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Experimental and computational studies on activated Bambara groundnut (*Vigna subterranean*) hulls for the adsorptive removal of herbicides from aqueous solution

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Abstract

Background: The excessive usage of herbicides to control herbs by farmers has become an issue of interest to the environmentalist due to the threat posed by such act to the ecosystem, and therefore, there is the need to curb such practices. The efficiency of Bambara groundnut shell for the removal of pendimethalin (PE) and paraquat dichloride (PQ) herbicides from aqueous solution was established in this work. The activated carbon was prepared via chemical activation method using trioxonitrate (v) acid by determining its void volume, moisture content, bulk density and Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) methods. Batch adsorption techniques were set to optimize the adsorption parameters such as solution pH, adsorbate concentration, contact time, adsorbent dosage and temperature in order to depict the best optimal conditions for the adsorption process. The adsorption process was examined in terms of its equilibrium data, kinetics, thermodynamics involved in the adsorption process as well as computational quantum chemical parameters evaluation.

Results: The batch adsorption experiments revealed that the amounts of PE and PQ adsorbed were found to vary with the contact time, adsorbent dosage, pH and initial concentration. The adsorption of PE and PQ decreased with increasing adsorbent dose but increases with increasing initial concentration of the PE and PQ solution. Isotherm studies revealed that the equilibrium data fitted to both Langmuir and Freundlich model with *R*-squared values of 0.976, 0.993 and 0.909, 0.978 for PE and PQ, respectively, which implied that Langmuir isotherm had a better fit. This was also found to be an indication that the uptake of PE and PQ by ACBGNS occurred through monolayer adsorption on identical homogenous sites. Also, kinetic modeling results obtained showed that the pseudo-second-order model explained the adsorption kinetics of PE and PQ by ACBGNS best, which meant that chemisorption was the slowest step and, thus, the rate determining step. The positive value of ΔH and the positive value of ΔG show the endothermic and spontaneous nature of adsorption of PE and PQ ACBGNS.

Conclusion: Batch adsorption experiment and characterization of the ACBGNS have indicated that Bambara ground nut shell can be used to produce activated carbon that can be applied effectively for adsorption of PE and PQ from an aqueous solution. Computational studies results obtained from quantum chemical analysis are consistent with the experimental results obtained from this study.

Keywords: Adsorption, Bambara groundnut shell, Isotherm, Thermodynamic, Computational

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Background

Farmers in developing countries like Nigeria are faced with various threats posed by unregulated and excessive usage of herbicides during farming processes which results in serious contamination and pollution of surface and ground waters (Neera 2009). These acts call for serious concern by environmentalists and their likes to curb such practices of the reckless use of these chemicals in crop farms, orchards, fields and forest lands (Neera 2009; Salman et al. 2011). Scientists have used several methods to control the unguided usage of these chemicals before, during and after farm practices of which adsorption finds an application. However, activated carbon usage in waste water treatments has been established to be more effective and efficient when compared to other adsorbent materials. This is due to its ease in experimental design and usage even though activated carbons which are commercially available are quite expensive (Ali et al. 2016; El-Shamy et al. 2018; Yanyan et al. 2018; Wei et al. 2019; Khan 2020; Alzhan et al. 2020; Liliana et al. 2020; Ahmed et al. 2020; Ahmed and Sayed 2020; Abdelhamid et al. 2020; Khalil and Kenawy 2020; El-Azazy et al. 2021). Reported studies on the use of Bambara groundnut shell do not involve using it to remove herbicides from an aqueous solution which could have led to understanding of the mechanism of the process (Ademola et al. 2019).

Pendimethalin was known as (3,4-dimethyl-2,6-dinitro-N-pentan-3-ylaniline) and that of paraquat dichloride (1,1-dimethyl-4,4-bipyridinium chloride). Pendimethalin and paraquat dichloride for their interaction with adsorbent surface. However, there is paucity in the usage of activated carbon sourced from Bambara groundnut shells (BGNS) for the adsorption of pendimethalin and paraquat dichloride. Bambara groundnut is an edible fruit that is cultivated mainly because of its high nutritional value. In northern Nigeria, large quantities of Bambara groundnut hulls are usually disposed as waste materials (Akinola et al. 2019). BGNS can be easily transformed and utilized as a good adsorbent. Most of the reported work on the use of BGNS product has to do with the ability of these adsorbents in adsorbing dyes (Akinola et al. 2019). There are few reports on the specific mode of action of the adsorbent and the extent of its adsorption (Akinola et al. 2019; Ayuba and Nyijime 2020).

In describing reactivity and illustrating chemical, molecular and electronic structure of compounds, quantum chemical methods have been found to find a lot of application (Kraka and Cremer 2000). This can assess the potentials and efficacy of the interaction between the adsorbent and adsorbate through mathematical intuitions and modeling. The correlation between structure and reactivity could be used to even predict the efficiency of compounds in adsorption which are yet to be

synthesized (Kareison and Lebanov 1996). The use of equations of mathematical origin and models could be used to establish and predict chemical phenomena of which adsorption is such an example (Hinchliffe 1994, 1999). In this previous study, it was shown that the activated Bambara groundnut shell is established to be an efficient adsorbent which can be applied for the adsorption of both pendimethalin and paraquat dichloride herbicides from aqueous solution. It functions through surface adsorption sites which depend on experimental parameters including solution pH, amount of adsorbent, time of contact and initial concentration of the herbicide. Physical process favors the adsorption of both PE and PQ herbicides on Bambara groundnut shell. Relatively based on the experimental data generated, the isotherm that fitted best was that of Langmuir model. The kinetics that best describes the adsorption process of both herbicides to the ACBGNS was that of second order (pseudo). Evaluated parameters obtained for both adsorption processes (ΔG , ΔH and ΔS) describe the process to be spontaneous and feasible in nature.

Furthermore, this approach can harness the structural and electronic parameters of these molecules in relation to adsorption to propose a suitable mechanism which may not be achieved experimentally (Growcock 1989; Wang et al. 1999). The aim of the present study was to investigate and established the adsorption efficiency of activated Bambara groundnut shell in the removal of pendimethalin (PE) and paraquat dichloride (PQ) herbicides from aqueous solution.

