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Original Research Paper

Adsorption of frequently used antibiotics from contaminated water using peanut shells

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Abstract:
The removal of pharmaceutical contaminants from water using cost-efficient and environmentally friendly adsorbents has proven to be extremely effective. The adsorption of amoxicillin (AMX) and tetracycline (TET) from wastewater using peanut shells (PS) were described in this study. The PS was characterized using Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX) techniques. The pH at the point of zero charge (pH_{pzc}) of PS was determined to be 6.5. The influence of operating parameters such as pH, time, initial concentration, adsorbent mass and temperature on the adsorption were evaluated. The adsorption data best fit the Sips isotherm with R^2 value of 0.999 for both AMX and TET and the maximum adsorption capacities of PS were obtained to be 42.47 mg g^{-1} for TET and 61.44 mg g^{-1} for AMX. Adsorption data were found to fit the pseudo first-order kinetic model for both AMX and TET. Thermodynamic parameters ΔG, ΔH and ΔS were determined to be 3.86, -8.88 and -41.36 for TET adsorption and -2.74, -16.64 and -45.15 for AMX adsorption. The negative ΔH values show that both adsorptions were exothermic while the ΔG values show that the adsorption was spontaneous for AMX and non-spontaneous for TET. The results show peanut shells is effective for the removal of AMX and TET from wastewater.

Keywords: Adsorption; antibiotics; emerging contaminants; peanut shells; wastewater treatment

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1. Introduction

Water pollution is a very prevalent challenge in communities where there is total or partial reliance on natural water bodies such as surface and underground water as sources of drinking water (Lin et al. 2022). About 70 – 80% of all illnesses in developing countries, accounting for about 1.7 million deaths (prevalently women and children) every year, are related to water contamination (Ahmed et al. 2020). Pharmaceuticals such as tetracycline (TET) and amoxicillin (AMX) are two of the most widely used and detected antibiotics in water streams globally (Ahmad et al. 2021; Mohammed et al. 2020; Offiong et al. 2019). They are used in medical therapy as well as the treatment and feeding of livestock (Kim et al. 2020) and are categorized as important emerging pollutants (Egbedina et al. 2021) owing to their low biodegradability, high persistence and severe adverse effects caused to living organisms (Soori et al. 2016; Vu et al. 2020). Their presence in the environment has been reported to inhibit the growth of aquatic species, adversely affecting human health causing diseases such as nephropathy, endocrine disruption and more recently, an increase in antibiotic-resistant infections (Xu et al. 2021; Yang et al. 2020).

Conventional methods used for the removal of pharmaceuticals include chlorination (Lang et al. 2022), ozonation (Asghari et al. 2021), chemical reduction (Yu et al. 2021) and membrane processes (Gao et al. 2021; Monachan et al. 2022; Zahoor et al. 2022). These techniques however are faced with limitations. Fouling of membranes causing contacts of adsorbents with oxidizing agents has limited the use of nanofiltration and reverse osmosis. Chlorination has been limited by the toxicity of its by-products which may be more harmful than the antibiotics

intended to be removed. Ozonation also produces biologically active chemical substances and its pH levels are not easily controlled (Mohammed & Kareem, 2019). Due to its effectiveness and cost-efficiency, adsorption is the most commonly used method in recent times. Adsorption processes are simple to design, easy to operate and can be easily incorporated with other wastewater treatment methods (Egbedina et al. 2021).

Graphene and its derivatives, carbon nanotubes (CNTs), zeolite, activated alumina, organoclays, silica gel, and activated carbon have all been explored as adsorbents for the removal of various water contaminants (Avc et al. 2019; Lu & Astruc 2020; Men et al. 2020; Miao et al. 2019). However, problems associated with these materials as adsorbents including high cost, difficulty in recovery and rapid blocking of pores have limited their application in water treatment (Kahya & Erim 2021).

Agricultural materials have received popularity since they are low-cost, highly efficient, abundant and environmentally friendly. Various agricultural waste materials are described in the literature for the removal of numerous contaminants. They include banana and coconut peels (Lazim et al. 2021) vetiver grass (Panja et al. 2020), sawdust (Nkansah 2019), orange peel, rice husk, and pistachio shell (Mohammed & Kareem 2019).

Nigeria is the largest producer of peanuts in Africa and this results in significant waste disposal problems when the shells are discarded (Bako et al. 2022). On the other hand, peanut shells have been reported to have high porosity and large surface areas (Li et al. 2018; Bobet et al. 2020) thus making them a potential alternative adsorbent for the treatment of polluted water while also solving the problem of waste accumulation. The objective of this study was therefore to study the efficiency of peanut shell powder (PS) in the treatment of water containing tetracycline (TET) and amoxicillin (AMX) using adsorption technique.

2. Materials and Methods

2.1 Materials

Peanuts were purchased from Bodija market in Ibadan, Oyo State, Nigeria. The pure form of the pharmaceuticals, Tetracycline (TET) and Amoxicillin (AMX) were obtained from Sagar Vitaceuticals, Lagos State, Nigeria. All chemicals were used as received.

