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Removal of Pendimethalin Herbicide from Aqueous Solution Using Untreated Bambara Groundnut Hulls as a Low Cost Adsorbent

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Abstract

In this work, untreated Bambara groundnut shell (UBGNS) waste was used to remove Pendimethalin (PE) herbicide from aqueous solutions through batch adsorption experiments after optimization as a low cost adsorbent. The UBGNS was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) methods. The effects of contact time, initial PE concentration, adsorbent dosage, solution pH and temperature were investigated and optimized. Isotherm studies, kinetics and thermodynamics of PE adsorption onto UBGNS were studied. Equilibrium data were fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherm models and the data best represented by the Langmuir isotherm indicating chemisorption mechanism. Thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) determined, showed that the adsorption of PE onto UBGNS was feasible, spontaneous and exothermic. The results obtained here show that UBGNS is an efficient adsorbent for the adsorptive removal of PE from aqueous solutions.

1. Introduction

The uncontrollable usage of herbicides by farmers to control herbs has become an issue of interest to the environmentalist and scientists due to the threat posed by such act, therefore the need to curb such practices. This is due to the extensive application of these chemicals in crop farms, orchards, fields and forest lands [1]. However, the wide spread of these chemicals has caused pollution of ground and surface water bodies due to leaching and runoff losses from farms, disposal of empty herbicide containers, unregulated discharge from manufacturing unit and various other sources [2]. Herbicides are established to be harmful to aquatic life because of their toxicity, carcinogenicity and mutagenicity [3]. The harmful influence of herbicides on human health and the environment has resulted to the imposition of stringent legislation on drinking water quality in many countries [4].

Pendimethalin is a chlorinated herbicide and at present, it has been used in more than 80 countries and probably the most commonly used herbicide in the world which exhibits acute, chronic toxicity and a carcinogen [5]. 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. It's almost non-volatile with half-life in soil condition of about 30- 90 days, but varies depending on various environmental factors including the pH, moisture, temperature and microbial and other activities [6]. Pendimethalin is a selective herbicide, 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 etc [6].

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 [7]. 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 [8].

Pendimethalin is highly toxic to fish and aquatic invertebrates [9]. The chemical also have the ability to bioaccumulate and biomagnify, and can bio-concentrate up to 70,000 times their original concentrations [10]. Conventional water supply unit process is unable to remove pendimethalin and therefore, specific unit, for example, adsorption tank is required.

From literature consulted, Bambara groundnut shell (BGNS) has been reported to be cheap, effective and efficient adsorbent in treating dyes and heavy metals removal [11-13]. This research work is aimed at investigating the efficiency of untreated Bambara groundnut shells in the removal of pendimethalin from aqueous solution. The influences of contact time, initial concentration of the herbicide, solution pH and temperature on the adsorption capacities of UBGNS on pendimethalin were investigated. In addition, thermodynamic, kinetic and isotherm modeling parameters were evaluated from the adsorption data generated to further elucidate the mechanism involved in the adsorption process.

2. Material and Methods

2.1 Collection and preparation of the adsorbent

Bambara groundnut shells (*Vigna subterranean*) (BGNS) were obtained from a farm located in Zaki-Biam, Ukum Local Government, Benue State of Nigeria. The shells 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 80^0 C to constant mass in the laboratory as described in literature [14]. 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 as adsorbent in the subsequent batch experiments.

2.2. Preparation of pendimethalin (PE) solution

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.

2.3. Characterization of the adsorbent

The surface morphological change of adsorbent sample was investigated using Scanning Electron Microscope (Phenom World Eindhoven). Scanned micrographs of adsorbents before and after adsorption were taken at an accelerating voltage of 15.00 kV and x500 magnification. FTIR analysis of adsorbents before and after adsorption was also carried out using Cary 630 Fourier Transform Infrared Spectrophotometer obtained from Agilent Technology. The analysis was conducted by scanning the samples through a defined wave number range of 650 – 4000 cm^{-1}; with 32 scans at $8cm^{-1}$resolution.

