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Effective Removal of Amoxicillin from Medical Wastewater Using an Eco-Friendly Modification of a Walnut Shell as an Adsorbent

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Abstract: This study is essential in correspondence with international initiatives to create sustainable wastewater treatment technologies. It highlights the need to address pharmaceutical pollutants in water, which significantly threaten human health and aquatic ecosystems. This study aimed to evaluate the efficacy of walnut shell-derived activated carbon (RWL) as a sustainable, economical source for activated carbon in the removal of the antibiotic Amoxicillin (AMX) from aqueous solutions. Activated carbon was prepared using H3PO4 as the activating agent and a conventional oven, resulting in a type of conditioner called (AHRWL). The adsorbent's structure and morphology were examined through scanning electron microscopy (SEM). The analysis demonstrated that the prepared adsorbent possessed pore structures that facilitated the efficient and rapid absorption of AMX. Several parameters were investigated, including the pH of the solution (ranging from 3 to 9), drug concentration (ranging from 10 to 60 mg/L), and adsorbent concentration (ranging from 0.025 to 0.25 g/100 mL for walnut shell), were investigated to evaluate the effect of AHRWL on AMX removal efficiency. The experimental results showed that the optimal removal of AMX occurred at a pH of 6, with an optimal amount of adsorbent around 0.25. The Langmuir isothermal model described the removal process well, and the kinetic data was found to correlate with a pseudo-second-order model. Overall, this study established that activated carbon derived from walnut shells serves as an excellent adsorbent for eliminating pharmaceutical pollutants from water, hence advancing environmental conservation and public health protection objectives.

Keywords: Amoxicillin, Wastewater treatment, Adsorption, Activated carbon, Isotherm, Kinetics, Walnut Shell, Sustainability

Introduction

The presence of pharmaceutical compounds, including antibiotics and their metabolites, in surface and subsurface waters can have harmful effects on the environment and human health (Orozco-Hernández et al., 2019; P. Sharma et al., 2022). Amoxicillin (AMX), an antibiotic widely employed in medical practice, is frequently detected in aquatic environments due to its limited ability to be absorbed by both humans and animals. Traditional water treatment plants are not efficient enough to eliminate antibiotics, making it challenging to ensure their complete removal from wastewater (Bago d'Uva et al., 2011; Michael & Miller, 2013).

Various treatment methods, including oxidation processes, membrane filtration, nan filtration, and adsorption, multiple strategies have been employed to remove antibiotics from wastewater (Ali et al., 2020; Michael & Miller, 2013). Among them, adsorption stands out as a promising technique due to its high effectiveness, scalability, and capacity to use agro-industrial waste as a source of activated carbon adsorbents (Machado et al., 2017; Michael & Miller, 2013) Recently, food agricultural by-products and waste have been shown to be low-cost sustainable adsorbents (Litefti et al., 2019; Serafin et al., 2023). These include such as rice husk (Shang et al., 2020), dried olive stone (Gameli et al., 2022), lemon peel (Anah & Astrini, 2018; Basu et al., 2018), orange peel (Gutierrez-Lopez et al., 2023), Cordia Myxa Fruits (Burdzy et al., 2022), pomegranate peels (De Gisi et al., 2016) and different other types of natural adsorbents.

Walnut biomass is a significant source of carbon-rich waste generated during Walnut oil production. While previous studies have focused on producing activated carbon from Walnut pulp or Walnut stone, this study aims to produce activated carbon using Walnut shells (RWL). The study uses a conventional furan to produce high surface area-activated carbon (Serafin et al., 2023). In previous study, we evaluated the adsorption capacity of activated carbon for AMX. It tests the adsorbent on a synthetic hospital effluent contaminated with various pharmaceutical compounds, sugars, and other organic and inorganic substances. The results of the study could contribute to the development of effective and sustainable methods for removing antibiotics from wastewater (Nordin et al., 2023).

Recent progress in healthcare practices has led to an observable increase in the usage of multiple pharmaceuticals. During pharmacological treatment, the primary components found in pharmaceutical products are primarily excreted from the patient's body, mostly in their unchanged state. (Bertuzzi et al., 2023). Patients will eliminate pharmaceutical residues in this manner, which will then make their way into the sewage disposal system and, ultimately, wastewater. Another potential route for pharmaceutical residues to reach the environment is improperly disposing of unused or out-of-date pharmaceuticals and depositing them in the municipal wastewater system or a landfill. The pharmaceutical pollutants that are discovered in hospital waste and effluents from the pharmaceutical sector most commonly include tetracycline (TEC), amoxicillin (AMO), and ciprofloxacin (CIP). Antibiotic compounds are not the problem until they reach concentrations higher than those at which they are hazardous to human health (Rogowska & Zimmermann, 2022). The presence of pharmaceuticals in water resources is a significant concern, and it is crucial to eliminate them from industrial influence to protect human health and the environment. Adsorption, a commonly used technique, has emerged as an effective method for treating water contaminated with pharmaceuticals (Ruziwa et al., 2023). The primary novelty of this study lies in the specific feedstock utilized for activated carbon production, which is an available and low-cost material. This work aims to investigate the adsorption of amoxicillin by activating carbon derived from the walnut shell. In addition, kinetic and equilibrium models were also studied.

Materials and Methods

Preparation of Raw Materials and Solutions

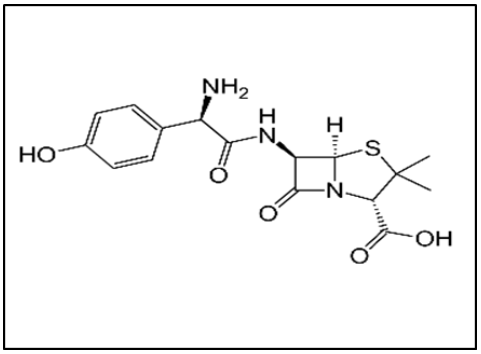

Figure 1. The chemical structure of AMX (Ghadim et al., 2013;. Sharma et al., 2009).

