

Adsorptive Capacity of *Prosopis Africana* Husks on Pesticides

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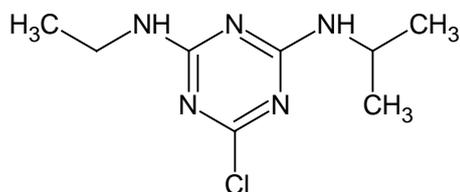
Abstract: The adsorptive capacity of ammonia-treated activated *Prosopis Africana* pod husks (APAPH) and carbonized activated *Prosopis Africana* pod husks (CPAPH) on atrazine was studied. All the adsorbents derived shows favorable physicochemical attributes (pH, bulk density, attrition, iodine adsorption number/surface area, titratable surface charge, SEM and FT-IR analysis). Batch adsorption studies were also carried out under the effect of operational parameters such as initial atrazine concentration (10-60 mgL⁻¹), initial solution pH (2-12), adsorbent dosage (0.5-2.5 g), contact time (30-240 Min), and temperature (300-350 K). Depending on the adsorbents, optimal removal of atrazine was: CPAPH (66.0 %) and APAPH (56.5 %). Equilibrium adsorption data obeyed isotherm models in the order (Langmuir > Dubinin-Radushkevich > Temkin > Freundlich).

Keywords: *Prosopis Africana*, Atrazine, activated carbon, adsorption, capacity

1. Introduction

Pesticides have been detected in soil, surface and groundwater throughout the world (Ijpelaar *et al.*, 2006) which is as a result of indiscriminate use of large quantity of pesticides to control, combat pests in order to ensure higher productivity of crops. Among the herbicides systematically monitored in our environments, atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) emerges as the most common and Prolific (Antonio *et al.*, 2010). Atrazine is a pre and post emergent herbicide used in the control of weeds mainly in crops of maize, sugar cane and sorghum (Chirside *et al.*, 2009). A significant amount of the pesticide may remain in the soil which in turn drains into surface waters. Pollution by pesticides has been revealed to affect aquatic life (Ijpelaar *et al.*, 2006). To address this, the World Health Organisation (WHO) has produced guidelines for exposure limits for individual pesticides in drinking water (Yokley and Cheung, 2000).

Although herbicides are the largest group of pesticides in terms of the number of compounds and total weight used, insecticides have historically posed the major environmental and health hazards (Yokley and Cheung, 2000). Atrazine is a selective systemic herbicide use for control of weed. The mode of action for atrazine is through inhibition of photosynthesis in the target plants. Atrazine is a soluble substances which can be transported in dissolved form from one place to other (Pathak and Dikshit, 2012).



Chemical Structure of Atrazine

Recent studies have shown that the aromatic structure of atrazine could be metabolized to gaseous end products in mixed cultures under methanogenic conditions (Raj and Anil, 2012). *Prosopis africana* is a leguminous plant of the Fabaceae family. It is a flowering plant that is locally called “kiriya” in Hausa, “okpehe” in Idoma and “gbaaye” in Tiv languages of Nigeria (Chidi *et*

al., 2012). It was originally found in the Sahel and Savannah forests of Senegal to Ethiopia. The trees of *P. africana* are common in the middle belt and northern parts of Nigeria (Aremu *et al.*, 2006). It grows to a height of 4-20 m, with slightly rounded buttress roots and dark stem bark, which is scaly, slash and has white streaks. It flowers once a year. The fruits are smooth, hard pod-like capsules having banana fruit shape and are brown-black in colour. The seeds are many, tiny and very hard, brownish-black in colour with high resistance to water and insect attack. It is traditionally used for formulation of animal feeds and preparation of local condiments through boiling and fermentation processes (Aremu *et al.*, 2006).

In Nigeria and many parts of West Africa, the seed hulls from this process lie as wastes and constitute environmental concern, therefore, good handling of the waste materials generated from this process could result in waste minimization and tremendous cost saving (Afidah and Zaharaddeen, 2015).

Prosopis africana tree is of great value to man and animal economically; it fixes nitrogen to enrich the top soil, generates timbers and produces protein rich leaves and sugary pods used as feed for animals (Annongu *et al.*, 2004). However, the disadvantage of *Prosopis* is of high content of anti-nutritive such as tannins, *prosopine* and toxic amino acids which are capable of causing adverse effect on simple stomachs when consumed without proper processing (Yusuf *et al.*, 2008). Consequently, the specific objectives of the present study were to prepare, characterize, and evaluate the effectiveness of adsorbents from *Prosopis Africana* pod husks (PAPH) (biomass) to remove Atrazin, a common herbicides from aqueous phase, with emphasis on adsorption equilibria.

