ADSORPTION AND KINETICS STUDY FOR THE REMOVAL OF PENDIMETHALIN FROM AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE

Ayuba AM, Nyijime TA∗

Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria

∗**Author for Correspondence:** : thomasnyijime@gmail.com

ABSTRACT

The wreak havoc pose by herbicide on the environment and the ecosystem has become an issue of interest to the environmentalist over the past years. Up till date, adsorption methods has been demonstrated to be an excellent technique to remediate herbicides by comparison with other traditional methods due to its high efficiency, low operating and maintenance cost, simple design, insensitivity for toxic substances, suitable for most contaminated waters and the complete removal of contaminants even from the dilute solutions. This paper is aim at investigating and establishing the adsorption efficiency of activated Bambara groundnut shells in the removal of pendimethalin (PE) herbicide from aqueous solution under different experimental conditions. The pore volume analysis of the adsorbent demonstrated good quality of the activated carbon. It also had low moisture content and bulky density respectively. The activated Bambara groundnut shell (ACBGNS) was also characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) analysis methods. The Effect of initial concentration (10 to 60mg/l), solution pH (3 to 8), adsorbent dosage (0.2 to 1.2g) and contact time (20 to 120) were optimized and reported. Adsorption capacity q_e (mg/g) of PE onto ACBGNS was found to be 14.93mg/g. A comparison of kinetic models applied to the adsorption of PE on the ACBGNS was evaluated for the pseudo first-order, the pseudo second-order, Elovich and intra-particle diffusion kinetic models, respectively. Results showed that the pseudo second-order kinetic model was found to relatively correlate the experimental data well when compared to other models tested.

Keywords: Pollution, Pendimethalin, Adsorption, kinetics, Environment

INTRODUCTION

Pendimethalin is a chlorinated herbicide and at present, it has been used in more than 80 countries and probably it is the most commonly used herbicide in the world which exhibits acute, chronic toxicity and carcinogen (EPA, 1997). Pendimethalin (3, 4-dimethyl-2, 6-dinitro-N-pentan-3-ylaniline) is a selective dinitroaniline herbicide which acts as a microtubule disruptor by inhibiting cell division and cell elongation in plants (WHO, 1987). It is almost non-volatile and its half-life in soil condition is about 30- 90 days but varies depending on various environmental factors like pH, moisture content, temperature and microbial activity (Ayuba and Nyijime, 2021). Furthermore, it is applied before emergence to cereals, maize, and rice, and with shallow soil incorporation before seeding bean, cotton, soy beans, and groundnuts. In vegetable crops, it is applied before emergence or transplanting, and it is also used to control suckers on tobacco (Salmana et al. 2011).

Due to its excessive usage, high persistence and mobility, pendimethalin is transported to surface and subsurface water bodies and had been found in ground water, rivers, high mountain lakes, drinking water supplies, and rain water and even in fog (Ayuba and Nyijime, 2021). Pendimethalin was found at a concentration below 0.1 μ/litre in one of 76 drinking-water supplies examined in the Veneto Region in Italy in 1987–88 (Funari and Smpaolo, 1989).

Several techniques have been used for herbicides removal including flocculation and coagulation, sedimentation (Navarro et al. 2009), ultra-centrifugation and micro-filtration (Jablonska, 2011), membrane separation and ozonation (Brose'us et al. 2009). However, these methods are associated with high operating costs and sludge generation which

