Preparation, Characterization, and Tetracycline Adsorption Efficiency of Tea Residue-Derived Activated Carbon

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Abstract

The process for preparing activated carbon (AC) made from tea residue was described in this paper. Investigated were the physicochemical characteristics and adsorption efficiency of the produced AC. Activation with potassium hydroxide (KOH) and carbonization at 350 °C are the two key steps in the manufacturing of AC. The activated carbon was used to adsorb Tetracycline (TC). Different parameters were studied at room temperature to show their effects on the adsorption efficiency of TC. These parameters are the initial concentration of adsorbate TC, solution acidity pH, time of adsorption, and adsorbent dosage. The prepared active carbon was characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET). The equilibrium of TC adsorption on the tea-activated carbon TAC is effectively represented by the Langmuir model. Tetracycline could be adsorbed onto the prepared activated carbon with a maximum capacity of 45.662 mg g^{-1}. Adsorption kinetics are well represented by pseudo-second-order. The investigation of adsorption thermodynamics demonstrates that TC adsorption on TAC is endothermic and spontaneous.

Keywords: Tea residue, Activated carbon, Tetracycline, Central Composite Design.

1. Introduction

The ecosystem of the earth is currently being continuously contaminated by various pollutants. Pharmaceuticals are released into water systems in large amounts through a variety of human activities, such as waste streams from hospitals and the pharmaceutical and veterinary sectors, which are one major cause of water contamination [1]. These chemicals can infiltrate aquatic bodies, including surface and groundwater [2], [3].

Pharmaceutical effluents containing antibiotics have recently received a lot of attention due to the increased use of antibiotics [4]. Since antibiotic resistance genes can be induced by prolonged exposure to relatively low quantities of antibiotics, the use of antibiotics rose quickly, raising concerns about their residues in the environment [5]. Tetracycline (TC) is a broad-spectrum antibiotic that has become one of the most commonly used antibiotics in the world due to its low cost, good quality, and useful antibacterial qualities [6]. It was

found in the 1940s and began to be utilized as a therapeutic agent to protect human health in the 1950s [7]. It has been extensively used in agriculture to prevent the pharmacological efficacy of infectious diseases and as a growth stimulant for microorganisms. Because Tetracycline (TC) does not quickly biodegrade, it poses a serious risk to both people and the environment [8]. Consequently, it is essential to remove TC residues from effluents before releasing them into the environment [7], [9]. The removal of TC from wastewater has been studied using a variety of methods, including biological treatment, coagulation, sedimentation, ozonation, photocatalysis, electrochemical degradation, and adsorption [10]. Adsorption technologies have been extensively used to remove pharmaceuticals from surface water and municipal wastewater compared to other water treatment methods because they can provide several advantages, such as simple design, simple operation, and high adsorption effectiveness [11]. Several materials have been studied as adsorbents for the adsorption of TC, such as resin, silica, clay, multi-walled carbon nanotubes, zeolite, graphene oxide, chitosan, and activated carbon [12]. Activated carbon is a powerful adsorbent because of its surface's numerous functional groups, porosity, and huge surface area. It also has a well-developed interior structure. It has been widely utilized to remove numerous organic and inorganic pollutants from contaminated streams that are biologically resistant [13], [14]. Commercial activated carbon is one of the most commonly used industrial adsorbents for separation, purification, and recovery procedures. However, it requires regeneration after each adsorption operation and has a high production cost. Utilizing biomass waste as a precursor to AC, such as groundnut husks, sugarcane bagasse, coconut shells, bamboo, rice husks, mango kernels, and tea residue, is a potential method for lowering the overall cost associated with its manufacturing [15], [16]. The two fundamental phases in the preparation of ACs are carbonization and activation. The goal of carbonization is to reduce the number of volatiles in the starting material. This is done by pyrolyzing the precursor at temperatures between 400 and 850 °C, which breaks it down into gases and tars made up mostly of hydrogen, oxygen, and nitrogen. The char created using this process will have a high fixed carbon content but little surface area and porosity. Therefore, an activation step is necessary to increase porosity and organize the structure, resulting in the extremely porous solid known as AC [17], [18]. There are two ways to make

activated carbon: physical activation and chemical activation. In the physical activation method, the raw material is carbonized at a high temperature and then activated with steam or carbon dioxide. In the chemical activation method, the precursor is soaked in chemicals like H_3PO_4, NaOH, K_2CO_3, KOH, $ZnCl_2$, etc. before being carbonized in an inert atmosphere [19].

In this study, tea residue was selected as a precursor to prepare activated carbon using chemical activation with KOH. The activated carbon was investigated as an adsorbent to adsorb Tetracycline from polluted water.

2. Materials and Methods
2.1 Materials

The tea residue was collected locally from leftover tea used in homes. Tetracycline (TC) was chosen as the target adsorbate, supplied by The State Enterprise for Drug Industries and Medical Appliances, Samara, Iraq. Tetracycline was directly used without any further treatment. Potassium hydroxide (KOH), used as the activating agent with a minimum assay of 85%, was purchased from Himedia, India.

