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Original Research

WALNUT SHELLS AS SUSTAINABLE ADSORBENT FOR THE REMOVAL OF MEDICAL WASTE FROM WASTEWATER

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Abstract: Adsorption has been demonstrated to be one of the world's most effective wastewater remediation techniques. This study attempts to use walnut shells as an adsorbent for the removal of the medications Amoxicillin, Ciprofloxacin, and Tetracycline from aqueous solutions. Many variables were studied to indicate walnut shells influence on the efficiency of removal; which included pH of the solution (3-9), drugs concentration (10-60 mg/L), adsorbent concentration (0.025–0.25) g/100ml for the walnut shell, contact time (5-120 min), and agitation speed (50-300 rpm). From the experimental results, the best removal at the most suitable pH value of Amoxicillin at pH 6, for Ciprofloxacin was at pH 5 and at pH 4 for the Tetracycline. With an optimum condition, for an amount of adsorbent of about 0.25, and an optimum time of 60 min for all adsorbs using 300 rpm. The best percentage of removal was 59.32% for Amoxicillin, 62.160% for Ciprofloxacin, and 61.55% for Tetracycline when 50 mg/l concentrations of all pharmaceutical solutions. The removal is well integrated into the Freundlich isotherm model. The correlation of kinetic data by a pseudo-second-order model was successful for three antibiotics. However, this study showed that walnut shells are an effective adsorbent in removing medical contaminants from an aqueous solution of the natural environment.

Keywords: *Adsorption; Amoxicillin; Ciprofloxacin; Isotherm; Kinetics; Tetracycline; Walnut shell; Wastewater treatment*

1. Introduction.

The global production of pharmaceuticals has experienced a significant surge in the last century, resulting in environmental degradation. [1,2]. Various pharmaceuticals enter the environment through human activities, posing immediate and long-term effects on the ecosystem [3]. These pollutants can be found in waterways, groundwater, wastewater treatment plants, and the ocean [4]. Traditional treatment methods struggle to effectively remove these persistent compounds, posing a threat to the environment [5].

The COVID-19 pandemic has highlighted the need to remove pharmaceutical residues from wastewater due to increased medication usage in hospitals [6]. However, the cost of pharmaceutical removal is a significant consideration, requiring the development of cost-effective materials and methods [7-10].

Adsorption has shown promise in removing pharmaceuticals from wastewater [11-15]. Various materials, including agricultural by-products, can serve as adsorbents [16-36]. These

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include such as orange peel [37], dried olive stone [38], broad bean peels [39], lemon peel [40, 41], rice husk [42], Cordia Myxa Fruits [43], walnuts shell [44], and others [45-47]. Recently, Walnut shells (WL) have been investigated as a potential low-cost adsorbent for removing drugs like Ciprofloxacin (CPF), Tetracycline (TYC), and Amoxicillin (AMX) [10]. The study examines parameters such as pH, contact duration, adsorbent doses, drug concentration (10-60 mg/L), and agitation speed, to determine optimal conditions for efficient removal [11].

The findings aim to contribute to the development of effective and sustainable methods for removing antibiotics from wastewater.

2.1. Chemicals.

Tetracycline powder (TYC) has the chemical formula C22H24N2O8, the molecular weight 444.440 g/mol, and a purity of 98%, Ciprofloxacin (CPF) (chemical formula: C17H18FN3O3, molecular weight: 331.34 g/mol, and purity: 97.5%), and Amoxicillin (AMX) Chemical formula: C16H19N3O5S, molecular weight: 365.404 g/mol, and purity: 99%. Original manufacturer: Merck, Germany. Fig. 1 shows how the chemicals in these three medicines are put together. Separate stock solutions of 1000 mg/L TYC, CPF, and AMX were prepared by dissolving the appropriate quantity of antibiotic powder in 1 L of deionized water. For thirty minutes, the stock solution is vigorously mixed until the solution is homogeneous. The original solution was then diluted to create working solutions. Because in vitro conditions were unstable during the pilot study, stock and liquid dilutions were created. During the experiments, the pH of the solutions was controlled by adding the buffer solution drop by drop.

2.2. Synthesizing of the Adsorbents

In this study, the walnut shells, shown in Fig 2, used as the target adsorbent (WL) were made in the lab using the following basic steps. First, a certain amount of (WL) was bought from a plant shop in Baghdad, Iraq.

Then, it was washed with deionized water, dried in an oven at 105 °C for one night, ground, and sieved [14]. And crushed into granules of different sizes, then sieved using sieves (type: Restch, Germany) to produce particles less than (425) μm; for their use in the experiment.