2.0 Experimental

2.1 Preparation and characterization of *P. Africana* pod husk adsorbents

P. africana pod husks (PAPH) were collected locally from different places in Otukpo and Adoka both in Benue State, Nigeria and were identified with LA 70874-4490 USA batch number. They were washed with water and raised with distilled water to remove dirt, air dried for 24 h, pulverized using a locally made grinder and sieved into particle size of 2 mm to generate the adsorbent precursor (Zaharaddeen and Afidah, 2014). The sieved material was chemically treated by steeping it in a saturated ammonium chloride solution for 24 h (Wuana *et al.*, 2016).

The slurry was filtered and the residue rinsed repeatedly with distilled water and air-dried to serve as the chemically (ammonium chloride) treated adsorbent (APAPH). A portion of APAPH was pyrolyzed in a muffle furnace at 350 K for 2 h. The resulting carbon was washed repeatedly with distilled water to remove ash, air-dried, and stored as the carbonized adsorbent (CPAPH).

The adsorbents were further characterized physico-chemically. Adsorbent pH was determined by dispersing 1.0 g triplicate samples of the adsorbent in distilled water for 4 h and measuring the pH of the resulting filtrate (Wuana *et al.*, 2015). Bulk density was determined by the tamping procedure of Ekpete and Horsfall, 2011. Attrition was determined by a procedure described by Toles *et al.*, 2000. Adsorbent surface area was determined by the iodine adsorption number method during which, a 0.5 g portion of the adsorbent was treated with an excess of standard iodine solution followed by back-titration of the unreacted iodine with

standard sodium thiosulphate solution (Wuana et al., 2015). A blank titration was also performed on an aliquot of iodine solution not treated with the adsorbent. The iodine number, n_{I_2} (i.e. amount in moles of iodine adsorbed per g adsorbent) was calculated using Eq. (1); while the adsorbent surface area, A (m^2/g) was calculated with the aid of Eq. (2), a modified form of that of Wuana et al., 2015

$$n_{I_2} \left(\frac{mol}{g} \right) = \frac{C_{S_2O_3^{2-}}(V_b - V_s)}{2 \times 10^3 M_a} \quad 1$$

$$A(m^2/g) = N_o \left(\frac{C_{S_2O_3^{2-}}(V_b - V_s)}{2 \times 10^3 M_a} \right) \sigma_{I_2} \quad 2 \quad \text{where } C_T \text{ is}$$

the concentration of the thiosulphate ($molL^{-1}$), V_B and V_S are, respectively, the titer values of the blank and adsorbent-treated iodine solutions (L); m_{AD} is mass of the adsorbent used (0.5 g); N_o is the Avogadro's number; and σ_{I_2} is the cross-sectional area of an iodine molecule (m^2), given as $3.2 \times 10^{-19} m^2$. Titratable surface charge was determined by the Boehm titrimetric method described by Van Winkle (2000). pH point of zero charge determination by Ekpete and Horsfall, (2011). Fourier transform infrared analysis utilized the FT-IR (Agilent-CARY-630), and was performed according to the manufacturer's specifications.

2.2 adsorption experiments

Batch adsorption experiments were designed to evaluate the effect of different operational parameters (initial solution pH, adsorbent dose, contact time, temperature) on aqueous phase abatement of atrazine by APAPH and CPAPH.

In order to study the effect of initial solution pH on adsorption of atrazine, separate 50 mL aliquots of atrazine solution (50 mg/L) were adjusted to pH 2, 5, 7, 9, and 11 by drop-wise addition of 0.1 M NaOH or 0.1 M HCl, as the case may be, with the aid of a pre-calibrated pH meter (HI96107, Hanna Instruments). The solutions were further contacted with 0.5 g of AMPH or CMPH adsorbents for 4 h with the aid of a mechanical shaker (HY-2, Jiangsu, China). The slurries were filtered and the residual atrazine concentrations in the filtrate determined using the GC-MS (Wuana *et al.*, 2015).