2.2 Preparation of Activated Carbon

The waste tea was boiled with distilled water for 0.5 h to remove water-soluble materials, then washed with distilled water until the washing water was colorless, and then dried at 110 °C in an air oven for 10 h with flipping. After pretreatment, the raw material was placed in a steel or porcelain crucible for carbonization in a furnace at 350 °C for 30 min under a flow of N_2 (150 cm^3/min). Next, the product is allowed to cool inside the furnace, with the nitrogen gas still flowing, until the temperature reaches 100 ^{C}. The carbonized product was then withdrawn from the furnace and allowed to cool to room temperature. Then, it was mixed with 30% KOH at a weight ratio of 2:3 (KOH: carbonized material) and mixed for 30 min using a shaker at 140 rpm. The sample was then filtered from the base residue. To prepare the activated carbon in its final step, the product was put in a closed crucible in a muffle furnace at 900 ^{C} for 1 h under a flow of N_2 (150 cm^3/min) [16]. The product is then allowed to cool to room temperature. Warm distilled water was used to thoroughly wash the obtained activated carbon (AC) until the solution's pH reached 7. The AC samples were dried overnight at 110 °C. The product was crushed with a mortar and pestle and

then sieved to get a 350 μm or smaller particle size. Finally, the product was preserved in a desiccator for the upcoming batch trials.

2.3 Activated Carbon Characteristics

To characterize the manufactured adsorbent, various characterizations were done. The surface morphologies were examined using scanning electron microscopy (SEM). The crystalline phase was identified using X-ray diffraction (XRD). EDX was used to analyze the absorbent's elemental composition. The above analysis was carried out locally at Al-Khoura Co. using KBr pellets in the range of 4000-400 cm^{-1}. Fourier transform infrared spectroscopy (FTIR 8400s Shimadzu) was employed to look into the functional groups on the adsorbent surface. The analysis was carried out at the Al-Nahrain University / College of Biotechnology Department. The surface area and porous structure were determined using the Brunauer-Emmett-Teller (BET) formula. The analysis was carried out at the Petroleum Research and Development Centre (PRDC).

2.4 Adsorption Study

Batch adsorption studies were carried out at room temperature using 25 ml of Tetracycline TC solution at different initial concentrations (30–150 mg/L), pH (2–11), time (20-300 min), and active carbon (AC) dosage (0.05–0.5 g/25 ml) at a constant speed of agitation (140 rpm). 25 ml of TC solution of the specified initial concentration was put in the Erlenmeyer flask (100 ml), and then a known amount of the AC was added to the solution. The mixture was shaken in an Orbital shaker (Edmund Buhler SM25, German) at 140 revolutions per minute. After that, filter paper (Whatman) was used to remove the adsorbent from the aqueous solution. A double-beam UV-visible spectrophotometer (PG Instruments, Model UV T80, England) was used to evaluate the TC's final concentration. The TC has a wavelength of 276 nm. The proportion of TC removed by the prepared activated carbon (AC) was calculated using Eq. (1)[20].

$$R \% = \left[\frac{C_0 - C_e}{C_0}\right] * 100\% \qquad \ldots (1)$$

Where R represents the removal percentage, C_o & C_e are the initial and equilibrium concentrations of TC (mg/l) respectively.

The equilibrium adsorption capacity of active carbon for Tetracycline, q_e (mg/g), was calculated using Eq. (2) [21], [22].

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \ldots (2)$$

Where q_e is (TC) adsorbed amount (mg/g); V is the volume of the sample (ml) and m is the quantity of the adsorbent added (g).

2.5 Adsorption Experimental Design

Four variables at five levels were experimentally designed using central composite design (CCD). These variables were: TC initial concentration Co, solution acidity pH, adsorption time T, and adsorbent dosage. The selection of the variable value ranges was informed by prior research conducted on the application of activated carbon to eliminate specific pharmacological pollutants. These variables were studied to investigate their impact on the adsorption efficiency of TC. Experimental design software was used to design, analyze, and optimize the affecting factors, as well as obtain an empirical model representing the adsorption efficiency of the TC.

Table 1 presents the independent factors with their coding and actual levels selected for process optimization.

Table 1,
Adsorption experimental design following CCD

run	A: Adsorption time (min)	B: pH	C: Dosage (g/25ml)	D:sa Initial Conc. (mg/L)	R% (Experimental)	R% Predicted	Residuals
1	230	4	0.39	60	85	80.68	4.32
2	90	9	0.16	120	67	69.51	-2.51
3	160	7	0.28	150	55	54.21	0.7917
4	160	7	0.05	90	62	62.99	-0.9861
5	90	9	0.39	60	65	66.35	-1.35
6	230	9	0.16	120	65	67.11	-2.11
7	90	4	0.39	120	55.333	55.24	0.0971
8	230	4	0.16	60	56	59.44	-3.44
9	230	4	0.16	120	45	41.85	3.15
10	160	7	0.28	90	77	77.67	-0.6667
11	20	7	0.28	90	54	55.71	-1.71
12	160	11	0.28	90	76	72.49	3.51
13	230	9	0.39	120	67	68.35	-1.35
14	230	4	0.39	120	52	54.17	-2.17
15	160	7	0.28	30	75	75.82	-0.8195
16	90	9	0.16	60	65	64.61	0.3889
17	230	9	0.16	60	90	88.29	1.71
18	90	4	0.16	60	46	42.85	3.15
19	90	4	0.39	60	56	55.67	0.3334
20	160	7	0.50	90	78	77.04	0.9584
21	160	7	0.28	90	78	77.67	0.3333
22	230	9	0.39	60	95	98.44	-3.44
23	90	9	0.39	120	64	62.33	1.67
24	160	2	0.28	90	33	36.54	-3.54
25	90	4	0.16	120	53	51.33	1.67
26	160	7	0.28	90	78	77.67	0.3333
27	300	7	0.28	90	80	78.32	1.68