2.4. Batch adsorption experiments

0.2g of adsorbent was added to $10cm^3$ of pendimethalin solution with an initial concentration of 60 mg/L and the content was shaken thoroughly for 80min at 25^oC. The solution was then filtered at particular time intervals and the residual concentration was measured with the aid of 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 during optimization experiments. The amount of PE adsorbed (qe) in the adsorbent phase was calculated according to mass balance of the **Eqn. 1** [15]:

$$\text{Pendimethalin uptake, } q_e = \frac{(Co-Ce)V}{m} \qquad \textbf{Eqn. 1}$$

Where C_o and C_e are the initial and equilibrium concentration (mg/l) respectively of pendimethalin solution, V is the volume of the pendimethalin solution (L), and m is the mass (g) of the adsorbent used. The percentage of removed pendamethalin (R_{em}%) in solution was calculated using **Eqn. 2** [16].

$$\%\ \text{Pendimethalin Removal} = \frac{(Co-Ce)}{Co} \times 100 \qquad \textbf{Eqn. 2}$$

2.5. Determination of adsorption parameters (Optimization)

i. Effect of pH

Adsorption experiments were conducted in the pH range of 3 to 8 keeping all other parameters constant (PE concentration 50mg/L; adsorbent dose 0.1g; contact time 24h; temperature 25◦C). The solution pH was adjusted to the required value using 0.1MHCl or NaOH, and pH was measured using a pH meter (MP220). The filtrates obtained from mixture were analyzed for residual un- adsorbed PE using UV visible spectrophotometer. The quantity adsorbed was calculated from the **Eqn. 1** [17].

ii. Effect of contact time

0.1 g untreated Bambara groundnut shells were weighed separately into a 100ml conical flasks. A 10cm^3 of the optimum concentration (60 mg/L PE) solution was added into the beaker. Each solution was agitated for different time intervals of 20, 40, 60, 80, 100 and 120 minutes to investigate the effect of contact time. After the completion of the reaction, the mixtures were filtered, followed by the determination of the residual PE concentrations using UV-visible spectrophotometer. The quantity of the pendamethalin adsorbed from the solution was calculated using **Eqn. 1** presented earlier [18].

iii. Effect of adsorbent dosage

The adsorption of PE onto UBGNS was studied by changing the quantities of the adsorbents from 0.2 to 1.2g in the test solution while keeping the initial PE concentration at 60 mg/L, temperature = 25 ◦C, pH 5 and equilibrium time 2hr constant. The mixtures were agitated with an orbital incubator shaker (Innova 4000 Model). At the completion of the contact, the solutions were filtered and the filtrates were analyzed for un-adsorbed PE using uv-visible spectrophotometer [18]. The amount of PE adsorbed was calculated from **Eqn. 1.**

iv. Effect of PE concentration

To establish adsorption isotherms and the effect of pendamethalin concentration, aqueous solutions of PE were prepared, in a concentration range from 10 to 60 mg/L while keeping all parameters at optimized conditions and initial pendamethalin concentrations. Once the equilibrium was attained, the quantity of adsorbed PE, as well as the residual concentrationin solution, was determined. The mixtures were filtered and the unabsorbed PE in the filtrate was analyzed by UV-visible spectrophotometer **[18]**. The quantity of pendamethalin adsorbed, qe, was calculated using **Eqn. 1**.

2.6. Adsorption isotherms

Four isotherm models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were used to test the fitting of the equilibrium data. The linear form of the Langmuir model is given in **Eqn. 3** [19]:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_{oKLC_e}}$$ **Eqn. 3**

Where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of PE 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 $\frac{1}{qe}$ versus $\frac{1}{Ce}$. The linear form of Freundlich isotherm which is also a model used in describing adsorption mechanism of herbicides however is given in **Eqn. 4** [20]:

$\log qe = \log K_f + (1/n) \log Ce$ **Eqn. 4**

Where K_f is a constant indicative of the relative adsorption capacity of the adsorbent and n is adsorption intensity related to the surface heterogeneity. Both K_f and *n* can be determined by the linear plot of log1/qe versus log1/Ce. The Temkin isotherm was also used in the form given **Eqn. 5** [21]:

$$q_e = \frac{RT}{b_T} lnA_{T+} \frac{RT}{b}$$ **Eqn. 5**

Where Temkin constant B = RT/b is related to the heat of adsorption, R the gas constant (J/mol*K), T* the temperature (K), b the variation of the adsorption energy (J/mol) and b_T the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. A plot of qe versus lnCe enables the calculating of isotherm constants B and b_T from the slope and the intercept, respectively. The linear form of the Dubinin- Radushkevich isotherm model used this research is as described by **Eqn. 6** [22]:

