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Apple peels as a natural adsorbent to remove antibiotics from wastewater.

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Abstract

Many researchers are interested in learning how to remove antibiotics from aqueous solutions because it is a major problem of pharmaceutical contamination for the development of bacterial resistance. In this study, adsorption studies were performed to remove antibiotics using agro-food waste [apple peels residue (APR)]. APR has such great potential filter for water treatment applications. A new generation of adsorbents has also been investigated for the elimination of the medicines tetracycline and amoxicillin. Several methods, like as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and Brunauer−Emmett−Teller (BET) specific surface area, were used to investigate the physical and chemical parameters of the APR surface before and after adsorption. The results of the batch studies demonstrate that the Freundlich isotherm equations and pseudo-second order kinetic rate equations were better suitable models for simulating the adsorption with a maximum absorbance of 84.38% or 91.12% amoxicillin and tetracycline respectively. According to thermos-dynamic parameters, adsorption processes are absorptive and exothermic in nature where ΔH^0 -1.57 and -0.773(kJ/mol) and$\Delta S0$ -0.011,-0.010 (KJ/mol) for Amoxicillin and tetracycline onto apple peels residue, respectively. Last but not least, the data from this study also confirmed the need to pay attention to the use of agricultural waste materials as cheap lignocellulose sorbents that can replace expensive sorbents in wastewater treatment.

Keywords: Apple peels residue , Agro-food waste , water treatment, Bio-sorption, Amoxicillin ,Tetracycline .

1. Introduction

Water is a natural resource required for life and the development of sustainable economy that is sustainable. The most popular medications for preventing or treating bacterial infections for human, animals, and plants are antibiotics [1]. The two primary ways that antibiotics enter the water supply are through wastewater from pharmaceutical firms and from municipal sewage treatment facilities [2]. Pharmaceutical wastewater is one of the emerging micro-pollutants which threaten the water quality and the ecosystem. Selection of the treatment process mainly depends on the chemical structure and solubility of the pollutant [3].

Antibiotic discharges need chemical or physical treatment to prevent harmful effects from contaminated water. Physical techniques are still the best stages of operation, and adsorption is the most popular method due to its ease of use, economy, directivity, excellent efficiency and absence of potentially dangerous byproducts [4]

Due to the nature of agro-industrial wastes, which includes cellulose, hemicellulose, and lignin as well as lipids, proteins, enzymes, and hydrocarbons, they have a high absorptive potential for many types of contaminants [5]. Additionally, they typically do not need pretreatment, which lowers the cost of preparation [6]. The use of apple peel residue (APR) leftover from the juice manufacturing process for this investigation. As economical and environmentally friendly natural adsorbent, and its results showed a high adsorption capacity of antibiotics in a short period [7]; which are produced in large quantities. In general, the apple plant is very sensitive to microbial deterioration due to the presence of polysaccharides; as a result, inappropriate management of these solid residues in the environment might cause considerable harm [8]. Therefore, utilizing it again as an adsorbent is advantageous from both angles and may be a strategy to manage solid waste. Waste from the manufacture of juices and derivatives and use it to address the problem of water pollution [9].

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Different authors have reviewed the removal of several contaminants from wastewater using agricultural waste adsorbents [10]. Only few works have been reported for removal of drugs by agricultural waste adsorbent [11]. The objective of this paper is research on adsorptive removal of antibiotics on such material with the aim of showing the effect of pH, APR dose, antibiotics concentrations, contact time and temperatures in the adsorption process. The study discusses the new trends of the adsorptive removal of antibiotics on natural sorbents.

2. Materials and Methods

2.1 Materials

All of the substances utilized in the study are reagents for analysis or laboratories. All tests utilized distilled water, HCl (0.1) N, NaOH (0.1) N, KNO_3, dried apple peel (DWP), amoxicillin (AC), and oxytetracycline HCl (TC) provided by Egyptian International Pharmaceutical Industry Company (EIPICO).

2.2. Methods

2.2.1. Apple peels residue collection and preparation

The wooden apple peel is gathered at the nearby market and rinsed several times with distilled water to remove dust and dissolved impurities. They are shade-dried at room temperature, then machine-milled, ground and passed through a standard sieve (SS) 0.85- mesh size and used as such is clearly shown in "Fig 1" [5].

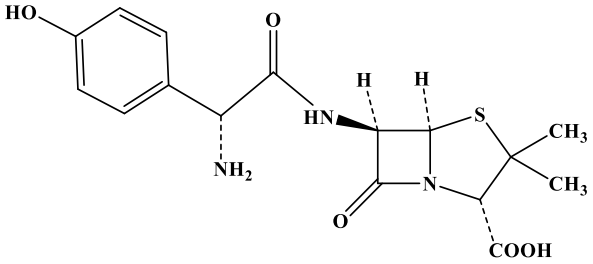
Fig.1 Images of apple peels residue collection and preparation

2.2.2. Characterization of Apple peels residue (adsorbent)

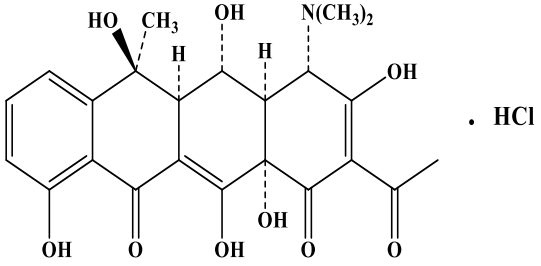
The adsorbent before and after adsorption of the antibiotics onto the surface of the bio-adsorbent, APR was characterized with (FTIR) (JASCO FTIR 6100 spectrometer), (SEM) (a Quanta FEG 250 Czcch Republic electron microscope), (EDX) (a Quanta FEG 250 Czcch Republic) and Brunauer−Emmett−Teller (BET) specific surface area. The zero point of charge pH_{PZC} of the APR sample was determined using the batch system equilibrium method by adding 50 mL of 0.01 mol/ L KNO_3 to several 100 mL flasks containing 0.10 g of adsorbent after adjusting the initial pH to a range of (1-10) with 0.10 mol/ L of NaOH or HNO_3 (APR). At a temperature of 25°C, the flasks were shaken at a speed of 120 rpm, and the subsamples were then allowed to adjust for 24 hours. The suspensions were then filtered, and a pH meter was used to record the solutions' final pH (pH f) values (Satorius Model PB-11). The pH_{PZC} value is the location where the curve of $\_pH$ ($pH_i - pH_f$) vs. pH_i crosses the line equal to zero [12].

2.2.3. Preparation of antibiotics stock solution (adsorbate)

Ac [$C_{16}H_{19}N_3O_5S$] & Tc [$C_{22}H_{25}ClN_4N_2O$] and chemical structure of antibiotics as shown in "Fig 2" were purchased from with molecular weight 365.4 and 496.9, respectively. To make the stock solution (1g/L), dissolve 1 g of each antibiotic powder in 1 L of distilled water. To create the necessary experimental concentration, the stock solution was diluted with distilled water. The wavelength was measured at 200 nm and 320 nm, respectively, and the final concentration was measured with a UV-Visible spectrophotometer (Model T60, UK) used at 190-900 nm to record the absorbance of the samples.