The effects of the parameter on TC sorption were modeled and designed using the CCD method, as illustrated in Table 1. The adsorption of TC (R%). The value of the coefficient of determination R^2 was used to assess the fit of the regression, Eq. (1), and it was found to be 0.9778, approving the model's accuracy.

$$R\% = -120.66 + 0.39\,A + 21.26\,B + 202.22C \\ + 1.21\,D + 0.011\,AB + 0.27\,AC \\ - 0.003\,AD - 10.95\,BC \\ - 0.013\,BD - 0.66\,CD \\ - 0.00054\,A^2 - 1.143\,B^2 \\ - 151.166\,C^2 \\ - 0.0035\,D^2 \qquad \dots (1)$$

time (A), pH (B), adsorbent dosage (C), and initial concentration of TC (D) were used to optimize the response removal.

Figure 1 plots the predicted vs. observed values of removal percent content in the five-factor CCD analysis. The predicted responses from the empirical function are almost identical to the measured values, where all points are close to the line in the range of the operating factors.
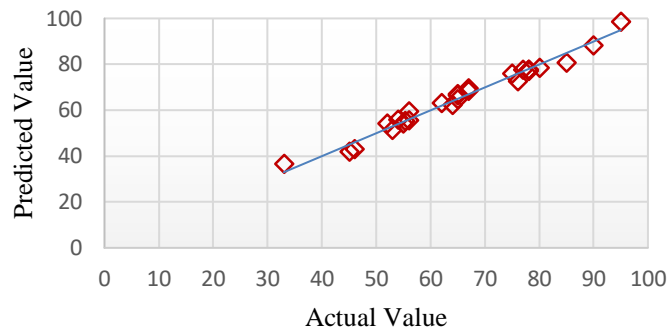
Fig. 1. Predicted vs. actual values of the percentage removal of Tetracycline adsorption.

3. Results and Discussion
3.1 Characterization of the activated carbon
3.1.1 Characterization using FT-IR

Figure 2 displays the FTIR spectra of both the raw material, tea residue, and the TAC. The O-H stretching vibration of the hydroxyl group is responsible for the bandwidth at 3415.99 cm^{-1}. The peak at 2898.9 cm-1 results from the C-H stretching of the benzene ring. The presence of a methoxy group band in the precursor is responsible for the broadband at 2850.54 cm^{-1}. The bands at 1727.74 cm^{-1} and 1639.24 cm-1 are due to the chemical formula C = O for carboxymethyl cellulose [23]. The low absorption at 1524.37 cm-1 is due to the oscillation of the aromatic skeletal structure. The peak at 1458.07 cm-1 represents the carboxylic groups [24]. The bands between 1000 and 1300 cm-1 are produced by the C-C and C-O vibrations of alcohols, phenols, and ethers. The band at 588.86 cm-1 is caused by the Si-O-Si vibration [25]. The peaks in activated carbons associated with the O-H, CH_3O, C-H, C=O, C-C, and C-O groups decreased or vanished after KOH activation [22].
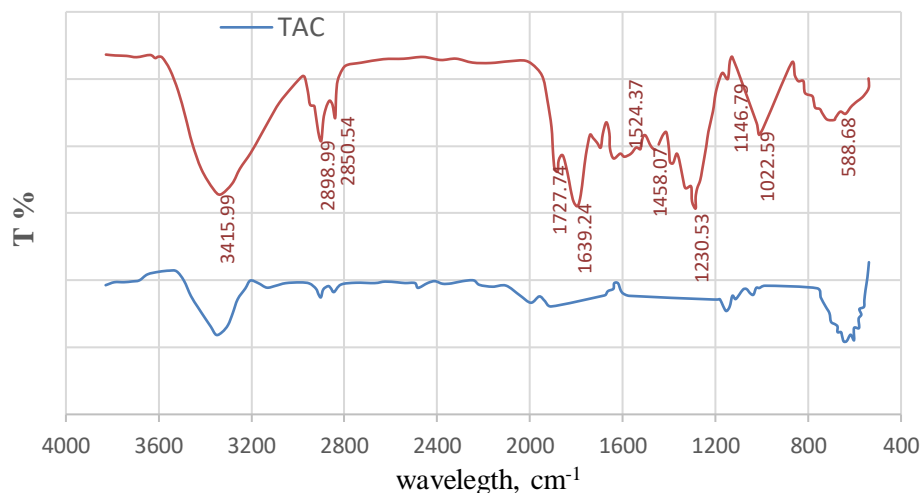

Fig. 2. FTIR spectra of the raw material, tea residue, and tea active carbon TAC.