2.2 Preparation of peanut shell powder

The peanut shells were removed and first washed with distilled water to remove dirt and sand. The washed shells were then air-dried for three days before being dried in an oven at 60 °C. The dried shells were then ground into powder using a grinder. The peanut shell powder was sieved with a 230-mesh size sieve to give a particle size of less than 63 μm, kept sealed in a glass container and labelled PS.

2.3 Characterization of the adsorbent

Fourier Transform Infrared (FTIR) spectrophotometer (Spectrum one, Perkin Elmer, USA) was used to determine the functional groups present on the peanut shell powder. Scanning Electron Microscope (SEM) connected to an Energy Dispersive X-ray (EDX) was used to reveal the surface structure of the adsorbent and elemental composition of PS using a JEOL JSM-7600F SEM-EDX instrument.

The point of zero charge (pH_{pzc}) of PS was determined according to the salt addition method outlined by Boumchita et al. (2017). In summary, 10 mL of 0.001 M NaCl was added to six (6) different sample bottles and the pH of the solutions were adjusted between 2 and 12 (pH_i) using HCl and NaOH as appropriate. 0.1 g of PS was added to each flask and the suspensions were shaken for 24 hours. The suspensions were filtered and their final pH values (pH_f) were noted. The change in pH was then plotted against the initial pH values and the point where ΔpH is zero was taken to be the pH_{pzc}.

2.4 Batch adsorption studies

2.4.1 Effect of contact time

Kinetic experiments were performed by adding 0.1 g of PS to 10 mL of 40 mg/L solutions of TET and AMX in sample bottles and shaken for different times from 5 min. to 1440 min. The results obtained were then fitted to

kinetic models: pseudo-first order and pseudo-second order kinetic models. The equilibrium time obtained in this experiment was used for subsequent experiments described below.

2.4.2 Effect of initial concentration

Equilibrium adsorption experiments were conducted by dispersing 0.1 g of the adsorbent in 10 mL TET and AMX solutions with different concentrations (5 - 100 mg/L) and shaken at their respective equilibrium times and filtered. Data obtained from the equilibrium experiment were subjected to Langmuir, Freundlich and Sips isotherm models to determine the nature and mechanism of the adsorption process of both pollutants by the adsorbent.

2.4.3 Effect of pH

The effect of pH was determined by adding 40 mg/L of the TET and AMX solution to 0.1 g of the adsorbent. The solutions' pH were varied (2-12) using 0.1 M HCl or 0.1 M NaOH.

2.4.4 Effect of adsorbent mass

The effect of adsorbent mass was also studied by adding 40 mg/L of TET and AMX solutions to 0.05, 0.1, 0.2, 0.3 and 0.4 g of the adsorbent. The solutions were shaken for their respective equilibrium times and filtered.

2.4.5 Data analysis

The concentrations of TET and AMX remaining in solution after adsorption were analysed with a UV/VIS spectrophotometer (Shimadzu UV-1650 pc) at a wavelength of 269 and 228 nm for TET and AMX respectively (Maximum wavelength values determined after scanning between 200 nm – 900 nm). The amount of pollutant adsorbed at equilibrium, q_e and the percentage removal (% adsorption) were calculated using equations (1) and (2) respectively (Men et al. 2020):

$$q_e = \frac{(c_o - c_e)V}{M} \quad (1)$$

$$\% \text{ adsorption} = \frac{C_O - C_e}{C_O} X\ 100 \quad (2)$$

Where V is the volume of the solution in L, C_o is the starting liquid-phase concentration in mg/L, C_e is the final equilibrium liquid-phase concentration in mg/L, and M is the mass of the adsorbent in grams.

3. Results and Discussions

3.1 Characterization of adsorbent

The pH_{pzc} is the pH at which the charge on the adsorbent in solution is zero. It determines the ease with which the adsorbent adsorbs pollutants (Egbedina et al. 2021). The pH at the point of zero charge (Fig. 1) was determined to be 6.5 suggesting that at a pH value below this, the charge on the adsorbent is positive and above this pH_{pzc} value, it becomes negative. A positive net surface charge favours the adsorption of anions while a negative surface charge favours the adsorption of cations due to electrostatic interactions between the adsorbent and the adsorbate (Egbedina et al. 2021).

The FTIR spectra (Fig. 2) show the absorption of C-H stretching vibration of methyl and methylene at 2917 cm-1. The band observed at 1731 cm-1 indicates the carbonyl (C=O) functional group and is attributed to the acetyl group or the ester present in hemicellulose or lignin. Peanut shells have been reported to consist of hemicellulose, cellulose and lignin (Bobet et al., 2020; Fermanelli et al. 2022). The peaks at 1457 and 1377 cm^{-1} are attributed to the C=C vibration of the sp2 hybridized carbon and the C-H in hemicellulose respectively.

The SEM images of the peanut shell as seen in Fig. 3 revealed a rigid structure with a rough surface. Pores of different sizes are also noticeable on the surface of the adsorbent. EDX analysis was carried out to determine the

elemental composition of PS. The results (Fig. 4) reveal calcium and carbon to be the dominant elements in PS with small amounts of potassium, sodium, oxygen and nitrogen.