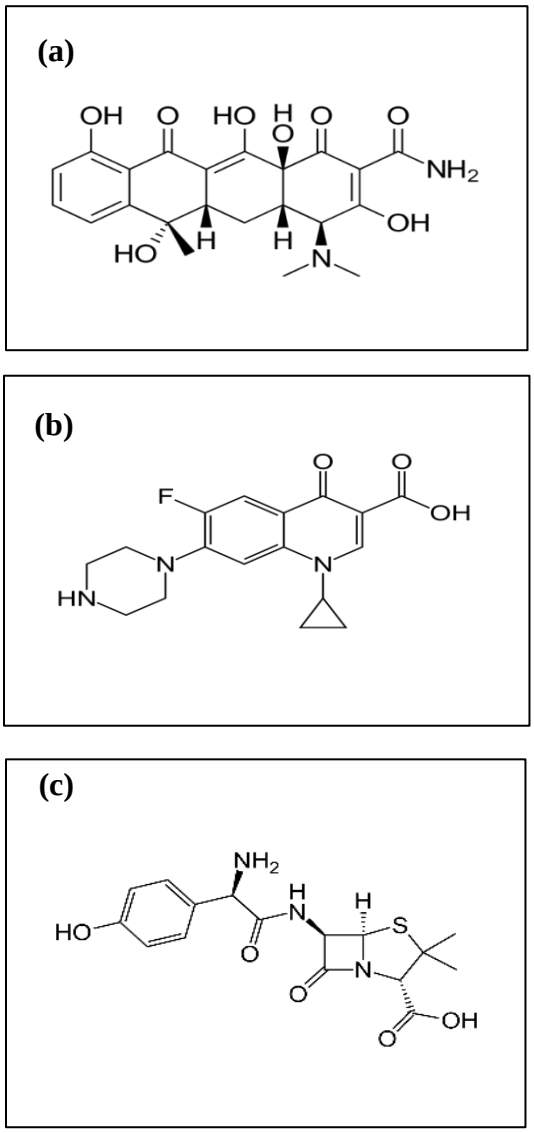


Figure 1. The chemical structure of (a) TYC, (b) CPF, (c) AMX [12,13].

Figure 2. Walnut shells before grinding

The material was divided into several samples, and each sample was handled separately and labeled to prepare different adsorbents, as shown in Fig. 3. It used the names Raw Walnut shells (WL) for brevity in this study.

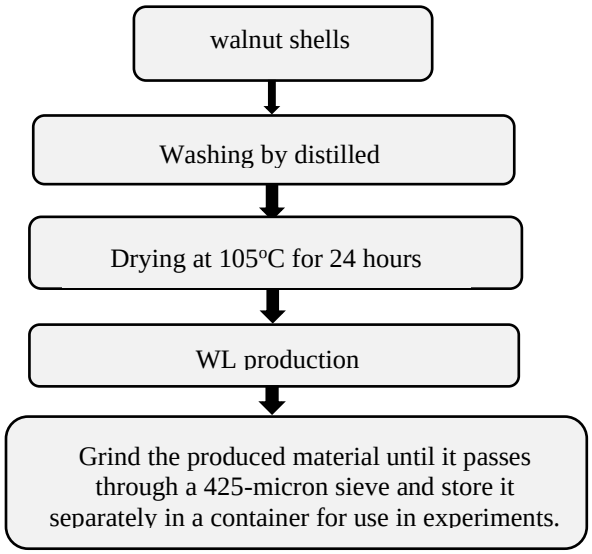
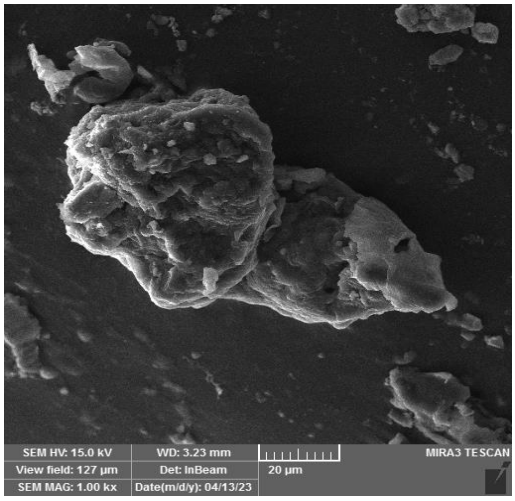


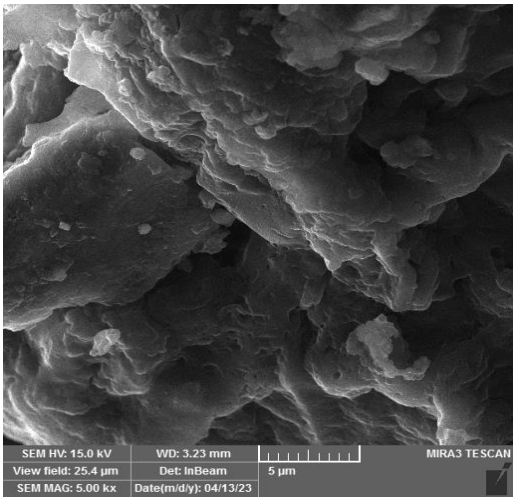
Figure 3. The production process for adsorbents from Walnut shells.