$\ln q_e = \ln(q_s) - (k_{ad}\varepsilon^2)$ **Eqn. 6**

Where q_e, K_{ad}, ε are the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_s is theoretical isotherm saturation capacity (mg/g), K_{ad} is the Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and ε is the Dubinin–Radushkevich isotherm constant in kJ/mol, and E is the Polanyi potential, where;

$\ln q_e = \ln q_m - \beta \varepsilon^2$ **Eqn. 7**

$$E = b\left[\frac{1}{\sqrt{2B_{DR}}}\right]$$ **Eqn. 8**

B_{DR} can be defined as the isotherm constant. The parameter *ε* can be calculated using the **Eqn. 9**:

$$\varepsilon = RTln\left[1 + \frac{1}{c_e}\right]$$ **Eqn. 9**

The values of the following constants including: R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature in Kelvin and adsorbate equilibrium concentration (mg/L), for respectively.

2.7. Kinetic studies

The study of adsorption kinetic of pendimethalin onto the untreated banbara groundnut shell 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. by keeping all other parameters (pH =5, adsorbent dosage 0.2g, initial PE concentration = 60mg/l, T = 298K) at optimized values. The rate constants of the adsorption process were determined from the pseudo – first-order and pseudo-second-order kinetic equations.

For the pseudo-first-order kinetics, the linear Lagergren expression given **Eqn. 10** was used [23]:

$\log (q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t$ **Eqn. 10**

Where k_1 is the first-order rate constant and qe and qt are the amounts of PE adsorbed at equilibrium and time t(mg/g), respectively. The values of log(qe− qt) were calculated from the experimental data and plotted against t. $k_1$was calculated from the slope of the plot. The linear form of the pseudo-second-order reaction kinetic model also used for adsorption studies can be given by **Eqn. 11** [24]:

$$\frac{t}{q_t} = \frac{1}{K_{2\,q_e^2}} + \frac{1}{q_e}\,(t) \qquad \textbf{Eqn. 11}$$

Where the equilibrium adsorption capacity (qe), and the second order constant k_2(g/mg h) were determined experimentally from the slope and intercept of plot t/qt versus t. The Elovich kinetic model was described in literature by many authors according to the following linear relation in **Eqn. 12** [25]:

$$qt = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t \qquad \textbf{Eqn. 12}$$

The parameters (α) and (β) were calculated from the slope and intercept of the linear plot of qt versus ln(t). The third kinetic model used is the intra particle diffusion and is described by **Eqn. 13** [26]:

$$qe = C + k_{int}^{1/2} \qquad \textbf{Eqn. 13}$$

The constant k_{int}(mg/g $min^{0.5}$) is the intra particle diffusion rate and C is the boundary layer thickness.

2.8. Thermodynamic parameters

The temperature of the working solution was varied between 30 to 60 °C (30, 40, 50 and 60 °C). 10cm^3 of the optimum concentration, 60 mg/L PE, was contacted with 0.2g of UBGNS for 80 min in 100cm^3 conical flasks. The mixtures were equilibrated at contact time at afore mentioned temperatures. The mixtures were filtered, and the filtrates were analyzed for PE using UV-visible spectrophotometer, and the quantities adsorbed were calculated by using **Eqn. 1** [15]. The thermodynamic parameters of adsorption such as changes in free energy (ΔG_a), enthalpy (ΔH_a) and entropy (ΔS_a) give useful view about the feasibility and the spontaneous nature of the adsorption process and generally can be described in **Eqns. 14, 15**:

$$\Delta G_a = -RT\ln k_c \qquad \textbf{Eqn. 14}$$

$$\ln k_c = -\Delta G_a/RT = -(\Delta H_a/RT) + (\Delta S_a/R) \qquad \textbf{Eqn. 15}$$

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 as in **Eqn. 16** [27]:

$$k_c = C_a/C_e \qquad \textbf{Eqn. 16}$$

Where C_a is mg of PE adsorbed per liter and C_e is the equilibrium PE concentration of solution (mg/L). Both ΔH_a and ΔG_a can be obtained from the slope and the intercept of van't Hoff plot of lnK_c versus 1/T.