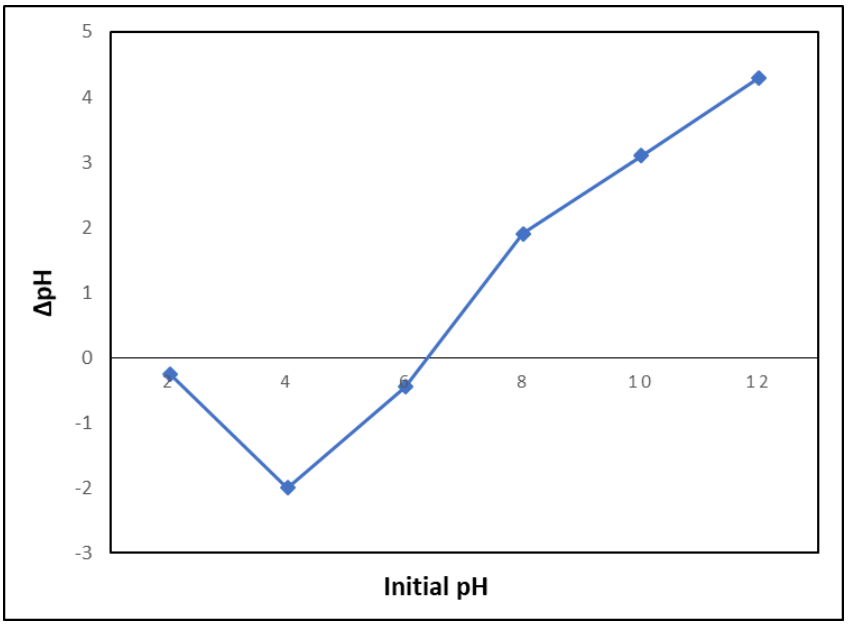

Figure 1: pH_{pzc} plot for peanut shell

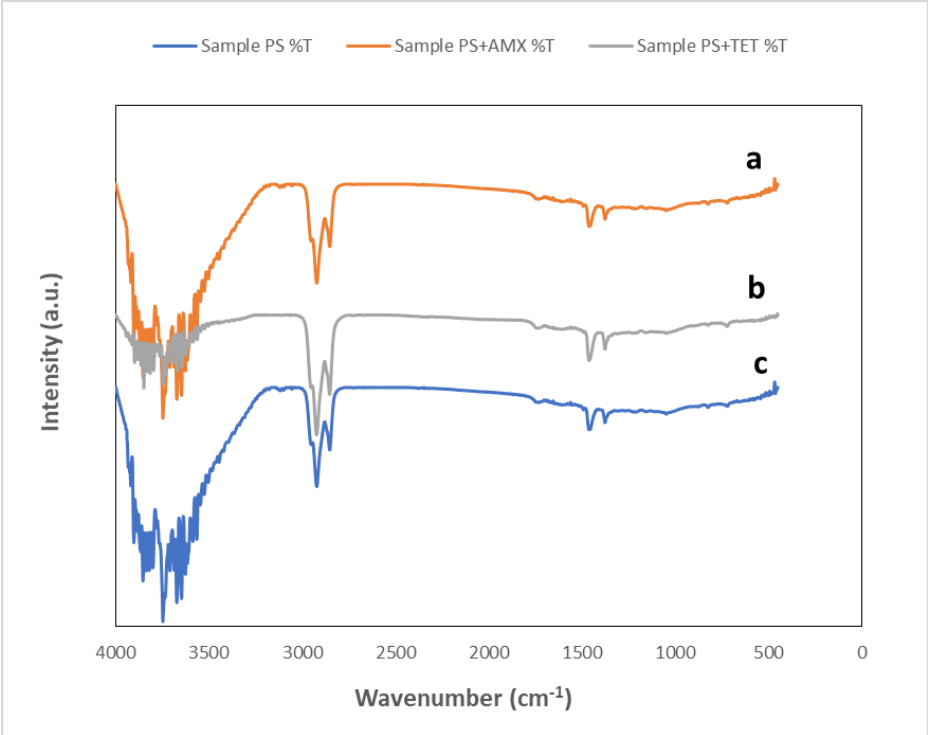

Figure 2: FT-IR spectra of (a) peanut shell + AMX (b) peanut shell + TET (c) peanut shell