Amoxicillin



Oxytetracycline HCl

Fig. 2 The chemical structure of the antibiotics

2.2.4. Batch adsorption studies of antibiotics

Adsorption tests were performed in batches. The most important factors affecting adsorption include temperature, pH, and dose of adsorbents, contact time, and contaminant concentrations. Batch pattern adsorption experiments of 20 mL Amoxicillin Ac and

Tetracycline Tc antibiotics onto APR were performed in 100 mL capped Erlenmeyer flasks and stirred.
Shaker (Memmert Waterbath, Model WNB7–45, Germany) at constant shaking speed of 120 beats min^{-1} and 30°C until equilibrium. Batch adsorption tests were run with different adsorbent dosages (0.01 to 0.4 g), pH values (3 to 10), starting antibiotic concentrations (25 to 150 mg/l), contact times (0 to 100 mins), and temperatures (10 to 50°C).Absorption conditions for antibiotics in order to identify the optimum adsorption conditions that are applied through isotherms, kinetics, diffusion and thermos-dynamic studies.
To quantify the adsorbed antibiotic, the supernatant of the APR-Ac, APR-Tc combination was collected separately using filter paper, as indicated in "Fig. 3" , and a photometer was used to measure the antibiotic concentration at various time intervals. Spectrum (model T60, UK) at the laboratory. Maximum absorption wavelength (λmax) at 200 nm and 320 nm. AC and TC are calibrated as shown in "Fig. 4". The same processes were used in the thermodynamic investigation at various temperatures while maintaining the other parameters constant, and the percentage removal, R (%) of the antibiotic was computed using the formulae [13]:

$$\text{Removal } \% = (C_0 - C_e / C_e) \times 100 \quad (1)$$

Where: C_0 and C_e are initial and final concentrations of the antibiotics in the solution respectively.

Fig. 3 Images of apple peels residue (a) before adsorption and (b) after adsorption Ac (c) after adsorption Tc.

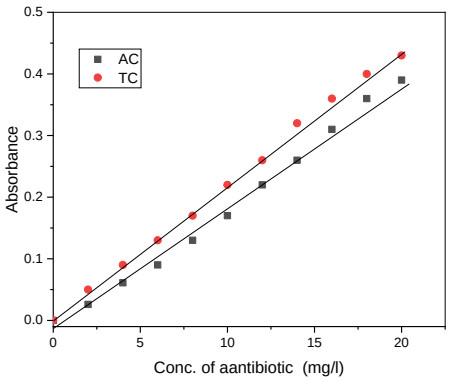


Fig. 4 Calibration curve of aqueous solutions of (a) AC (b) TC antibiotics.

3. Results and Discussion

3.1. Characterization of the apple peels residue

3.1.1 Point zero charge (pH pzc) of the apple peels residue

Adsorbents with positive surface charges enhance the ability of negatively charged compounds to adsorb at pH levels below pH_{PZC}; when the pH is less than pH_{PZC}, adsorbents with negative surface charges promote the adsorption of positively charged compounds. Therefore, it may be inferred that medium having a pH lower than 6.7, as indicated in "Fig. 5" should be favored for the adsorption of this antibiotic by APR. [5].

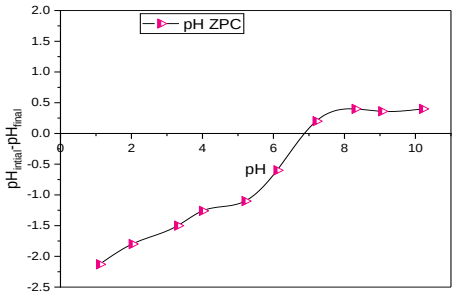


Fig. 5 Point zero charge of dried apple peels.

3.1.2 FTIR Spectrum Analysis

The FTIR spectrum of the APR "Fig. 6a" has shown the various functional groups with respect to their peak value. Peak at 3388 and 2925 cm^{-1} indicates the functional group OH and C–H, respectively. The peak values at 1772, 1620, 1249, and 1048 cm^{-1} confirm the functional groups C = O stretch, C = C, C–C, C–H bending, respectively. "Fig.6b" shows the FTIR spectrum of Ac and Tc antibiotics absorbed on APR, where the peaks were slightly shifted values to 2932 ,2871, 1833, 1687, 1261, 1035 cm^{-1} respectively for Ac and 2912, 2836, 1943, 1659, 1241, 1032 cm^{-1} respectively for Tc [14].
This shift in peak values may be due to the formation of a bond between functional groups present in APR and (antibiotics Ac and Tc). In addition to the observation of intense bands at 1677, 1679 and 1792, 1773 cm^{-1}, this corresponds to N-C=O and HO-C=O, respectively [15]. Other intense bands are those of 1450 and 1969 cm^{-1}, mainly dedicated to N-C stretching and N-H bending, and 1108 and 1128 cm^{-1}, mainly dedicated to O-C stretching and HO-C=O bending vibration for AC and TC respectively, that these bands appeared after adsorption of AC and TC onto APR "Fig. 7b".
Also new absorption bands appeared at 1280 and 1031 cm^{-1} for the asymmetric and symmetric stretching of the O=S=O group, respectively for AC. On the basis of FTIR one can confirm the adsorption of AC and Tc antibiotics on APR [7].

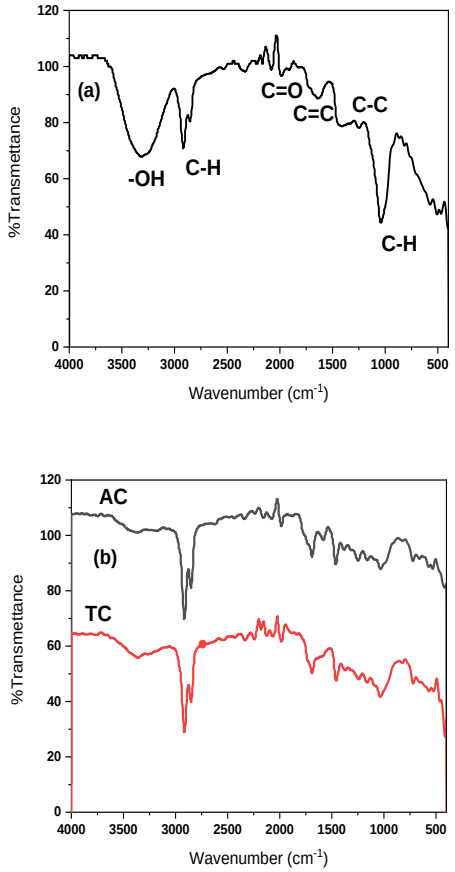
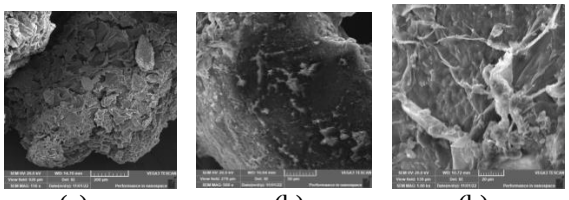


Fig.6 FTIR spectrum of dried apple peels (a) before adsorption and (b) after adsorption of Ac and Tc antibiotics.

