

Sorption Energies for Atrazine onto Devolatalized *Vitellaria paradoxa*

Itodo, Adams Udoji**

Department of Chemistry, Kebbi State University of Science and Technology, Aliero, NIGERIA

Abdulrahman, Funke Wosilat

Department of Chemistry, University of Abuja, NIGERIA

Hassan, Lawal Gusau

Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto, NIGERIA

Happiness, Ugbede Itodo

Department of Chemistry, Benue State University, Makurdi, NIGERIA

ABSTRACT: We utilize isotherm models in contributing to scholarly knowledge in simple terms, to measure the forces or energy defining certain adsorption phenomenon. Gas Chromatography coupled with Mass Spectrophotometer detector (GCMS) was utilized to measure equilibrium phase atrazine after adsorption onto Shea nut Shells (SS) acid derived activated carbon. Data were fitted into the D-R and Temkin isotherm relationships for energy data estimation of Sorption energy value (B_D), mean free energy (E_D) and heat of sorption (B). They were estimated as $0.7600\text{mol}^2\text{KJ}^{-2}$, 0.8111 kJmol^{-1} and 0.790Jmol^{-1} respectively. The parameter predicting the type of adsorption was evaluated B_D , $B < 20\text{kJ/mol}$ and $E_D < 8$ which is an indication that physisorption (Non specific adsorption) dominates chemisorption and ion exchange. The D-R model with a higher correlation coefficient values, $R^2 = 0.979$ proves a better choice in explaining sorption energies. Generally, shea nut shells can be used as alternative precursors for activated carbon production via the two steps and acid treatment method..

KEY WORDS: Isotherm, Atrazine, Sorption energies, *Vitellaria paradoxa*, Dubinin-radushkevich, Temkin.

INTRODUCTION

The quality evaluation of activated carbon with parameters like adsorption capacity, intensity, thermodynamics and kinetics are as vital as the

estimation of certain energy parameters namely mean free energy, sorption energy etc. An approximation from such energy parameters gives a clue to the type of adsorption

* To whom correspondence should be addressed.

+E-mail: itodoson2002@gmail.com

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as either physisorption, chemisorptions, ion exchange or complexation.

Previous studies have shown that herbicide (atrazine) disrupt the production and functionality of human hormones and a higher incidence was reported for cases of cancer in humans and laboratory animals [1]. The use of active carbon was prescribed by USEPA as the best available technology for the removal of atrazine from drinking water. Many studies have revealed adsorption of atrazine using conventional activated carbon granules and fibres. A chemical activation using activating agents is a new generation of adsorption fibre development. Adsorbents obtained with this method provides higher yield, high surface area, high mesopores volumes and some unusual pore surface chemistries [1,2,3]. The sorption of herbicide by activated carbon were previously reported [1,2,4]. This present study reports atrazine sorption, not in a micro quantity ($\mu\text{g/L}$) but within a quantity range (g/L) that could account for both the topical and systemic level of poisoning reportedly associated with atrazine [5].

Basics of adsorption

Adsorption is actually a mechanism in which the forces of interaction between surface atoms and the adsorbate molecules are similar to Van der Waals forces that exist between all adjacent molecules. There are both attractive forces and repulsive forces with the net force depending on the distance between the surface of the adsorbent and the adsorbate molecule [6]. Adsorption is also defined as a process in which a soluble chemical (the adsorbate) is removed from fluid by contact with a solid surface (the adsorbent). It is the trapping of impurities by strong physical bond within the porous structure of carbon. It is one of the many processes used to purify, concentrate, or separate component [7]. Adsorption competes with other processes like evaporation, solvent extraction, distillation, sublimation, drying, sedimentation, filtration, screening, ion exchange, centrifugation, and absorption [7]. It is used in industry for product separation and waste treatment. In general, adsorption is the process by which a component moves from one phase to another while crossing some boundary. It was found that the observed effect of adsorption was achieved within porous solids and that adsorption was the result of interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase [8].