3.1.2 Characterization using SEM

The SEM examination was conducted to investigate surface morphology and the shape of the active carbon (TAC), as shown in (Figure 3a). The micro-surface morphologies of TAC are depicted in Figure 3. The internal structure of the activated carbon depressions has several etched pores and channels, in addition to a random distribution of depressions of different sizes. This turned out to agree with recent reports [16] that studied the removal of o-Cresol by activated carbon derived from waste tea. EDS analysis was used to evaluate the adsorbent's elemental composition. According to this observation, the primary components of TAC were C (76.7%), O (14%), Mg (0.9%), Al (0.4%), and Ca (5.9%) (Figure 3b).
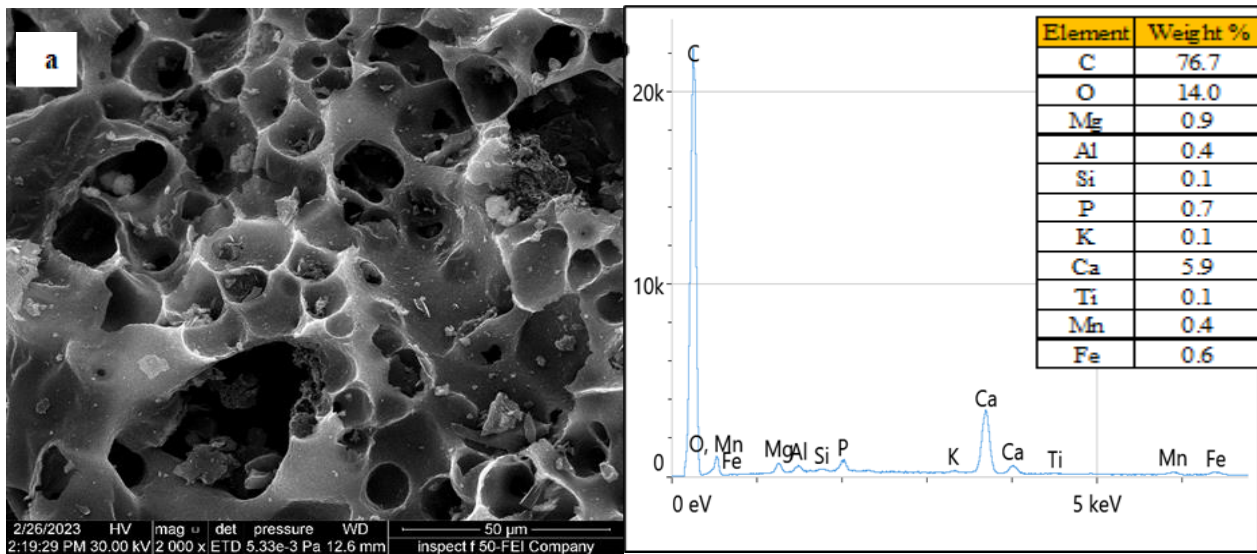
Fig. 3. (a) SEM image of Active carbon, (b) EDS.

3.1.3 Surface area and pore structure

Brunauer-Emmett-Teller (BET) characterization showed that the activated carbon made from tea residue (TAC) had a specific surface area of 747 m^2/g and an average pore volume of 0.477 m^3/g.

3.1.4 Characterization using XRD

Powder XRD analysis was used to describe the crystallinity of the TAC surface. The TAC sample's XRD spectrum is displayed in Figure 4. These spectra showed weak peaks at 22° and 44°. These peaks demonstrate the presence of a graphite crystal structure in TAC. This turned out to be consistent with recent reports [26].
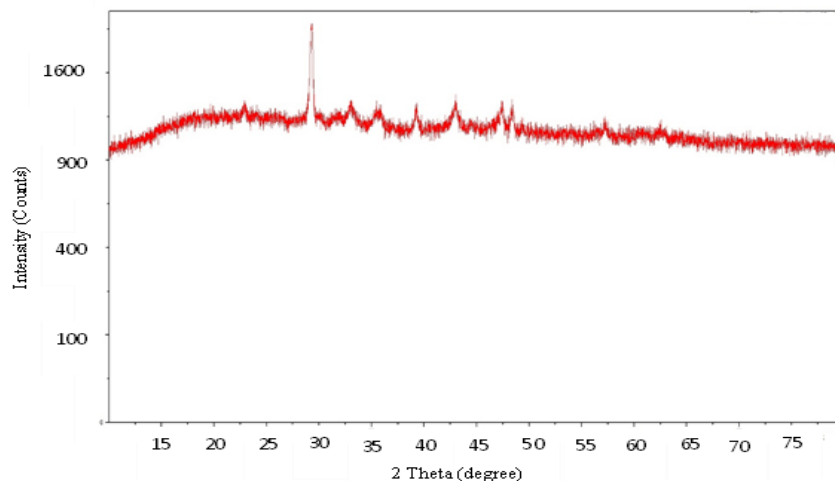

Fig. 4. X-Ray diffraction patterns of tea residue activated carbon TAC.

3.2 ANOVA analysis

The analysis of variance displayed in Table 2 records the actual results of ANOVA evaluations. The significance of a parameter was indicated by its P-value. The model's F-value of 37.69 and P-value of 0.0001 imply the model is significant. In this case, A, B, C, D, AB, AD, BC, CD, A², B², C², and D² are significant model terms. Values greater than 0.05 indicate the model terms are not

significant. The analysis results in Table 2 indicate the significant effect of each variable in the model on the removal efficiency. It can be observed that the pH parameter in the linear form **B** (F-value = 186.64) has the most significant effect on removal efficiency, followed by the linear term of the mixing time **A** (F-value = 73.86). In interactive terms, the most significant effective parameters are mixing time and initial concentration **AD** (F-value = 65.52), and the other is the pH and TAC dosage **BC** (F-value = 11.83).