3.1.3 Scanning Electron Microscopy (SEM).

SEM characterization of APR, before and after adsorption, showed complete change in surface texture. Before adsorption there was the rough surface morphology was observed in “Fig 7a”, while after adsorption of Ac and Tc antibiotics on the APR, layer on the surface of adsorbent and smoother morphology. The build-up of Ac and Tc particles on a APR surface is clearly shown in "Fig 7b,c" which demonstrates how the adsorbent surface entirely changed and the pore diameters shrank, proving that two antibiotics were successfully adsorbed on the surface of APR [7]



(a) (b) (b)

Fig.7 SEM image of apple peels residue (a) before adsorption and (b) after adsorption Ac (c) after adsorption Tc.

3.1.4 Energy-dispersive spectroscopy X-ray (EDX)

Before and after antibiotics uptake by APR, the qualitative composition of the elements was elucidated by EDX analysis (Quanta FEG Republic 250 Czcch). APR discharged with Ac has a chemical composition (by weight percent) of 56.34% for carbon and 43.66% for oxygen, as measured by X-ray spectrometry. The chemical composition of APR loaded with Ac and TC was 46.94% and59.63% for carbon, 48.99% and 38.17% for oxygen, 3.40% and1.98% for nitrogen, 0 % and 0.22% for chloride and0.38% and 0% for sulfur respectively as shown in “Fig. 8a,b,c” and Table 1 (in weight ratio). The chemical composition of APR was altered as a result of efficient adsorption of Ac and TC molecules onto the pores of APR, as indicated by the clear weight changes between APR loaded and unloaded with Ac and TC [16].

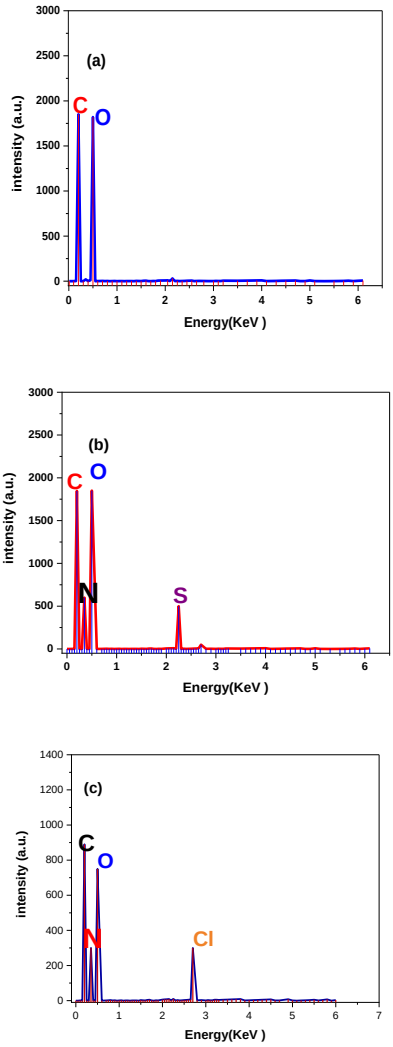


Fig. 8 EDX analysis of apple peels residue (a) before adsorption and after adsorption (b) AC and (c) TC process.

Table 1: Elemental composition of apple peels residue before and after adsorption process

Element %	Before adsorption	After adsorption for AC	After adsorption for TC
Carbon	56.34%	46.94%	59.63%
Nitrogen	-	3.40%	1.98%
Oxygen	43.66%	48.99%	38.17%
Chlorine	-	0 %	0.22%
Sulfur	-	0.38%	-

3.1.5 BET Surface area and pore diameter properties.

The N_2 adsorption isotherms for APR are shown in the" Fig. 9a". The APR sample displays a type I isotherm curve, indicating the formation of meso-pores and macro-pores in the adsorbent. In addition, the pore diameter and pore size distribution in APR "Figure 9b" show that the pores are mostly porous as they lie in the range of 2–50 nm with an average pore diameter size of 4.09 nm. In addition, the total pore volume and the average surface area (BET) of APR are 0.042 cm^3/g and 268.41 m^2/g respectively [17].

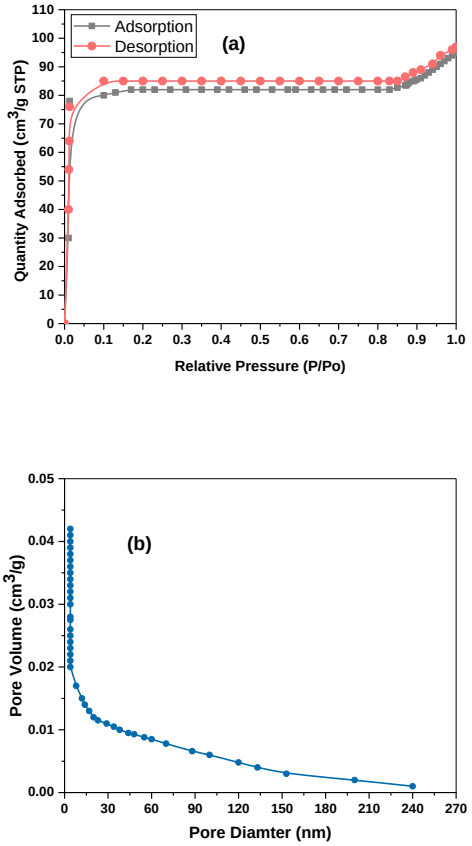


Fig. 9 (a) N_2 adsorption–desorption isotherms and (b) the pore diameter for APR

3.2. Effect of some parameter on sorption of antibiotics

3.2.1 Effect of pH

The pH of the adsorption medium is a key factor that influences the adsorption capacity [6]. APR adsorbent was used in this study to remove Ac and Tc from aqueous solutions at various pH values between (3 and 10) as seen in "Fig.10". The R% removal from APR for antibiotics showed an increase at low pH. The following explanations apply to this phenomenon:

The first step involved the protons of the functional groups on the APR in the solution at a low pH. The negatively charged antibiotics in solution and the positively charged APR surface are electrostatically attracted to each other, increasing the amount of time the antibiotic is in contact of the antibiotic with APR [6].