The effect of adsorbent dose on adsorption of atrazine was investigated by dispersing accurately weighed portions (0.5, 1.0, 1.5, 2.0, and 2.5 g) of APAPH or CPAPH in 50 mL aliquots of atrazine (50 mg/L) solution with the aid of a mechanical shaker for 4 h. all samples were removed after and filtered, then stored in a glass bottle for further analysis (Taha *et al.*, 2014).

The effect of initial concentration was carried out with different initial atrazine concentration of 10-60 mgL^{-1} . 0.1 g of adsorbents (APAPH and CPAPH) were contacted with different concentrations was placed on a mechanical shaker and agitated at 150 rpm, at room temperature for 4 hrs to ensure equilibration. The suspension was then filtered using Whatman filter paper (Wuana *et al.*, 2015).

The effect of contact time on adsorption of atrazine was investigated by dispersing 0.5 g of adsorbents (APAPH and CPAPH) was placed in five well labeled 250 mL Erlenmeyer flasks, each containing 50 mL of atrazine solution. The flasks were placed on mechanical shaker for 30, 60, 90 120, 180 and 240 Minute. Resulting mixture was filtered using Whatman filter paper and stored in a well labeled glass bottles at normal room temperature for further analysis (Venkatraman *et al.*, 2011).

Lastly, the effect of temperature on adsorption of atrazine was assessed by contacting 0.5 g of adsorbents (APAPH and CPAPH) was contacted with 50 mL of atrazine solutions using the Gallenkamp temperature controlled water bath. The instrument was set at 30°C for 4 hrs, after which the sample was taken off and filtered using the Whatman filter paper, stored in a well labeled glass bottle at room temperature for further analysis. The same procedure was repeated for samples at temperatures of 40°C, 50°C, 60°C and 70°C for 4 hrs each (Verma and Mishra, 2010).

In all batch adsorption experiments, the quantity of Atrazine adsorbed, Q (mg/g) was calculated by the mass balance equation:

$$Q(\text{mg/g}) = \frac{(C_i - C_f)V}{m_{AD}} \quad 3$$

where C_i and C_f are the initial and final (residual) Atrazine concentrations (mgL^{-1}), respectively; V is the aliquot of Atrazine solution used; and m_{AD} is the mass of adsorbent (g) that will be used for this particular batch treatment.

The percentage removal of Atrazine by PAPH was calculated as:

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad 4$$

2.3 Aqueous Phase Analysis of Atrazine using Gas chromatography

A gas chromatography-mass spectrometer (GC/MS) is used for separation and quantization of Atrazine using selected ion monitoring (SM) in the electron ionization (EI) mode, the GC/MS gives superior specify and similar sensitivity compared to NIST library.

Quality control was achieved by good laboratory practices. All glassware and plastics were appropriately washed with acid (1 + 1 HNO_3) and finally with distilled water and oven-dried. Procedural blank samples were subjected to similar treatments using the same quantity of reagents. In all cases, measurements were done in triplicate.

3.0 Results and discussion

3.1 Physicochemical attributes of *P. Africana* pod husk adsorbents

The physicochemical attributes of *P. africana* pod husks adsorbents (i.e. CPAPH and APAPH) are recorded in Table 1. CPAPH and APAPH had pH of 7.10 ± 5.0 and 7.30 ± 5.2 mean and standard deviation values respectively. Adsorbents with pH 6–8 are acceptable for applicability for water and wastewater treatment (Wuana *et al.*, 2016). Bulk densities of 0.66 and 0.49 kgm^{-3} were showed in table 1 for CPAPH and APAPH; respectively if the density of activated carbon is high then it

will provide greater volume activity and hence better quality of activated carbon (Kibami *et al.*, 2014). Among the samples, the densities of CPAPH are higher than APAPH. The results shows that all the adsorbents used for the study have higher apparent densities. Attrition has values of 13% and 17% for CPAPH and APAPH respectively which are shown in table 1, somewhat higher than adsorbents from moringa oleifera pod husk (Wuana *et al.*, 2016). Both adsorbents showed acceptable attrition loss after preparation.

The iodine number indicates the extent of micropore volume distribution within the adsorbents matrices, hence the surface area and Iodine numbers ($\times 10^{-4} \text{ molg}^{-1}$) were 640 and 395 for CPAPH and APAPH; respectively. CPAPH particularly had high ash content indicative of low carbon content. Titratable surface acidic groups ($\text{mmol H}^+_{\text{eqg}^{-1}}$) were determined by the selective neutralization with a series of bases of varying strength: NaHCO_3 , Na_2CO_3 and NaOH . NaHCO_3 neutralizes carboxylic groups wherein, those neutralized by Na_2CO_3 but not by NaHCO_3 are lactones. The weak acid groups neutralized by NaOH but not by Na_2CO_3 were postulated as phenols (Wuana *et al.*, 2013).