2.3. Characterizations.

The adsorbent samples were characterized by examining their surface using scanning electron microscopy (SEM). The SEM images, depicted in Fig. 4, provided a visual representation of the surface morphology of the samples. The images indicated the presence of fine particles with irregular shapes and varying sizes. These particles displayed different dimensions and multiple steps, kinks, and broken edges on their outer surfaces [15].



(a)



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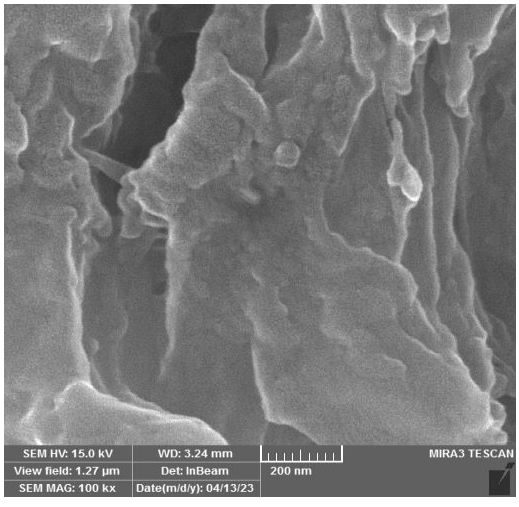


(c)

Figure 4. SEM images were taken of walnut shell samples with magnification (a) x 20 mm, (b) x 5 mm, and (c) x 20 mm.

Furthermore, the FT-IR analysis was conducted to gain qualitative insights into the functional groups present on the material surfaces. Infrared spectra were obtained for each adsorbent sample in its raw state before the adsorption process and after being used for the adsorption of AMx, CPF, and TYC, following pH adjustments. Table (1) presents the identified functional groups on the surfaces of the adsorbent (WL) and their corresponding assignments in the infrared spectra [16]. The FT-IR analysis is illustrated in Fig. 5.

2.4. Sorption Experiments.

The sorption of ciprofloxacin (CPF), tetracycline (TYC), and amoxicillin (AMX) by selected reactive materials was studied using batch experiments under different conditions. The batch experiments were done by adding a certain amount of the sorbents to (100) mL of pharmaceutical solutions with different concentrations of (10-60) mg/L, and then shaking the mixture with a thermostatic shaker. For practical reasons, batch tests were done with different contact times (15–120 minutes), initial pH of the solution (3–9), agitation speed (50–300 rpm), and sorbent dosage (0.25–0.25 g/100 mL). A fixed volume (100 mL) of the solution was withdrawn from each flask, and filtered using filter paper type (Whatman No. 40) to separate the adsorbent from the aqueous solution, then the filtered solution was analysed using double beam UV-visible spectrophotometer (PG Instruments, Model UV T80, England) at λmax (CPF) =272 nm, λmax (TYC) =360 nm, λmax (AMX) =227 nm to determine the remain pharmaceutical concentration.

Table 1. Function groups before and after Walnut shells (WL) loaded with Amoxicillin (AMX), Tetracycline (TYC), and Ciprofloxacin (CPF).

Walnut shells (WL)				
Wave number cm^{-1}	**Assignment Groups**	**After adsorption of Amoxicillin (AMX) cm^{-1}**	**After adsorption of Tetracycline (TYC) cm^{-1}**	**After adsorption of Ciprofloxacin (CPF) cm^{-1}**
3383.90	Carboxylic acid, Amides	3402.24	3401.76	3392.51
2926.20	Carboxylic acid	2925.87	2923.97	2924.33
2856.12	Carboxylic acid	2855.08	2854.04	2854.95
2151.61	Alkynes	1729.67	1735.15	2143.48
1730.51	Carboxylic acid	1635.81	1631.45	1736.22
1615.52	Carboxylic, Hydroxyle, Alkanes	1515.95	1514.67	1634.46
1516.72	carboxylates, Carboxylic acid	1374.42	1449.84	1514.83
1420.59	phosphorus oxide, Aromatic	1336.58	1420.44	1451.39
1263.30	phosphorus oxide, carboxylic acids, ethers, phosphorus oxide	1237.10	1376.48	1426.86
1072.05	Carboxylic acid	1057.50	1058.82	1055.74
927.11	Aromatic	818.48	898.52	897.27
632.10	Aromatic	-	607.10	608.14