Methods

Chemicals and reagent

Adsorbate tested pendimethalin (PE) and paraquat dichloride (PQ) herbicide were obtained from Yankura market, Kano, Nigeria. Pendimethalin [CAS number = 40487-42-1, chemical formula = $C_{13}H_{19}N_3O_4$, molecular weight = 281.312 g mol⁻¹] and paraquat dichloride [CAS number = 1910-42-5, chemical formula = $C_{12}H_{14}Cl_2N_2$, molecular weight = 257.16 g mol⁻¹. Bambara groundnut shells (BGNS) were collected as a waste material from some farms in Benue, Nigeria. The collected BGNS were washed with distilled water to eliminate any dirt. All chemicals used were of the analytical grade. Sodium hydroxide, phosphoric acid, hydrochloric acid were the products of Sigma-Aldrich (Darmstadt, Germany).

Preparation of adsorbent

The BGNS sourced after removing the seeds from the pods were thoroughly washed to clear off impurities using water. Shells obtained were subjected to drying at 80°C to obtain constant weight. Pulverization and

subsequent sieving of the dried shells into fine particles were conducted as described by Ayuba and Nyijime (2021). The final product was kept for further usage in an air safe container. 100 g of the fine powder was mixed with 10% phosphoric acid (H_3PO_4) (100 g sample + 100 mg/l of 10% H_3PO_4 , wt/v). Pyrolysis in an electric muffle furnace of the fine particles was conducted for 1 h at 450 °C and subsequently removed and cooled at room temperature. Before drying at 110 °C at a period of 24 h, the pyrolyzed carbon was subjected to washing using 2% HCl and distilled water to achieve a neutral pH sample (Ayuba and Nyijime 2021).

Preparation of herbicides solutions

The stock herbicides solution was prepared by mixing 3.6 ml of the 276 mg/l of PQ solution and 2 ml of 500 mg/l of PE solution separately each to a 1-L flask and further diluting to the mark. Serial dilution was carried out using distilled water to give solution concentration of 10, 20, 30, 40, 50 and 60 mg/l of each herbicides solution.

Batch adsorption experiments

Adsorption experiments for PE or PQ onto the prepared adsorbent were studied by weighing 0.1 g of the adsorbent (ACBGNS), and 10 cm³ of 50 ml initial concentration (PQ or PE) was introduced into a 250-ml beaker and was tightly covered and placed in an incubator shaker (Innova model) and run at 25 °C for 2 h. After equilibration, samples were withdrawn and filtered through Whatmann filter paper and the absorbance of the residual herbicides was measured using a Uv-visible spectrophotometer (PerkinElemer) at λ_{max} 243 and 257 nm for pendimethalin and paraquat dichloride, respectively. The same method was used while varying the initial concentration, the contact time, the adsorbent dosage and temperature of adsorption during optimization experiments. The optimized values were used to conduct the main batch adsorption experiments at varying temperatures (60 mg/l concentration, 0.2 g dosage, pH 6 and pH 8, 80 min contact time for PE and PQ, respectively). The amount of the herbicide adsorbed for each gram was obtained using Eq. (1) (Fouodouo et al. 2017).

$$\text{Herbicide uptake, } q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

The initial and equilibrium concentration (mg/l) are defined as C_o and C_e , volume of the herbicide solution (L) is V , and the mass (g) of ACBGNS is m .

Characterization of the adsorbent

The adsorbent (ACBGNS) was characterized using Cary 630, Agilent Technology model of Fourier Transform Infrared Spectrophotometer and Scanning

Electron Microscope (Phenom World Eindhoven). The conducted FTIR experiment used a range of wave numbers (650–4000 cm⁻¹) with 32 scans at 8 cm⁻¹ resolution, while the SEM analysis was performed by scanning the micrographs of ACBGNS before and after adsorption using 15.00 kV voltage of acceleration with an $\times 500$ magnification.

Computational details

All the geometries of the molecules have been fully optimized using the B3LYP method within the framework of density functional theory (DFT) housed in Materials Studio 7.0 software (Accelrys, Inc.) in conjunction with the double numerical polarization (DNP) basis set (Lee et al. 1988; Becke 1993). After obtaining the geometry optimized herbicide molecules, quantum chemical parameters were computed which were later used to predict the adsorption mechanisms (Tao et al. 2010; Mohammed et al. 2017; Zohdy et al. 2021). This method has been used to provide useful information about useful quantum chemical parameters (Khaled et al. 2005; Emreguland and Hayvali 2006; Zohdy et al. 2021), through density functional theory (DFT) to predict the structural nature of the adsorbate and adsorbent interaction processes (Lashkari and Arshadi 2004; Mohan and Joseph 2018). The electron affinity (EA) and ionization potential (IP) of the neutral herbicide molecules were calculated in relation to the lowest energy of the unoccupied molecular orbital (E_{LUMO}) and the highest occupied molecular orbital energy (E_{HOMO}), respectively, using Koopman's theory (1993).

$$IP = -E_{HOMO} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

Energy gap ΔE was calculated using Eq. (4):

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (4)$$

Calculated ionization potential and electron affinity values were used to determine the values of the absolute electronegativity χ , the absolute hardness (η) and the softness (σ) using expressions in Eqs. (5) and (6): (Pearson 1963).

$$\chi = \frac{1}{2}(IP + EA) = \frac{1}{2}(-E_{HOMO} - E_{LUMO}) \quad (5)$$

$$\eta = \frac{1}{2}(IP - EA) = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \quad (6)$$

Value of the global softness (σ) is the reciprocal of the global hardness (Pearson 1963).

$$\sigma = 1/\eta \quad (7)$$

For a reaction made of adsorbent and adsorbate having varying electro negativities, the flow of electrons is expected from the adsorbate molecule having lower electronegativity toward that with a higher negativity (adsorbent surface) till equilibrium of the chemical potentials of both systems is attained (Parr and Szentpaly 1999).