Additionally, raising the pH increased the density of negative charges on APR's surface, which also decreased adsorption capability [18]. Furthermore, it is noted that pH 6 yields the highest absorption of the Ac and Tc antibiotics as well as the desired APR absorption sequence for antibiotics. As a result, it was decided that a pH of 6 would be optimum for the adsorption of Ac and Tc antibiotics on APR.

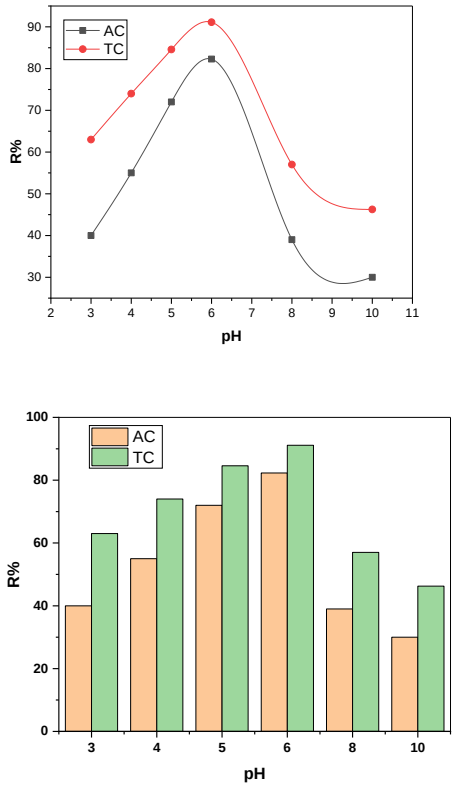


Fig.10 Effect of pH on the adsorption of Ac and Tc antibiotics onto apple peels residue

3.2.2 Effect of agro-food waste apple peels residue (Dosage)

As the adsorbent dosages were adjusted from 0.01 to 0.40 g at (50 mg/l) antibiotic concentration on equilibrium duration of 100 min., the % adsorption and quantity adsorbed increased. With 0.30 g of adsorbed antibiotics, clearance rates of Ac and Tc antibiotics were 84.38% and 91.12%, respectively. It is clear from "Fig. 11" that increasing the adsorbent dose results in a rise in accessible adsorption sites and the surface area, which in turn increases the quantity of antibiotics adsorbed. It was noted that the quantity of adsorption decreases steadily when equilibrium is reached. This may be caused by the adsorption sites overlapping or aggregating, this lengthens the diffusion channel and decreases the total amount of antibiotic-accessible adsorbent surface area [19]. The saturation of adsorption sites during the adsorption process is the major cause of the constant adsorption capacity with increasing dosage of adsorbent [20]. Therefore, 0.30 g can be regarded as the ideal dosage for APR loading. Due to the development of a balance between the antibiotic molecules on the adsorbent and in the solution, no noticeable removal of antibiotics was seen above the saturation point [21].

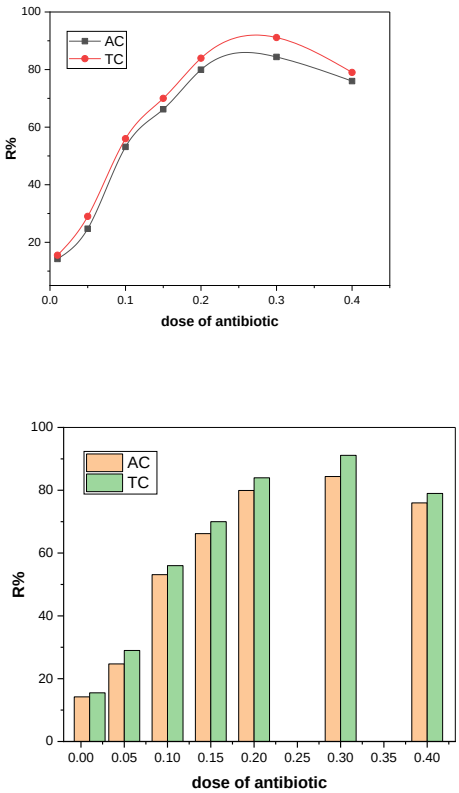


Fig.11 Effect of adsorbent dosage on the adsorption of Ac and Tc antibiotics onto apple peels residue.

3.2.3. Effect of antibiotics concentration

The relationship between initially antibiotic concentrations, removal percentage has been examined. The adsorption of antibiotics was performed at pH 6 and various starting antibiotic concentrations ranging from 25 to 150 mg/l. The effect of different initial antibiotics concentration on adsorption of antibiotics onto APR is presented in "Fig. 12". The results showed that as the initial antibiotic concentration is increased up to 50 mg/l, the percentage of antibiotic elimination decreases. This can be explained by the fact that the adsorbent's surface contains more active sites at low initial antibiotic concentrations compared to high initial antibiotic concentrations. As a result, APR's surface has absorbed the majority of the antibiotics molecules, resulting in a larger removal %. In contrast, with high initial concentrations of antibiotics, molecules have a poor likelihood of being adsorbed since there lack many binding locations on the adsorbent's surface. As a result, some antibiotics molecules do not become adsorbed and instead stay in the solution [11].

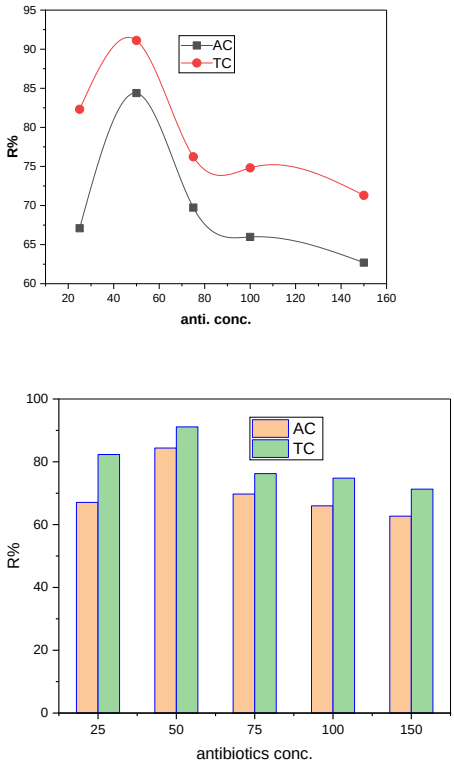


Fig.12 Effect of initial antibiotics concentration on the adsorption of Ac and Tc antibiotics onto apple peels residue

3.2.4. Effect of contact time

In the context of the economic issues of treating contaminated water, the contact time of the adsorption process is a crucial component. For the uptake rate of the antibiotics Ac and Tc, APR

investigated the link between antibiotics uptake and reaction time. By producing the adsorbent-adsorbent solution with a set amount of 0.30 g of APR as shown in "Fig.13" it is possible to implement the contact time effects on the adsorption of the two antibiotics. In general, increasing the contact time slightly increases the antibiotic adsorption capacity. Since the antibiotic deposits are present at the adsorption site on the adsorbent, extending the contact period does not result in an increase in adsorption. The initial antibiotic adsorption rate was greater because the APR adsorbent had a relatively wide surface area accessible for antibiotic adsorption. After some time, there was only a very slight improvement in antibiotic absorption since there weren't many active sites on the adsorbent surface. It then reaches equilibrium at a point where it stabilizes and becomes constant due to the completely occupied surface of the sorbent and stable absorption [22]. A shaking time of 100 min was found to be sufficient to achieve antibiotic equilibrium beyond the exposure time studied.