Enhance adsorption via surface activation

The surface of an adsorbent is typically composed of various Surface Functional Groups (SFGs). Adsorption of organic adsorbate is greatly dependent on the amount and nature of surface oxide groups [6]. Surface functional groups (carbon/oxygen) are created by oxidation occurring during the activation process of an adsorbent. Some of the common basic functional groups created are lactones, quinones, and carboxylates [8]. while some of the common acidic functional groups created are phenolic, hydroxyl, carbonyl, and carboxylic acids [8]. The presence of oxygen-containing basic groups such as are a key factor in promoting irreversible adsorption [9]. Strongly dissociated adsorbates are weakly adsorbed when compared to non-dissociated [9]. The more non polar an adsorbate, the higher the adsorption capacity. This is attributed to the fact these adsorbate molecules tend to prefer the adsorbent surface rather than being in the solution [6]. It has also been shown that an increase in the molecular weight of the adsorbate will generally enhance adsorption until the size of the adsorbate is larger than the pore size of the adsorbent. Typically, aromatic compounds are more adsorbable than aliphatic compounds of similar molecular size and branched-chain molecules are generally more adsorbable than straight-chain molecules [6]. In addition, solubility of the adsorbate is also an important factor. In general, the lower the solubility of the adsorbate, the higher the adsorption capacity since the forces of attraction between the adsorbate molecules and the adsorbent surface molecules will be greater than the forces of attraction between the adsorbate and the solvent molecules [6].

Classes of adsorption based on energy values

Chemisorption

This is a shorter way of writing chemical adsorption. It is also called specific adsorption and limited to monolayer coverage of the substrate. Here, a covalent bond is formed between the adsorbate and adsorbent. The enthalpy of chemisorption is within the range of 200kJ/Mol [10].

Physisorption

This stands for physical adsorption. It is also called non specific adsorption which occurs as a result of long

range weak Van der Waals forces between adsorbates and adsorbents. The energy released when a particle is physisorbed is of the same magnitude as the enthalpy of condensation. The enthalpy of physisorption is measured by monitoring the rise in temperature of a sample of known heat capacity. Typical values are in the region of 20 kJ /Mol [10].

Chemisorption occurs at high temperatures with a significant activation energy. Thus, it involves strong bonds and the process is irreversible. The heat of adsorption is typically high in chemisorption and it is similar to heat generated during a chemical reaction. There are several factors that impacts physical adsorption [6,11]. The major factors which affect physical adsorption include the surface area of the adsorbent, pore structure of the adsorbent, surface chemistry of the adsorbent, nature of the adsorbate, pH of the solution, and the presence of competing adsorbates. It is due to these factors, physical adsorption is considered to be a complex phenomena. Surface area of the adsorbent is one of the most important factors in which adsorption greatly rely. The surface area is comprised of two types, the external surface area and the internal surface area (pore walls). When molecules are larger than the pore diameter, lesser adsorption would take place because of steric hindrances.

Adsorption isotherm

Isotherms are empirical relationship used in predicting how much solute can be adsorbed by activated carbon [12]. Chilton *et al.*, [13] defined adsorption isotherm as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent (activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium. It maps out the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations [13]. The adsorption isotherm is based on data that are specific for each system and the isotherm must be determined for every application. An adsorption isotherm beside providing a panorama of the course taken by the system under study in a concise form indicate how efficiently a carbon will allow an estimate of the economic feasibility of the carbons' commercial application for the specific solute [13].

Dubinin-Radushkevich (D-R) isotherm

This isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is represented by the Eq. (1) below:

$$q_e = q_D \exp (- B_D [RT \ln (1 + 1/C_e)] \quad (1)$$

Where, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface [14,15]. The linear form of equation 1 is given as Eq. (2);

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

A plot of $\ln q_e$ against $RT \ln (1 + 1/C_e)$ for modified sorbents is expected to yield a straight line and this is an indication of a good fit of the D-R isotherm for the experimental data. The apparent energy (E_D) of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relation given as Eq. (3) below [14].

$$E_D = \sqrt{1/2B_D} \quad (3)$$

Temkin adsorption isotherm

The Temkin isotherm was tested for equilibrium description at room temperature. The model was respectively represented by equations 4 and 5 below. Therefore, a plot of q_e versus $\ln C_e$ enable the determination of the constants A and B. Where B is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K), b is Temkin isotherm constant and T is the temperature (K). [16,17].