Fukui indices were used to establish the reactive sites on the herbicide (adsorbate) which shows chemically reactive regions of the electrophilic and nucleophilic character of the studied herbicide molecules (Verma et al. 2018). Chemically, where the function of the Fukui is found to have large values predicts a region of higher reactivity than where the value is small. To further predict the sites which can serve as hard and soft acid and bases, the HSAB principle can be invoked in relation to the evaluated Fukui indices. To define Fukui function $f(r)$ for nucleophilic attack (Eq. 8) and electrophilic attack (Eq. 9) depending on the direction of electron transfer, the scheme of finite difference approximations obtained from Mulliken population analysis of atoms in the herbicide molecules was used (Alibakhshi et al. 2018; Verma et al. 2018; Zohdy et al. 2021).

$$f_k^+ = q_{k(N+1)} - q_{k(N)} \quad (8)$$

$$f_k^- = q_{k(N)} - q_{k(N-1)} \quad (9)$$

Value of q_k is the molecule's gross atom charge, the number of electrons (N) in the molecule, the anion is $N+1$ describing the LUMO of the neutral molecule with an added electron, and the cation is defined with respect to $N-1$ showing a new HOMO after electron removal from the neutral molecule. The ground state geometry of the herbicide molecules resulting from local minima was used for all calculations.

Results

The spectroscopic and micrograph results of this study are reported in Figs. 1 and 2, respectively. The optimized adsorption density of various adsorption parameters including solution pH, contact time, adsorbent dosage, initial herbicide concentration is reported in Figs. 3, 4, 5 and 6. The calculated adsorption isotherm, kinetics study, thermodynamic as well as the calculated quantum chemical parameters and Fukui indices of pendimethalin and paraquat dichloride molecule are reported in Tables 1, 2, 3, 4 and 5, respectively. Figure 7 shows the optimized geometry, HOMO, LUMO of PE and PQ molecules.

Discussion

Spectroscopic characterization of the adsorbent

FT-IR spectra of pendimethalin and paraquat dichloride (Fig. 1a–c) before and after adsorption show five important peaks which include O–H broad peak at 3117 cm^{-1} , C≡C vibration at 2322 cm^{-1} , 2084 cm^{-1} and 2113 cm^{-1} , peaks at 1994 cm^{-1} and 1871 cm^{-1} which can be assigned to C=O group; such assignments can be affected by neighboring aromatic C–C ring stretched vibrations. At 1562 and 1063 cm^{-1} , the following stretch assignments of C=C and C–O were observed. The peaks at 970 cm^{-1} , 873 cm^{-1} and 676 cm^{-1} correspond to C–H in alkenes and C–H in aromatic rings. There was a minor difference that was observed prior to and after adsorption, which resulted in a shift and broadening of adsorption peaks. The shift of the –OH peak from 3117 to 3339 cm^{-1} for pendimethalin and 3117 cm^{-1} to 3119 cm^{-1} for paraquat dichloride indicates the involvement of the hydroxyl groups in the adsorption of the herbicides (Abbas and Ahmed 2016; Jawad et al. 2018).

The micrograph of the surface of ACBGNS before adsorption (Fig. 2a) shows the morphology of the surface adsorbent having pores, cracks, holes which are expected to enhance adsorption. After adsorption of the two herbicides differently (Fig. 2b, c), the surfaces showed the formation of clusters, patches, with filled cracks on the ACBGNS surfaces which shows the participation of ACBGNS in the adsorption of PE and PQ.

Some of the obtained physical properties of the activated carbon produced 11.2 moisture content (%), 0.242 g/cm^3 density and 1.78 cm^3 pore volume. 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 activated carbon that though it might not give up to 100% adsorption, it will be good for adsorption of organic and inorganic materials to a large extent (Fito et al. 2019). Maximum weight loss was observed in the present study; 51.82% of the activated carbon was obtained after activation.

Effect of pH variation on PE and PQ adsorption

Figure 3 shows the variation in PE and PQ amount adsorbed onto ACBGNS with solution pH. Removal of PE and PQ by ACBGNS is observed to be at optimum pH of 6 and 8. It can be observed from the plots that ACBGNS possesses high removal of PE at lower pH, while PQ was more adsorbed at higher pH condition. The presence of pectin on the surface of ACBGNS favored the adsorption of PQ which is cationic in nature; this is as a result of negatively charged ions increase in alkaline medium