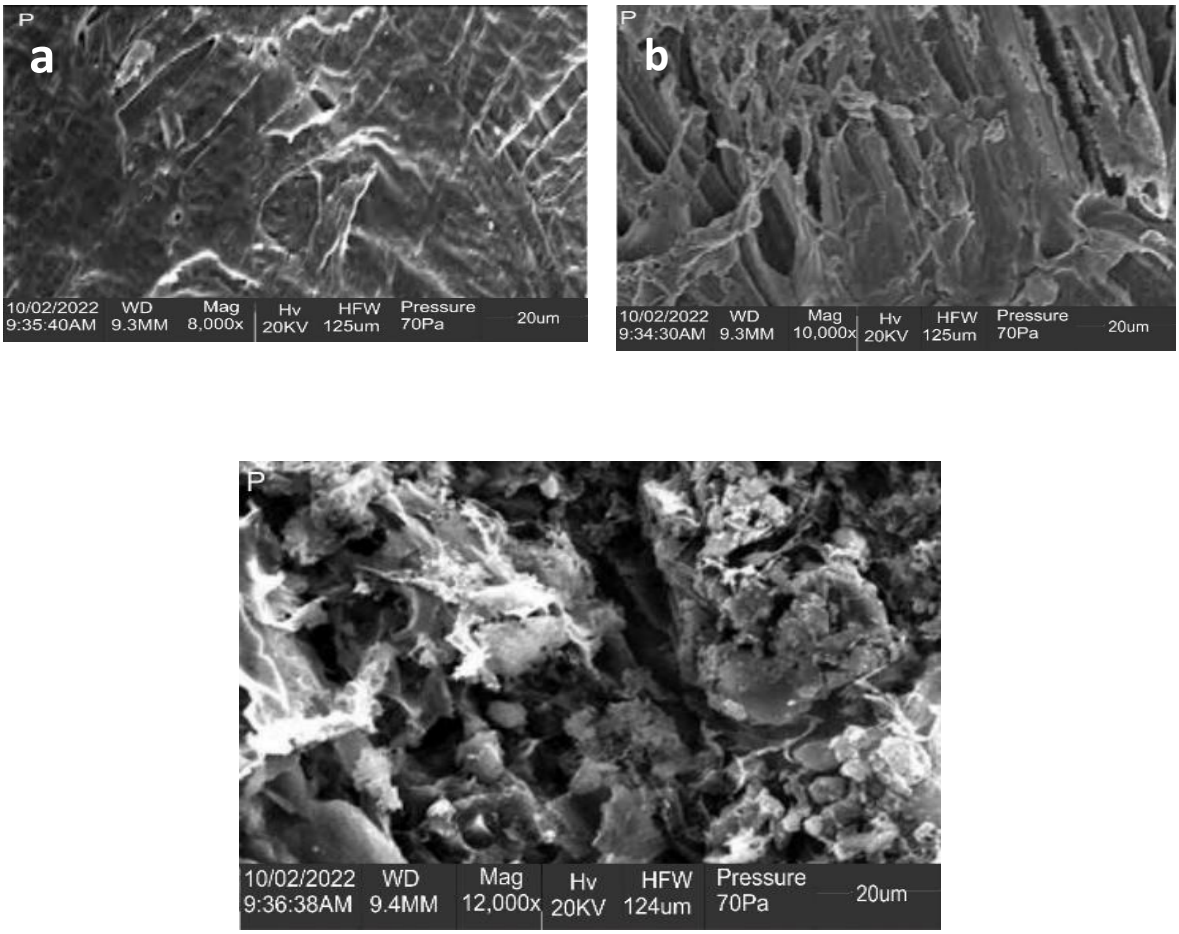

Figure 3: SEM images of peanut shell at (a) 8,000x (b) 10,000x and (c) 12,000x

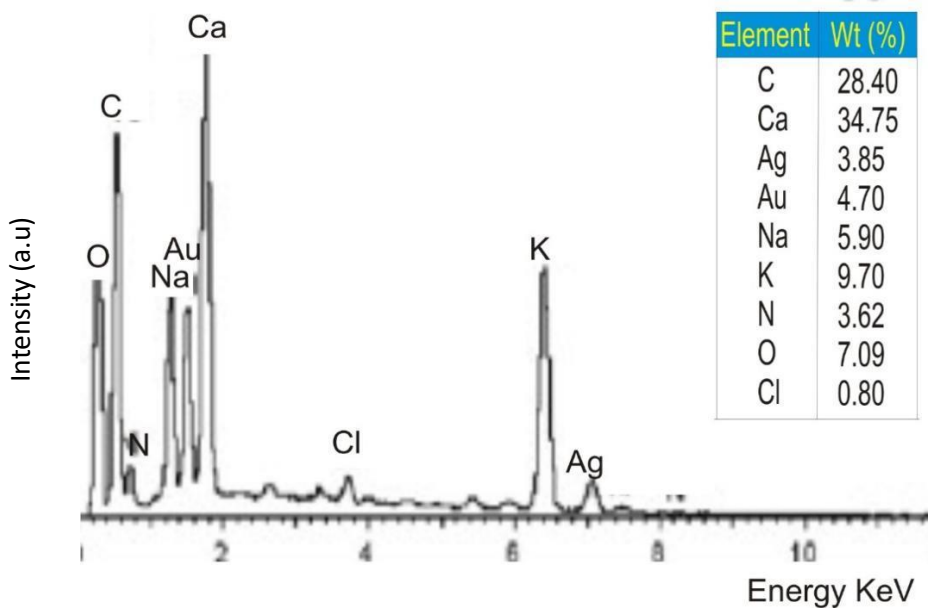

Figure 4: Elemental composition of peanut shell

3.2 Batch adsorption studies

3.2.1 Effect of pH

It is important to consider the influence of pH on the removal of AMX and TET on PS. pH affects the chemistry of the adsorbent and the adsorbate (Adebowale & Egbedina 2022). The adsorption capacity of AMX is greatest at pH 7 (3.3 mg/g) and lowest at pH 2 (2.83 mg/g) as shown in Figure 1.5. AMX can either be cationic, zwitterionic, or anionic depending on the pH of its solution. When the pH is below 2.68, it is primarily cationic (AMX+); when the pH is between 2.68 and 7.49, it is zwitterionic ($AMX^{\pm}$) and when the pH is between 7.49 and 9.63, it is anionic (AMX-) (Imanipoor et al. 2020).

Additionally, the pH_{pzc} for the adsorbent was determined to be 6.5. At lower pH, both the adsorbent and AMX are positively charged which could result in electrostatic repulsion leading to the lower adsorption capacity observed at this pH. With reducing cationic character as pH increased, there was a steady increase in adsorption because the PS can adsorb organic pollutants which exist in their zwitterionic form explaining the higher adsorption capacity observed. However, with pH > 7, the electrostatic attraction between the negatively charged AMX and the adsorbent causes the adsorption capacity to decline (Imanipoor et al. 2021).

At pH 10, TET adsorption was at its highest (Fig. 5). At this pH, TET and PS are negatively charged in the basic medium, with TET occurring as a divalent anionic species (Egbedina et al. 2021). Therefore, it is anticipated that in these circumstances, the repulsion mechanism will be engaged, resulting in a reduction in adsorption. The amount of adsorption increased, indicating a stronger attraction of the adsorbent for anionic TET. Therefore, in this instance, the adsorption capacity is unaffected by the electrostatic force of attraction. As the pH increased from 10 to 12, adsorption capacity reduced and this is attributed to a reduction in the hydrophobicity of TET suggesting that hydrophobic interactions between the PS and TET could be a major form of interaction.