$$q_e = B \ln (A + C_e) \quad (4)$$

$$\text{Where } B = RT/b \quad (5)$$

Choice of equipment

The gas chromatographic technique is at best a mediocre tool for qualitative analysis. It is best used with other technique to answer the question of what is present in a sample. Besides the simplicity of the instrument, ease of operation. GC also provides the answer to how much? It is an excellent quantitative analytical tool in quantifying micrograms in a litre or one volume in

millions of volumes [18]. The sample herbicide (containing atrazine) is a multicomponent mixture containing atrazine (test sample) and other organochlorine moieties, which are very similar to atrazine. Secondly, the GC column has a very high efficiency which was claimed to be in excess of 400,000 theoretical plates. The column is about 100m long, a very dispersive type of stationary phase retaining the solute approximately in order of increasing boiling point. Helium carrier gas was selected since it can realize high efficiencies with reasonable analysis time [19]. Techniques of external standardization entails the preparation of standards at the same levels of concentration as the unknown in the same matrix with the known. These standards are then run chromatographically under ideal conditions as the sample. A direct relationship between the peak size and composition of the target component is established and the unknown was extrapolated graphically

Aim of this work

In this present work, chemically activated carbon was formulated to adsorb atrazine traces from water. This research was based on an initial qualitative study based on atrazine sorption as earlier predicted by FTIR analysis [20] and to further compliment the kinetic study of the same sorption process earlier investigated [21]. The specific objectives include; Generation of activated carbon thereby adding values to the wastes and to predict sorption energies by evaluation of the mean free and apparent energy using both Temkin and D-R isotherm models.

EXPERIMENTAL SECTION

Branded named herbicide (atrazine[®]) presumably 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine, with specification of 50% atrazine was procured from a retailer's stand of the agro-chemical wing of Sokoto central market, Nigeria. The substrates, Shea nut Shells (SS) was randomly collected from waste depots within Rikoto- Zuru in Kebbi. Gas chromatography coupled with Mass spectrophotometer detector (Shimadzu GC/MS QP2010 Plus model, Kyoto Japan) located at the National Research Institute for Chemical Technology, Zaria was implored for equilibrium phase atrazine estimation. Activating agents and all other reagents of analytical grades were procured from Prolabo Chemicals and supplied by the general research laboratory of

Usmanu Danfodiyo University, Sokoto Nigeria. They were used as received.

Sample treatment and preparations

The method of sample treatment by Fan *et al.*, [22] and that of Itodo *et al* [15, 20] were adopted. The shea nut shells were washed with plenty of water to remove surface impurities and sundried, then, dried in an oven at 105°C overnight [23]. The samples were separately pounded/ grounded followed by sieving with a <2mm aperture sieve. The less than 2mm samples were stored in airtight containers. About 3g of each pretreated biosolid (< 2mm mesh size) were introduced into six (6) different clean and pre weighed crucibles. They were introduced into a furnace at 500°C for 5 minutes after which they were poured from the crucible into a bath of ice block. The excess water was drained and the samples were sun dried. This process was repeated until a substantial amount of carbonized samples were obtained [24]. The carbonized sample was washed, using 10% HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid [22]. The solids were then sun dried, then, dried in the oven at 100°C for one hour. Accurately weighed 2g each of already carbonized samples were separately mixed with 2cm³ of each 1M activating agent (H₃PO₄ and ZnCl₂). The samples were introduced into a furnace, heated at 800°C for 5 minutes. The activated samples were cooled with ice cold water. Excess water was drained and samples were allowed to dry at room temperature [24]. The above procedure was repeated for different residual time (5min and 15 min). Washing of the above sample was done with 10% HCl to remove surface ash, followed by hot water and rinsing with distilled water to remove residual acid [22]. Washing was completed when pH of the supernatant of 6-8 was ascertained [25]. The sample were dried in an oven at 110°C overnight and milled or grounded, followed by filtration to different mesh size and stored in air tight container.

Atrazine standard solution for equilibrium studies

For the sorption/equilibrium studies, several concentrations viz; 10, 20, 30, 40 and 50g/L Herbicide equivalent of 5, 10, 15, 20 and 25g/L Atrazine was prepared by respectively dissolving 0.25, 0.5, 0.75, 1.0 and 1.25g of herbicide into a conical flask, poured gently

into a 25cm³ volumetric flask, homogenized and made to the mark with chloroform (i.e. 5,000ppm – 25,000ppm atrazine).