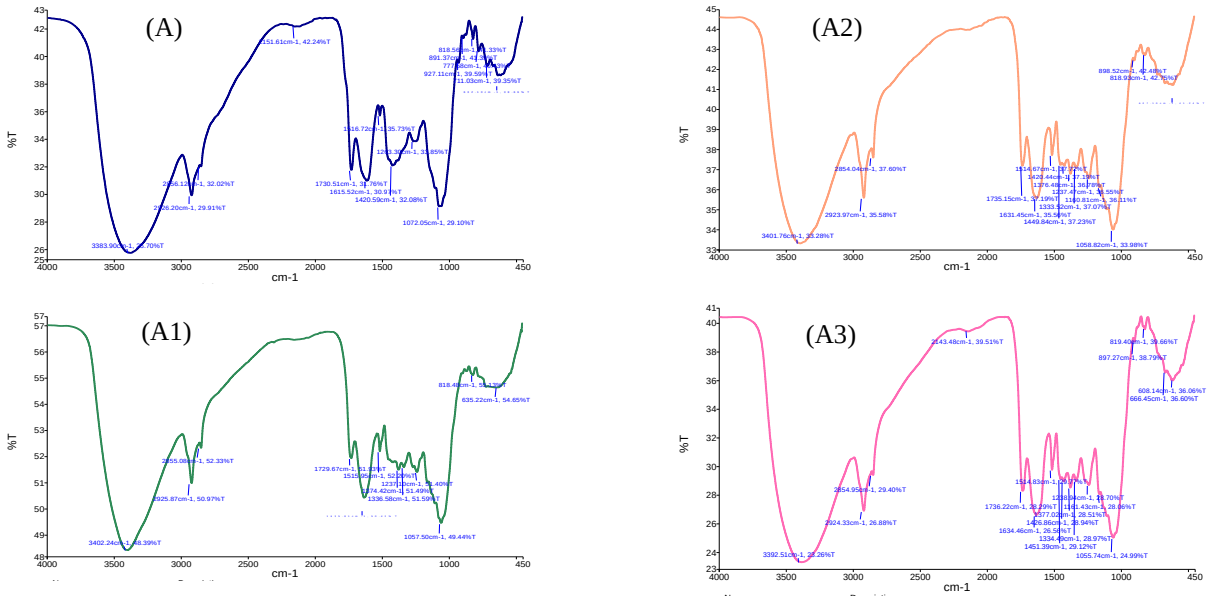


Figure 5. FTIR analysis: (A) RAW Walnut shells (WL) before adsorption of the drugs and after adsorption: A1: Amoxicillin (AMX) loaded Walnut shells (WL); A2: Tetracycline (TYC) loaded Walnut shells (WL) and A3: Ciprofloxacin (CPF) loaded Walnut shells (WL).

The mass balance was used to figure out how much of the drug was absorbed by the reacting material, qe (mg/g). Eq.1 [17].

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

Where: qe is the amount of drug adsorbed per unit mass of sorbent (mg/g), C_0 and Ce are the starting and equilibrium drug concentrations (mg/L), V is the volume of the drug solution (L), and m is the mass of the sorbent (g). Eq.2 was used to figure out the removal rate (R%) of the drug from the sorbent at time t. [18].

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

3. Results and Discussion

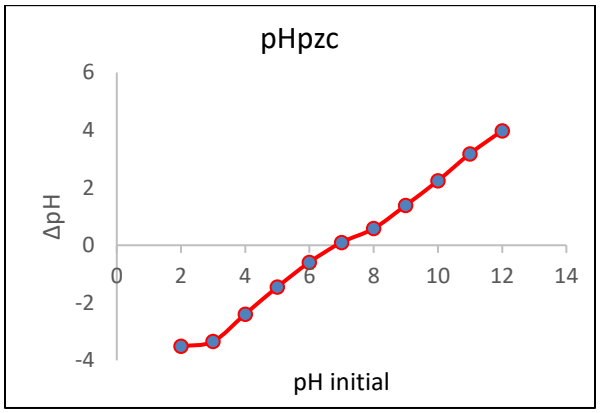
3.1. Effect of pH

In order to find the best pH value, the pH of a solution with 100 mg/L each of AMX, CPF, and TYC was changed separately, and pH values from 3 to 9 were taken and rocked for 1 hour at room temperature with 0.025 g of adsorbent and 200 rpm of shaking speed. As sorbent material, (WL) has been used in the tests. In general, the ability of an adsorption system to remove pollution depends on the surface properties of the adsorbent used and the type of the adsorbate at a certain pH value. The study of pH at the point of zero charges (pHpzc) is crucial in understanding the charging behavior of the adsorbent surface. It indicates the pH value at which the surface of the adsorbent material becomes neutral, with no net charge. This means that when the pH is higher than the pHpzc, the surface charge of the adsorbent is negative, and vice versa [19].