3.2.2 Effect of adsorbent dosage

Optimizing the dosage of the adsorbent is important from an economic perspective (Imanipoor et al. 2021). At fixed initial AMX and TET concentrations, the influence of this parameter was studied. Fig. 6 shows that the adsorption capacity of PS for the pollutants under study declined as the dosage was increased from 0.1 to 0.5 g. This might be a result of the aggregation of adsorbent particles which occurs as mass increases and reduces the overall effective surface area while increasing the diffusion path (Marzbali et al. 2016).

3.2.3 Kinetic studies

The adsorption kinetics of TET and AMX onto PS were examined using the pseudo-first order (Equation 3) and pseudo-second order (Equation 4) kinetic models. The design and operation of the adsorption process are influenced by its kinetics, which also provides information on the mechanism of adsorption (Brouers & Al-Musawi 2018).

$$q_t = q_e\,(1 - e^{-k1^t}) \qquad (3)$$

$$q_t = \frac{k_2\, q_e^2 t}{1 + k_2\, q_e t} \qquad (4)$$

where t is the adsorption time (minutes), q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium, and k_1 (min^{-1}) and k_2 ($g.mg^{-1}\ min^{-1}$) denote the adsorption rate constants of the pseudo-first and pseudo-second order kinetic models respectively (Abodif et al. 2020; Brouers & Al-Musawi 2018).

The kinetic studies of the adsorption of TET and AMX (Table 1 and Fig. 7) revealed that the q_e values obtained using pseudo first-order kinetic model was similar to the experimental qe of 3.57 mg g^{-1} for TET and 3.55 mg g^{-1} for AMX. This shows that the adsorption of the pollutants followed the pseudo first-order kinetic model and therefore adsorption proceeded via multilayer adsorption. Also, the rate constant, k_1 for TET adsorption was observed to be less than that of k_2 while the k_1 of AMX adsorption is higher than its k_2. When k_1 is greater than k_2, it suggests that internal diffusion contributed to the adsorption of AMX in addition to the surface adsorption which occurred in both cases (Chaba & Nomngongo 2019).