GC/MS conditioning

The GC/MS column was held at 60°C in injection volume of 1μL and then programmed to 250°C. It was set at a start m/z of 40 and end m/z of 420. The detector (mass spectrophotometer) was held at 250°C above the maximum column temperature. The sample size was 1μL, which was split 100⁻¹ onto the column and so the total charge on the column was about 1. Helium was used as the carrier gas at a linear velocity of 46.3cm/sec and pressure of 100.2kPa. Ionization mode is electron ionization (EI) at a voltage of 70eV. In this analysis, Amplification and resolution for test herbicide was achieved by adjusting the threshold to 6000. Thus, worse interference and solvent peaks were screened out leaving majorly the deflection of target compound (atrazine) as it was made pronounced on the chromatogram. Sorption efficiency of an adsorption process was defined based on the fractions of extracted and unextracted sorbates [18]. A three point calibration curve was made from 1.0, 5.0 and 10.0g/L atrazine solution. These standards were run chromatographically under ideal conditions. A direct relationship between the peak height or size and concentration of target was established. The unknown was extrapolated graphically [18].

Batch equilibrium experiment

5g of substrate was diluted to the mark of 100cm³ volumetric flask. This concentration of 50g/L herbicide is equivalent to 25g/L or 25,000ppm atrazine stock. 10cm³ of the atrazine solution was interacted with 0.1g of each sorbent and allowed to stand for 12hours. The mixture was filtered and the filtrate was analyzed with a GCMS for atrazine equilibrium phase concentration [26].

The amount of atrazine at equilibrium, q_e was calculated from the mass balance equation described as Eq. (6) [27].

$$q_e = (C_0 - C_e) V/W \quad (6)$$

C_0 and C_e are the initial and final dye concentrations (mg/L) respectively. V is the volume of dye solution and M is the mass of the acid catalyzed Poultry waste sorbent (g).

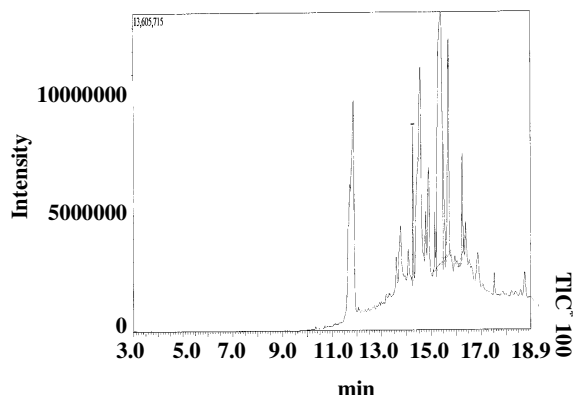


Fig. 1: GC/MS chromatogram of equilibrium concentration atrazine after adsorption onto SS/A/5g/L⁻¹ sorbent (Carrier gas-Helium 100.2 kpa, Column temperature -60°C, Injection temperature-250°C, Injection volume—1μL, Flow rate-1.61mL/min, Injection method- split, Linear velocity- 43.6cm/sec.)

While t is the equilibrium contact time, when $q_e = q_t$, Eq. (6) will be expressed as Eq. (7) below:

$$q_t = (C_0 - C_t) v/w \quad (7)$$

where $q_e = q_t$ and C_t is the concentration at time, t . The percent dye removal (RE %) was calculated for each equilibration by the expression presented as Eq. (8):

$$RE(\%) = (C_0 - C_e) / C_0 \times 100, \quad (8)$$

Where RE (%) is the percent of dye adsorbed or removed. The % removal and adsorption capacities were used to optimize the activation condition. The test were done at a constant temperature of 27±2°C [28]. The equilibrium concentration of atrazine (herbicide), q_e and Adsorption efficiency (% Removal) were estimated. The extent of atrazine removal (by difference) from chloroform spiked with 25g/L of atrazine was expressed as Eq. (3) [27].