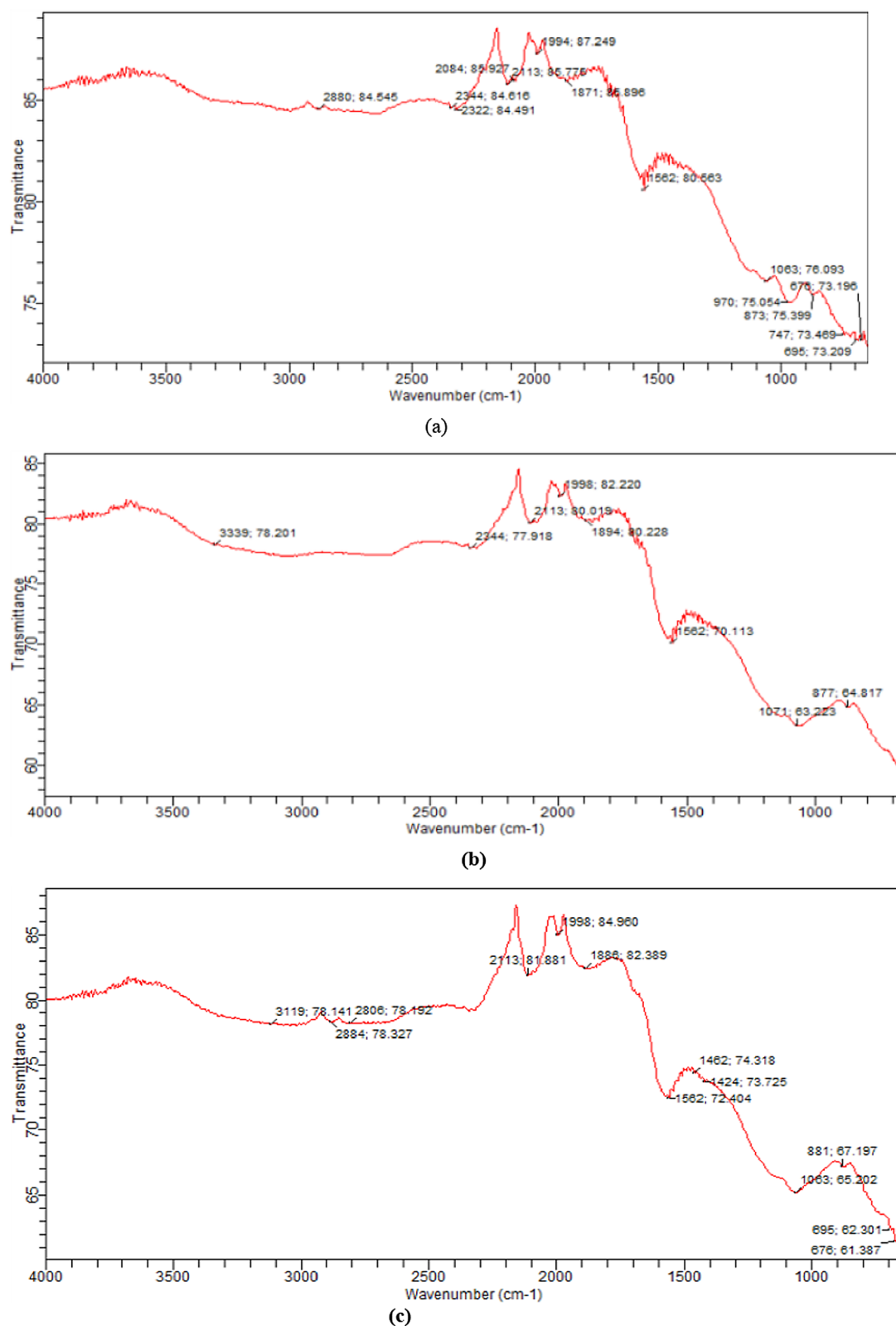


Fig. 1 FT-IR spectra of ACBGNS (a) before adsorption, (b) and (c) after the PE and PQ adsorption. The adsorbent (ACBGNS) was characterized using Cary 630, Agilent Technology model of Fourier Transform Infrared Spectrophotometer. The conducted FTIR experiment used a range of wave numbers ($650\text{--}4000\text{ cm}^{-1}$) with 32 scans at 8 cm^{-1} resolution

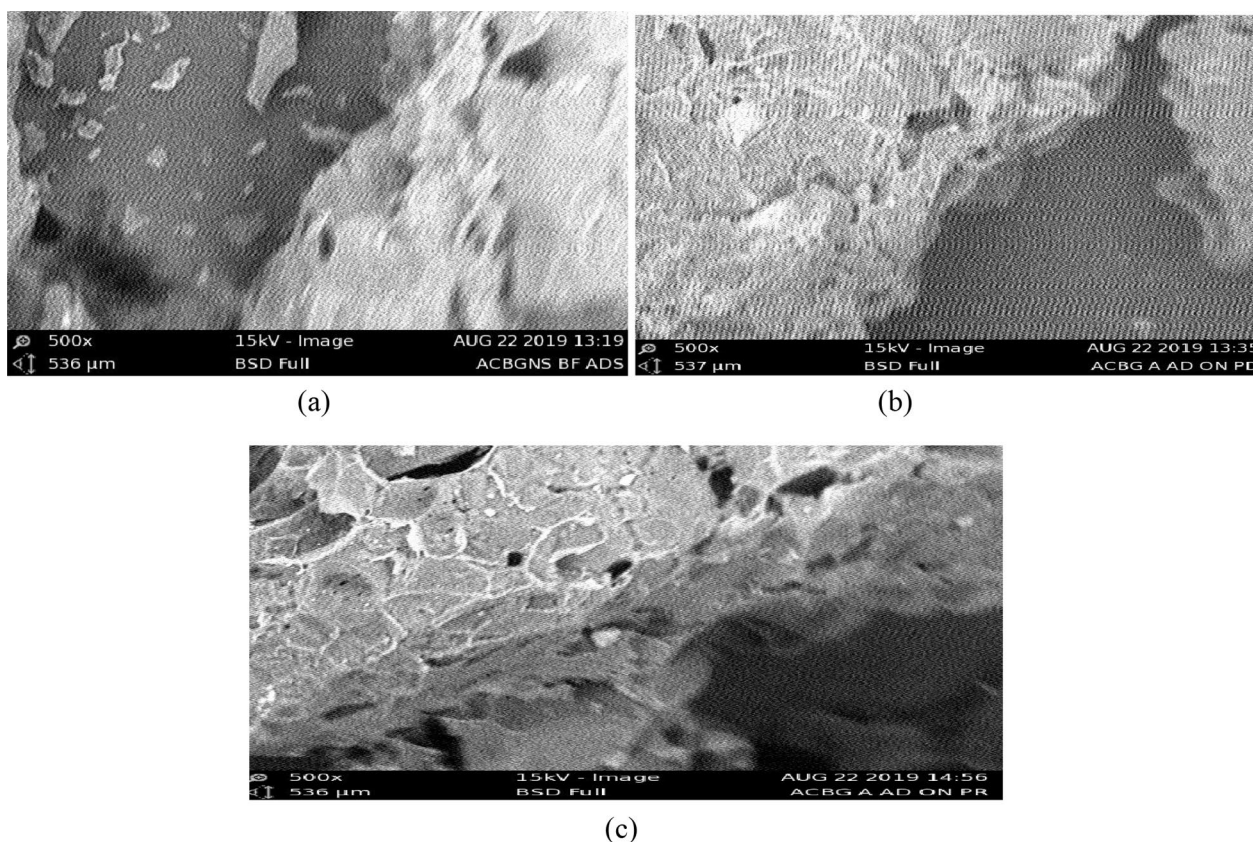


Fig. 2 SEM micrograph of ACBGNS (a) before adsorption and (b) after adsorption on PQ (c) after adsorption of PE. The adsorbent was characterized using scanning electron microscope (Phenom World Eindhoven). The SEM analysis was performed by scanning the micrographs of ACBGNS before and after adsorption using 15.00 kV voltage of acceleration with an $\times 500$ magnification