Pharmanostra (Pelotas, Brazil) provided the Amoxicillin antibiotic (AMX) for this study. The molecular formula of AMX is $C_{16}H_{19}N_3O_5S$, with a molecular weight of 365.40 g/mol and a water solubility of approximately 13 mM at pH = 7. The AMX molecule contains two ionization sites with different affinities for protons, which can result in deprotonation and protonation, leading to the existence of three distinct ionization forms (in varying concentrations in solution): zwitterion, cationic, and anionic in Figure 1.In order to generate simulated contamination of the aqueous solution, 1 gram of (AMX) was dissolved separately in 1 liter of distilled water to reach a concentration of 1000 mg/L. Then, using dilution law, other concentrations were prepared.

Activated Carbons from Walnut Shell Production

Figure 2. The (RWL) before and after grinding

Figure 2 shows the Walnut shells before and after grinding. The preparation of raw, modified, and activated carbon from walnut shells, which are used as adsorbent material to remove pharmaceutical contaminants, were as follows: washed with distilled water several times and dried at 105C° for 24 hrs, then crushed into granules of different sizes, after that sieved using sieves (type: Restch, Germany) to produce particles ≤ (425) µm (Al-sharify & Onyeaka, 2023). The material produced was given the name Raw Walnut Shells (RWL). The Raw Walnut shells (RWL)material was impregnated with 10.0 ml of a 38% H_3PO_4 solution at a ratio of 3:1 (H_3PO_4: RWL) in flasks under magnetic stirring for two hours before being dried at 105 C° for twenty-four hours. We used the name (HRWL) for the produced materials. To produce an inert environment, a dry mixture of HRWL was heated to 600 C° using nitrogen gas. This is done to avoid undesirable reactions that could happen if oxygen were present, such as oxidation or spoiling. Because nitrogen is inert, it acts as an effective barrier, guaranteeing the intended result of the two-hour carbon preparation procedure in a reactor (Oliveira et al., 2025). The activated carbon was separated using a 425 µm filter and dried at 105 C° for 24 hours. We used the name (AHRWL) for the produced materials. Last, we prepared the investigational materials by placing them in a container after grinding the produced material until it passed through a 425-micron sieve (Halysh et al., 2020). Figure 3 depicts the production process for adsorbent from Walnut shells. Figure 4 shows the (AHRWL) powder as activated carbon.

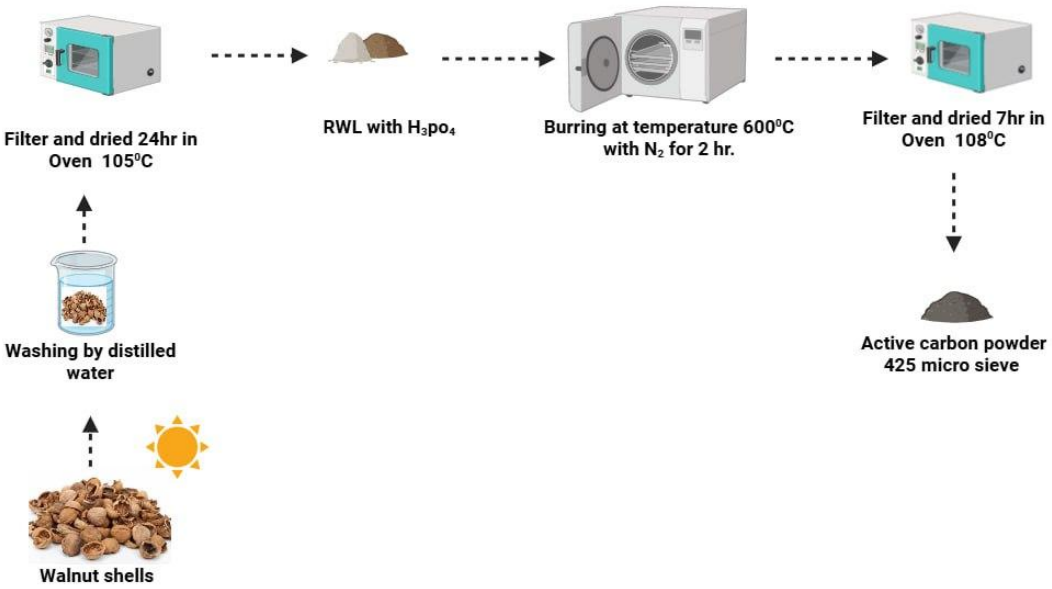

Figure 3. Showing the production process for adsorbents from (AHRWL).

Figure 4. The (AHRWL) powder activated carbon.