RESULTS AND DISCUSSION

The chromatogram shown as Fig. 1 stands for unadsorbed atrazine out of the 5g/dm³ atrazine which was interacted with SS/A sorbent. The chromatogram was characterized by a baseline disturbance. This is caused by either hydrocarbon impurities or by impure carrier gas [18]. The former could be linked to the fact that the sorbate concentration (5g/dm³) is too low for the 0.1g carbon dose. Unoccupied pore size could as well, lead to

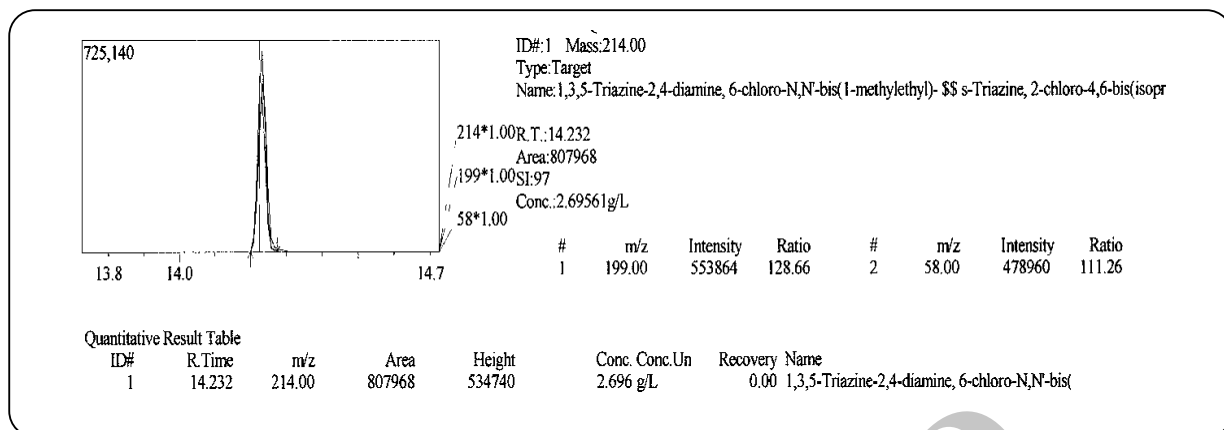


Fig. 2: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/5g/L⁻¹ sorbent.

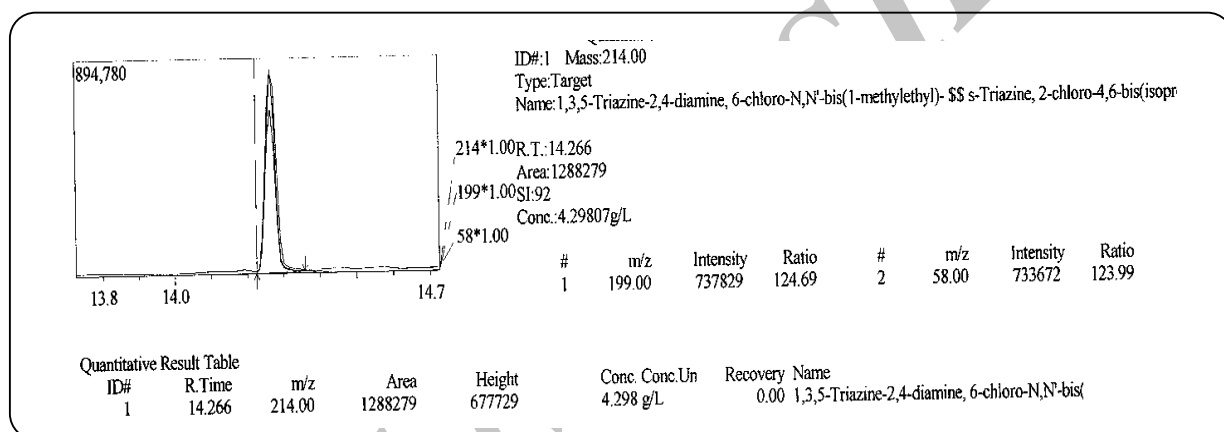


Fig. 3: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/10g/L⁻¹ sorbent.

desorption of the sorbate with a resultant poor percentage removal (46.08%).

The equilibrium experimental data from Figs. 2 to 6 were treated as Table 1.

Effect of initial atrazine concentration on removal efficiency

Table 1 presents the role played by initial sorbate concentration and its effect on sorption efficiency. The highest percentage atrazine removal was observed with the interaction of 0.1g atrazine with 10cm³ of a 25g/L atrazine solution. Hence, out of the 25g/L, 20g/L, 15g/L, 10g/L and 5g/L initial atrazines concentration, a total of 16.581, 12.538, 9.007, 5.702 and 2.696g/L atrazine was attracted onto the sheanut shell (SS) bioadsorbent. These

accounts for a 66.324, 62.69, 60.007, 57.020 and 46.080% removal efficiency respectively.