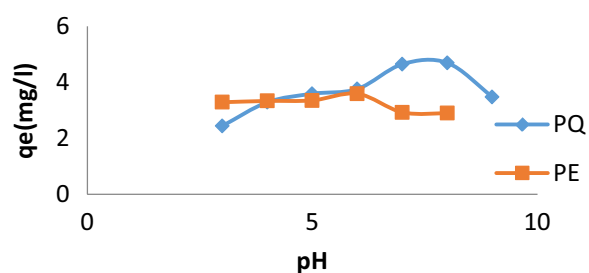


Fig. 3 Effect of pH on adsorption of PE and PQ (adsorption conditions: concentration of PE and PQ = 50 mg/l, $m = 0.1$ g, $t = 24$ h, $T = 25$ °C, volume of solution = 10 cm³, agitation speed = 150 rpm)

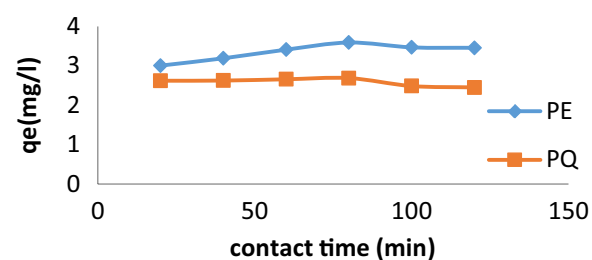


Fig. 4 Effect of time on adsorption of PE and PQ (adsorption conditions: concentration of PE and PQ = 50 mg/l, $m = 0.1$ g, $T = 25$ °C, volume of solution = 10 cm³, agitation speed = 150 rpm)

(Bello et al. 2017), while the surface of ACBGNS which also contains phenolic or carboxylic functional groups may be the reason for increased adsorption of PE at low pH (Bedin et al. 2015).

Effect of PE and PQ adsorption duration

Variation in the amount of PE and PQ molecules adsorbed with respect to duration is presented in Fig. 4. It was found that the adsorption rate of PE and PQ by ACBGNS was initially fast reaching equilibrium within 80 min. PE and PQ molecules were firmly attached onto the ACBGNS resulting in a higher rate of adsorption. At

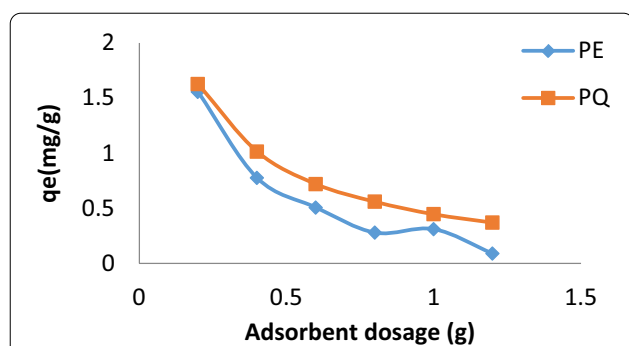


Fig. 5 Effect of adsorbent dosage on adsorption of ACBGNS onto PE and PQ, (adsorption conditions: concentration of PE and PQ = 50 mg/l, $t = 2$ h, $T = 25$ °C, m = varied, volume of solution = 10 cm³, agitation speed = 150 rpm)

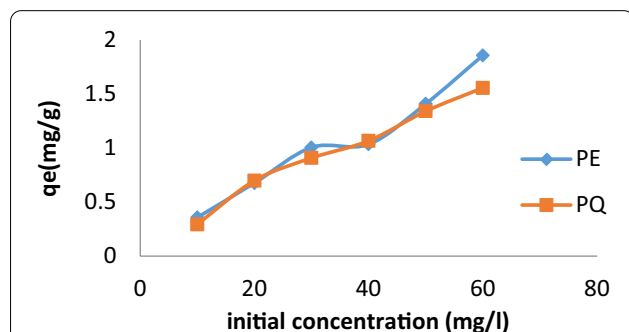


Fig. 6 Effect of initial concentration on adsorption of ACBGNS onto PE and PQ (adsorption conditions: concentration of PE and PQ = 10–50 mg/l, $m = 0.2$ g, $t = 2$ h, $T = 25$ °C, volume of solution = 10 cm³, agitation speed = 150 rpm)

Table 1 Calculated Freundlich, Temkin and Langmuir Isotherm constants for the PQ and PE Adsorption onto ACBGNS

Isotherm model	Parameter	Pendimethalin	Paraquat dichloride
Langmuir	Q_o (mg/g)	52.63	142.86
	K_L (L/mg)	0.056	0.0107
	R_L	0.186	0.379
	R^2	0.976	0.993
Freundlich	$1/n$	1.486	1.190
	N	0.673	0.840
	k_f	3.689	1.923
	R^2	0.909	0.978
Temkin	A_T (L/mg)	0.6358	0.376
	b_T	223.81	201.76
	B	11.07	12.28
	R^2	0.780	0.971

a later stage, the rate of PE and PQ removal was found to be constant. The available surfaces for binding the molecules became almost exhausted, and therefore, repulsive forces either between PE or PQ with the ACBGNS surface made the herbicide molecules difficult to occupy the vacant sites (Mondal and Kar 2018).

Effect of adsorbent amount on adsorption of PE and PQ

Figure 5 reveals the variation in equilibrium amount of PE and PQ adsorbed with adsorbent dosage (0.2–1.2 g). From the plots, the amount of PE and PQ adsorbed increased with an increase in the adsorbent amount used, while the amount adsorbed for a given amount of the adsorbent decreased considerably for both PE and PQ. This decrease observed for the herbicides in terms of adsorption per unit mass with respect to increasing adsorbent dosage could be attributed to possible overlapping of adsorption sites with an increase in adsorbent dosage. This is an indication that ACBGNS has a high adsorption capacity at low dosage.

Effect of initial herbicide concentration on adsorption of PE and PQ

Figure 6 presents an increase in amount per gram of PE and PQ adsorbed as their initial concentration increases. Driving forces of molecules in solution are low at a lower concentration, therefore resulting in a lower adsorption rate, while when concentration increases, it is expected that the PE and PQ would have higher driving forces which enable them to easily occupy the active sites on the ACBGNS surface from the aqueous phase. This was reported by other researchers (Mondal and Kar 2018; Lee et al. 2019).