itself requires further treatment. Though adsorption using activated carbon (Moradi et al. 2014), is undoubtedly an effective adsorbent for treating inorganic and organic pollutant-contaminated water, the high cost associated with it often limits its large-scale application (Srivastava et al. 2009) to reduce the operational costs, the search for alternative materials for environmental engineering has intensified in recent years. The technology for the purification of water can benefit from the utilization of renewable biomaterials with performance properties comparable to synthetic materials (Cara and Jit, 2015). Use of agricultural-based materials as adsorbent is a potential alternative for the effluents treatment as it has several advantages, namely low production cost, abundance in availability, simple preparation steps, and high removal efficiency with the possibility of reuse (Kushwaha et al. 2013). A number of these type of nonconventional adsorbents such as Banana peel (Chaparadza and Hossenlopp, 2012), wood charcoal, fly ash, coconut charcoal, saw dust, sunflower seed shells and rice husk (Rojas et al. 2014), were used for atrazine removal from water. Since, Bambara groundnut shell (BGNS) is abundant in Nigeria and constitute a waste disposal problem, it can be easily processed and utilized as a good adsorbent. Most of the reported work on the use of BGNS product is on the removal of dyes, herbicides and has to do with the ability of these adsorbent in adsorbing the herbicides. There are few reports on the specific mode of action of the adsorbent and the extent of adsorption (Ayuba and Nyijime, 2020). It is against this background that the present study set out to investigate the adsorption of pendimethalin from aqueous solution using activated carbon obtained from Bambara groundnut shell as well as proposed the mechanism from the insight obtained from the kinetic evaluation.

MATERIALS AND METHODS

Collection and Preparation of the Adsorbent

Bambara groundnut shell (*Vigna subterranean*) (BGNS) were obtained from farm in Zaki-Biam, Ukum Local Government area of Benue State, Nigeria. The shells obtained, after removing the seeds from the pods, were thoroughly washed with water to remove dust and other impurities. These shells were then air-dried and oven-dried at 80 $^{\circ}$C to constant mass in the laboratory. The dried shells were then pulverized and sieved into fine particles. The final product was stored in a clean, air-tight container for further usage. 100g of the fine powder was mixed with 10% phosphoric acid (H_3PO_4) (100g sample + 100mg/l of 10% H_3PO_4, wt/v). The treated samples were pyrolyzed at 450°C for 1 h in an electric muffle furnace. After activation, the mixture was removed from the furnace and allowed to cool to room temperature. The pyrolysed carbons were washed with 2% HCl (v/v) several times with distilled water until a neutral pH was achieved. Later the carbon paste was dried in an electric oven at 110°C for 24 h (Ash et al. 2006). The carbon preparation experiments were carried out several times to obtain enough activated carbon samples for further analysis and characterization. The activated carbon yield was calculated with the help of Equation (1):(Cui et al.2007)

$$X(\%) = \frac{m}{m_o} \times 100 \qquad (1)$$

Were; X is char or activated carbon yield (%), m is the char or activated carbon mass (g), m_o is the raw sample mass (g).

Preparation of Pendimethalin (PE) Herbicide Solution

1000mg/l of the PE solution was prepared by mixing 2ml of the 500mg/l pendimethalin 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 pendimethalin solutions (Ayuba and Nyijime, 2021).

Adsorbent Surface Characterization

The surface morphological change of adsorbents samples was investigated using Scanning Electron Microscope (Phenom World Eindhoven). The Scanned micrographs of adsorbents before and after adsorption were taken at an accelerating voltage of 15.00 kV and x 500 magnification (Ayuba and Nyijime, 2021).

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Fourier transform infrared (FTIR) analysis of adsorbent before and after adsorption was carried out using Cary 630 Fourier Transform Infrared Spectrophotometer Agilent Technology. The analysis was done by scanning the sample through a wave number range of 650 – 4000 cm^{-1}; 32 scans at 8cm^{-1}resolution (Ayuba and Nyijime, 2021).

Determination of Bulk Density

The bulk density of ACBGNS was determined using Archimedes's principle by weighing 10cm^3 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 (2) (ASTM, 2008).

$$\text{Bulk density} = \frac{w_2 - w_2}{v} \quad (2)$$

Were; 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 in literature (Onwuka, 2018). 5g of ACBGNS 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 (3):

$$\text{\% moisture content} = \frac{w_2 - w_2}{w_2 - w_2} \times 100 \quad (3)$$

Were; 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 ACBGNS, 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).**