Batch Adsorption Studies

The adsorption of amoxicillin (AMX) onto the reactive material was studied through batch experiments conducted under various conditions. In each experiment, a specified amount of the sorbent was added to 100 mL of pharmaceutical solution with concentrations ranging from 10-60 mg/L. The mixture was then shaken using a thermostatic shaker for different contact times (15-120) minutes, at varying initial pH values (3-9), agitation speeds (50-250 rpm), and sorbent dosages (0.025-0.25 g/ 100 mL). To measure the amount of pharmaceutical adsorbed onto the reactive material, a fixed volume of 50 mL of the solution was withdrawn from each flask and filtered using What Man No. 70 filter paper to separate the adsorbent from the aqueous solution. The filtered solution was then analyzed using a double-beam UV-visible spectrophotometer (PG Instruments, Model UV T80, England) at λmax(AMX) = 230 nm to determine the remaining pharmaceutical concentration. A 1000 mg L^{-1} stock solution of Amoxicillin (AMX) was made. AMX was diluted to proper concentrations (10–400 mg L^{-1}) from the stock solution and detected by a UV–vis spectrophotometer. The calibration curve was calculated by measuring absorbance values of AMX standard solutions (5–25 mg L^{-1}) between pH 7.04–7.5. The data (Figure 5) drew a straight line with high correlation coefficient (R^2 = 0.998); it confirmed the constancy of molar absorptivity over the concentration range being studied. This confirmed the accuracy of AMX concentration determinations. Equilibrium concentrations in samples were then calculated using the calibration plot. The amount of pharmaceutical adsorbed onto the reactive material (qe) in mg/g was calculated using the mass balance equation (Eq.1) as described by Bondarev et al. (2001).

$$q_e = \frac{(C_o - C_e)V}{m} \qquad \text{Eq.1}$$

The amount of pharmaceutical adsorbed per unit mass of sorbent (q_e) in mg/g was calculated using the mass balance equation (Eq.1), where C_0 and C_e (mg/L) represent the initial and equilibrium pharmaceutical concentrations, V (L) is the volume of pharmaceutical solution, and m (g) is the mass of the sorbent. To determine the removal efficiency (R %) of pharmaceuticals onto the sorbent at a particular time (t), Eq.2 was used, as described by Bondarev et al. (2001).

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \text{Eq.2}$$

Statistical analyses, consisting of correlation coefficient analysis and simple linear regression analysis, were performed on the experimental results of this study to confirm the relationship between the different conditions and the resulting removal ratios, as well as to evaluate the statistical significance at a threshold of 0.05.

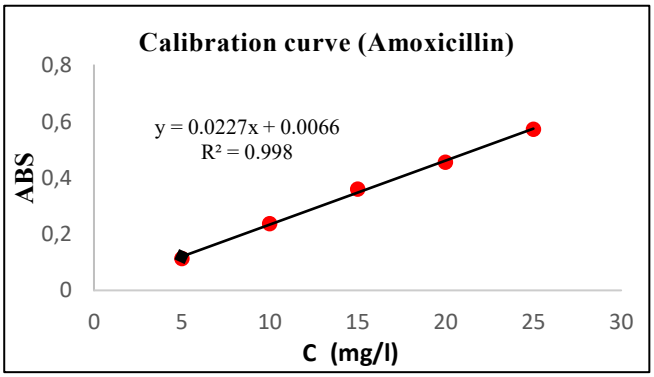

Figure 5. Calibration curves for (AMX).

Results and Discussion

Characterization of Adsorbents

For the activated carbon, several test methods were used to identify prepared from AHRWL. These inspection techniques consist of SEM (Ali et al., 2020). SEM analysis was employed to display the surface morphology and microstructure of AHRWL before and after modification, as depicted in Figure 6. The figure revealed that significant changes occurred in the surface morphology of the natural sorbent after modification. The AHRWL had a porous structure with a rough and irregular appearance, featuring scattered and differently-sized block structures. However, the surface morphology of this material differed after the modification process. The modified activated carbon produced from walnut shells had a smooth surface with numerous holes and a crystal-like appearance, with edge-shaped pores of varying sizes. In contrast, the pores in the H_3PO_4-treated activated carbon were uniformly distributed. The formation of a highly porous structure can be attributed to the significant reduction of organic and inorganic matter during the pyrolysis and washing steps (Anirudhan & Ramachandran, 2007; Chou et al., 2016; Wang et al., 2019). Figure 6 shows SEM images taken at varying magnifications to examine the changes in an activated carbon sample before and after modification. The images labelled (a) show the sample at a magnification of x 100 prior to modification, while the images labelled (b) display the sample at a higher magnification of x 5000 after modification.

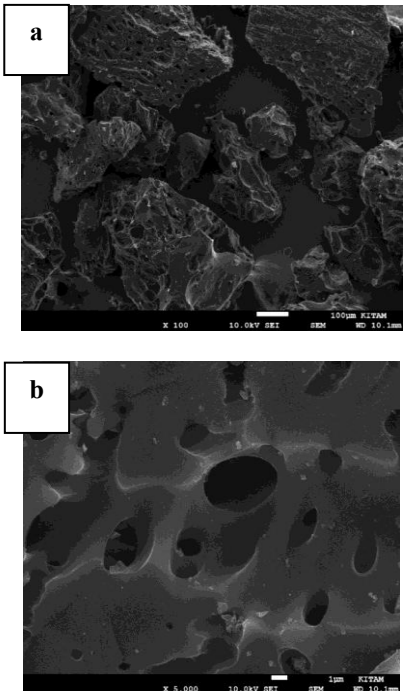

Figure 6. SEM images taken at (a) x 100, (b) x 5000, magnification of the activated carbon sample.

The Brunauer–Emmett Teller equation (BET) was used to calculate the surface area, or SBET, of activated carbon samples made from AHRWL activated carbon by N_2 isotherms. The volume of liquid nitrogen that corresponded to the amount adsorbed at a relative pressure of $P/P_0 = 0.99$ was known as the total pore volume, or V_T. V_μ is the micropore volume. According to (Kowalczyk et al., 2024), the difference between V_T and V_μ was used to compute the mesopore volume V_m. Table 1 contains a list of the outcomes that were gathered for this purpose.

Table 1. Physical characteristics of AHRWL.