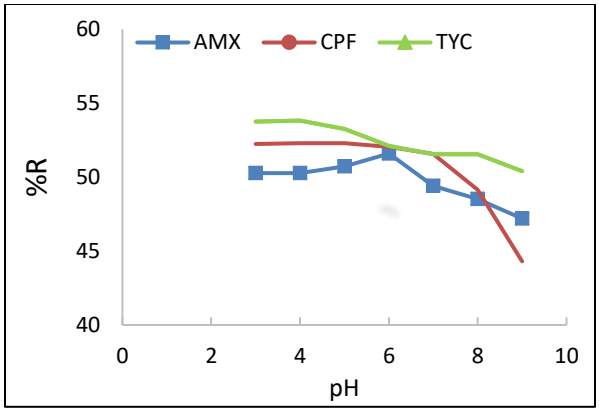
To determine the pHpzc of the raw material (WL), a series of 0.1 M KNO_3 solutions were prepared in closed conical flasks. The initial pH of each solution was adjusted within the pH range of 2-12 using HCl or NaOH solutions and

measured with a pH meter. Subsequently, 0.4 g of the raw material was added to each solution and agitated at room temperature for 48 hours. The suspension was then filtered using filter paper, and the pH of the resulting filtrate was determined. By plotting the curve pH = f (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 found to be 6.93. The results for the determination of pHpzc are shown in Fig. 6.

Referring to the experiments, it can be shown from find through the calculations that the removal rate R% for AMX maximum of 51.6% at pH = 6, but for CPF the best pH value is 5, and was obtained removal rates of 52.298, for TYC the best rate removal was 53.828 in pH= 4, The results of the experiment for all pharmaceutical samples have been shown in Fig 6. Clearly, the amount of each antibiotic adsorbed onto the (WL) in each drug system increases, showing a pH increase from 4 to 6, and subsequently, it decreases with the increase in pH. Such adsorption behavior can be explained according to the electrostatic interactions between antibiotic molecules and the surface of the (WL) with the opposite charges [20].



(a)



(b)

Figure 6. (a) pH_{PZC} of walnut shells (b) Effects of the initial value of pH on removal efficiency of (AMX, CPF, TYC) (C_0:50 mg/L, contact time 1-hour, adsorbent dose 0.025g, solution volume100ml, agitation speed 200rpm).

3.2. Effect of Amount of Walnut Shell

The impact of the adsorbent dosage is a significant factor that has been investigated to determine the removal efficiency and adsorption capacity of the adsorbent material. The study found that the optimum percentage of pharmaceutical material removal was achieved when using a dosage of 0.25 g. This information is depicted in Fig.7. The experimental results for all samples were obtained under identical conditions, except for the pH values, which were 6, 5, and 4 consecutively. Previous studies explained that the reason for removal efficiency has been increased with an increase in the dose, on the other hand, adsorption capacity decreased with the increase in dose. The explanation for the difference in the removal capacity and the dose of the adsorbent is due to the presence of many active sites on the surface of the adsorbent, and the percentage of these sites available, is higher when using fewer quantities of the adsorbent. Also, with the increase in the amount of the adsorbent substance, the rate of collisions between the granules of the adsorbent substance with each other increases, and therefore there is adsorption of ions on the surface of the solid substance, and then they

return to the solution again due to the collisions, which is called the process of (desorption), and with the increase in the quantity of the adsorbent substance, there are layers of the substance on top of each other, and thus a shift between the adsorption sites and between the ions of the pharmaceutical substances, thus decreasing the adsorption capacity [21,22].

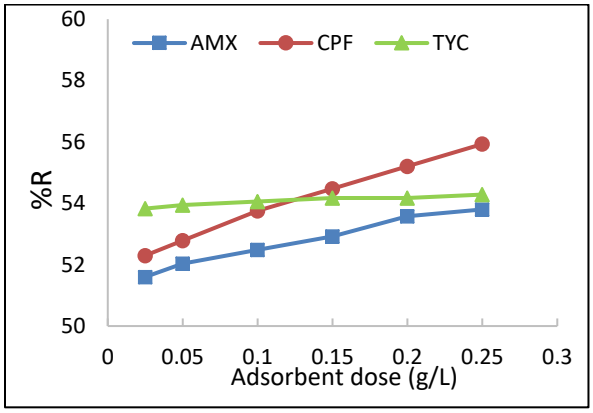


Figure 7. Effects of adsorbent dosage value on removal efficiency of (AMX, CPF, TYC) (C_0:50 mg/L, contact time 1 hour, pH value (6,5,4) consecutively, solution volume100ml, agitation speed 200rpm).

3.3. Effect of Contact Time

Contact time has a significant impact on efficiently removing pharmaceutical ions using different adsorbents. Fig. 8 shows. The impacts of the contact time on the capacity of adsorption of pharmaceutical ions AMX, CPF, and TYC by (WL), it finds through the calculations that the removal rates %R increasing with time for all samples. Considering the contact, time then increases from 5 to 120 minutes. The results clearly show that the adsorption rate is higher in the beginning as a result of the availability of a large part of the active sites on adsorbents. When those sites are depleted, the rate of adsorption is regulated by the rate at which an adsorbate is transferred from outside to the inner sites of adsorbent molecules [23]. Maximal removal has been achieved within the 2-hour stirring times in experiments. There should not appear to be much advantage after this time.