Batch Adsorption Experiment

The known weight of adsorbent was added to 10cm^3 of the pendimethalin solution with an initial concentration of 60 mg/L, and the content was shaken thoroughly. The solution was then filtered at particular time intervals and the residual concentration was measured with the aid of uv-visible spectrophotometer (Perkin-Elemer). The maximum wavelength of the pendimethalin was found to be 243nm. The same method was used while varying the initial concentration, the contact time, the adsorbent dosage, and temperature of adsorption. The amount of pendimethalin adsorbed (*qe*) in the adsorbent phase was calculated according to mass balance of the Equation (4) (Adekolaet al. 2012).

$$\text{Pendimethalin uptake, qe} = \frac{(Co - Ce)v}{m} \quad (4)$$

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

Optimization of Adsorption Parameters
Effect of pH

Adsorption experiments were conducted in the pH range of 3 to 8 while keeping all other parameters constant (PE concentration 60 mg/L; adsorbent dose 0.1 g; contact time 24 h; temperature 25^{0}C). The solution pH was adjusted to the required value using 0.1MHCl or 0.1MNaOH, and pH was measured using a pH meter (MP 220). The mixtures were filtered, and the filtrates were analyzed for PE using UV visible spectrophotometer. The quantity adsorbed was calculated using Equation (4)

(Abdus-salam and Itiola, 2012).

Effect of Contact Time

0.1 g of ACBGNS was weighed separately in 100ml conical flasks. A 10cm^3 of the optimum concentration (60 mg/L PE) solution was added in the beaker. Each solution was agitated for different time interval of 20, 40, 60, 80, 100 and 120 min to investigate the effect of contact time. After the completion of the reaction, the mixtures were filtered and followed by the determination of the residual PE concentrations using UV-visible spectrophotometer. The quantity adsorbed was calculated using Equation (4) (Saidat et al. 2018).

Effect of Adsorbent Dosage

The adsorption of PE onto ACBGNS was studied by varying the quantities of the adsorbents from 0.2 to 1.2g in different beakers while keeping all other parameters at optimized value.The mixtures were agitated with an orbital incubator shaker (Innova 4000 Model). At the completion of the contact, the solutions were filtered and the filtrate was analyzed for PE using Uv-visible spectrophotometer (Saidatet al. 2018). The quantity adsorbed, qe, was calculated using Equation (4).

Effect of PE Concentration

10 cm^3 of 10, 20, 30, 40, 50 and 60 mg/L of pendimethalin solution were prepared by serial

dilution of the stock solution and were added separately to 0.2 g of ACBGNS to form a mixture at room temperature. The pH was maintained at optimized value while adsorbent dosage was kept constant and sample were agitated for 80min and the mixtures were filtered and analyzed for remaining pendimethalin concentration with the UV-Vis spectrophotometer (Pathak and Anil, 2012).