Sample name Characterization	AHRWL
Surface Area S_{BET} **(m²/g)**	1205.771 m²/g
Total pore volume V_T **(cc/g)**	6.244e-01 cc/g
Average pore Radius	1.03577e+01 Å
Micropore volume V_μ **(cc/g)**	0.510 cc/g
Micropore area	1104.602 m²/g
External surface area	101.168 m²/g
Mesopore volume V_m **(cc/g)**	0.114 cc/g

Effect of pH

To identify the most effective pH for removing AMX, a solution containing 100 mg/L of AMX was prepared and adjusted to pH values ranging from 3 to 9. The solution was then mixed with 0.025 g of (AHRWL) at 200 rpm for 1 hour at room temperature. The success of an adsorption system in eliminating pollutants relies on the surface properties of the adsorbent and the nature of the adsorbate at a specific pH. Thus, determining the point of zero charge (pHpzc) is crucial, as it signifies the pH at which the adsorbent's surface carries no charge. Above the pHpzc, the surface charge of the adsorbent is negative, while below pHpzc, it is positive (Litefti et al., 2019). In order to determine the pHpzc of the raw material (RWL), a series of 0.1 M KNO_3 solutions were prepared in closed conical flasks. The initial pH of each solution was adjusted and measured within the pH range of 2-12 using HCl or NaOH solutions. Then, 0.4 g of the raw material was added to each solution and agitated at room temperature for 48 hours. The resulting suspension was filtered, and the pH of the filtrate was measured. By plotting the curve pH = **(**pH initial) (where pH = pH initial - pH final), the intersection points of this curve with the x-axis provided the pH value at the point of zero charge, which was determined to be 6.93. The results of the pHpzc determination are presented in Figure 7.

The experimental results demonstrate that the maximum removal rate (R%) of AMX reached 79.32% at pH 6, as depicted in Figure 7. The adsorption of the antibiotic on AHRWL increased when the pH elevated from 4 to 6, but thereafter decreased with further pH rises. Mechanism of pH Influence: The pH of the solution markedly affects the surface charge of the adsorbent and the ionisation state (speciation) of the adsorbate, Amoxicillin (AMX). The pHpzc of AHRWL was ascertained to be 6.93. This number signifies that below pH 6.93, the adsorbent surface is primarily positively charged due to the protonation of its functional groups, whereas above pH 6.93, the surface becomes largely negatively charged due to deprotonation. Amoxicillin (AMX) is an amphoteric antibiotic, capable of existing in cationic, zwitterionic, or anionic forms contingent upon the solution's pH, attributable to the protonation and deprotonation of its amine (pKa ≈ 7.4) and carboxylic acid (pKa ≈ 2.4) moieties (Gupta et al., 2024). The adsorption phenomenon results from the electrostatic interactions between antibiotic molecules and the negatively charged surface of AHRWL. The correlation coefficient (r) of -0.674 signifies a negative correlation, although the p-value derived from linear regression analysis (>0.05) suggests that the association between the reduction in removal rate (R%) and the elevation in pH is not statistically significant (Shang et al., 2020).

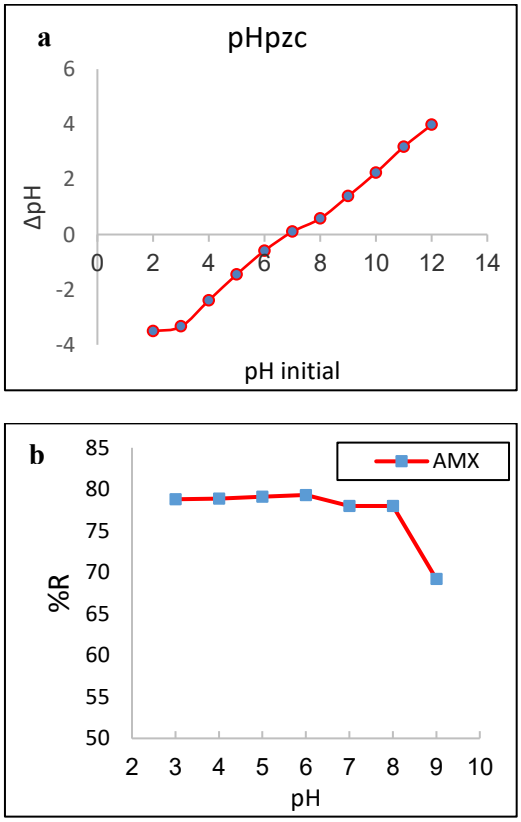

Figure 7. (a) pH_{pzc} of walnut shells (b) Effect of pH on the removal of AMX using (AHRWL) (W=0.025 g/100ml; contact time 1 hour; Ci = 50 mg/L; rpm =200).

Effect of Dosage

Figure 8 illustrates that augmenting the AHRWL dosage from 0.025 to 0.25 g/100 ml led to an enhancement in AMX elimination efficiency from 79.32% to 81.08%. The efficiency of AMX removal is positively associated with the sorbent's surface area. As the mass of the sorbent grows, the quantity of adsorption sites or surface area enlarges, leading to a higher percentage of sorbent removal (Gameli et al., 2022). The correlation analysis yielded a r value of 0.98, signifying a robust positive linear association. The measured p-value corroborates this assumption, as it is markedly low (< 0.05), specifically 0.0005. The association between the sorbent's weight and the removal percentage is statistically significant and not coincidental. To achieve maximum removal efficiency, mass ratio or surface loading of adsorbate materials relative to the adsorbent dosage has to be kept below the ideal threshold for maximum adsorption. This optimal value corresponds to the combination of the best removal rate and the highest capacity of the adsorbent. Consequently, a dose of 0.25 g/100 mL was chosen as optimal for achieving high removal efficiency.