Table 2,
ANOVA Results of Tetracycline Adsorption Findings

SOURCE	SUM OF SQUARES	MEAN SQUARE	F-VALUE	P-VALUE	
MODEL	5478.72	391.34	37.69	< 0.0001	significant
A-TIME	766.9	766.9	73.86	< 0.0001	significant
B-PH	1938.01	1938.01	186.64	< 0.0001	significant
C-DOSAGE	296.34	296.34	28.54	0.0002	significant
D-CO	700.56	700.56	67.47	< 0.0001	significant
AB	50.17	50.17	4.83	0.0483	significant
AC	70.84	70.84	6.82	0.0227	
AD	680.34	680.34	65.52	< 0.0001	significant
BC	122.84	122.84	11.83	0.0049	significant
BD	12.84	12.84	1.24	0.2879	
CD	79.51	79.51	7.66	0.0171	significant
A²	151.31	151.31	14.57	0.0025	significant
B²	714.74	714.74	68.83	< 0.0001	significant
C²	78.09	78.09	7.52	0.0179	significant
D²	213.46	213.46	20.56	0.0007	significant
RESIDUAL	124.6	10.38			
PURE ERROR	0.6667	0.3333			
COR TOTAL	5603.32				

3.3 Adsorption parameters interactions
3.3.1 Interaction between Adsorption time and initial concentration of TC

Figure 5 shows the 3D response surface and contours of how the most important factors, adsorption time and initial concentration of TC, interact at pH =9. The p-value and F-value are indicators of these outcomes, as shown in Table 2. Figure 5 shows that the adsorption time is the most important factor in the absorption process. When the initial concentration of Tetracycline (Co) was between 30 and 90 ppm, increasing the adsorption time led to a higher percentage of Tetracycline being removed. When the concentration of Tetracycline is greater than 100 ppm, the adsorption capacity gradually
slows down over time. This observation is because increasing concentrations require more time to be adsorbed. This behavior is in agreement with [28]. The optimum values for mixing time and initial concentrations are 230 min and 60 ppm, respectively.

The non-significant factors in Eq. (1) are eliminated, and only the significant factors are included in Eq. (2).

$$R\% = -120.66 + 0.39\,A + 21.26\,B + 202.22C$$
$$+ 1.21\,D + 0.011\,AB$$
$$- 0.003\,AD - 10.95\,BC$$
$$- 0.66\,CD - 0.00054\,A^2$$
$$- 1.143\,B^2 - 151.166\,C^2$$
$$- 0.0035\,D^2 \qquad ... (2)$$

An analysis of variance was used to assess the suitability of the model. The quadratic model was found to be very significant, with the values of R-squared, adjusted R-squared, and Predicted R-squared correlation coefficients equal to 0.9778, 0.9518, and 0.8723, respectively. This value indicates the proportionality of the experimental values and the predicted adsorption removal values. The ANOVA analysis of Tetracycline adsorption nearly agrees with that of [27], which studied the adsorption of Tetracycline onto AC and analyzed the results using RSM.
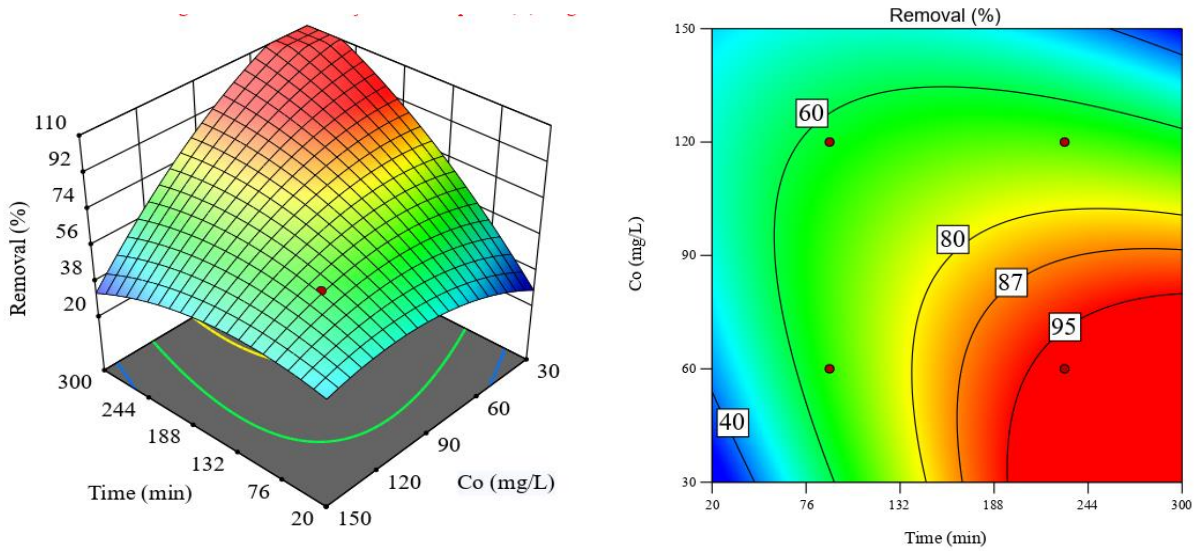
Fig. 5. Counter plots and 3D of removal percent (%) of TC as a function of time (min) and initial concentration of TC (ppm).