For a 1hour interaction time and within the 0.1g sorbent dose per 10cm³ sorbate solution, The following was evidently observed

(i) Adsorption efficiency increases with initial sorbate concentration.

(ii) Adsorption within the low sorbate concentration (5 - 10g/dm³) range could possibly be followed by desorption. Hence, a less than 50% adsorption was investigated.

(iii) Adsorption of fairly high concentrated atrazine (15 - 25g/L) could be governed by a multilayer adsorption with resultant intraparticle attraction. In light of this, sorption efficiency or percentage sorbate uptake is greater than 60%.

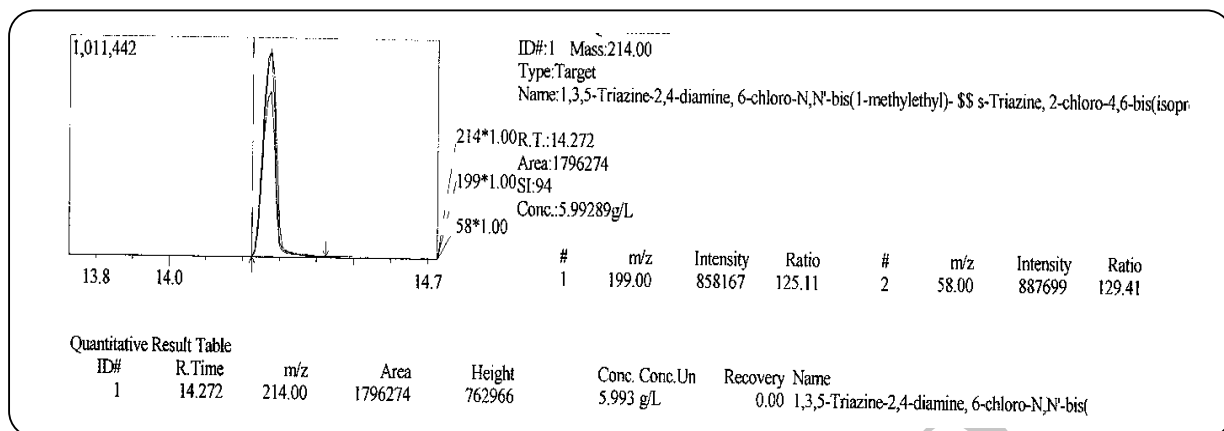


Fig. 4: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/15g/L⁻¹ sorbent.

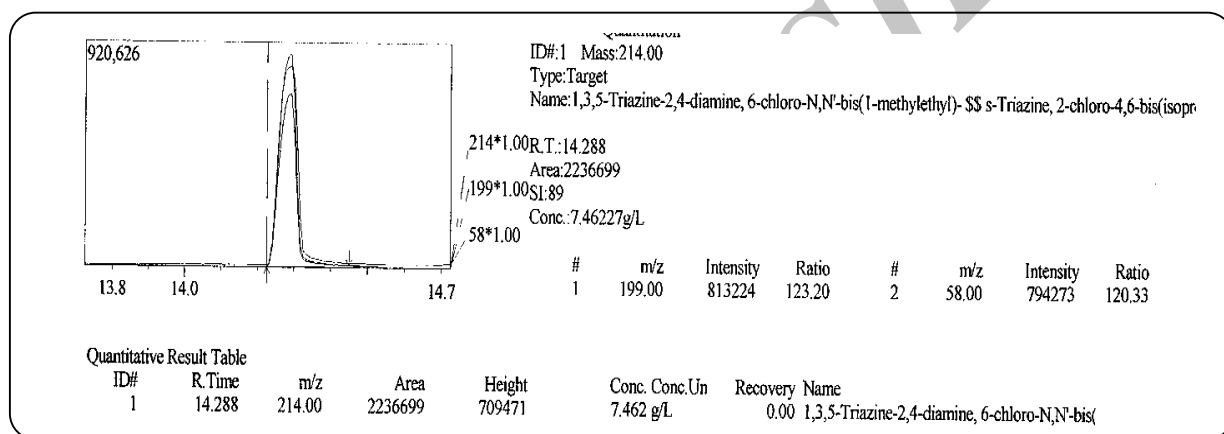


Fig. 5: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/20g/L⁻¹ sorbent.