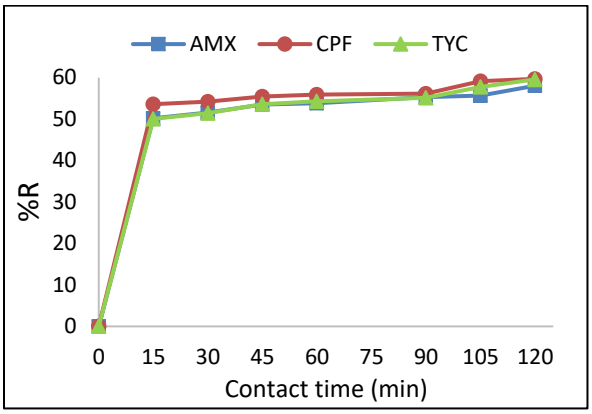


Figure 8. Effect of the contact time upon the efficiency of (AMX, CPF, TYC) removal efficiency (C_0:50 mg/L, adsorbent dose 0.25g, pH value (6,5,4) consecutively, solution volume100ml, agitation speed 200rpm).

3.4. Effect of Initial Concentration

The study of the effects of the initial concentration of pharmaceutical substances AMX, CPF, and TYC on adsorption capacity is crucial. Fig. 9 depicts the concentrations measured, the percentages of removal, and the results of an experiment demonstrating that the adsorption capacity at equilibrium (Qe) increased as the initial concentrations of pharmaceutical materials increased, as the mass thrust force increased so that the adsorption continues with increasing concentration until all the sites are filled. The presence of attractive forces (static electricity, van der Waals, etc.) causes the molecules of pharmaceuticals to bind more strongly to the adsorbent, particularly at the active sites. However, as concentrations increase, they decrease, allowing for a greater difference to be observed between initial and final concentrations; consequently, the proportion of pharmaceutical materials removed decreases [24,25].

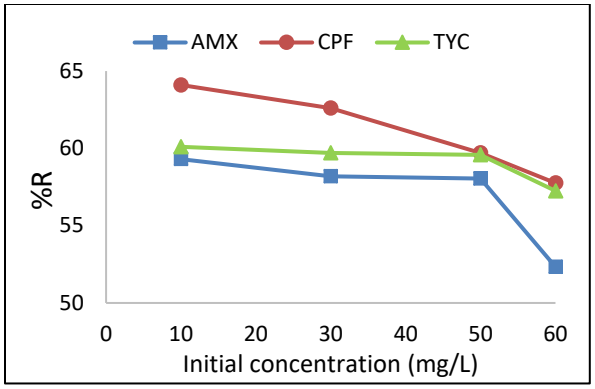


Figure 9. Effects of the initial concentration values of pharmaceutical material (AMX, CPF, TYC) on removal efficiency (Adsorbent dose 0.25g, contact time 1 hour, pH value (6,5,4) consecutively, solution volume100ml, agitation speed 200rpm).

3.5. Effect of Agitation Speed

The literature showed that there is an optimum speed, which must be checked for each absorbent material. Fig 10 shows the effect of the rpm on the absorption of pharmaceutical substances (WL) at different agitation speeds, and it is found through the calculations that the removal rates R% will increase with increased action speed [26]. This results from the fact that with the increase of turbulence, a change in the thickness of the boundary layer around adsorbent particles occurs, it may be observed from the figure that at 300 rpm, the capacity of the adsorption of adsorbent is maximal, which means that the best absorbance was obtained for all samples with increasing speed [27].

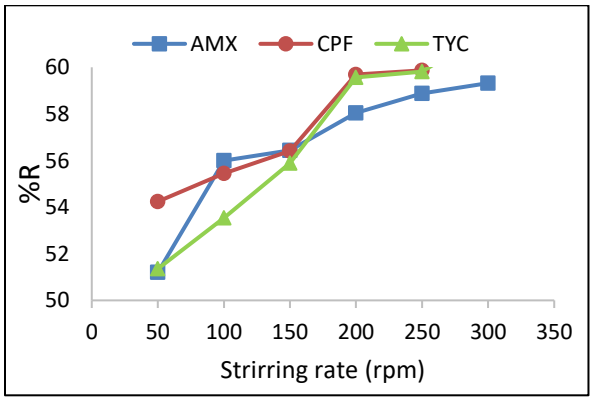


Figure 10. Effects of the speed of agitation on the efficiency of removal of (AMX, CPF, TYC) (C_0:50 mg/L, adsorbent dose 0.25g, contact time 1 hour, pH value (6,5,4) consecutively, solution volume100ml).