RESULTS AND DISCUSSION
Adsorbent Surface Characterization

Figure 1 shows spectra of ACBGNS before and after adsorption of PE. Figure 1a contains the broad peak at 3117cm^{-1} is attributed to the stretching vibration of -OH group. The stretching of the - OH group bond to methyl radical is associated with the signal at 2880cm^{-1}. Peaks at 2322cm^{-1}, 2084cm^{-1} and 2113cm^{-1} are associated with stretched vibration of C=C in alkynes. While the peaks at 1994cm^{-1} and 1871cm^{-1} are ascribed to C=O group which is affected by minor overlapping with C-C aromatic ring stretched vibration. The peak at 1562cm^{-1} correspond to C=C aromatic rings while the peak at 1063cm^{-1} is due to C-O bond. The peaks at 970cm^{-1}, 873cm^{-1} and 676cm^{-1} correspond to C-H in alkenes and C-H in aromatic rings. There were a minor difference between before and after adsorption (Figure1), the shift of the -OH peak from 3117cm^{-1} to 3339cm^{-1}indicates the involvement of the hydroxyl groups in the adsorption the PE.
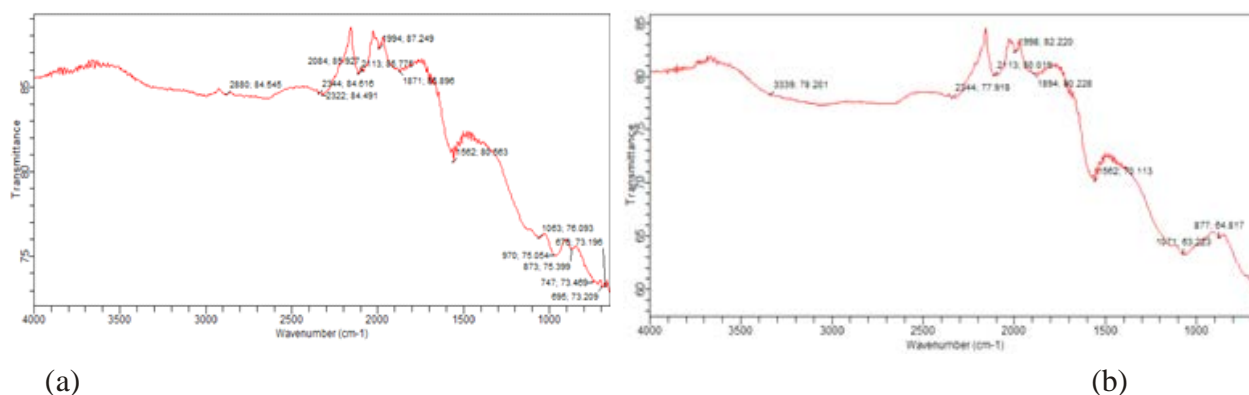
(a)   (b)
Figure 1: FTIR Spectra of ACBGNS (a) before and (b) after adsorption onto PE

The micrograph of ACBGNS before and after adsorption on PE shows that the surface of the adsorbent before adsorption have rough, holes, crack which enhance adsorption (Figure

2a). While after adsorption it was observed that there was formation of clusters, patches, cracks on the adsorbent surface which shows the participation of ACBGNS in the adsorption of PE (Figure 2b).
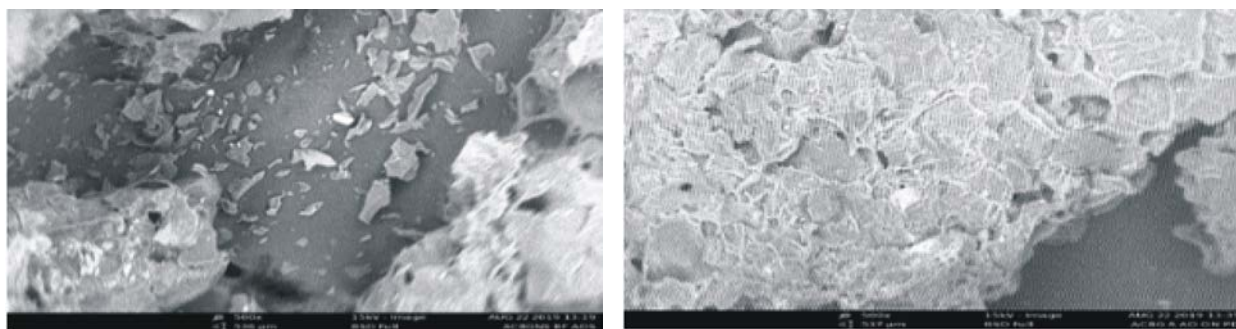
Figure 2: SEM Micrographs of ACBGNS (a) before and (b) after adsorption onto PE

Physical Properties of the Produced Activated Carbon

Some physical properties of the *ACBGNS* produced are given in the Table 1. The value of the moisture content, pore volume and the bulk density of the produced untreated carbon revealed that it had good adsorptive properties. It was noticed from the properties of the *ACBGNS* 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 1: Physical Properties of the ACBGNS

Moisture	Density	Pore volume
11.2%	0.242g/cm^3	1.78cm^3

Batch Adsorption Optimizations

Figure 3 shows plots for the variation of the amount of PE adsorbed with pH. The optimum pH for removal of PE on ACBGNS is observed to be 6. It can be observed from the plot that ACBGNS showed good removal in acidic condition which may be due to the cellulosic compounds (carboxylic and phenolic groups) present on the adsorbent surface (Ferrero, 2014). At higher solution pH (5.0–6.0), the electrostatic repulsions between the surface of adsorbents and the positively charged PE molecules are depressed, which increase the amount of PE removal (Hassan et al. 2014).The decrease in the adsorption capacity at pH values (6.0–8.0) could be related to the repulsion between the negative charge of anionic species in solution and negative surface charge of the adsorbent.