3.3.2 Interaction between pH and TAC Dosage

The solution pH is an important factor that can greatly affect the adsorption process because it changes the adsorbent's surface charge and ionization behavior. Figure 6 shows the 3D response surface and contours of how pH and the amount of active carbon affect the adsorption of Tetracycline. These are the two most important factors. Figure 6 shows that the adsorption percentage increased with increasing pH. This can

be due to the competition for adsorption sites between Tetracycline and H^+ that occurs on the surface of the adsorbent at a low pH. With increasing pH, the adsorbent gradually gains more adsorption capacity and reaches its maximum adsorption of 97% at pH 9 and an Ac dose of 0.39 g per 25 mL solution. However, with pH = 11, the adsorption capacity of TAC fibers tends to decrease slightly because of the attenuation of hydrogen bonding due to the generation of OH^{-1}. This behavior is in agreement with [28].
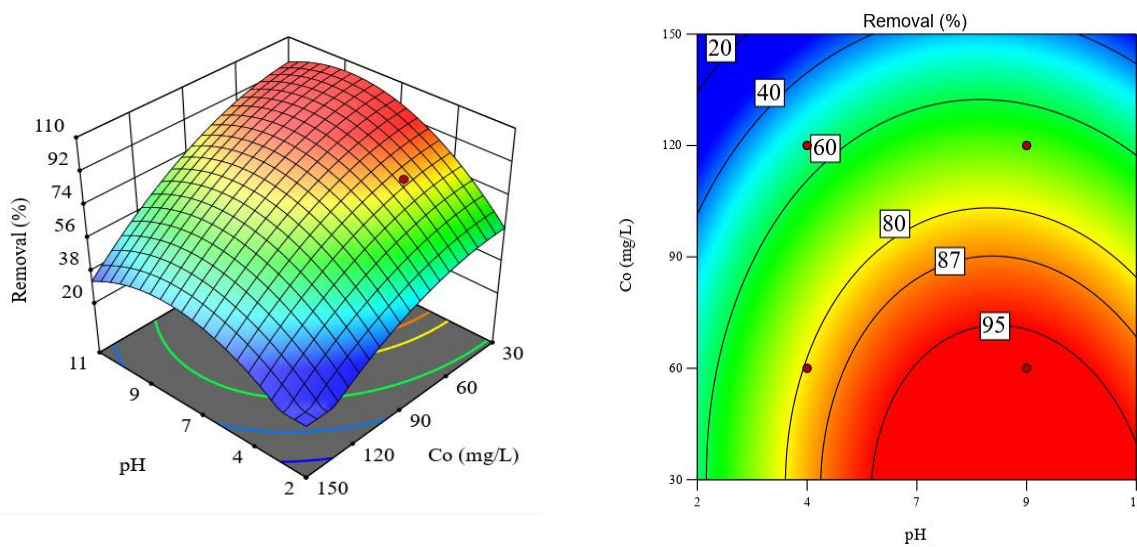

Fig. 6. Counter plots and 3D of removal percent (%) of TC as a function of pH and TAC dosage (g/25ml).

8

3.4 Optimization of process variable

The model accuracy was validated by optimizing the process parameters of the adsorption of Tetracycline on TAC. The obtained experimental result confirmed the validity of the model, as shown in Table 3, with 85% removal.

Table 3,
Adsorption of Tetracycline on TAC optimization following the designed model.

Process Parameters (Coded)	A	B	C	D	Predicted R^2	Actual R^2	Error %
Best Values	230	9	0.39	60	0.8723	0.9518	0.08

4. Adsorption Isotherms

The equilibrium data is used to calculate the adsorption isotherms, which are the basic requirements for designing adsorption systems. The sorption data for Tetracycline is fitted with two linearized forms of isotherm models (Langmuir and Freundlich), as shown in Figure 7. Accordingly, the empirical coefficients in Table 4 for each model were determined from the slope and intercept of the linear plot. Eq. (3) represents the mathematical expression of the Langmuir isotherm [29].

$$q_e = \frac{K_L \, q_m \, C_e}{1 + K_L C_e} \qquad \ldots (3)$$

The linearized form of Eq. (3) is given by Eq. (4)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \qquad \ldots (4)$$

Where

q_e: Amount of Tetracycline adsorbed per unit mass of AC at equilibrium (mg/g).

q_m : Maximum capacity of adsorption (mg/g).

K_L : Constant in Langmuir isotherm (L/mg).

C_e: The equilibrium concentration of the Tetracycline in the solution at equilibrium (mg/L). The values of both K_L and q_m can be calculated using adsorption experimental data and Eq. (4).

The isotherm model of Freundlich is based on the assumption of heterogeneous surface energies and multi-layer adsorption. The Freundlich isotherm is given by Eq. (5) [21].

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \ldots (5)$$

Eq. (6) represents the linearization form of the Freundlich model

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \qquad \ldots (6)$$

The constant parameters of the Freundlich isotherm (K_F and n) represent the adsorption capacity and the adsorption intensity, respectively. These values can be predicted from the experimental data using Eq. (6).