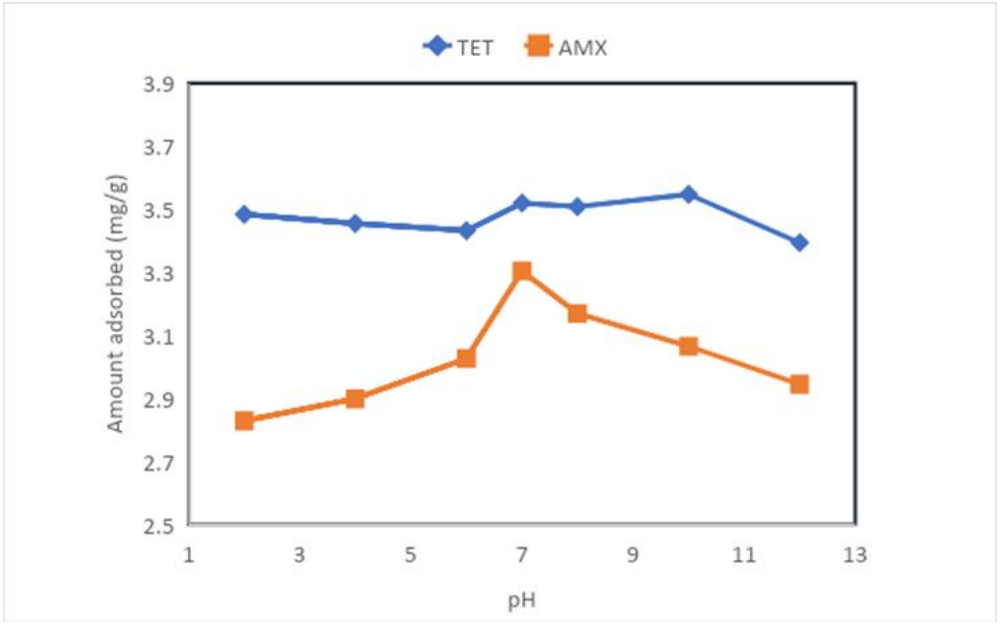

Figure 5: Effect of pH on the adsorption of AMX and TET (Initial concentration = 40 mg/L; adsorbent mass = 0.1 g; Contact time = 240 min. for TET and 60 min for AMX; Temperature = 298 K)

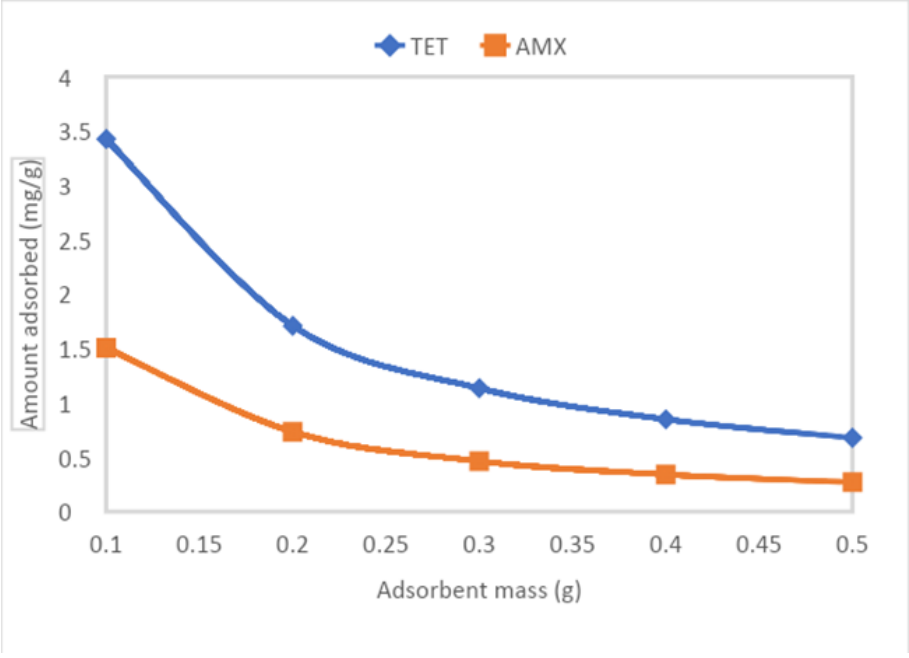

Figure 6: Effect of adsorbent dosage on the adsorption of TET and AMX (Initial concentration = 40 mg/L; pH = 7; Contact time = 240 mins for TET and 60 min for AMX; Temperature = 298 K)

Table 1: Kinetic parameters for the adsorption of TET and AMX on PS

Model	Parameters	TET	AMX
Pseudo first order	k_1 (min^{-1})	0.317	0.336
	q_{e1} (mg g^{-1})	3.559	3.498
	R^2	0.852	0.901
Pseudo second order	k_2 ($g.mg^{-1}min^{-1}$)	0.673	0.284
	q_{e2} (mg g^{-1})	3.571	3.554
	R^2	0.801	0.734