Variation of the amount of PE molecule adsorbed with time is shown in Figure 4. It is evident that the rate of adsorption of PE on ACBGNS was rapid and the equilibrium was reached within 80 minutes and there after the rate of PE removal remained almost stable. Initially there was large number of vacant active binding sites available at the first phase of experiment and large amount of PE molecule were bound rapidly on the adsorbents at a faster adsorption rate. The binding site was shortly become limited and the remaining vacant surface sites were difficult to be occupied by PE molecule due to formation of repulsive forces between the PE on the solid surface and the liquid phase (Anwar et al. 2010).
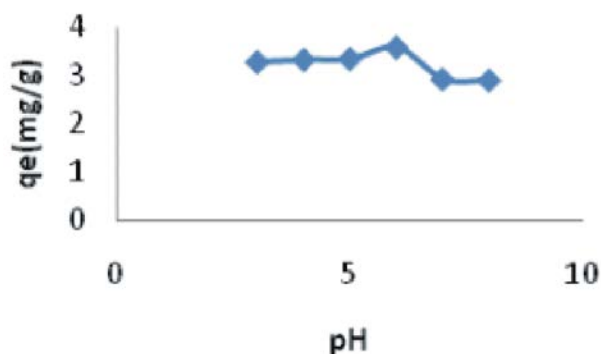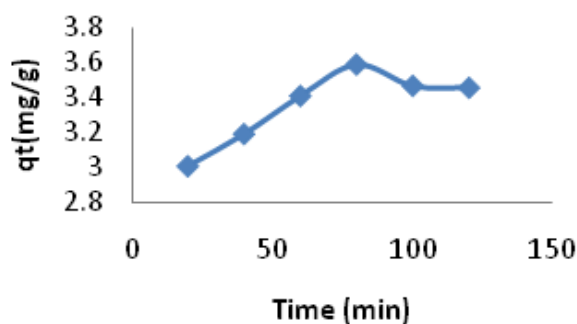

Figure 3: Effect of pH on Adsorption of PE

Figure 4: Effect of time on Adsorption of PE

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Figure 5 reveal plot showing the variation of equilibrium amount of PE adsorbed with adsorbent dosage. From the plot, it is observed that as the adsorbent dosage was increased, the amount adsorbed also increased but the amount adsorbed per unit mass of the adsorbent decreased considerably. The decrease in adsorption per unit mass with increasing dosage of adsorbent is attributed to possible overlapping of adsorption sites as adsorbent dosage increases. The amount of PE molecule adsorbed is dependent upon the initial concentration, and at higher concentrations, the available sites of adsorption become fewer (Gueu et al. 2006).