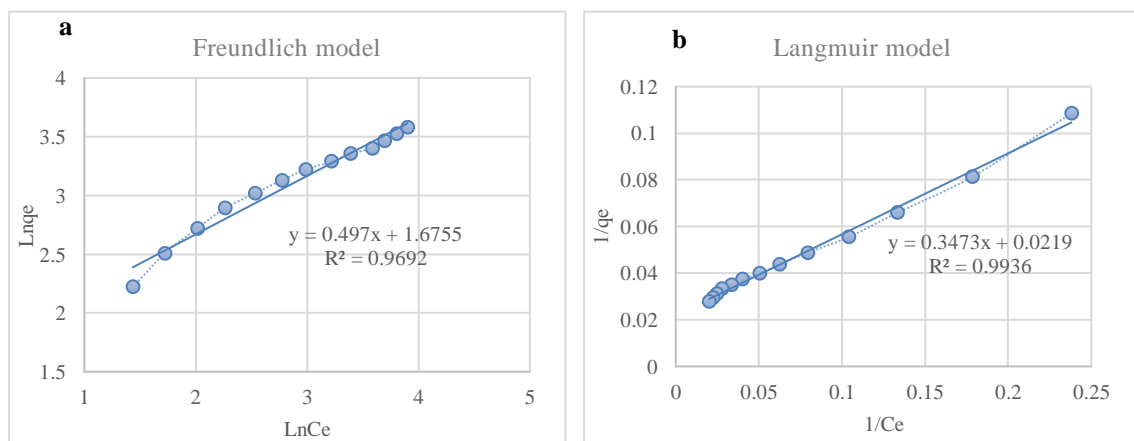The fitting of experimental data according to Langmuir and Freundlich isotherm models is shown in Figure 7.

Fig. 7. Linear form of the isotherm models for sorption of Tetracycline onto TAC, (a) Freundlich, (b) Langmuir.

The values of Langmuir isotherm parameters (q_m, K_L) and Freundlich isotherm (n, K_F) as well as the correlation coefficient (R^2) are listed in Table 4.

Table 4,
Parameters of Langmuir and Freundlich equations.

Langmuir			Freundlich		
K_L (L/mg)	q_m (mg/g)	R^2	K_F	n	R^2
0.063	45.662	0.9936	1.644	0.597	0.9692

From the values of the correlation coefficients (R^2), it is concluded that the Langmuir model fits the experimental data better than the Freundlich model, which suggests a high monomolecular layer on the surface of the TAC.

4.2 Adsorption kinetics

To understand the controlling mechanism and the adsorption rate, the adsorption kinetics of Tetracycline onto TAC were studied using two kinetic models: pseudo-first-order and pseudo-second-order. Eqs. (7) and (8) represent the non-linear forms of pseudo-first-order and pseudo-second-order kinetics, respectively [29], [30].

$$\left(\frac{dq_t}{dt}\right) = K_1 (q_e - q_t) \qquad ...(7)$$

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad ...(8)$$

The parameters q_t and q_e (mg/g) represent the amounts of the TC that were adsorbed on the TAC at any time (t) and equilibrium, respectively. The parameters K_1(min^{-1}) and K_2($g/mg.min$) are the rate constants of the pseudo-first-order and pseudo-second-order kinetics, respectively.

The linearized form of the pseudo-first-order and pseudo-second-order is given by Eqs. (9) and (10), respectively [22][31].

$$ln(q_e - q_t) = \ln q_e - K_1 t \qquad ...(9)$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e{}^2}\right) + \left(\frac{t}{q_e}\right) \qquad ...(10)$$

Figure 8 shows the graphical presentation of the experimental adsorption data according to the pseudo-first-order and pseudo-second-order kinetics models.
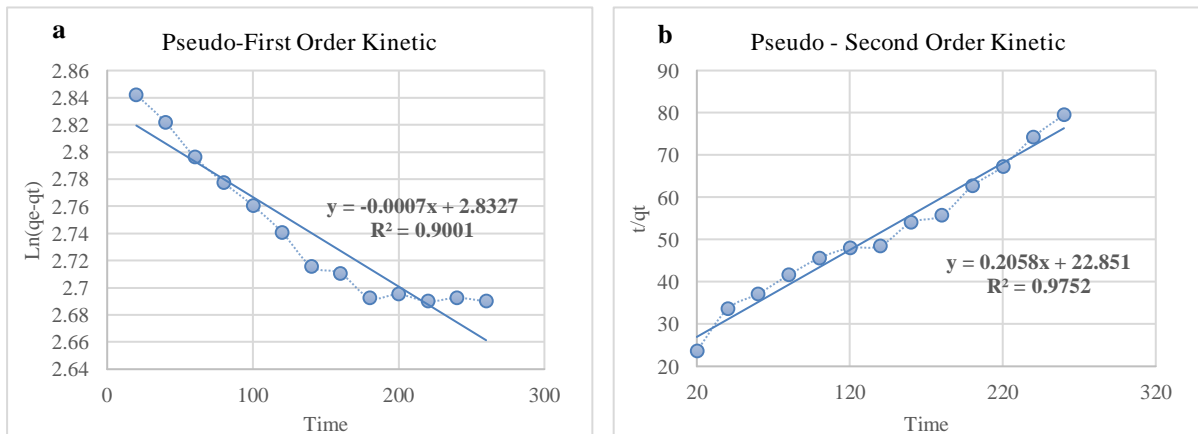

Fig. 8. (a) Pseudo-first-order and (b) Pseudo-second-order kinetics models for adsorption of Tetracycline onto TAC.

Based on the values of correlation coefficients (R^2) presented in Table 5, it was concluded that the pseudo-second-order kinetic model describes the experimental data for the adsorption of the Tetracycline onto the TAC.