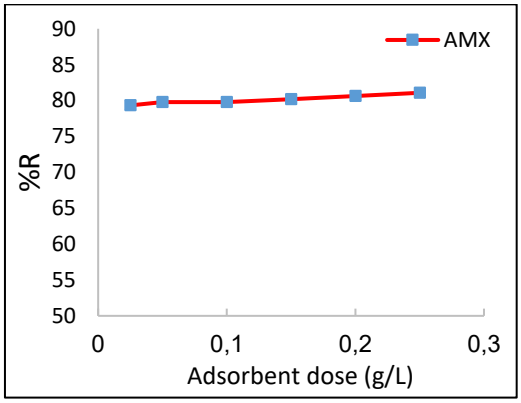

Figure 8. Effect of adsorbent dosage on the removal of AMX using (AHRWL) (pH =6, contact time 1 hour; Ci = 50 mg/L; rpm=200).

Equilibrium Time

This experiment aimed to determine the time required for the adsorption process to reach equilibrium between the selected adsorbent and the pharmaceutical material (AMX). Figure 9 depicts the uptake of the material over time. The results indicated that the sorption of AMX on the AHRWL adsorbent was initially high, and the adsorption rate reached a nearly constant state after a contact time of 15 minutes. The differences observed in the extent of adsorption can be attributed to the presence of unoccupied sites on the surface of the adsorbent and the significant concentration gradient of the solute (Basu et al., 2018). However, as the binding sites became limited in the later stages, the remaining sites were left unoccupied, resulting in the system reaching equilibrium (Anah & Astrini, 2018). The removal efficiency gradually approached a constant value of 82.84% for AHRWL at an AMX concentration of 50 mg/L, indicating that equilibrium was achieved after 60 minutes. In this study, time is regarded as a significant component for enhancing the elimination %; nonetheless, its impact is constrained. A p-value of 0.131 signifies that the link lacks statistical significance at a 95% confidence level ($\alpha = 0.05$), as noted by (Koirala, 2025), suggesting that time alone may not be the principal factor affecting the removal percentage.

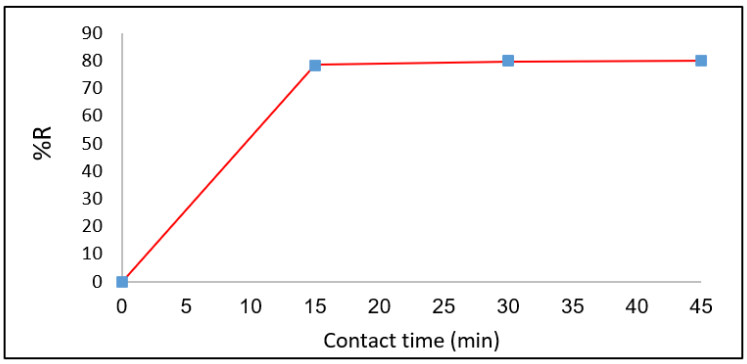

Figure 9. Effect of equilibrium time on the removal of AMX using (AHRWL) (pH =6; Ci = 50 mg/L; rpm=200; W=0.25g).

Effect of Initial Concentration

The rate of adsorption is a crucial factor in determining the effectiveness of adsorption, and the initial concentration of the adsorbate is an essential consideration in this regard. Figure 10 illustrates the effect of various initial concentrations of AMX on the adsorbent. The AHRWL adsorbent was able to remove 84.6% of AMX at an initial concentration of 10 mg/L, indicating that there are enough adsorption sites available for pharmaceutical adsorption at lower initial concentrations (Pehlivan & Altun, 2006). As the initial concentration of pharmaceuticals in the aqueous solution rises, there is a decrease in the value of removal efficiency. This occurrence can be attributed to the involvement of energetically less favourable sites as the pharmaceutical concentration increases. The adsorption process is regulated by various factors, including internal structures, ion exchange processes, and the velocity at which pharmaceuticals traverse through the system. (Lucas et al., 2004). Furthermore, as the concentration of pharmaceuticals rises, the driving force for their removal from the bulk solution and attachment to the adsorbent surface strengthens. This medium leads to a higher amount of pharmaceuticals being adsorbed per unit mass of the adsorbent. However, the curve in the graph demonstrates that as the concentration increases, the adsorption efficiency actually decreases. This decline in adsorption efficiency can be attributed to various factors. One possible explanation is that at higher concentrations, there is greater competition among solute particles for the available adsorption sites on the surface of the adsorbent material. Consequently, the probability of each solute particle successfully adsorbing onto the surface diminishes, resulting in an overall decrease in adsorption efficiency (Yasemin & Zubeyde, 2006). This study indicates that the removal rate depends on the initial concentration, although not significantly, as shown by the results of the correlation coefficient analysis and linear regression analysis of r = 0.79 and p value 0.2, when compared to the removal results for each concentration.

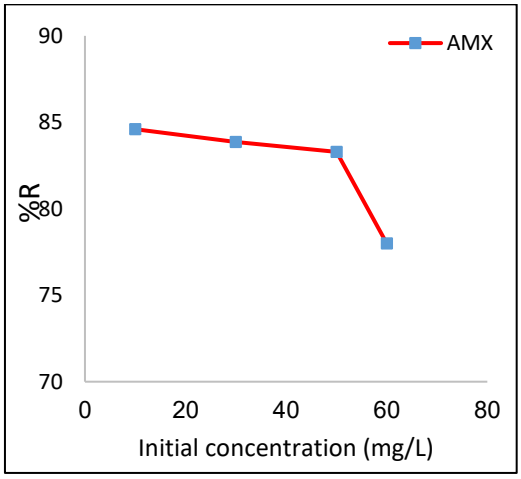

Figure 10. Effect of initial concentration on the removal of AMX using (AHRWL) (pH =6; contact time 1 hour; rpm=200; W=0.25g/100ml).