The pH at zero point charge is above 7.0 for both CPAPH and APAPH. The results in Table 1 show that $\text{pH} > \text{pH}_{\text{zpc}}$ for CPAPH and APAPH, This indicates the surface is negatively charged for both CPAPH and APAPH which arises from both basic/acidic sites that combine with protons from the medium.

Table 1: Selected Physiochemical Parameters of Adsorbents.

Parameter	CPAPH	APAPH	RPAPH
Bulk Density (gcm^{-3})	0.66±0.47	0.49±0.35	0.44±0.31
Iodine number (m gg^{-1})	640	395	245
Iodine number ($\times 10^{-3} \text{ molg}^{-1}$)	2.52	1.56	0.97
Surface area (m^2g^{-1})	485.92	299.90	186.02
Ash Content (%)	10%	-	-
pH_{pzc}	7.6	7.2	6.4
Attrition (%)	13%	17%	30%
pH	7.10±5.0	7.30±5.2	6.83±4.8
Titratable surface charge ($\text{mmol H}^+_{\text{eqg}^{-1}}$)			
NaOH	0.89	0.88	0.64
NaHCO_3	0.97	0.68	0.93
Na_2CO_3	0.54	0.26	0.15

CPAPH= carbonized *P. africana* pod husks, APAPH= ammonium chloride-treated *P. africana* pod husks and RPAPH= raw *P. africana* pod husks

FTIR spectrum for Ammonium-modified *P. africana* pod husk (APAPH) showed four absorbance peaks with high intensity at 3257.7 mL⁻¹, 2922.2 mL⁻¹, 1613.9 mL⁻¹ and 1028.7 mL⁻¹ as well as four other peaks with lower intensity at 2050.0 mL⁻¹, 1214.2 mL⁻¹, 1319.5 mL⁻¹ and 723.1 mL⁻¹. The strong peaks at 3257.7 mL⁻¹ was typical of vibration originating from O-H stretching frequency of hydroxyl functional groups with hydrogen bonding. The peaks at 2922.2 mL⁻¹ could be assigned to C-H stretching of aldehyde or alkane. Also, the peak at the range of 1613.9 mL⁻¹-1438.8 mL⁻¹ could be ascribed to N-H bend of amine. The peaks at the range of 1319.5 mL⁻¹-723.1 mL⁻¹ were attributed to C-O stretching of alcohol or ether. While the peak at 1028.7 indicate the presence of C-H of alkanes. The peak at 2050.0 is assigned to -C≡C- stretching of alkyne or C≡N stretching of nitrile.

The highest intensity peak for Carbonized- *P. africana* pod husk (CPAPH) was obtained at the range of 3652.8 - 3548.4 mL⁻¹, indicated the presence of weak O-H alcohols or phenol groups. The peak at 2322.1 -2108.7 mL⁻¹ was ascribed to C≡N symmetric, while the peak 2108.7-2072.4 mL⁻¹ was attributed to C≡N nitrile and -C≡C- of alkynes. The lower intensity peak of 1561.8 mL⁻¹ was attributed to C=C stretching vibration of alkenes (Wuana *et al.*, 2016).

The micrographs from SEM analysis of the *P. africana* showed a heterogeneous and irregular texture with an eroded surface for all the adsorbents derived from *P. africana* pod husk (RPAPH, CPAPH and APAPH).