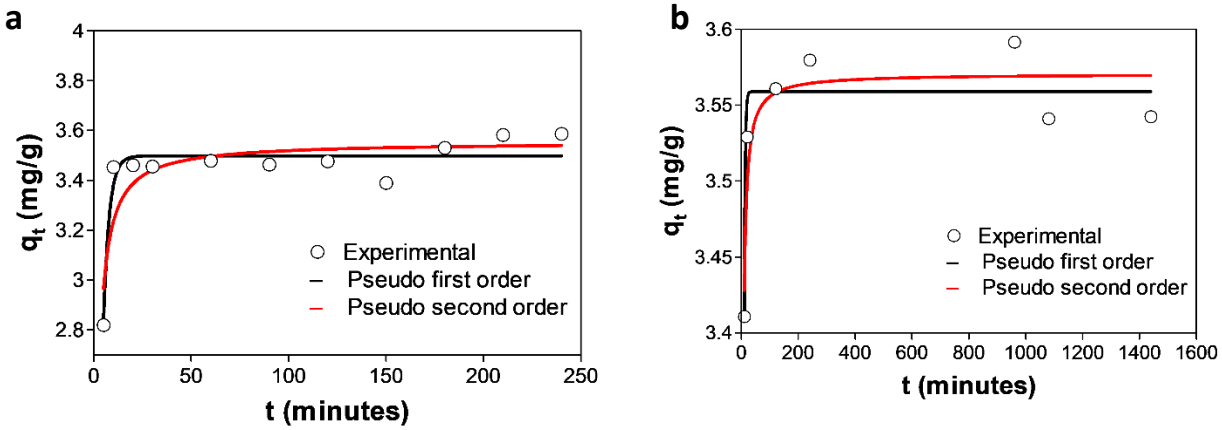

Figure 7: Kinetic plots for the adsorption of (a) AMX (b) TET on the peanut shell

3.2.4 Equilibrium studies

The adsorption of TET and AMX on PS was modelled using non-linear isotherm equations to explain the interaction between the pollutants and the adsorbent. The models are Langmuir, Freundlich and Sips models (Equations 5-7) (Ahsan et al. 2018; Chaba & Nomngongo 2019) and their plots are shown in Fig. 8.

Langmuir isotherm model: $q_e = \frac{Q_O b C_e}{1 + b\, C_e}$ (5)

Freundlich isotherm model: $q_e = K_f\, C_e{}^{1/n}$ (6)

Sips isotherm model: : $q_e = \frac{(K_S C_e)\, Q_s{}^n}{1 + (K_S C_e)^n}$

Sips isotherm model: $q_e = \frac{(K_S C_e) Q_s{}^n}{1 + (K_S C_e)^n}$ (7)

Where q_e is the quantity of solute adsorbed (mg/g) at equilibrium, C_e is the concentration remaining in solution (mg/L), Q_o is the Langmuir's monolayer adsorption capacity (mg/g); b is a constant that indicates the affinity of the adsorbate for the adsorbent; K_F is the Freundlich's empirical constant that indicates the relative adsorption

capacity of the adsorbent; n is the adsorption constant that shows the heterogeneity of adsorption, K_s is the Sips isotherm model constant and Q_s is the Sips isotherm adsorption capacity.

From the data obtained, the adsorption of TET and AMX were observed to best fit the Sips isotherm model with correlation coefficient values of 0.999 for TET and AMX adsorption. The limitation of the Freundlich model which occurs with high pollutant concentration is avoided by using the Sips model to predict adsorption occurring on heterogeneous surfaces (Ayawei, 2017). Therefore, this suggests that adsorption occurred on heterogeneous active sites on the surface of PS with adsorption proceeding via multilayer (diffused adsorption) at low concentrations but proceeds via monolayer as concentration increases (Muntean, et al, 2018) and is in correlation with the results obtained from kinetic modelling of the adsorption data. The maximum adsorption capacities qmax of TET and AMX on PS according to the Sips isotherm were recorded as 42.47 mg g^{-1} and 61.44 mg g^{-1} respectively (Table 2).

Table 3 shows a comparison of the adsorption capacities of the PS adsorbent with other agricultural adsorbent materials. The results displayed show that the peanut shell is a good adsorbent material for the removal of TET and AMX, having a greater adsorption capacity than those obtained using these other adsorbents.