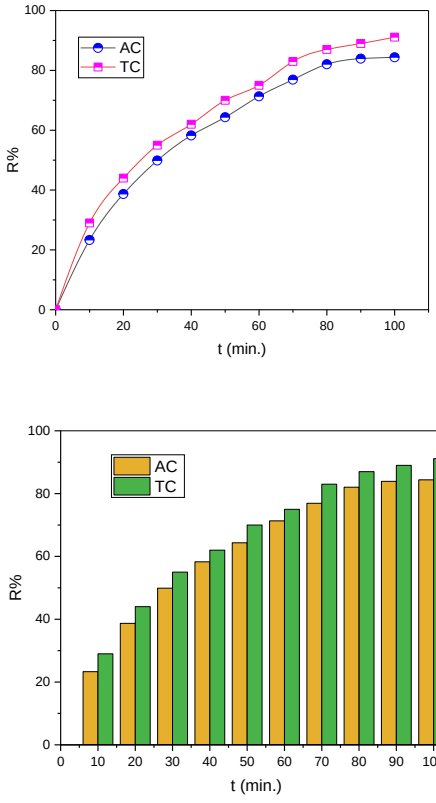
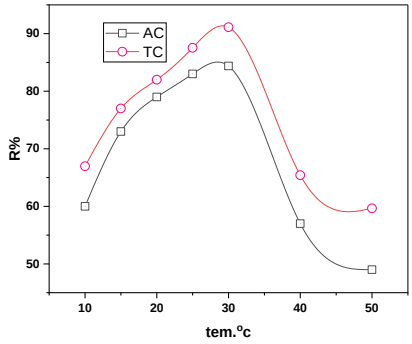


Fig.13 Effect of contact time on the adsorption of Ac and Tc antibiotics onto apple peels residue

3.2.5. Effect of temperature

For the adsorption of Ac and Tc antibiotics at 50mg/l on the APR surface at constant weight, "Fig. 14" shows the effect of temperature on the fitting adsorption capacity. From temperatures 30°C to 40°C The removal rate of Ac and Tc antibiotics decreased from 91.12% to 58.61% and from 84.38% to 55.11%, respectively, with the temperature increase from 30 to 50°C due to increased adsorbent migration from solid phase to bulk phase. This causes the adsorbent surface to inactivate or destroy some of the active sites and absorb instead of adsorb [23].



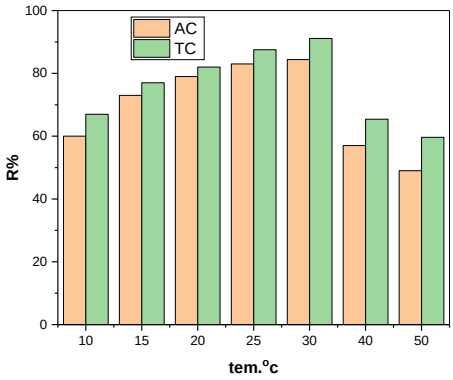


Fig. 14 Effect of temperature on the adsorption of Ac and Tc antibiotics onto apple peels residue

Table 2 Comparison of removal % of different adsorbents for antibiotics

Adsorbents	Antibiotics name	Adsorbent dosage	%Removal	Refs
Carbon materials	Amoxicillin	0.05-0.5 g/L	39.5-75.6	24
AC-siris seed	Metronidazole	0.15-0.8 g/L	35.2- 64.2	25
AC	Tetracycline	0.05-0.6 g/L	44.6-78.9	26
NiO nanoparticle	Amoxicillin	0.1-0.5 g/L	54.3-87.9	27
Azolla filiculoides	Tetracycline	0.5-5 g/L	69.8-87.9	28
Granular sludge	Oxytetracycline	0.4-2 g/L	39.8-79.8	29
Chestnut shell G	Penicillin	0.5-3 g/L	28.7-81.4	30
Apple peels residue	Amoxicillin	0.01-0.3g/l	14.2-84.3	This study
Apple peels residue	Tetracycline	0.01-0.3g/l	15.5-91.1	This study

3.3. Adsorption isotherm

The isothermal adsorption model is commonly employed to describe and study the adsorption mechanism. Data on equilibrium were examined using *Langmuir, Freundlich isotherm and Temkin adsorption isotherm model***.**

3.3.1. Langmuir adsorption isotherm

The Langmuir model addresses monolayer adsorption at several local adsorption locations. Assuming that the monolayer adsorption energy is uniform throughout the surface of the adsorbent, it is demonstrated that there is no adsorbent migration along the plane of the surfaces [31,32]. The following is how to express Langmuir's equation in its linear form:

$$\mathbf{Ce/\ q_e = 1/q_{max}\ K_L + Ce\ /q_{max}} \qquad \mathbf{(2)}$$

Where qe (mg/g) is the quantity of Ac and Tc adsorbed by the APR at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity corresponding to monolayer coverage, K_L (L/mg) is the Langmuir constant, and Ce (mg/L) is the concentration of Ac and Tc at equilibrium. A plot of Ce /qe versus Ce may be used to determine the values of q_{max} and K_L. The parameters are provided in Table 3 along with the Langmuir plots for Ac and Tc adsorption onto the cloth that were produced in"Figure15a,b ". For the Langmuir plots, the correlation coefficient values fluctuated between 0.84 and 0.90.This indicates that the Langmuir model was not followed in the adsorption of Ac and Tc onto the APR.

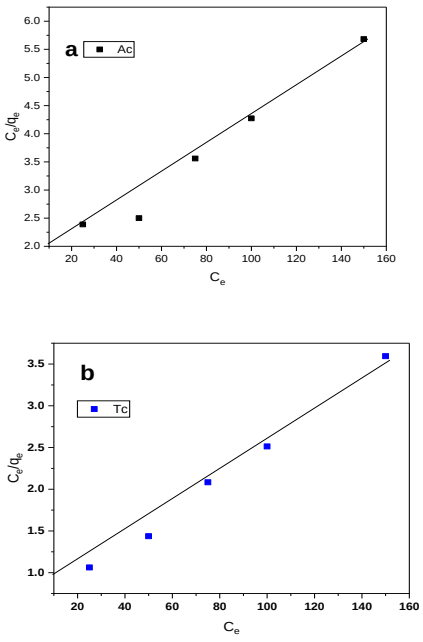


Fig.15 Langmuir adsorption isotherm of (a) Ac and (b) Tc antibiotics onto apple peels residue. [contact time 100 min., dose 0.30 g , pH= 6 and antibiotics conc. 50 mg/l] .