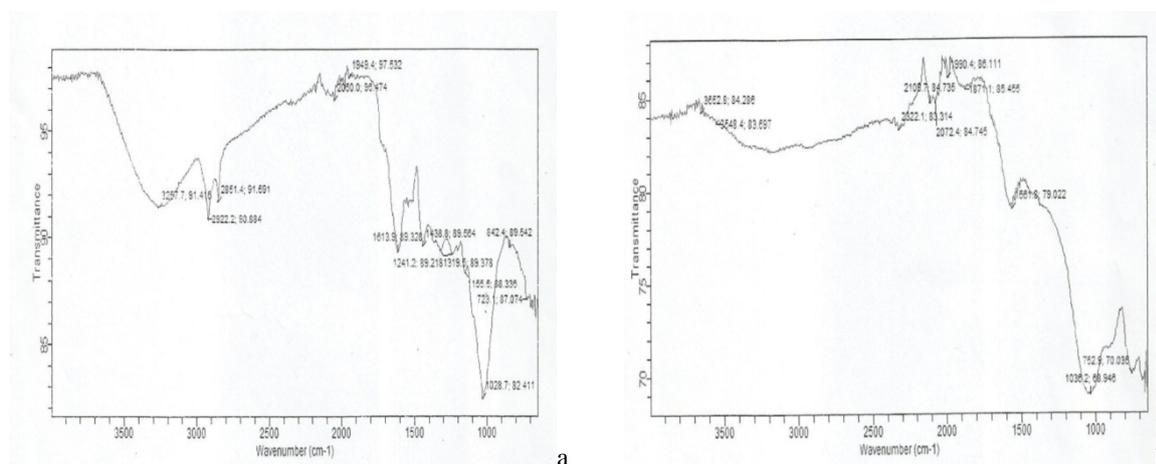


Figure 1: FTIR Spectrum of (a) carbonized (b) Ammonium-Chloride Modified *P. Africana* pod husks.

Table 2: Comparative FTIR spectra characteristics of CPAPH, APAPH and RPAPH

Vib. Freq(cm ⁻¹) Ranges	Observed		Functional groups	Assignment
	CPAPH	MPAPH		
1000-690	1036.2-752.9	1028.7-842.4	-	Alkanes

1320-1000	-	1319.5-723.1	1230.0-845.8	C-O	Alcohol, Carboxylic acid and ester.
1640-1550	1561.8-1475	1613.9-1438.8	1613.9-1435	N-H Bend, -C=C-	Amines, Alkenes.
2260-2100	2108.7-2072.4	2050.0	2214.0-2105.9	-C≡C- stretch C≡N stretch	Alkynes Nitrile
2410-2280	2322.1-2108.7	-	2325.9-2214.0	C≡N	Nitrile
3000-2850	-	2922.2-2851.4	2922.2	C-H, stretch C-H stretch	Alkanes Aldelyde
3000-2500	3652.8-3548.4	3257.7-3000	3280.1-3000	O-H stretch, O-H stretch O-H broad	Carboxylic acids Alcohol.

CPAPH= carbonized *P. africana* pod husks, APAPH= ammonium chloride-treated *P. africana* pod husks and RPAPH= raw *P. africana* pod husks

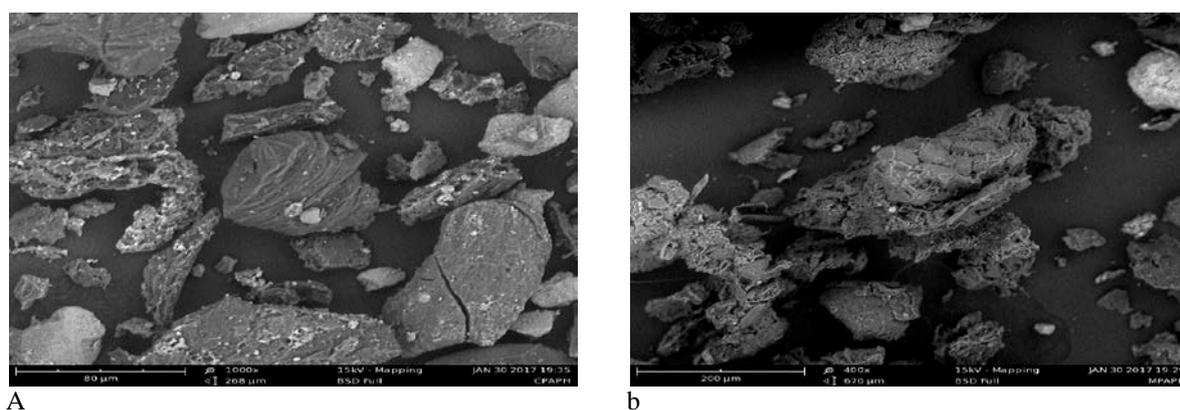


Figure 2; SEM micrograph of (a) Carbonized and (b) Ammonium-Chloride treated *P. Africana* pod husks.