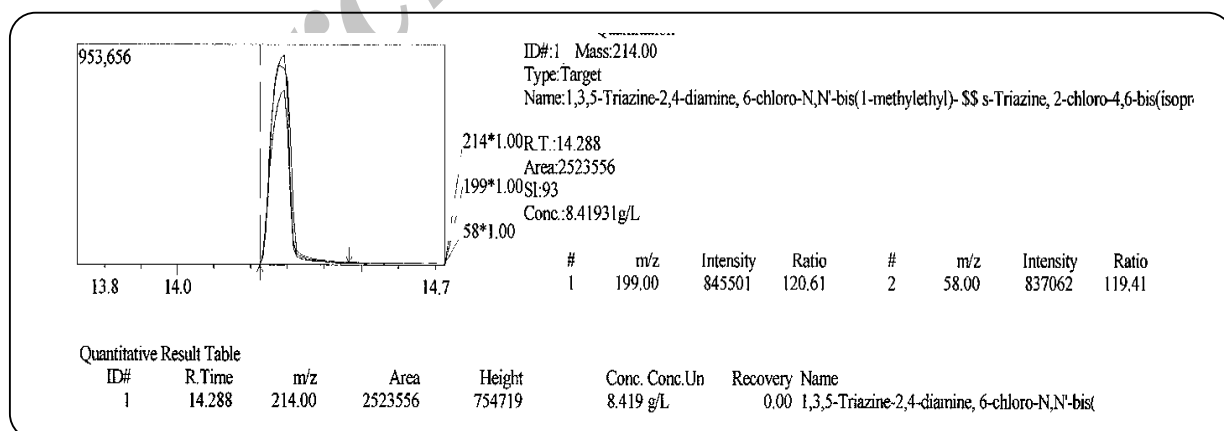


Fig. 6: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/25g/L⁻¹ sorbent.

Table 1: Adsorption experimental data of atrazine uptake by fixed mass of SS-sorbents at different initial sorbate concentration, using GC/MS

Sorbent	Co (g/dm ³)	Ce (g/dm ³)	Ca (g/dm ³)	% RE	Ads.m (mg.10 ⁻³)	q _e (mg/gx 10 ⁻³)	K _c
SS/A/5	5	2.696	2.304	46.08	0.0230	0.230	0.854
SS/A/10	10	4.298	5.702	57.02	0.0570	0.570	1.327
SS/A/15	15	5.993	9.007	60.047	0.0901	0.901	1.503
SS/A/20	20	7.462	12.558	62.69	0.1254	1.254	1.680
SS/A/25	25	8.419	16.581	66.324	0.1658	1.658	1.969

SS/A/15 -Sheanut shells, treated with H₃PO₄ activated for 15 minute dwell time, SS/A/25 -Sheanut shells, treated with H₃PO₄ activated for 25 minute dwell time

Table 2: Temkin and R-D Adsorption experimental GC/MS data for atrazine uptake by chemically modified SS-sorbent.

Isotherms	Relationship (Y=)	R ²	Parameters (constant)	Values.
Temkin	0.790x - 0.947	0.927	b (Unitless) B(J/mol) A(Lg ⁻¹)	3158.794 0.790 3.316
R-D	-9.466x-2.360	0.979	q _D (mgg ⁻¹)	4.37x10 ⁻³
			B _D (Mo1 ² KJ ⁻²)	0.7600
			E _D (kjmo1-2)	0.8111

Sorption isotherm modeling

The high regression or determination coefficient, R² value (0.979) for Dubinin-Radushkevich model was an indication that D-R isotherm gave very good description of the sorption process, over the range of chosen concentrations. The apparent energy of adsorption and Dubinin-Radushkevich isotherm constants are shown on Table 2. Their values were obtained from the plot of type in Fig. 7. The high values of q_D shows high sorption capacity. The values of the apparent energy of adsorption (E_D < 8.0) also depict physisorption process [29].

The two isotherms experimental data on Table 2 were used to estimate certain energy parameters. The Dubinin-Radushkevich, (R-D) isotherm model is more general than the Langmuir isotherm as its deviations is not based on ideal assumptions such as equipotential of sorption sites, absence of steric hindrances between sorbed and incoming particles and surface homogeneity on microscopic level [29]. The estimated constant, B_D, related to adsorption energy was presented as 0.7600 mol²kJ². This constant gives an idea about the mean free energy which was valued as E_D= 0.811 kJmol⁻¹. E_D is a parameter used in predicting the type of adsorption. An E_D value < 8 kJmol⁻¹ is an indication of physisorption [29].