3.3.2. Frendlich adsorption isotherm

According to multilayer adsorption and equilibria, the Freundlich isotherm is utilised to describe the adsorption processes taking place on heterogeneous surfaces and active sites with different energies [33]. In linear form, the Freundlich equation is written as follows:

$$\mathbf{\log q_e = Log\ K_f + 1/n \log Ce} \qquad \mathbf{(3)}$$

Where Ce (mgL^{-1}) is the equilibrium concentration of Ac and Tc in solution, qe is the equilibrium concentration of Ac and Tc on the APR, and Kf ($dm^3\ g^{-1}$) and 1/n are Freundlich constants relating to adsorption capacity and adsorption intensity, respectively. The slope and intercept in "Fig 16a,b" are used to determine Freundlich constants, which are listed in Table 3. The experimental data and the Freundlich model exhibit strong agreement, as indicated by the correlation coefficients (R^2 >0.99). The 1/n numbers (0.71, 0.85) are smaller than 1, so they represent the favourable adsorption conditions [36].

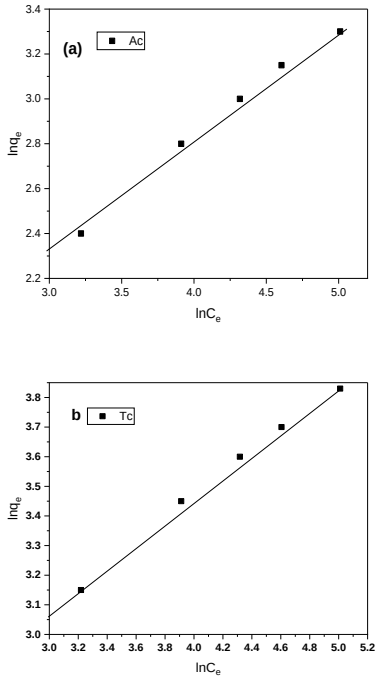


Fig.16 Freundlich adsorption isotherm of (a) Ac and (b) Tc antibiotics onto apple peels residue. [Contact time 100 min., dose 0.30 g, pH= 6 and antibiotics conc. 50 mg/l].

3.3.3. Temkin adsorption isotherm

Temkin's model is based on the hypothesis that, for gas phase adsorption, the heat of adsorption brought on by interactions with the adsorbate decreases linearly with recovery rate. This application of the Gibbs relation to adsorbents is based on the theory

that their surfaces contain homogeneous energy [34, 35]. The Temkin model's equation is:

$$Qe = q_m \ln K_t + q_m \ln Ce \quad (4)$$

Where: K_t and q_m are the Temkin constants related to adsorption capacity in (L mg^{-1}) and heat of sorption in (J mol^{-1}) respectively [37]. The values of q_m and K_t can be obtained from the slope and intercept of the linear plot of Qe versus ln Ce as displayed in "Fig 17 a,b". The correlation coefficient values (R^2) fluctuated between 0.89 and 0.90.This indicates that the Temkin model was not followed in the adsorption of Ac and Tc onto the APR.

3.4. Kinetic study

Using a linear regression analysis technique, four kinetic models were utilized to fit the experimental data at an initial antibiotic concentration of 50 mg/l. (Table 4) lists the parameters of these models in brief. The pseudo-first-order rate expression is provided as: [38,39]

$$\log(qe\_ qt) = \log(qe) \_ k_1\, t /2.303 \quad (5)$$

Where: q_t is the current quantity of antibiotic adsorbed on the adsorbent, *t* (min) is the contact time and K_1 is the first-order rate constant. A "Fig.18a,b" of log (qe_qt) versus t gives a linear relationship from which the value of K_1 and qe may be calculated from the slope and intercept.

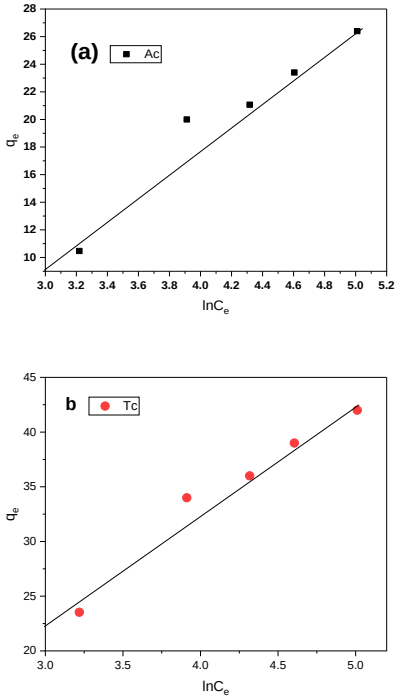


Fig.17 Temkin adsorption isotherm of (a) Ac and (b) Tc antibiotics onto apple peels residue. [Contact time 100 min., dose 0.30 g, pH= 6 and antibiotics conc. 50 mg/l].

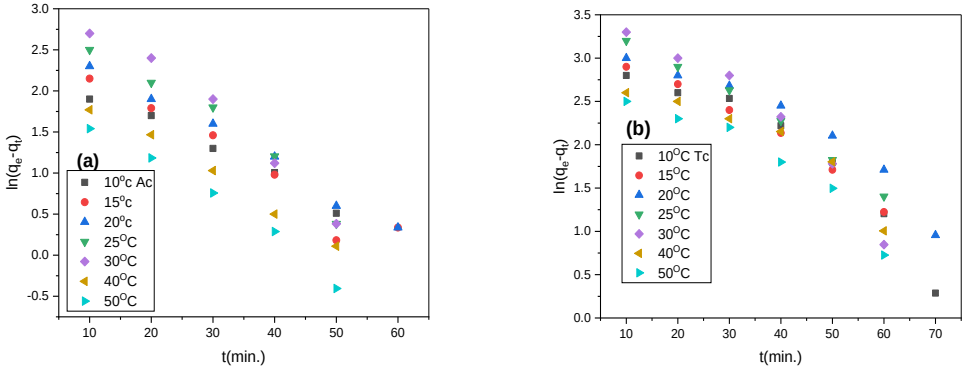


Fig. 18 First-order kinetic model for adsorption of (a) Ac and (b) Tc antibiotics onto apple peels residue at different temperatures

Table 3. Langmuir, Freundlich and Temkin isotherm constants of adsorption of Ac and Tc antibiotics onto apple peels residue at 30°C .