3.2 Effect of initial solution pH on aqueous phase abatement of atrazine

Figure 3 shows the effect of initial solution pH on the aqueous phase sorptive abatement of atrazine by CPAPH and APAPH. The effect of initial solution pH (Figure 3) was investigated over the pH ranges of 2, 4, 7, 9, and 12 at a fixed initial concentration of atrazine (50 mg L^{-1}). The amount of atrazine adsorbed decreased with increase in pH for APAPH adsorbents, while CPAPH slightly increased with increase in pH. The highest atrazine uptakes: APAPH (65%) and CPAPH (72%) were recorded at pH 2; while the least: PAC (69%), APAPH (30%) and CPAPH (70%) were achieved at pH 12.

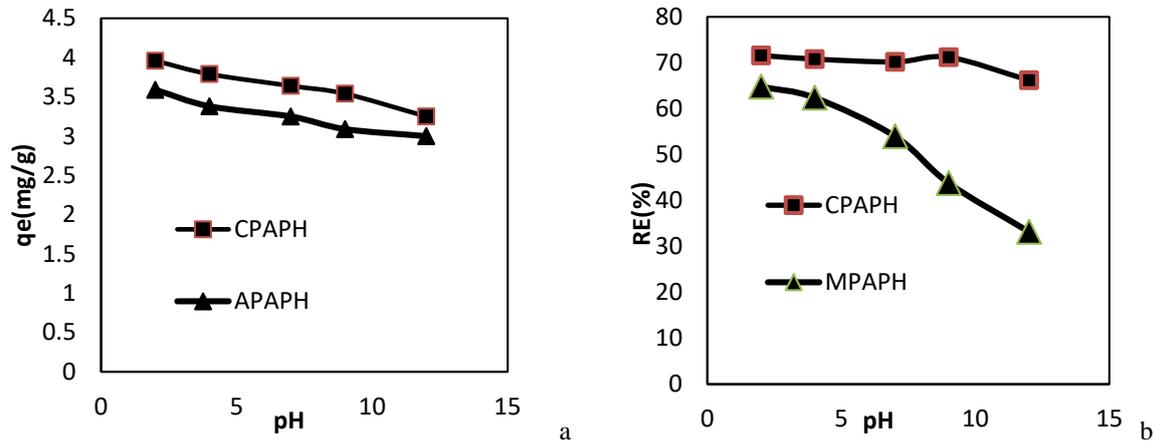


Figure 3: Effect of Initial Solution pH on Equilibrium Adsorption of Atrazine onto Carbonized *Prosopis Africana* pod husks (CPAPH) and Ammonium-chloride treated *Prosopis Africana* pod husks (APAPH). a=Equilibrium phase adsorption and b= Percentage Removal efficiency

3.3 Effect of adsorbent dose on aqueous phase abatement of atrazine

The effect of adsorbent dosage was studied at 30°C by varying the sorbent amounts from 0.5 to 2.5 g; Figure 4 shows that the adsorption of atrazine onto CPAPH and APAPH decrease as dose increases. From the results, it is revealed that CPAPH was better on adsorption uptake of atrazine than APAPH. The percentage of atrazine adsorption on *P. africana* is determined by the sorption capacity of the *P. africana* and the maximum removal of atrazine was obtained at the adsorbent dose of 0.5 g for both CPAPH and APAPH.

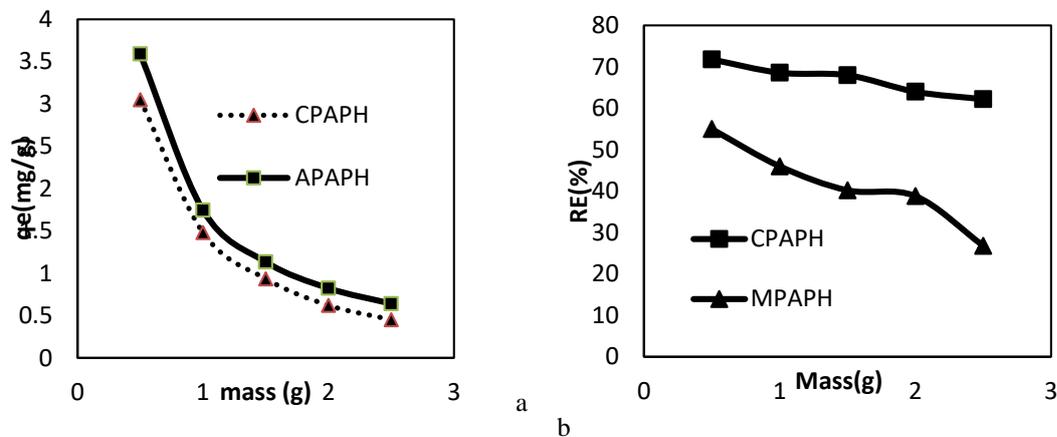


Figure 4: Effect of adsorbent dosage on Equilibrium Adsorption of Atrazine onto Carbonized *Prosopis Africana* pod husks (CPAPH) and Ammonium-chloride treated *Prosopis Africana* pod husks (APAPH). a=Equilibrium phase adsorption and b= Percentage Removal efficiency