Adsorption isotherm

Three different isotherm models, Temkin, Freundlich and Langmuir, were used to treat the generated isotherm data with the intention of proposing adsorption process mechanism. The Langmuir's model has been used to describe the adsorption of monolayer which occurs on the outer surface of an adsorbent with infinite number of active adsorption sites.

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (10)$$

C_e is the concentration of PE or PQ in mg/L at equilibrium, q_e , the amount of herbicide adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_o is maximum monolayer coverage capacity (mg/g), K_L is the isotherm constant (L/mg) for Langmuir. From the slope and intercept, the values of q_{\max} and K_L were evaluated through extrapolation of the Langmuir plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$. The

Table 2 Parameters for the kinetic adsorption of PE and PQ onto ACBGNS

Kinetic models	Numerical values			
Pseudo-first order	q_{eExp} (mg/g)	q_{eCal} (mg/g)	K_1 (min ⁻⁵)	R^2
PE	14.89	0.432	0.0023	0.098
PQ	13.01	1.236	0.021	0.781
Pseudo-second order	q_{eExp} (mg/g)	q_{eCal} (mg/g)	K_2 (min ⁻⁵)	R^2
PE	14.89	14.93	0.897	1
PQ	13.01	13.16	0.058	0.999
Intra particle diffusion		K_3	C	R^2
PE		0.094	15.74	0.049
PQ		0.172	11.28	0.614

Table 3 Parameters for the thermodynamic adsorption of pendimethalin (PE) and paraquat dichloride (PQ) onto ACBGNS

Adsorbate	T (K)	K_c	ΔG (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
PE	303	81.08	-11.07	5.67	30.50
	313	55.07	-10.43		
	323	52.33	-10.62		
	333	29.96	-9.413		
PQ	303	1.606	-1.193	0.80	40.0
	313	1.495	-1.046		
	323	1.490	-1.071		
	333	1.402	-0.935		

Table 4 PE and PQ quantum chemical parameters

Properties	Pendimethalin	Paraquat dichloride
HOMO (at orbital number)	75	43
LUMO (at orbital number)	76	44
E_{HOMO} (eV)	-5.306	-3.085
E_{LUMO} (eV)	-3.280	-0.963
ΔE (eV)	2.026	2.122
Dipole moment (Debye)	2.730	2.190
Binding energy (kal/mol)	-4695.753	-2999.686
Ionization potential (I) (eV)	5.306	3.085
Electron affinity (A) (eV)	3.280	0.963
Global hardness (η)	1.013	1.061
Global softness (ϕ)	0.987	0.943
Absolute electronegativity (χ)	4.293	2.024
Polarizability (Π^*) (Å ³)	78.439	27.597
Surface area (SA) (Å ²)	307.88	302.58
Surface volume (SV) (Å ³)	281.65	258.86

Langmuir adsorption parameters obtained from the plots (figures not shown) are reported in Table 1. From the presented results, the value of Q_0 is higher for PQ than

for PE. Q_0 is generally equivalent to the coverage of maximum adsorption capacity, indicating an increasing Q_0 value toward better adsorption. Hence, higher Q_0 obtained for PQ confirms that ACBGNS adsorbed PQ better than PE. Freundlich isotherm model's empirical Eq. (11) can be used to describe the adsorption over heterogeneous surface of herbicides (Guo and Wang 2019).

$$\log Q_e = \log kf + \frac{1}{n} \log C_e \quad (11)$$

K_F in the Freundlich's equation describes adsorption capacity constant. The adsorption intensity's empirical parameter can be defined by $1/n$. From this study, it is clear that the capacity adsorption can depend on major factors including the nature of adsorbent and the type of herbicide used. The calculated values of R_L for the two herbicides are given in Table 1 which shows PE and PQ adsorption onto ACBGNS surface is favorable. As tabulated in table, values of n ranged between 0 and 1 qualifying a favorable adsorption.