3. Results and discussion

3.1. FTIR spectroscopy and scanning electron microscopy

The FT-IR analysis provides information on the chemical structure of the adsorbent materials. This analysis is performed in the range of 400–4000 cm^{-1}. FT-IR spectra of untreated Bambara groundnut shell before and after adsorption are depicted in **Figure 1**. A broad adsorption peak at 3272 cm^{-1} is attributed to –OH stretching and also prominent peaks at 2918cm^{-1} assigned to C – H bands of methyl and methylene groups [28]. Peak at 1514cm^{-1} is ascribed to carbonyl C-O group which is affected by minor overlapping with C-C aromatic ring stretching vibration. The peak observed at 1019cm^{-1} to 1242cm^{-1} are due to carbonyl groups C-O bonds. Peak at 1443cm^{-1} correspond to C-H vibrations in

methane. The presence of OH group and carbonyl group is attributed to the presence of carboxylic acids group present in the adsorbent. The stretching of the C-O group to aromatic ring is attributed to the signal at 835cm^{-1}. The hydroxyl, carboxyl and carboxylic acids are important adsorption sites [29].
There was minor difference between before and after pendimethalin adsorption. The shift of the OH From 3272cm^{-1} to 3279cm^{-1} indicates the involvement of the hydroxyl groups in the adsorption the pendimethalin herbicide. The shift of the carbonyl group peak from 1611cm^{-1} to 1622cm^{-1} shows that the carbonyl group participated in the adsorption of PE. The result of the FTIR spectrum shows the participation of carbonyl and hydroxyl groups present on the surface of the raw (untreated) Bambara Groundnut shells used as an adsorbent as active binding sites to improve adsorption of pendimethalin.

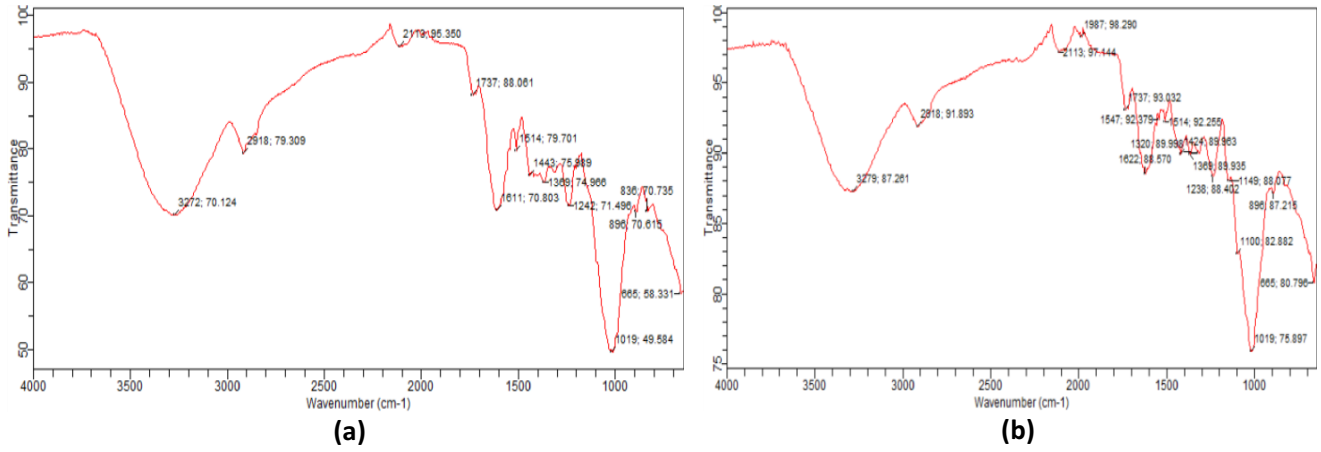
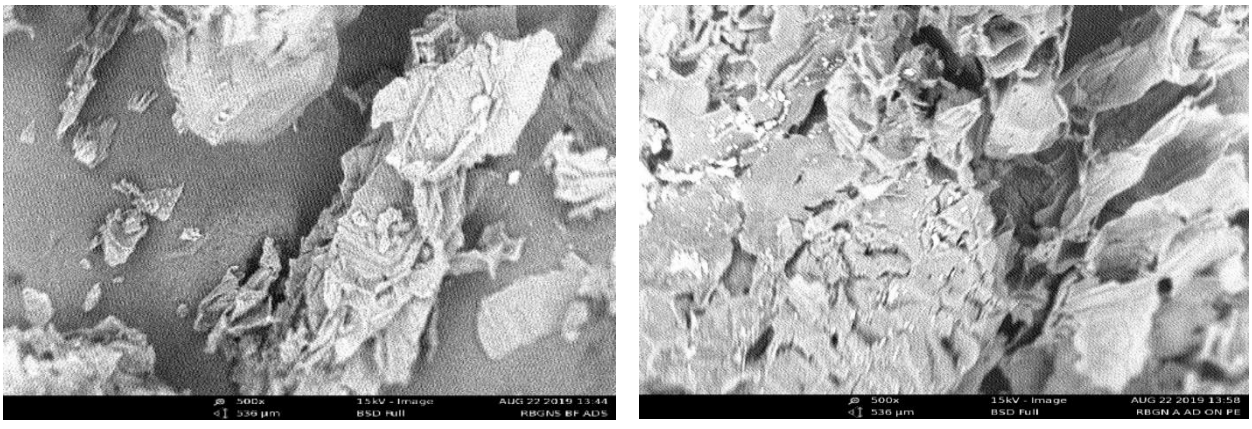