3.4 Effect of initial solution concentration on atrazine

The adsorption removal capacity was determined at different Atrazine concentrations ranging from 10-60 mgL⁻¹. Figure 5 shows the adsorption uptake at different Adsorbents (CPAPH and APAPH). It is shown that the adsorption was fast during the early period of sorption but began to slow down gradually at the end for all the Adsorbents. The initial faster rates of adsorption may be attributed to the presence of a larger number of binding sites available for adsorption, and the

gradually reduced adsorption rates at the end were caused by the saturation of the binding sites and attainment of equilibrium.

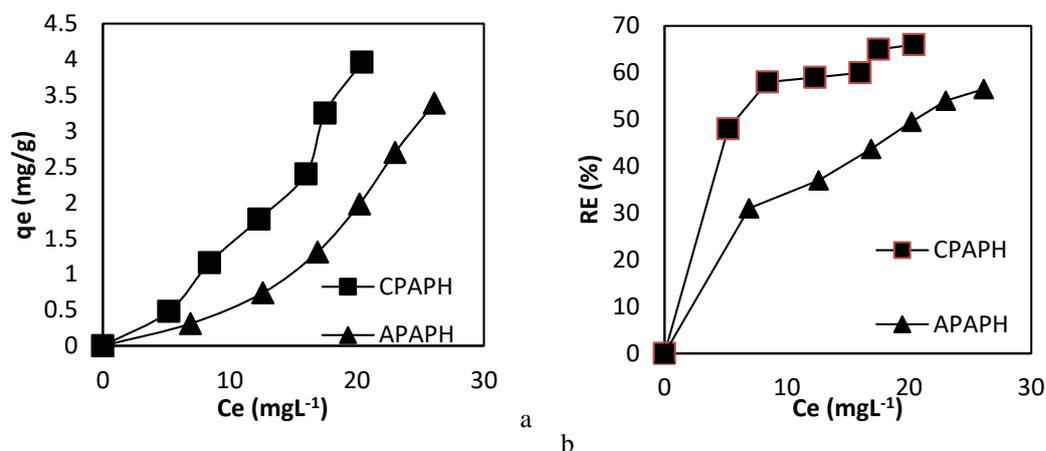


Figure 5: Effect of equilibrium concentration on Equilibrium Adsorption of Atrazine onto Pure Activated carbon (PAC), Carbonized *Prosopis Africana* pod husks (CPAPH) and Ammonium-chloride treated *Prosopis Africana* pod husks (APAPH). A=Equilibrium phase adsorption and B= Percentage Removal efficiency

3.4.1 Isotherm Studies of atrazine adsorption

Adsorption isotherm is invaluable curves, which explain the phenomenon of mobility or release of a substance from the aqueous phase or aquatic environments to a solid-phase at a constant temperature and pH (Allen *et al.*, 2004). It is important to determine the most appropriate correlation for equilibrium adsorption isotherm, to optimize the design of a sorption system (Wuana *et al.*, 2015). The Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich isotherm models were used to analyze the adsorption equilibrium.

Langmuir isotherm: The model predicted a maximum values that could not be reached in the experiments. A K_L (Lmg^{-1}) value indicates are; 0.45 and 0.85 for CPAPH and APAPH. The monolayer saturation capacity, q_m , is shown to be 20.57 and 33.33 mgg^{-1} at a temperature of 30 °C for the adsorbents (CPAPH and APAPH) respectively. As shown in Table 1, the values of R_L for atrazine adsorption on the adsorbents (0.49, 0.49 and 0.48) were less than 1 and greater than zero for (PAC, CPAPH and APAPH) indicating favorable adsorption.

Table 2: Isotherm Experimental Constants for Adsorption of Atrazine onto PAC, CPAPH and APAPH.