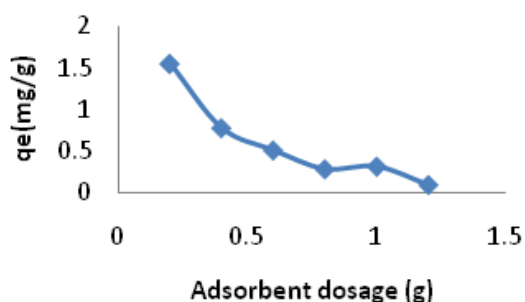It is also observed that as the adsorbents dose increased from 0.2 to 1.2g, the quantity adsorbed (mg/g) decreased from 1.5554 to 0.089mg/g. This showed the high adsorption capacity of the ACBGNS at low dosage. Figure 6 reveals plots showing the variation of equilibrium amount of PE herbicide adsorbed with time. It is evident from the plots that the amount of herbicide adsorbed by ACBGNS increases with increase in the concentration of the herbicide. At low concentration, the available driving force for transfer of PE onto the adsorbent particles is low, while at high concentration, there is a corresponding increase in the driving force, thereby enhancing the interaction between the PE in the aqueous phase and the active sites of the adsorbent. As a result of this, there was an increase in the uptake of PE molecule. Therefore, there was an increase in the quantity of PE adsorbed (qe) with an increase in the initial concentration.
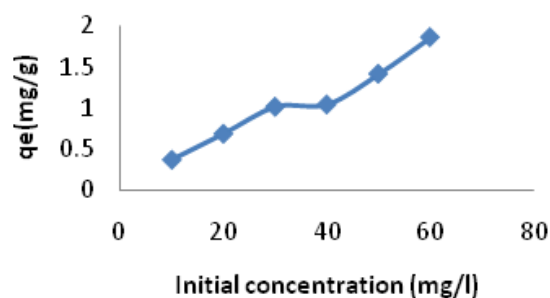

Figure5: Effect of Dosage on Adsorption of PE

Figure6: Effect of Concentration on Adsorption of PE

Kinetic Studies

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 PE were studied by varying the contact time as 5, 10, 15, 20, 30, 40, 50, 60, 80, 100 and 120min. and keeping all other parameters (pH=6, adsorbent dosage 0.2g, initial PE concentration= 60mg/l, T= 25 °C) at optimized values. The kinetics of pendimethalin adsorption on the ACBGNS were analyzed using pseudo first-order (Lagergern, 1898), pseudo second-order (Hoys and Wase, 2000), Elovich (Guo et al. 2010) and intra particle diffusion (Ahmed and Dhedan, 2012) kinetic models. The conformity between experimental data and the model predicted values was 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 pendimethalin adsorption onto ACBGNS.

Pseudo First-Order Equation

The pseudo first-order equation (Anwar et al. 2010) is generally expressed as follows:

$$\frac{\partial a t}{\partial t} \quad = \quad k1 \ (q_e - q_\tau) \tag{5}$$

Where:

q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg·g^{-1}), k_1 is the rate constant of pseudo first-order adsorption(l·min^{-1}). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation (5) becomes:

$$\log (q_e - q_t) = \log (q_e) \frac{k1}{2.303} t \qquad (6)$$

The values of *log (q_e – q_t)* were linearly correlated with *t*. The plot of *log (q_e – q_t)* vs. *t* gave a linear relationship from which k_1 and q_e were determined from the slope and intercept of the plot respectively. The linear plots were made for pseudo-first-order model (figure not shown) The correlation coefficient values in addition to *q*e values (experimental and calculated) for PE removal by ACBGNS are given in Table 2. The low value of correlation coefficient and the non-reasonable difference between the experimental and calculated adsorption capacity *(q*e) show that this model fails to interpret the experimental data.

The Pseudo Second-Order Equation

The pseudo second-order adsorption kinetic rate equation is expressed as (Hoys and Wase, 2000).

$$\frac{\partial \alpha \tau}{\partial \tau} = k_2 (q_e - q_t)^2 \qquad (7)$$

k_2 is the rate constant of pseudo second-order adsorption (g·mg^{-1}·min^{-1}). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the Integrated form of Equation (7) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + Kt \qquad (8)$$

This is the integrated rate law for a pseudo second-order reaction Equation (8) can be rearranged to obtain Equation (9), which has a linear Form:

$$\frac{t}{q_t} = \frac{1}{k_{2q^2e}} + \frac{1}{q_e} \qquad (9)$$

If the initial adsorption rate, *h* (mg·g^{-1}·min^{-1}) is;

$$h = k_{2q^2e} \qquad (10)$$

Then equation (10) becomes

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{t}{q_e} (t) \qquad (11)$$

The plot of *(t/q_t)* and *t* of Equation (11) gave a linear relationship from which q_e and k_1 *were* determined from the slope and intercept of the plot respectively. The values of *t/qt* are plotted