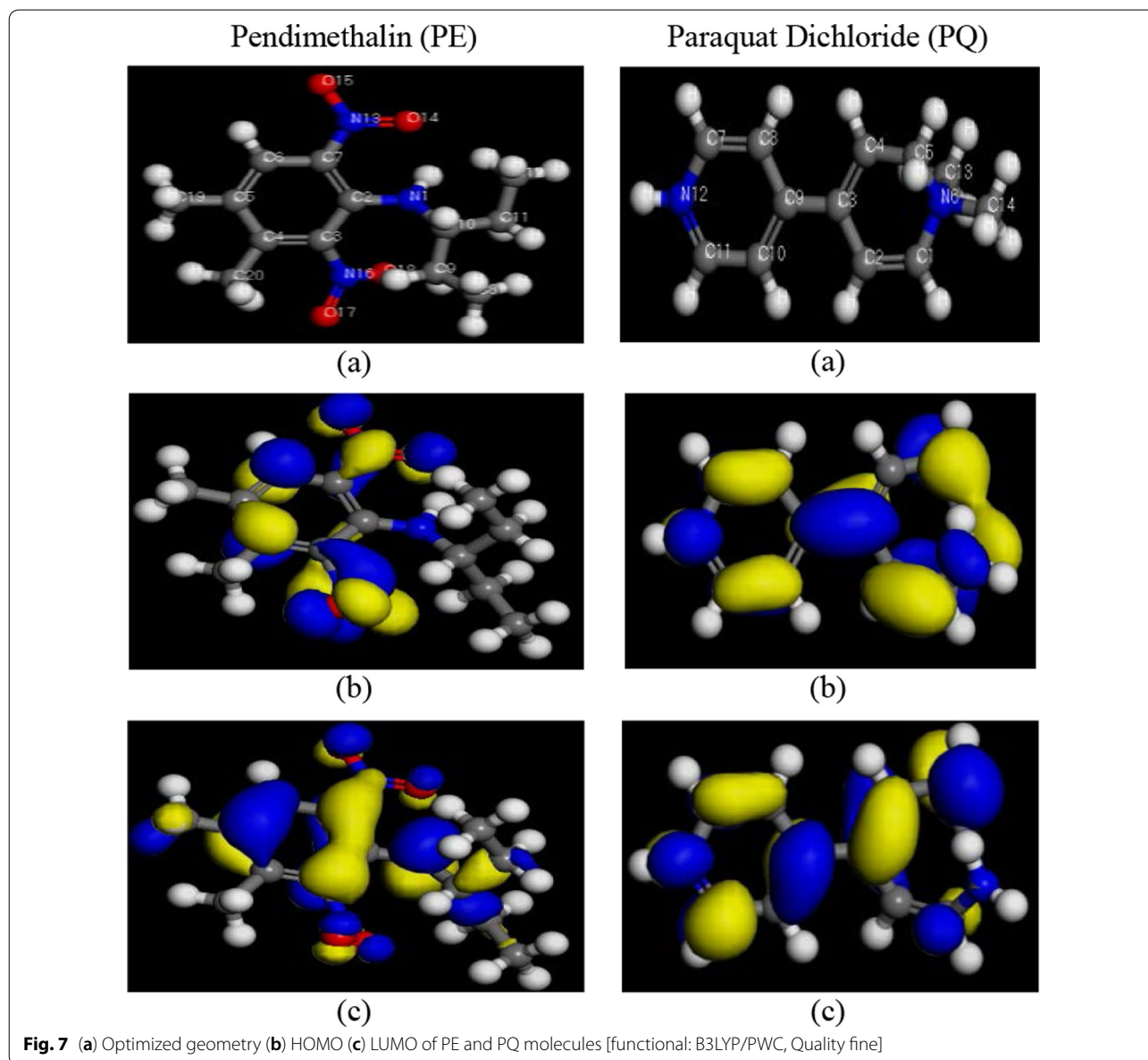
When the surface coverage is related to the adsorption free energy during the interaction of the herbicides with the adsorbent surface, we consider the isotherm described by the Temkin model. In addition, the heat of adsorption associated with the herbicide molecules on the layer is found to decrease proportionately because of adsorbent-adsorbate interaction. This type of adsorbate-adsorbent interaction is associated with uniformly associated binding energies, to reach a maximum value (Al-Saad et al. 2019). This statement is as presented by the following relation in Eq. (12):

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T} \right) \ln C_e \quad (12)$$

The Temkin constant $B = RT/b$ is related to the heat of adsorption, the molar gas constant is R (J/mol K), the temperature is T (K), the adsorption energy variation is

Table 5 Calculated Fukui indices for the studied inhibitor molecules

Molecule	Electrophilic (F^-)				Nucleophilic (F^+)			
	Mulliken		Hirshfeld		Mulliken		Hirshfeld	
	Atom	Value	Atom	Value	Atom	Value	Atom	Value
PE	N(1)	0.105	N(1)	0.096	O(17)	0.124	O(17)	0.100
	O(15)	0.079	O(15)	0.077	O(18)	0.123	O(18)	0.114
PQ	C(5)	0.079	H(13)	0.075	C(11)	0.094	C(11)	0.095



b (J/mol) and the binding constant at equilibrium is b_T (L/mg) which is equivalent to binding energy at maximum value (Araujo et al. 2018). Table 1 contains the

summary of all parameters calculated for Temkin isotherm. From Table 1, both b_T and B values for PE and PQ were reported as 223.81 and 11.07, respectively. The

regression equation and R^2 value observed for this model favorably described the adsorption process of the herbicides onto ACBGNS, across the experimental variables applied. When the values of the correlation coefficient, R^2 , were compared for the three tested isotherms, relatively, the Langmuir model fitted better among others for the adsorption data of herbicide onto ACBGNS.

Kinetic study

The kinetic studies of systems involved in adsorption describe how fast the adsorbate uptake onto the adsorbent is which controls the amount of equilibration time. The adsorption kinetic curves of the PE and PQ molecules on ACBGNS were obtained by subjecting the experimental data obtained to three models of kinetics comprising pseudo-first and second-order and intraparticle diffusion.

(a) Kinetic model of the pseudo-first-order

Equation (13) can be used to define the model (Benkaddour et al. 2018).

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \quad (13)$$

k_1 is the rate constant and q_e is the amounts (mg/g) of PQ while q_t is that of PE adsorbed at equilibrium and time t , respectively. $\log(q_e - q_t)$ was plotted against t , and values associated with k_1 were evaluated from the graph's slope. R^2 values, calculated and experimental q_e values obtained for PE and PQ adsorption onto ACBGNS are presented in Table 2. R^2 was observed to be very low coupled with a reasonable difference established between the adsorption capacity (q_e) values for experimental and calculated, showing failure in experimental data interpretation.

(b) Kinetic model of the pseudo-second-order

This type of second order has been widely to predict kinetics of adsorption processes and the expression is as in Eq. (14) (Hameed et al. 2009).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} (t) \quad (14)$$

Adsorption rate constant is given by k_2 (g/mg min), while t/q_t values were plotted against t (figure not shown). According to the kinetic model of the pseudo-second order, parameters of adsorption of herbicides onto ACBGNS are given in Table 2. From the results, parameters obtained were found to fit the equation with the R^2 values close to unity. There was good correlation between the

calculated and experimental values. The use of this model in adsorption process describing the adsorption of PE and PQ herbicides onto ACBGNS was proved based on such comparison.

(iii) Intraparticle diffusion model

Weber–Moris Eq. (15) predicts the possibility of the sole mechanism through the intra particle diffusion model (Raul et al. 2011).

$$q_e = C + K_{\text{int}} t^{1/2} \quad (15)$$

The constant k_{int} (mg/g min^{0.5}) describes rate of diffusion, while the boundary layer thickness is defined by C . If the rate-limiting step is only through intra particle diffusion, then a linear plot would be obtained when q_t versus $t^{1/2}$ is extrapolated to the origin. If not, there is involvement of other mechanism. The values of the constant C from Table 2 were found to 15.74 and 11.28 for PE and PQ, respectively. It can be concluded that PQ and PE adsorption by the ACBGNS cannot be predicted by this model.