Waste type	Langmuir adsorption isotherm			Freundlich adsorption isotherm		Temkin adsorption isotherm				
	Q_{max}(mg/g)	$R_L x10^4$	$k_L \times 10^{-2}$ L mg^{-1}	R^2	K_F ($dm^3 g^{-1}$)	1/n	R^2	q_m	K_t	R^2
Ac	36	0.66	1.98	0.85	2.20	0.50	0.99	8.52	0.15	0.89
Tc	48	0.93	4.18	0.91	7.31	0.36	0.99	10.1	0.47	0.90

The pseudo-second-order model's linearized version is provided as: [40,41]

$$t/q_t = (1/(K_2\, q_e^{\,2})) + t/q_e \qquad (6)$$

Where: K_2 is the pseudo-second order rate constant. The plot of t/qt versus t in "Fig 19 a,b" gives a linear relationship from which q_e and K_2 can be determined from the slope and intersection of the graph, respectively. The correlation coefficients R^2 greater than (0.99); suggest that the adsorption of AC and Tc on APR mainly follows the "pseudo-second-order" kinetic model. The pseudo-second rate constants for the AC and Tc adsorption on the APR show a steady increase with increasing solution temperature (10^oC-30^oC). This finding shows that the elimination of the antibiotics Ac and Tc is an endothermic process in which the mobility of large antibiotic molecules rises with temperature. The rise in k_2 with temperature is also a sign of greater pore penetration of antibiotic compounds at higher temperatures, which results in more adsorption sites being accessible. The values of k_2 decreased with the increasing of temperature from (30^oC -50^oC) this suggested that the adsorption process was exothermic in this stage [42] due to increased adsorbent migration from solid phase to bulk phase. This causes the adsorbent surface to inactivate or destroy some of the active sites and absorb instead of adsorb [40].

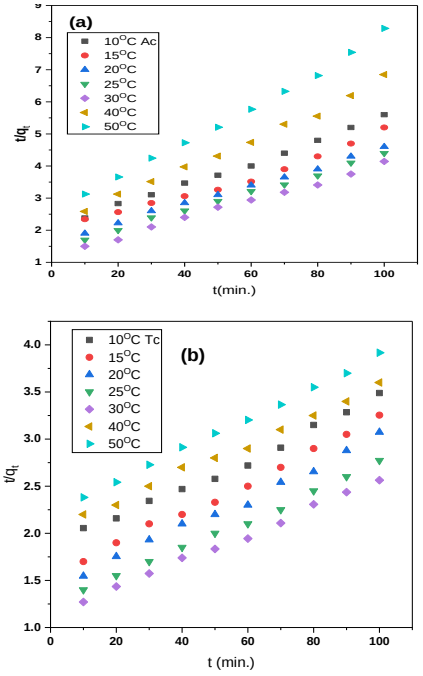


Fig. 19. Second- order kinetic model for adsorption of (a)Ac and (b) Tc antibiotics onto apple peels residue at different temperatures.

The intra-particle diffusion model is used here to refer to the theory proposed by Weber and Morris based on the following equation: [43]

$$q_t = k_P\, t^{1/2} + C \qquad (7)$$

Where: qt (mg/g) is the amount of dye adsorbed at time t, K_P (mg/g min1/2) is the particle diffusion rate constant obtained from the slope, of the q_t vs. $t^{½}$ as shown in "Fig. 20 a,b". The diffusion rate constant in the k_p particle increases with increasing temperature from 10^oC to 30^oC because increasing temperature leads to increased dynamics force, which will increase the diffusion rate of Ac and Tc and from 30^oC - 50^oC the K_P particle decreases with increasing temperature due to increased adsorbent migration from solid phase to bulk phase. This causes the adsorbent surface to inactivate or destroy some of the active sites and absorb instead of adsorb [44]. While the C value indicates the thickness of the boundary layer. The larger C indicates a larger boundary layer effect, which accounts for the larger part from the surface absorption during the rat limitation period [42].

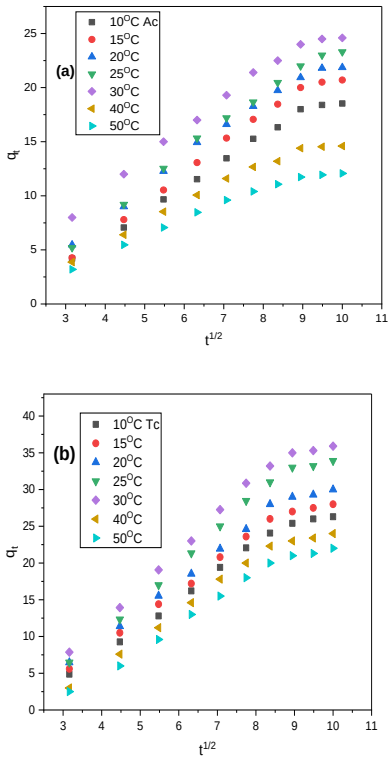


Fig. 20 Intra-particle diffusion model for adsorption of (a) Ac and (b) Tc antibiotics onto apple peels residue at different temperatures

The Elovich model is generally expressed as:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \, Ln\, t \quad (8)$$

Where: α is the initial adsorption rate constant (mg/(g min) and the parameter β is the desorption constant (g/mg). The plot of qt vs ln t at various concentrations, as shown in "Fig. 21a,b", provides a linear relationship with a slope of "1/β" and an intercept of 1/β ln (αβ), from which the constant may be calculated. As the temperatures rises from 10°C to30°C, the value of β drops while the value of α grows. This may be as a result of the function that adsorption processes play in regulating the rate of Ac and Tc adsorption on the APR surface, demonstrating that α is regulated by the number of available adsorption sites [45].

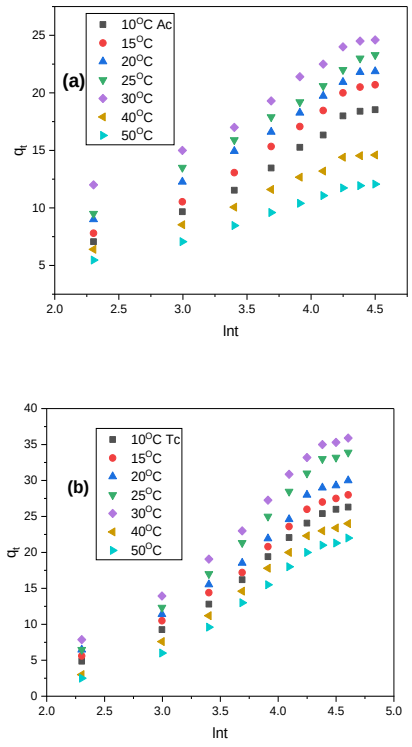


Fig. 21 Elovich kinetic model for adsorption of (a) Ac and (b) Tc antibiotics onto apple peels residue at different temperatures.