Isotherm model	Constants	Values		
		PAC-ATR	CPAPH-ATR	APAPH-ATR
Langmuir	R^2	0.842	0.974	0.998
	K_L (Lmg^{-1})	0.80	0.45	0.85
	R_L ($Lmol^{-1}$)	0.49	0.49	0.48
	q_m (mgg^{-1})	10.87	28.57	33.33
Freundlich	R^2	0.874	0.988	0.842

	N	0.59	0.67	0.81
	K_f (mgg ⁻¹)	11.16	23.01	4.07
Temkin	R^2	0.955	0.900	0.836
	β_T (KJmol ⁻¹)	-100.12	-100.12	-36.79
	$1/\beta_T$	-9.98x10 ⁻⁰³	-9.9x10 ⁰³	2.7x10 ⁰²
Dubinin-Radushkevich	R^2	0.968	0.914	0.951
	β (KJmol ⁻¹)	-8x10 ⁻⁰⁶	1 x 10 ⁻⁰⁵	-6x10 ⁻⁰⁵
	E	250	223.6	91.23

PAC= pure activated carbon, CPAPH = carbonized *P. africana* pod husks and APAPH= ammonium- chloride *P. africana* pod husks.

Freundlich adsorption isotherm The model parameters and R^2 values are presented in Table 2. The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ versus $\ln C_e$ plot, as shown in Figure 11 and the model parameters are shown in Table 2. The magnitude of K_f (23.01 and 4.07) showed that CPAPH had a high capacity for atrazine adsorption from the aqueous solutions studied. As shown in table 2, $1/n_F$ value is less than 1 for all the adsorbents (CPAPH and APAPH) indicated that atrazine is favorably adsorbed by all the adsorbents used. As shown in Figure 11. The n values for all adsorption systems studied were less than unity, which reflects the favorable adsorption of the reactive atrazine over the entire concentration range used in this study (Wuana *et al.*, 2016).

Temkin adsorption isotherm The model parameters are listed in Table 2. The correlation coefficients of (CPAPH and APAPH) 0.900 and 0.951, Temkin isotherm appears to provide a good fit to the atrazine adsorption data.

The adsorption energy in the Temkin model, β_T , is negative for atrazine adsorption from the aqueous solution, which indicates that the adsorption is exothermic. Consequently, the adsorption isotherm of atrazine on CPAPH and APAPH can be described reasonably well by the Temkin isotherm.

Dubinin-Radushkevich (DRK) Isotherm DKR isotherm is used to determine the apparent energy of atrazine adsorption onto PAC, CPAPH and APAPH. The DKR parameters are calculated from the slope of the plot of $\ln q_e$ versus ε^2 , yielded straight lines and indicates a good fit of the isotherm to the experimental data. Values for β (mol⁻²J⁻²) are shown in Figure 13. The linear regressions are shown on Table 9, the values of q_m and β calculated from the intercepts and slopes of the plots respectively are shown on Table 9. Also shown on the same table 9 is the apparent energy (E) of adsorption from the Dubinin-Radushkevich isotherm.

From the linear plot of DRK model, q_m was determined to be very high for all the adsorbents (CPAPH and APAPH), the mean free energy, $E = 250$ KJmol⁻¹, 223.6 KJmol⁻¹ and 91.23 KJmol⁻¹ indicating a physisorption process and the $R^2 = 0.968$, 0.914 and 0.951 higher than that of Tempkin.

4. Conclusion

The adsorbents prepared in this study showed favourable physicochemical attributes (pH, bulk density, attrition, iodine adsorption number/surface area, titratable surface charge, and FT-IR analysis). Batch sorption experiments conducted to investigate the effects of operating conditions such as initial Atrazine solution, pH (2–11), adsorbent dosage (0.5–2.5 g), initial solution concentration (10–60 mgL⁻¹), contact time (30–240 min), and temperature (300–350 K) on Atrazine removal showed that at equilibrium, optimal Atrazine uptake (mg g⁻¹) occurred at pH 2 and sorbent dose of 0.5 g for all adsorbents. Langmuir isotherm described the equilibrium adsorption data better than the Freundlich model, the fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the pulp waste surface, and since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

The Dubinin–R and Langmuir isotherms model provided a better fit of the equilibrium the R²= 0.968, 0.914 and 0.951 higher than that of Tempkin. The Temkin isotherm appears to provide a good fit to the atrazine adsorption data as well.

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