Figure 1. FTIR Spectrum of UBGNS (a) before and (b) after adsorption on PE

Scanning electron microscopy micrographs of UBGNS before and after adsorption of PE are shown in **Figure 2**. The SEM micrographs show that the surfaces of UBGNS before and after adsorption are different from each other. The surface before adsorption has pores and patches while after adsorption the surface was devoid of pores, cavities, cluster and patches, which is due to the adsorption of PE.



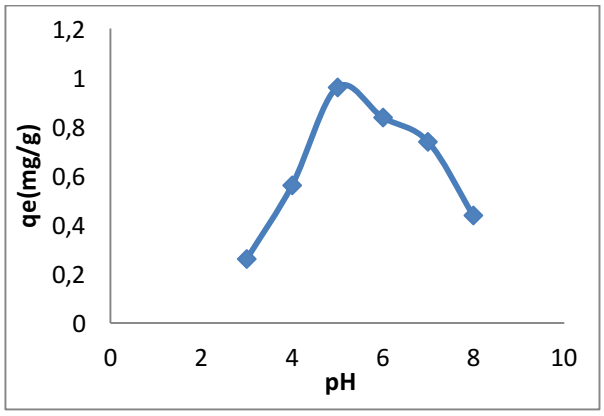
(a) (b)

Figure 2. SEM micrographs of UBGNS (a) before and (b) after adsorption of PE onto UBGNS

3.2. Optimized adsorption parameters

Figure 3 shows plots for the variation of the amount of PE herbicide adsorbed with pH. The effects of pH of solution on PE removal are evaluated by varying initial pH of solution from 3 to 8. As can be seen

from **Figure 3**, the PE removal was somewhat evidently dependent on pH with the better adsorption occurring under acidic conditions (pH 5) and decreased with increase in solution pH. This means the adsorbed amount of PE decrease as pH increased from 5 to 8 due to electrostatic repulsion between adsorbent and negatively charged species in solution [29-30]. Similar trend was reported by Mitiku [31]. On the other hand, **Figure 4** shows plot for the variation of the equilibrium amount of PE adsorbed with adsorbent dosage. It was evaluated by varying amounts of adsorbents dosage (0.2–1.2 g) while adsorbate initial concentration was fixed. It is indicative 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 adsorbent dosage of adsorbent is attributed to possible overlapping of adsorption sites as adsorbent dose increases which will equally reduce the effective adsorption sites. Concentration factor involving low PE-to-adsorbent ratio at low PE concentrations can be considered in explaining the dependence of adsorption on adsorbent dose. The percentage of PE molecule adsorbed is found to dependent upon the initial concentration, and at higher concentrations, the available sites of adsorption become fewer [32, 33].



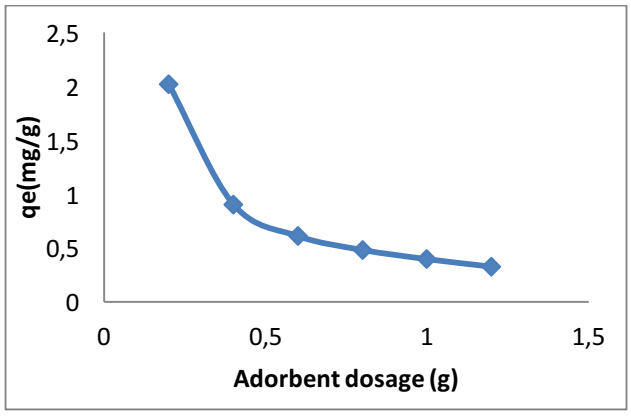
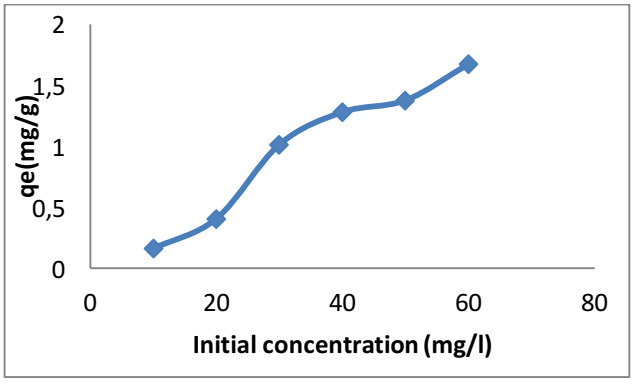