The Influence of Agitation Speed

The speed of agitation plays a pivotal role in affecting the outer boundary layer. It can be utilized to predict the removal of pharmaceutical compounds, such as AMX, at different velocities. The influence of agitation speed on the elimination of pharmaceutical substances by the selected adsorbent is illustrated in Figure 11. The experimental results demonstrated a significant impact of stirring rate on the adsorption of pharmaceuticals. Increasing the stirring rate from 50 to 300 rpm led to an increase in the percentage of AMX removed from AHRWL, rising from 79.32% to 83.28%. This rise in the removal percentage of pharmaceutical material at higher stirring rates can be attributed to the reduction of the boundary layer thickness around the adsorbent particles, consequently resulting in an increased concentration of pharmaceutical materials near the adsorbent surface (Piccin et al., 2011). Increasing the stirring rate enhances the movement of pharmaceuticals from the bulk solution to the adsorbent surface, leading to superior mass transfer and a shorter time to reach adsorption equilibrium. However, the removal efficiency reaches a nearly constant value beyond 250 rpm, indicating an optimal stirring speed.

An increased stirring rate can lead to a higher removal efficiency for pharmaceuticals. Still, it comes at the cost of greater energy consumption and a greater risk of damage to the physical structure of adsorbents (Piccin et al., 2011). As depicted in Figure 11, the efficient removal of pharmaceuticals at 250 rpm was not considerably

different from that at 300 rpm. Hence, a stirring rate of 300 rpm is sufficient to make sure that all available surface binding sites are accessible for lead uptake. Statistical analyses indicate a positive correlation, with a coefficient of determination (R^2) of 0.89 and a statistically significant p-value of 0.01, which is below the threshold of 0.05.

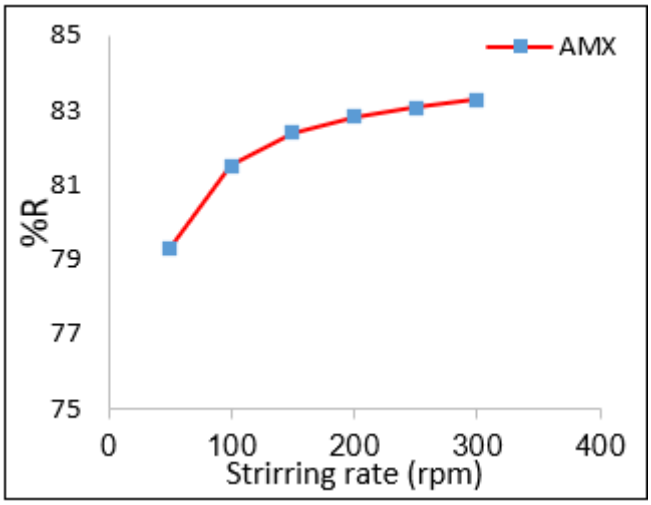

Figure 11. Effect of agitation speed on the removal of AMX using (AHRWL) (pH =6; contact time 1 hour; Ci = 50 mg/L; W=0.25g/100ml)

Sorption Isotherms

Sorption isotherms are valuable tools for understanding the sorption process. They establish the relationship between the equilibrium content and the amount of adsorbate adsorbed per unit mass of adsorbent at a constant temperature (Rao et al., 2009). The Langmuir and Freundlich isotherm models are typically used to study the sorption process. The model parameters can provide insight into the sorption mechanism, surface properties, and affinity of the adsorbent (Yuh-Shan, 2004). Table 2 lists the estimated parameters for the isotherms and coefficients of correlation R^2, while Figures 12 and 13 summarize the findings. The Langmuir adsorption model is valid for single-layer adsorption. It assumes that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Abbas et al., 2016). The Langmuir isotherm equation (3) is used to describe the data obtained from the experiment.

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \qquad \text{Eq.3}$$

The linear form of Eq. (4) is:

$$\frac{C_e}{qe} = \frac{1}{(bq_m)} + \frac{C_e}{(bq_m)} \qquad \text{Eq.4}$$

The sorbed amoxicillin on the sorbent in (mg/g) is represented by q_e, while qm stands for the maximum sorption capacity for monolayer coverage in (mg/g). The constant b in (L/mg) is related to the affinity of the binding site, and Ce in (mg/L) denotes the AMX concentration in the solution at equilibrium. The Langmuir isotherm is commonly used to describe the adsorption isotherm, which is limited by the assumption of uniform energies of adsorption on the surface of the adsorbent. On the other hand, the Freundlich isotherm is suitable for heterogeneous surfaces (Debord et al., 2023), and it follows equation (5).

$$q_e = K_F\, C_e^{\,1/n} \qquad \text{Eq.5}$$

The capacity and intensity of adsorption are represented by the Freundlich constants K_F and n, respectively. Unlike the Langmuir model, the Freundlich isotherm provides information about the monolayer adsorption capacity. The K_F and n values can be obtained from the plot of ln q_e versus ln Ce, which yields a straight line with an intercept of ln K_F and a slope of 1/n (Piccin et al., 2011). The batch equilibrium data were obtained using an initial concentration of 50 mg/l for amoxicillin and amounts of adsorbent, ranging from 0.025-0.25 g/100ml. However, as Figure (12) illustrates, the batch equilibrium data of AMX on AHRWL fit the Langmuir model better than the

Freundlich isotherm, with a correlation coefficient (R2) above 0.95. According to multiple authors, these findings are consistent with earlier research that used agricultural precursors for antibiotic adsorption (Getenew & Misganaw, 2024). This medium implies that some homogenous spots are the sites of monolayer adsorption. According to the Freundlich isotherm model, the adsorption of surface energy is heterogeneous. Figure (13) depicts the correlation between the number of pharmaceuticals adsorbed per unit mass of adsorbents (q_e) and the equilibrium pharmaceutical concentration (Ce), as predicted by the Freundlich isotherm models. The slope (1/n) values for both adsorbents ranged from 0 to 1, indicating that bond energies increase as the planar density increases. A 1/n value less than one suggests favourable chemisorption of the adsorption process (El Hammari et al., 2023).