The R-D Theoretical saturation capacity, q_D and the Langmuir maximum adsorption capacity, q_m were both estimated as q_D = 4.37x10⁻³mgg⁻¹ and q_m = 0.772x10⁻³mgg⁻¹. No known and proven reference could make us conclude that the theoretical saturation capacity, q_D is always higher than the maximum adsorption capacity as the case was made evidence in this research.

The Temkin constant related to heat of sorption, B was estimated as 0.790 J/mol. The unitless quantity, b (3158.794) and Temkin constant, A (3.3159 Lg⁻¹) were in good agreement with values presented by Hameed [17] on the Evaluation of papaya seed adsorbent.

In the energy parameter models, R-D and Temkin were used to present sorption energy value (B_D), mean free energy (E_D) and heat of sorption (B). They were estimated as 0.7600mol²KJ⁻², 0.8111 kJmol⁻¹ and 0.790Jmol⁻¹ respectively, the parameter predicting the type of adsorption which was evaluated as E_D<8.0 is an indication that physisorption dominates chemisorption, ion exchange etc. The R-D model with a higher correlation coefficient values, R² = 0.979 proves a better choice in explaining sorption energies. Besides the E_D validation test, The mean free and energy values and heat of sorption values (kJ/mol) were less than 20KJ/mol. This

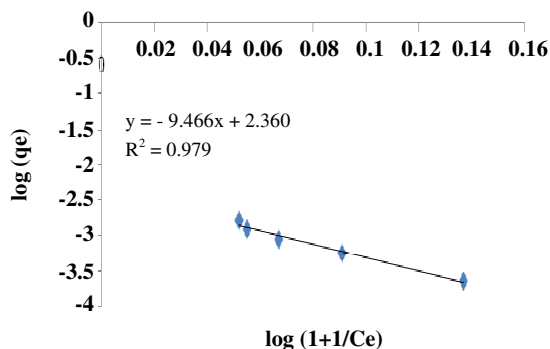


Fig. 7: GC/MS analysis for D-R adsorption isotherm of atrazine uptake onto acid catalyzed shea nut shell biosorbent.

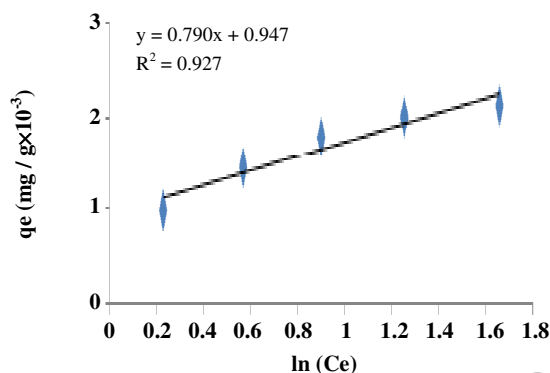


Fig. 8: GC/MS analysis for D-R adsorption isotherm of atrazine uptake onto acid catalyzed shea nut shell biosorbent.

situation, according to *Atkins* [10] is a characteristics of physisorption. In his report, the enthalpy of physisorption was measured by monitoring the rise in temperature of a sample of known heat capacity to give typical values in the region of less than 20kJ /Mol [10]. He also argued that chemisorption is a specific adsorption and limited to monolayer coverage of the substrate. Here, a covalent bond is formed between the adsorbate and adsorbent. The enthalpy of chemisorption is within the range of 200kJ/Mol [10]. Reports (Unpublished) on surface coverage in this experiment fitted best into the Freundlich isotherm (sorption on heterogeneous surface). Hence, adsorption is not restricted to monolayer coverage as purposed for chemisorption.

CONCLUSIONS

Highlights of this research showed that sheanut shells can be used as alternative precursors for activated carbon

production via the two steps and acid treatment method. On the same fashion, sorption quantification was feasibly observed for a multicomponent system (Herbicide) using a gas chromatography coupled with mass spectrophotometer detector. A physisorption type of adsorption was predicted for the process, a controlled zero emission and waste management alternative was also arrived at adding value to the sheanut shells .

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