Figure 3. Effect of pH on adsorption of PE onto UBGNS. **Figure 4.** Effect of dosage on adsorption of PE onto UBGNS

It was observed from **Figure 5** that the total amount of PE molecule adsorbed per gram of the UBGNS increased with increasing concentration. At low concentration, the available driving force for transfer of PE molecule 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 molecule 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. Trend was earlier reported [34]. Effect of contact time on adsorption of PE is presented in **Figure 6**.



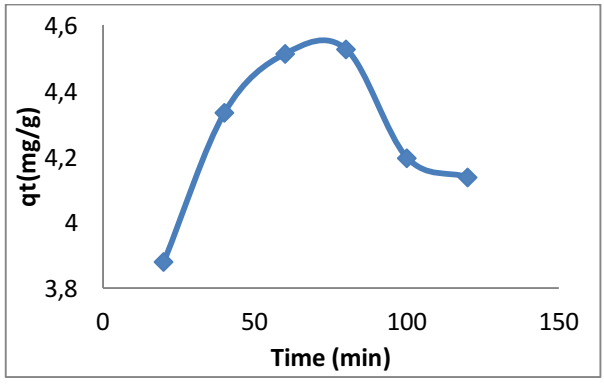


Figure 5: Effect of concentration on PE onto UBGNS **Figure 6:** Effect of contact time on PE onto UBGNS

Uptake of PE was rapid in first 20- 80 minutes and declined after 80 minutes. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage whereas after 80 minutes decreasing effect is due to vacant surface sites are not easy to be occupied due to repulsive forces. Later on the process becomes relatively slower and equilibrium conditions are reached at 80 min. At this point, the amount of the PE desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the PE being adsorbed onto the adsorbent. Similar work was reported by Jude *et al*. [35]. Therefore, throughout further batch experiments were carried out using the optimized 80 minutes PE and adsorbent UBGNS contact time.

3.3. Adsorption isotherms

Adsorption isotherm studies were carried out using four isotherm models: The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models.The linear plot of specific adsorption (1/qe) against the equilibrium concentration (1/Ce) for Langmuir model, (logqe) against the (logCe) for Freundlich model, (lnCe) against the equilibrium adsorption (qe) for Temkin model and (lnqe) against ε^2 for Dubinin-Radushkevich model (Figures not shown) show that the adsorption obeys the Langmuir model having the highest value of correlation coefficient R^2. **Table 1** summarizes the monolayer adsorption capacities according to the Langmuir model and the parameters of the four isotherms together with their correlation coefficients at different concentration. It was observed that the Langmuir model yielded the best fit since the R^2 value were relatively high (0.940) and this confirmed that the Langmuir isotherm was favorable for adsorption of pendimethalin on UBGNS. For Freundlich isotherm model, the 1/n value obtained is below one. This indicated that the adsorption process followed a normal Langmuir isotherm and conforms to the experimental data when fitted into the Langmuir isotherm equation [36]. This is an indication of homogeneous nature untreated carbon surface in which the pendimethalin molecule/carbon adsorption had equal adsorption activation energy (AAE). The results also demonstrated the formation of monolayer coverage of pendimethalin molecule at the outer surface of the carbon. Most studies from the literature have also reported similar observations where adsorption of pesticides on activated carbon was well represented by the Langmuir isotherm such as adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran on the surface of carbon slurry and blast furnace slag, dust, and sludge [37] and Removal of insecticide carbofuran from aqueous solutions by banana stalks activated carbon [38]. As shown in **Table 1**, both equilibrium binding constant (b_T) and heat of adsorption constant (B) values were found to be 131.77 and 18.80 respectively. The regression equation and R^2 value for Temkin model were observed that this isotherm also gave very good description of the adsorption process of PE onto UBGNS, over the range of concentration studied. As shown in **Table 1** the value of linear regression coefficient, R^2, is 0.859, suggesting that these experimental data fitted worse with the Freundlich followed by Temkin model. This finding indicates that PE adsorption on UBGNS does not follow the Dubinin–Radushkevich sadsorption model. The apparent energy of adsorption and Dubinin–Radushkevich isotherm constants are shown in **Table 1**. The high value of q_s shows high adsorption capacity. The value of the apparent energy, *E*, of PE adsorption on UBGNS is 0.158 kJ/mol. On comparing the values of the correlation coefficient, R^2, for the four tested isotherms, it can be observed that the adsorption data of PE herbicide on UBGNS fitted well with the Langmuir isotherm followed by Dubinin–Radushkevich, Temkin isotherm and the least in Freundlich. By comparison with other adsorbents for herbicides removal, many studies using various adsorbents were reported in the literature [11], [39-41] and their performances were compared in terms of adsorption capacity. As presented in