3.5 Thermodynamic study

Thermochemical investigate were looked at to provide a standard for judging the viability or spontaneity of the adsorption process. Equation is used to compute the terms enthalpy (ΔH^o) and entropy (ΔS^o).

$$K_c = q_e/C_e \quad (9)$$

$$Ln K_c = \Delta S^0/R - \Delta H^0/(RT) \quad (10)$$

Where: k_c is the distribution coefficient, *qe* is the concentration of AC and TC adsorbed onto APR at equilibrium (mg/L), *Ce* is the equilibrium of AC and TC in the liquid phase (mg/L), *R* is the universal gas constant (8.314 J/mol K), and *T* is the absolute temperature (K). By using Van't Hoff plot ($\ln k_c$ vs. 1/*T*), the values of Δ*H*° and Δ*S*° were calculated from the slope and intercept as shown in " Fig 22" and presented in (Table 5).

It is observed that the removal of Ac and Tc increased with increasing temperature from 283 to 303 K. However, the exothermic character of the adsorption process was verified by the negative value of ΔH° -1.57, -0.773k J mol-1, demonstrating the existence of physical forces during the adsorption of Ac and Tc onto APR, respectively. This agrees well with the n value obtained from the Freundlich isotherm.

The adsorption of Ac and Tc onto APR resulted in a reduction in the rando mness at the solid-solution interface, as shown by the negative values of ΔS° -0.011,-0.010 k J mol $^{-1}K^{-1}$entropy for Ac and Tc, respectively. This demonstrates that adsorption improves the order of the antibiotics at the solid-liquid interface during the adsorption process on APR, supporting the interaction between two antibiotics and APR. The ions flow from the solid phase into the liquid phase when the temperature rises due to the mobility of antibiotic molecules [39]. Equation (12) may be used to compute the Gib bs free energy change, G^0, in terms of enthalpy and entropy [46].

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \quad (11)$$

It produces positive results at all temperatures, indicating that the adsorption of Ac and Tc on apple peel residue APR is a physical adsorption since the free energy values fall within the range of (48 to 0 kJ mol-1). Therefore, Vander Waals forces or electrostatic attraction may be responsible for the binding between antibiotic molecules and the adsorbent surface [47].

Table 4 Kinetics parameters of (a) Ac and (b) Tc antibiotics onto apple peels residue.

antibiotics Type	Tem. (^{0}C)	Pseudo first-order model		Pseudo second-order model		Intraparticle Diffusion model			Elovich equation model		
		$k_1\times10^2$ (min^{-1})	R^2	$K_2\times10^4$ (g/mg min)	R^2	K_p mg /g min$^{-1/2}$	C (mg g^{-1})	R^2	A (mg(g min)$^{-1}$)	$\beta\times10^2$ (g mg^{-1})	R^2
Amoxicillin Ac	10	3.47	0.93	4.21	0.99	2.41	-3.63	0.99	1.82	19.15	0.98
	15	4.10	0.90	4.87	0.99	2.77	-4.55	0.99	1.95	16.55	0.96
	20	4.31	0.94	5.02	0.99	2.83	-4.69	0.99	2.79	15.80	0.95
	25	5.13	0.89	5.80	0.99	2.94	-5.51	0.99	3.15	15.01	0.98
	30	5.91	0.94	6.40	0.99	2.99	-6.08	0.99	4.97	14.44	0.99
	40	4.28	0.93	5.91	0.99	1.85	-1.79	0.99	0.18	25.50	0.97
	50	4.07	0.96	5.71	0.99	1.59	-1.41	0.99	0.16	31.41	0.96
Tetracycline Tc	10	4.32	0.93	1.32	0.99	3.76	-6.76	0.99	1.40	9.95	0.95
	15	4.41	0.94	1.53	0.99	3.93	-7.08	0.99	1.55	9.55	0.97
	20	3.44	0.91	1.75	0.99	4.07	-7.40	0.98	1.69	9.22	0.96
	25	4.01	0.86	1.84	0.99	4.78	-8.05	0.99	1.84	7.83	0.97
	30	4.51	0.93	1.90	0.99	4.96	-8.91	0.99	2.09	7.55	0.96
	40	4.06	0.80	1.44	0.99	3.71	-8.31	0.99	1.18	9.91	0.95
	50	3.98	0.87	1.27	0.99	3.45	-8.06	0.99	1.01	10.90	0.96

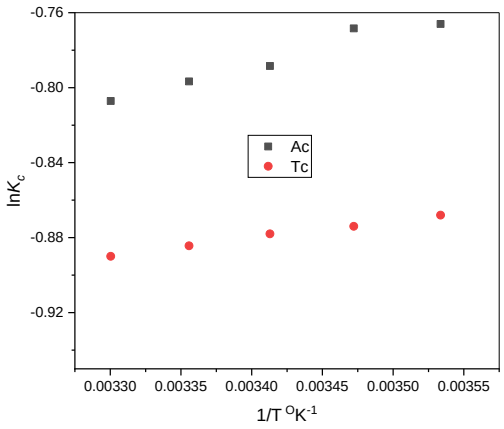


Fig.22 Variation of ln*Kc* with 1/T (K^{-1}) for estimation of the enthalpy and entropy antibiotics onto apple peels residue

Table 5 Thermodynamic parameters for the adsorption of Ac and Tc onto apple peels residue.

Antibiotics Type	Temp. ºC	Temp. ºK	ΔH^0 kJ/ mol	ΔS^0 kJ/ mol	ΔG^0 kJ/ mol
Amoxicillin Ac	10	283	-1.57	-	1.76
	15	288		0.011	1.82
	20	293			1.88
	25	298			1.94
	30	303			2.01
Tetracycline Tc	10	283	-	-	2.05
	15	288	0.773	0.010	2.10
	20	293			2.15
	25	298			2.20
	30	303			2.25

4. CONCLUSION

APR apple peel, a solid waste product from fruit, has been effectively employed as a great, economical alternative to remove antibiotics from wastewater. The results showed that the removal of amoxicillin Ac and tetracycline Tc was 84.38% and 91.12% respectively at the initial concentration of 50 mg/l at pH 6 for 100 min. by shaking at 120 rpm at 30^{o}C. The SEM study was supported by observing the difference in the surface geometry of the adsorbent before and after AC and Tc adsorption. The adsorption equilibrium data show a better agreement with the Freundlich isotherm model than with the Langmuir isotherm model. The adsorption kinetics followed the pseudo-second kinetics equation for the adsorption of Ac and Tc on the APR. Research demonstrates thermodynamics. Spontaneous and exothermic in nature, is the result of a change in the positive value of the free energy and the negative value of the change in enthalpy, respectively. It was finally concluded that APR, a readily available, cheap and effective material, could replace other expensive adsorbents used to remove antibiotics in wastewater treatment.

Finally, the data obtained in this work confirmed the benefits of using a suitable adsorbent might be agricultural industry wastes because of their capacity to remove antibiotics. It is considered an effective, widely available, and low-cost alternative to other expensive adsorbents used to remove antibiotics in wastewater treatment.

5. Conflicts of interest

There are no conflicts to declare.

6. Formatting of funding sources

No funding sources.

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