Arjun, S., & Subhose V. (2018). Spectral, structural and energetic study of acephate, glyphosate, monocrotophos and phorate: an experimental and computational approach, *Journal of Taibah University for Science*, 12(1), 69-78, DOI: 10.1080/16583655.2018.1451109
- Voudrias, E., Fytianos, F., and Bozani, E. (2002). Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials, *Global Nest, The Int.J.* 4(1), 75-83
- Weber, W.J., Morris, J.C. (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Proc. Am. Soc. Civil. Eng.* 89, 31–59.
- Zuhra, G.M., Moghala, M.J., Memona, R., Nusrat, N., Memona, B.M. I. (2014). Adsorption of Selected Pesticides from Aqueous Solutions Using Cost effective Walnut Shells *IOSR Journal of Engineering (IOSRJEN)* www.iosrjen.org ISSN (e): 2250s-3021, ISSN (p): 2278-8719, 10(1); 43-56.