Table 2, for comparison sake, the removal efficiency of PE onto UBGNS was quite comparable to others reported.

Table 1: Adsorption isotherms parameters for the adsorption of pendimethalin onto UBGNS

Isotherm Model	Parameters	Numerical values
Langmuir	Q_o(mg/g)	10.42
	K_L(L/mg)	0.036
	R_L	0.247
	R^2	0.940
Freundlich	1/n	0.714
	n	1.400
	K_f(mg/l)	0.423
	R^2	0.692
Temkin	A_T(l/mg)	0.228
	b_T	131.77
	B	18.80
	R^2	0.859
DRK	q_s(mg/g)	42.95
	K_{ad}(mol^2/K^2)	2×10^{-5}
	E(KJ/mol)	0.158
	R^2	0.914

Table 2. Comparison of pendimethalin Langmuir adsorption capacities with various adsorbents

Herbicide	Adsorbent	Adsorption capacity	Reference
Bantazon	Oxidized activated carbon cloth	17	**[41]**
Atrazine	Fe-Zr-Mnnanocomposite	0.30	**[39]**
Carbenazim	Spent coffee grounds	11.918	**[40]**
Pendimethalin	Bambara groundnut shell	10.42	This study
Linuron	Spent coffee grounds	5.834	**[40]**
Atrazine	Bambara groundnut hulls	3.5236	**[11]**

3.4. Adsorption thermodynamics

The studies of temperature influence on pesticide adsorption available in the literature reveal that the relation between temperature and adsorption depends on the adsorbent/adsorbate pair [42]. In order to study the nature of adsorption, the thermodynamic parameters for the adsorption process, such as the Gibbs free energy (ΔG_a), the enthalpy (ΔH_a) and the entropy (ΔS_a) were calculated using **Eqns 14, 15**. The values of ΔH_a and ΔS_a were calculated from the slope and intercept of plot between lnKc versus 1/T are shown in **Table 4**. The negative value of ΔH_a indicated the exothermic nature of the adsorption interaction. The negative value of ΔS_a showed the affinity of the UBGNS for pendimethalin and the decreasing randomness at the solid–solution interface during the adsorption process. The negative value of ΔG_a indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of pendimethalin on the surface of the studied adsorbent. ΔG_a values were found to decrease as the temperature increased, indicating higher driving force and hence resulting in more adsorption capacity. Similar result was reported elsewhere by other authors [43].

Table 4. Thermodynamic parameters for the adsorption of PE on CBNS

T(K)	ΔG_a(kJ/mol)	ΔH_a(kJ/mol)	ΔS_a(J/mol.K)
303	-2315.09		
313	-2274.39	-5.623	-10.87
323	-2035.55		
333	-2032.12		

Conclusion

The present investigation showed that the untreated carbon prepared from Bambara groundnut shell is a promising adsorbent for the removal of herbicide, pendimethalin from aqueous solution over a wide range of concentrations. Adsorption equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models and the equilibrium data for UBGNS were best represented by the Langmuir isotherm. The adsorption kinetics was found to follow closely the pseudo second-order kinetic model. Thermodynamic parameters such as enthalpy (ΔH_a), entropy (ΔS_a) and free energy (ΔG_a) were evaluated. Adsorption capacities of UBGNS for PE were high when compared with other adsorbents showing that UBGNS as a potential adsorbent for the adsorptive removal of pendimethalin.

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