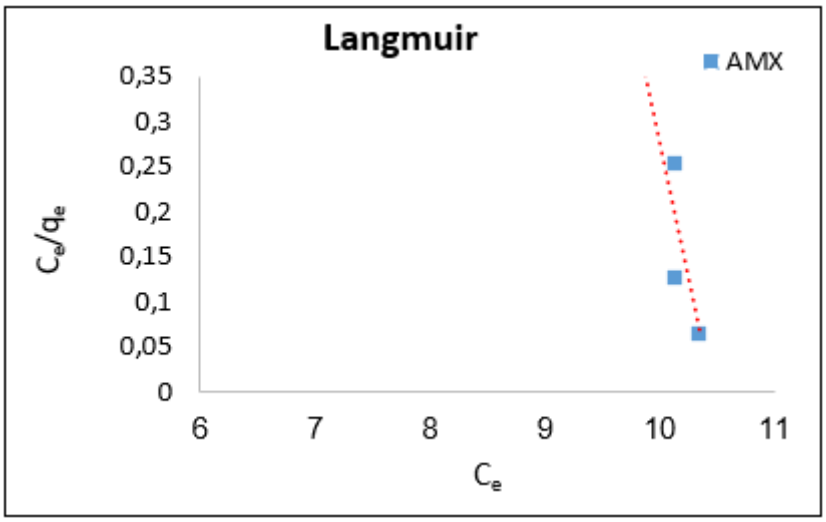

Figure 12. Linear Langmuir adsorption isotherm of (AMX) sorption onto (AHRWL).

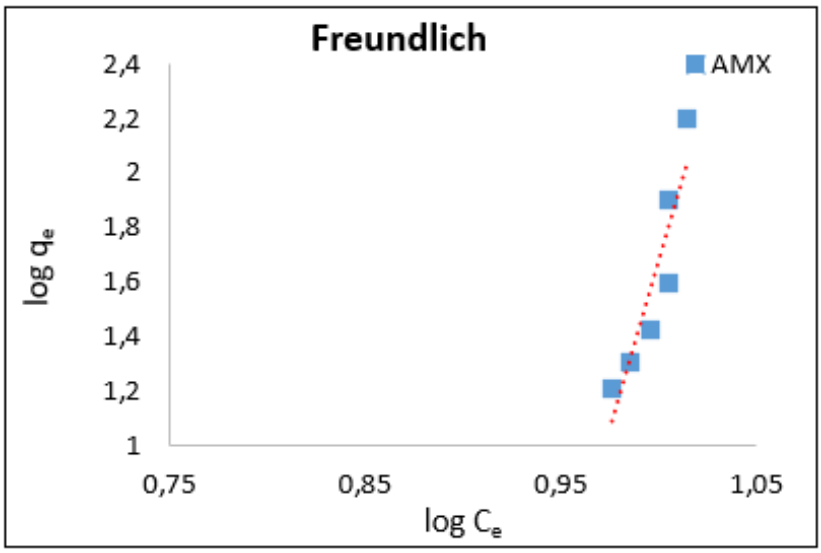

Figure 13. Linear Freundlich adsorption isotherm of (AMX) sorption onto (AHRWL).

Absorption Kinetics

The kinetic study assesses the rate of adsorption, which various mass transfer conditions may limit. These conditions are dependent on factors such as the type of adsorbate and adsorbent, as well as pressure and temperature. Solid materials typically have two main types of resistance: (i) Resistance to external diffusion, which concerns the mass movement from a bulk fluid to an outer surface, and (ii) Resistance to interparticle diffusion, which pertains to the transfer of mass from an outer surface to the surface between pores. Different models have been developed to investigate these processes and determine the likely rate-determining steps. Typically, the pseudo-first-order (eq. 6) and pseudo-second-order (eq. 7) models are used to elucidate the kinetics of pharmaceutical adsorption.

$$q\,(t)\;=\;q\,(1\;-\;e^{-\,Kt_1}\,)\,e \qquad \text{Eq.6}$$

$$q\;=\;\frac{K_2\,{q_e}^2 t}{1+K_2 q_e t} \qquad \text{Eq.7}$$

The amount of adsorbate adsorbed onto the adsorbent at any time t (in mg/g) is represented by q(t). In contrast, K_1 (in min^{-1}) and K_2 (in g/mg.min) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively. The amount of solute adsorbed onto the adsorbent at equilibrium is represented by q_e (mg/g), and t (min) denotes time (Rao et al., 2009; Yuh-Shan, 2004).

Table 2 and Figures 14 and 15 provide a comprehensive overview of the findings. The experimental data were found to be well-suited to the pseudo-second-order kinetic model, as indicated by the higher R^2 (0.99) values obtained. The computed q_e (equilibrium adsorption capacity) values closely matched the experimental values, further supporting the suitability of the pseudo-second-order model. In contrast, the pseudo-first-order model yielded lower R^2 (0.86) values and exhibited a significant disparity between the calculated and measured adsorption capacity, suggesting its poor performance. These results align with previous studies that utilized agricultural precursors for adsorbing antibiotics, as reported by several authors (Abbas et al., 2016).

Table 2. Parameters of. Langmuir, Freundlich, isotherms, and kinetic models for (AMX) adsorption onto (AHRWL).