against t (not shown). Fitting kinetics parameters of adsorption of PE onto ACBGNS according to pseudo-second-order model (Equation 11) are given in Table 2. As seen from figure 7, the pseudo-second-order kinetic model fits the experimental data very well; the correlation coefficients values, R^2, is equal to unity, and the experimental and theoretical uptakes are in good agreement. This indicates the applicability of the second-order kinetic model to describe the adsorption process of PE onto ACBGNS.
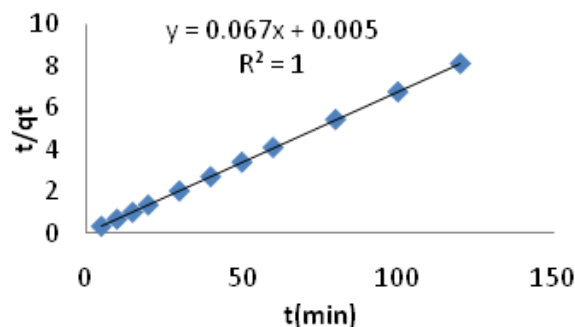

Figure 7: Pseudo-second order linear plot on Adsorption of PE onto ACBGNS

Elovich Equation

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

$$qt = 1/\beta In (a\beta) + 1/\beta Int \qquad (12)$$

This model gives useful information on the extent of both surface activity and activation energy for chemisorptions process. The parameters *(α)* and *(β)* were calculated from the slope and intercept of the linear plot of *q*t versus ln(t). The obtained R^2 value of this model is given in (Table 2) and the figure not shown. The great deviation from linearity reflects that this model suggested by Elovich does not fit kinetic data.

Intra-Particle Diffusion Equation

The slowest step in an adsorption process is usually taken as the rate determining step. This step is often attributed to pore and intra particle diffusion. Since pseudo first and pseudo second order models cannot provide information on effect of intra particle diffusion in adsorption, intra particle diffusion model can be used (Ahmed and Dhedan, 2012). Possibility of

involvement of intra particle diffusion model as the sole mechanism was investigated according to Weber–Moris, (1963) Equation (13)

$$qe = C + K_{int} t^{½} \qquad (13)$$

Where the constant k_{int}(mg/g min$^{0.5}$) is the intra particle diffusion rate and C is the boundary layer thickness. If the rate-limiting step is only due to the intra particle diffusion, then qtversus

$t1/2$ gave a linear and the plot passes through the origin. From Table 2 and figure not shown, the constant C was found to be 15.74. This indicates that the intra particle diffusion model is not applicable for PE removal by an ACBGNS. Since the plots of qt versus $t1/2$ did not pass through origin and depending on the poor determination coefficients, R^2, it can be concluded that the intra particle diffusion is not the rate-determining step of the adsorption mechanism.

Table 2 Kinetic parameters for the adsorption of PE onto ACBGNS

Kinetic model	Parameters/Values			
Pseudo first-order	q_e(mg/g)$_{cal}$	q_e(mg/g)$_{Exp}$	K_l	R^2
	14.89	0.432	0.0023	0.0.98
Pseudo-second order	q_e(mg/g)$_{cal}$	Q_e(mg/g)$_{EXP}$	K_2	R^2
	14.89	14.93	0.897	1
Elovich	α	B		R^2
	4.7×10^{33}	5.00		0.027
Intra - particle diffusion	K_3(mg/(g.min$^{0.5}$))	C(mg/g)		R^2
	0.094	15.74		0.049

CONCLUSION

The results of this study indicated that the activated Bambara groundnut shells is a good adsorbent for the removal of pendimethalin from aqueous solution. The adsorbent was investigated on the effect of initial PE concentration, adsorbent dosage, contact time, temperature and pH which are highly dependent on the efficiency of adsorption. The obtained adsorption kinetics fitted well with pseudo-second order model, while Pseudo-first order, Elovich and Intra particle were non-linear. Activated carbon from Bambara groundnut shell appears to be a promising adsorbent for the removal of pendimethalin herbicide from aqueous solution.

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