3.6. Absorption Isotherms

Sorption isotherms are very useful tools for figuring out how the sorption process works. Find the relationship between the equilibrium content and the amount of adsorbate adsorbed per unit mass of adsorbent at a constant temperature [28]. The sorption process is typically studied using the Langmuir and Freundlich isotherms models. The model parameters can be interpreted in greater detail to provide insight into the sorption mechanism, surface properties, and affinity of the adsorbent [29]. The estimated parameters for the isotherms and coefficients of correlation R^2 have been listed in Table 2 and Fig. 11 shows a summary of the findings. The Langmuir adsorption model is valid for single-layer adsorption. It is based on the assumption that 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 [30]. The Langmuir isotherm equation is.

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \quad (3)$$

The linear form of Eq. (4) is:

$$\frac{C_e}{qe} = \frac{1}{(bQ_0)} + \frac{C_e}{(bQ_0)} \quad (4)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the maximum sorption capacity for monolayer coverage (mg/g), b is the constant related to the affinity of the binding site (L/mg), and Ce is metal ions concentration in the solution at equilibrium (mg/L). The Langmuir isotherm is used most frequently to describe the adsorption isotherm which is limited by the assumptions of uniform energies of adsorption on the surface of adsorbent.

The Freundlich isotherm is valid for heterogeneous surfaces [31], and it follows the equation (5).

$$q_e = K_F\, C_e^{\,1/n} \qquad (5)$$

Where: K_F and n are the Freundlich constants concerning the capacity and intensity of adsorption, respectively. In contrast, the Langmuir model provides no information about the monolayer adsorption capacity. The K_F and n values will be obtained from the plot of ln q_e versus ln Ce that gives a straight line with an intercept ln K_F and a slope 1/ n [32]. The lines of the linear regression that have been obtained have highly important coefficients of correlation R^2 (0.987 - 0.997), which indicates a good fit to the Freundlich equation in all samples.

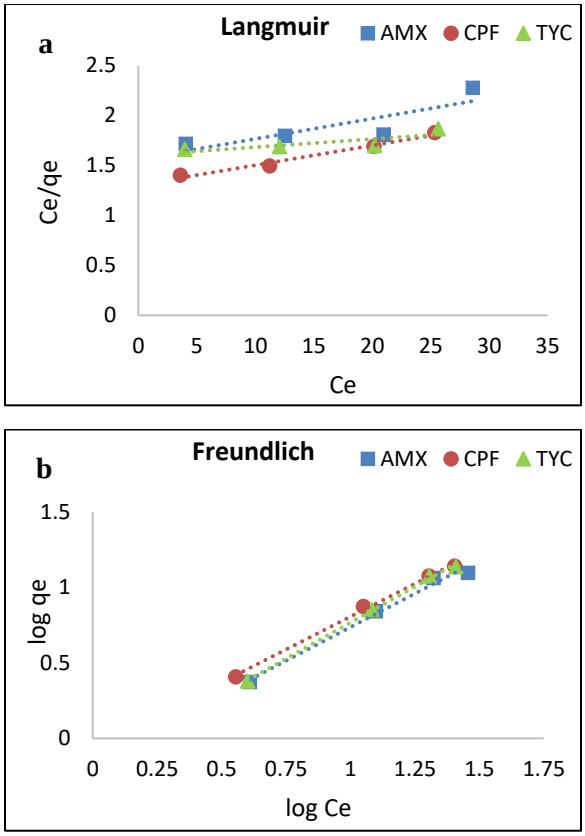


Figure 11. Linear isotherm of (AMX, CPF, TYC) sorption onto (WL) (a) Langmuir adsorption (b) Freundlich adsorption.

3.7. Absorption Kinetics

The kinetic study measures the rate of adsorption, which may be limited by different mass transfer conditions. These conditions depend on the type of adsorbate and adsorbent, as well as the pressure and temperature.

Table 2. Parameters of. Langmuir, and Freundlich, Isotherms for (Amoxicillin, Ciprofloxacin, Tetracycline) adsorption onto (WL).

Isotherm				
Model	**Parameter**	**AMX**	**CPF**	**TYC**
Freundlich	**K_F(mg/g)**	0.857701	0.93763	0.829859
	n	1.122334	1.146921	1.047779
	R^2	0.9872	0.9968	0.9977
Langmuir	**q_{max}(mg/g)**	49.26108	50.50505	123.4568
	K_L(L/mg)	0.012994	0.015177	0.005056
	R^2	0.7125	0.9783	0.6671

There are two main types of resistance in a solid material: (i) Resistance to external diffusion, which has to do with the mass movement from a bulk fluid to an outside surface. (ii) Resistance to interparticle diffusion, which is related to the transfer of mass from an outside surface to the surface between pores. Several models have been made to look into processes and find the likely rate-determining steps. Most of the time, pseudo-first-order (eq. 6) and pseudo-second-order (eq. 7) models are used to explain the kinetics of pharmaceutical adsorption.