Model	**Isotherm Parameter**	**AMX**
Langmuir	q_{max}(mg/g)	-1.644
	K_L(L/mg)	-0.095
	R^2	0.950
Freundlich	K_F(mg/g)	1.28E-10
	n	0.040
	R^2	0.839
	Kinetics Parameter	**AMX**
Pseudo first order	q_e experimental(mg/g)	16.6
	q_e calculated (mg/g)	1.403
	K_1(min^{-1})	0.0248
	R^2	0.861
Pseudo-second order	q_e calculated (mg/g)	16.583
	K_2 (g mg-1 min-1)	0.066
	R^2	0.999

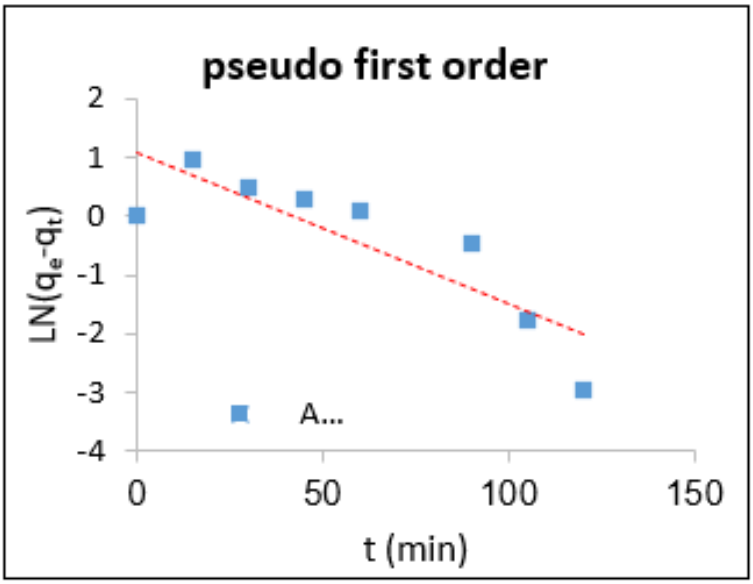

Figure 14. Pseudo-1st-order linear plot of (AMX) sorption onto (AHRWL).

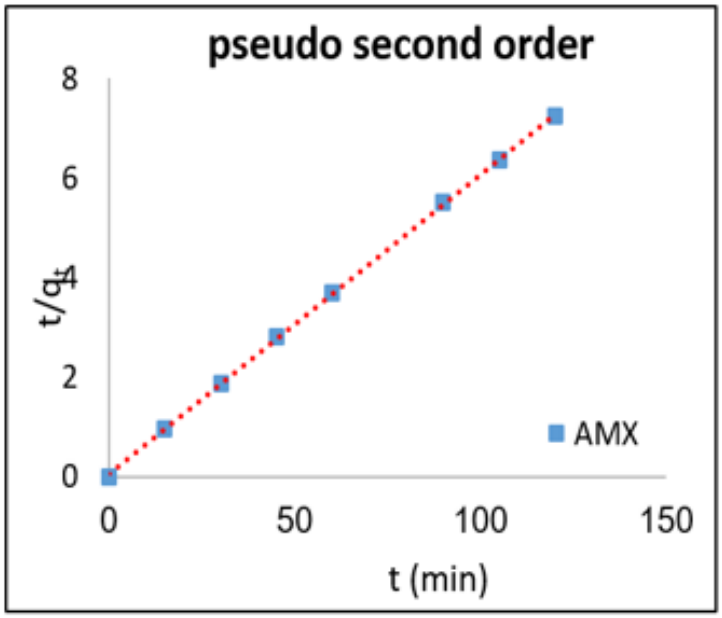

Figure 15. Pseudo – 2nd-order linear plot of (AMX) sorption onto (AHRW)

Conclusion

The current study explained the effectiveness of activated carbon prepared from walnut shells (AHRWL) as a sustainable and economically viable adsorbent for the removal of Amoxicillin (AMX) from aqueous solutions. By adopting an environmentally friendly approach toward the valorization of agricultural waste materials, the present study paces up global efforts to develop eco-friendly wastewater treatment technologies. The findings of this study emphasize the potential of AHRWL as a realistic solution for addressing pharmaceutical contamination, which poses significant risks to human health and aquatic ecosystems. According to the experimental findings, AHRWL demonstrated a high adsorption efficiency under ideal circumstances. When the initial concentration was 50 mg/l, with an adsorbent dose of 0.25g/100ml, pH 6, contact time of 1 hour, and speed of 300 rpm, the removal rate reached 83.28%. The process also fit the Langmuir isotherm model and pseudo-second-order kinetics very well, which undoubtedly supported the material's potential to provide quick and efficient pollutant removal. Furthermore, this study has provided an aspect of optimizing adsorbent dosage, pH levels, and contact time, thus making it useful in practical applications for real-world purposes.

In summary, the present study enhances not only the understanding of sustainable adsorbent technologies but also aligns with broader environmental and public health objectives. The use of walnut shells in water treatment has a dual benefit: it relieves agricultural waste. It reduces pharmaceutical contaminants in water sources, thus helping to create a healthier and more sustainable future.

Nomenclature

Ce	Equilibrium condentration of AMX, mg/l
Ct	concentration of AMX at time t(min), mg/l
KF	Freundlich isotherm constant, (mg/g).
KL	Langmuir isotherm constant, l/mg
K1	The adsorption rate constant of the pseudo-first-order model, 1/min
K2	The rate constant of the pseudo-second-order model, mg/g.min
qe	Uptake of AMX at equilibrium, mg/g
q_t	Uptake of AMX at time t(min), mg/g
V	Volume of AMX solution, ml
W	Weight of activated carbon, mg

Scientific Ethics Declaration

* The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Conflict of Interest

* The authors declare that they have no conflicts of interest.

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