Thermodynamic adsorption study

Notably parameters obtained from thermodynamic evaluations give vital information about the adsorption nature with respect to feasibility and spontaneity of the process. Temperature effects associated with PQ and PE adsorption onto ACBGNS were studied by temperature variation from 303 to 333 K while keeping all other parameters (pH=6 and 8, respectively, for PE and PE, adsorbent dosage 0.2 g, initial PQ concentration=60 mg/l, $t=80$ min) at optimized values. The thermodynamic constants for adsorption which can be used to describe the spontaneity and feasibility of an adsorption process are described entropy (ΔS), free energy (ΔG) and enthalpy (ΔH) changes. Equations (16) and (17) describe them thus:

$$\Delta G = -RT \ln K_c \quad (16)$$

$$\ln k_c = -(\Delta H/RT) + (\Delta S/R) = -\Delta G/RT \quad (17)$$

the temperature being $T(K)$, the gas constant, R , 8.314 J/mol K and k_c the constant of equilibrium which can be obtained from the relation in Eq. (18) (Calvete et al. 2010).

$$k_c = C_a/C_e \quad (18)$$

where C_a is the adsorbed herbicide in mg/L and the equilibrium herbicide concentration is C_e (mg/L). The slope from the van't Hoff's plot and intercept and the values of ΔS and ΔH were evaluated, and Table 3 contains all the

calculated values. ΔH values which were found to be positive show that an endothermic process is involved for the adsorption of the herbicides onto ACBGNS. The positive value of ΔS indicates high randomness at PQ and PE molecules adsorption interphase onto ACBGNS (Gunay et al. 2007). Physical adsorption has values in the range of 2.1–20.9 kJ/mol, which describes the type of adsorption for both herbicides involved in this research, while higher range of 80–200 kJ/mol can be used to qualify chemisorption mechanism. ΔG values which are negative show the adsorption is thermodynamically feasible and spontaneous (Mustapha et al. 2019).

Computational study

Quantum chemical parameters of PE and PQ molecules calculated are presented in Table 4 which shows smaller energy gap (ΔE) of PE as compared to PQ. This gap in energy (ΔE) can be used to describe softness and hardness of a molecule. Lower ΔE (and vice versa) describes soft molecules with tendency of better adsorption compared to hard molecules. Therefore, lower values of ΔE correlate well with the ease of adsorption of molecules onto an adsorbent. Eigen values of E_{HOMO} and E_{LUMO} as presented in Table 4 describe that PQ herbicide adsorption is higher than that of PE which may be due to the presence of chloride ion in solution and lone pairs of nitrogen increase its activity which is in good agreement with that earlier reported here experimentally. Relationship between adsorption and dipole moment is yet to be fully established in literature with most adsorption processes reported to favor lower μ as shown in Table 4. The μ for PQ is lower than that of PE and therefore better adsorbed. The adsorption ability of a chemical compound can be controlled by its binding energy (E_{B}), surface volume (SV), surface area (SA). The higher the values of SV, SA, E_{B} obtained, then the process of protonation, hydration and subsequent adsorption on a surface for a given molecule becomes more difficult. Therefore, lower values of these parameters associated with PQ herbicide show that it is better protonated, hydrated and adsorbed on ACBGNS than PE herbicide.

In the presence of charge atmosphere, polarizability can be defined as a measure of the behavior of molecular species. Tendency of the ease of a molecule to be adsorbed is related to better response. This explains why PQ herbicide is better adsorbed on ACBGNS than PE herbicide. Better adsorption of PQ is also favored by their SV and SA values which are low. It is established that molecules compete with difficulty to fit into the adsorption matrix of the adsorbent when the values of surface area and volume of the adsorbate are large.

An index, the function of Fukui can be used to assess the local reactivity (hence adsorption) of a molecule on

the basis of the constituent atoms which are electronic in nature (Alokut et al. 2017). Based on electrophilic and nucleophilic nature of the chemical reactivity of a molecule, Fukui indices provide useful information about the reactive centers (Mohan and Joseph 2018; Zohdy et al. 2021). Threshold values of f_k^+ and f_k^- control nucleophilic and electrophilic centers of in a given molecule. PE and PQ herbicide's Fukui functions are shown in Table 5. F^- for PE and PQ molecule have their highest Mulliken and Hirshfeld charges on N(1) and H(13), C(5) while for the nucleophilic (F^+), PE herbicide on O(17), O(18) and PQ herbicide are on the aromatic ring N(5) shown in Table 5. Therefore, the adsorption of PE on ACBGNS occurs through the nitrogen atom while that of PQ occurs via the aromatic ring of the molecule. Optimized geometry, Frontier orbital diagrams of PE and PQ herbicides are reported in Fig. 7. Within the diagrams, red loop shows positive sites while negative charges are displayed in blue loops on the molecules.

Conclusions

The present study has demonstrated that activated Bambara groundnut shell can be used as a natural, promising, economic and environmentally friendly adsorbent for PE and PQ removal from aqueous solutions. FTIR, SEM, moisture content, pore volume and bulky density were used to analyze for the functional groups and surface area that are responsible for the herbicide ion removal from aqueous solutions. The batch adsorption method is dependent on the contact time, dosage, solution pH and initial herbicide ion concentrations. The experimental data in the adsorption process indicated good correlations with the pseudo-second-order kinetic model and Langmuir isotherm. The thermodynamic study showed that the process is highly endothermic in nature, with positive value of ΔH and change in ΔS . Based on this study, the readily available Bambara groundnut shell which is cheaply available to the environment could be used as a natural adsorbent, due to its high removal efficiencies of the herbicide ion involved in this study. Studied computational parameters and that of the experimental supported each other with high degree of similarities.

Abbreviations

PE: Pendimethalin; PQ: Paraquat dichloride; ACBGNS: Activated Bambara groundnut shells; DFT: Density functional theory; ΔG : Change in Gibbs's energy; ΔH : Change in enthalpy; ΔS : Change in entropy.

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Authors' contributions

AMA did the conception and designed of the work, TAN performed the experiment and interpreted the data and was a major contributor in writing the manuscript, and HFC substantively revised the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing of interests.

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