$$q\,(t) = q_e\,(1 - e^{-K_1 t}) \qquad (6)$$

$$q = \frac{K_2 q_e^2 t}{1+K_2 q_e t} \quad (7)$$

Where: q(t) - amount of adsorbate adsorbed onto adsorbent at any time t (mg/g), K_1 - rate constant of pseudo-first-order model (min^{-1}), K_2 - rate constant of the pseudo-second-order model (g/mg.min), q_e - amount of solute adsorbed onto the adsorbent at equilibrium (mg/g), t - time (min) [33,34]. Table 3 and Fig. 12 show a summary of the findings. The pseudo-second-order kinetic model is a better fit for the experimental data because it gave higher R^2 values, while the pseudo-first-order model gave low R^2 values. Also, there is a big gap between the calculated and measured adsorption capacity for the pseudo-first-order model, which shows that the model isn't very good. These results are in agreement with several authors who used agricultural precursors for the adsorption of antibiotics [35,36].

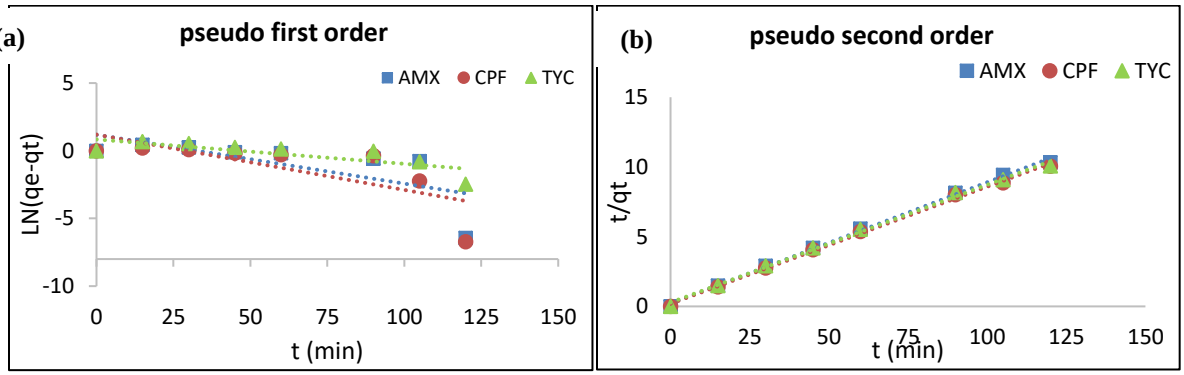


Figure 12. Adsorption kinetic models (a) Pseudo-1st-order and (b) Pseudo-2st-order.

Table 3. Parameters of kinetic models for (Amoxicillin, Ciprofloxacin, and Tetracycline) adsorption onto (WL).

kinetics				
Model	**Parameter**	**AMX**	**CPF**	**TYC**
pseudo first order	**q_e**	3.255	3.297617	2.310583
	$K_1(min^{-1})$	0.0361	4.09E-02	0.018
	R^2	0.4794	0.5628	0.5983
pseudo-second order	**q_e**	11.520737	11.91895	11.84834
	K_2 (g mg^{-1} min^{-1})	0.0351247	0.037703	0.025661
	R^2	0.9981	0.9978	0.9964

4. Conclusions

This study explored the potential use of walnut shells (WL) as a sustainable adsorbent for the removal of medical waste, specifically the medications Amoxicillin (AMX), Ciprofloxacin (CPF), and Tetracycline (TYC), from aqueous solutions. The experimental results indicated that walnut shells have shown effectiveness in removing these pharmaceutical contaminants from wastewater. Several variables were investigated to assess the influence of walnut shells on the removal efficiency. These variables included the pH of the solution, drugs concentration, adsorbent concentration, contact time, and agitation speed. Optimal conditions for efficient removal were determined, such as pH 6 for AMX, pH 5 for CPF, and pH 4 for TYC. An adsorbent amount of approximately

0.25 and a contact time of 60 minutes at 300 rpm agitation speed yielded the best percentage of removal. The study found that the removal of pharmaceuticals using walnut shells followed the Freundlich isotherm model, indicating a well-integrated removal process. Additionally, the kinetic data correlated well with a pseudo-second-order model for all three antibiotics. Walnut shells were characterized through surface examination using scanning electron microscopy (SEM), which revealed fine particles with irregular shapes and varying sizes. The Fourier-transform infrared (FT-IR) analysis provided qualitative insights into the functional groups present on the material surfaces. Overall, this research contributes to the development of effective and sustainable methods for wastewater treatment by offering walnut shells as a low-cost adsorbent for the removal of medical contaminants. Further studies can explore the scalability of this method and its application in larger-scale wastewater treatment systems.

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Author contributions

Al-Sharify and Faisal M proposed this research and supervised the work. Faisal M and Al-Sharify designed and carried out the work in collaboration with Marwa Mahdi S[1]. All authors worked on methodology and developing the theory and result analysis. All authors contributed to the final version of the manuscript.

Conflict of interest

The authors confirm that there is no conflict of interest.

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