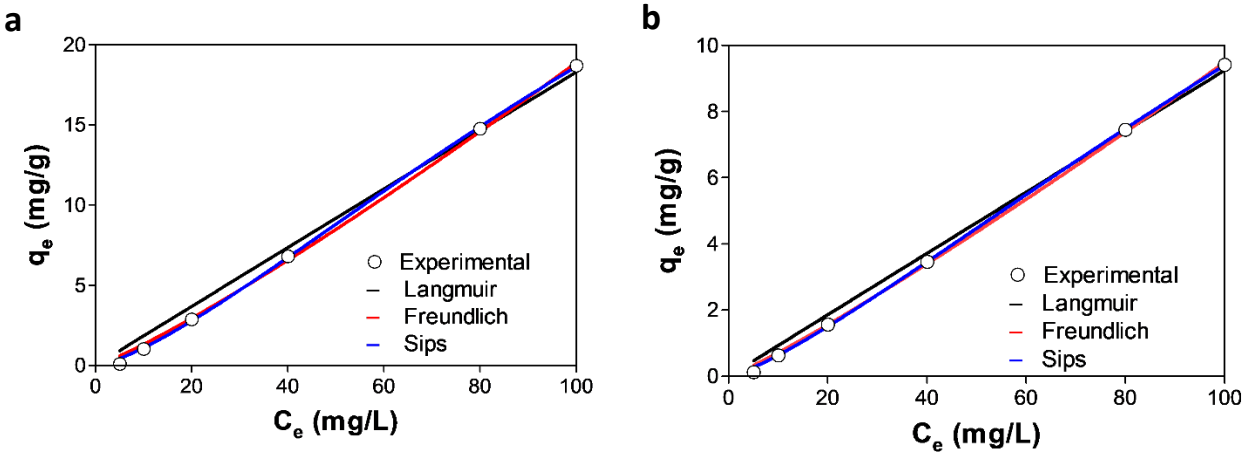

Fig. 8: Isotherm plots for the adsorption of (a) AMX (b) TET on the peanut shell

Table 2: Values of the parameters for equilibrium adsorption models

Model	**Parameter**	**TET**	**AMX**
Langmuir	q_o	1145.23	2359.416
	K_L	8.13 x 10^{-5}	7.8 x 10^{-5}
	R^2	0.994	0.990
Freundlich	n_F	0.893	0.866
	K_F	0.0545	0.0928
	R^2	0.998	0.998
Sips	q_s	42.465	61.443
	n_s	1.271	1.379
	K_s	0.0037	0.00545
	R^2	0.999	0.999

Table 3: Comparison of the adsorption efficiencies of low-cost adsorbents for AMX and TET removal from aqueous solutions

Adsorbent	Pollutant	q_{max} (mg g^{-1})	Reference
Algae biomass	TET	20.50	Abd & Mohammed-Ridha 2021
Zeolite	TET	20.40	Zou et al. 2019
Pine bark biochar	TET	15.50	Ryenchindorj et al. 2022
Pistachio shell	TET	95.06	Mohammed & Kareem 2019
Peanut shell	TET	42.47	This study
Algae biomass	AMX	17.4	Abd & Mohammed-Ridha 2021
Aloe vera leaf waste	AMX	29.11	Hashemzadeh et al. 2022
Chitosan	AMX	73.52	Mangla et al. 2022
Magnetic graphene nano-platelets	AMX	14.10	Kerkez-Kuyumcu et al. 2016
Peanut shell	AMX	61.44	This study

3.3.5 Thermodynamic studies

To find out how temperature affected the adsorption of AMX and TET onto PS, adsorption experiments were conducted between 298K and 338K. The experimental results obtained were utilized to calculate the thermodynamic parameters of the adsorbent. Equations (8) and (9) were used to compute the Gibb's free energy (ΔG°, kJ·mol^{-1}·K^{-1}), enthalpy (ΔH°, kJmol^{-1}), and (ΔS°, J·mol^{-1}):

$$\text{In } K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

Where $K_d = q_e/C_e$ is the distribution coefficient, R is the universal gas constant and T is the temperature in Kelvin (Boumchita et al. 2017). ΔH° and ΔS° were obtained from the slope and intercept respectively of the plot of ln K_d against 1/T.

The value of ΔG° in the case of AMX is negative, indicating that AMX adsorption is spontaneous (Table 4). The positive value of ΔG° in the case of TET shows that the spontaneity of the process is only achieved at lower temperatures, hence the process is non-spontaneous. This is supported by the fact that the values of ΔG° become increasingly positive at elevated temperatures suggesting that the adsorption process is more likely to proceed spontaneously at lower temperatures. On the other hand, the ΔG° of AMX was negative, demonstrating the spontaneous nature of the adsorption. The negative values of the ΔH° and ΔS° for the adsorption of both pollutants suggest that the processes are exothermic and that there is order at the surface of the PS adsorbent, respectively (Boumchita et al. 2017).

Table 4: Thermodynamic parameters of the adsorption of TET and AMX on the peanut shell

Parameters	TET	AMX
Δ*H*° (kJ/mol)	-8.88	-16.64
ΔS° (J·mol^{-1})	-41.36	-45.15
Δ*G*° (kJ·mol^{-1}·K^{-1})		
298 K	3.442	-3.186
308 K	3.855	-2.735
318 K	4.269	-2.283
328 K	4.682	-1.832
338 K	5.096	-1.380

4. Conclusion

This study revealed the efficiency of peanut shells for the removal of TET and AMX from wastewater. The point of zero charge of the adsorbent was determined to be 6.5 and the presence of functional groups that signify the presence of cellulose and lignin was confirmed by FT-IR spectroscopy. Batch adsorption experiments have also shown that different experimental conditions affect the adsorption process. For TET and AMX, the ideal pH for adsorption was 10.0 and 7.0, respectively. AMX and TET were further shown to have maximal adsorption capabilities of 61.44 mg/g and 42.47 mg/g, respectively. The adsorption of both pollutants onto PS was revealed to follow the pseudo first-order kinetic model. Adsorption isotherm studies also revealed that the adsorption of TET and AMX followed the Sips model suggesting the occurrence of multilayer interactions between the adsorbent and the adsorbate. The enthalpy values of the adsorption of both pollutants further revealed that the adsorption process was exothermic. The increasingly positive ΔG values for TET and AMX adsorption show the spontaneity of the adsorption at lower temperatures showing that tetracycline and amoxicillin removal from wastewater can be accomplished using peanut shell as an adsorbent.

Authors' contribution

Abisola Egbedina: Conceptualization, Methodology, Formal analysis, Supervision, Writing - review & editing.
Hassan Sulaimon: Methodology, Formal analysis, Investigation, Writing - original draft.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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