Table 5,
Adsorption kinetics parameters of pseudo-first-order and pseudo-second-order rate equations

Pseudo-first-order			Pseudo-second-order		
K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg. min)	q_e (mg/g)	R^2
0.0007	9.2	0.9	0.0018	9.2	0.9752

4.3 Thermodynamics study

Three thermodynamic parameters, including enthalpy change ΔH^0, Gibbs free energy change ΔG^0, and entropy change ΔS^0, were studied to investigate the thermodynamic behavior of the adsorption onto the TAC. The Gibbs free energy change ΔG^0 was determined by Eq. (11) [32].

$$\Delta G^o = RTln(K_c) \qquad \ldots (11)$$

Where R is the universal gas constant ($R = 8.314 \, kJ/kmol.K$), T is the absolute temperature of the solution (K), and K_c is the distribution coefficient that can be calculated by Eq. (12).

$$K_c = \frac{q_e}{C_e} \qquad \ldots (12)$$

Where qe is the amount of Tetracycline adsorbed per unit weight of active carbon at equilibrium concentration (mg/g) and Ce is the equilibrium concentration of TC (mg/l). The relation between the thermodynamic parameters enthalpy change ΔH^o, entropy change ΔS^o, and Gibbs free energy change ΔG^o is given by Eq. (13) [32].

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \ldots (13)$$

Substitution Eq. (13) in Eq. (11) gives

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \ldots (14)$$

The values of $\ln(K_c)$ were calculated by Eq. (12) at different temperatures. Plotting $\ln(K_c)$ vs. $\frac{1}{T}$ gives a linear relation from which the values of ΔH^o and ΔS^o can be calculated. Figure 9 shows that the value of K_c increases as the temperature increases. Table 6 summarizes the thermodynamic parameters $\Delta G^o, \Delta H^o, $ and ΔS^o at various temperatures for the adsorption of Tetracycline onto TAC.
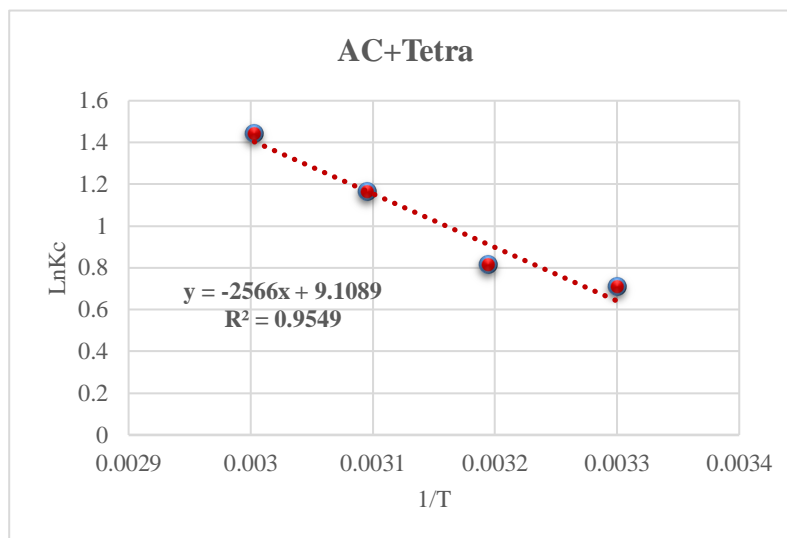

Fig. 9. $\ln K_d$ versus $^1/_T$ for the adsorption of Tetracycline on TAC.

Table 6,
Thermodynamic parameters for the adsorption of Tetracycline by the Active Carbon

ΔG^o (kJ/mol)				ΔS^o (kJ/mol K)	ΔH^o (kJ/mol)
30 ^oC	40 ^oC	50 ^oC	60 ^oC		
-1.776	-2.114	-3.121	-3.987	75.73	21.333

The negative values of ΔG^o indicate the spontaneous nature of the sorption process. The enthalpy change ΔH^o has a positive value, which indicates that the adsorption process is physisorption and endothermic. The adsorption process will be favored by increasing the temperature. The entropy change has a positive sign, which reveals that the randomness at the interface of solid and liquid will increase during the adsorption of Tetracycline [33].

5. Conclusion

In this work, tea residue was successfully converted into activated carbon, which was then used to effectively adsorb Tetracycline from an aqueous solution. The following parameters are the best for the adsorption process, which gives a removal percent of Tetracycline of 97%: mixing duration of 230 min, acidity pH of 9, dosage of 0.39 g/25 ml of active carbon, and initial Tetracycline concentration of 60 ppm. Tetracycline's equilibrium adsorption on the prepared active carbon is accurately modeled using the Langmuir model, with a maximum adsorption capacity of 45.662 mg/g. The pseudo-second-order model describes the adsorption kinetics and the reaction rate constant K_2 is 0.0018 g/(mg. min). Tetracycline adsorption on tea-activated carbon is endothermic and spontaneous, according to a thermodynamics study.

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تحضير وتوصيف وكفاءة امتصاص التتراسيكلين للكربون المنشط المشتق من بقايا الشاي

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الخلاصة

في هذه الدراسة، تم تحضير الكربون المنشط (TAC) من بقايا الشاي المستخدم. تمت دراسة الخصائص الفيزيائية والكيميائية وكفاءة الامتصاص للكاربون المنشط المنتج. ان عملية التنشيط تمت باستخدام هيدروكسيد البوتاسيوم (KOH) والكربنة عند 350 درجة مئوية، وهما الخطوتان الرئيسيتان في عملية التحضير. تم استخدام الكربون المنشط المحضر لامتصاص التتراسيكلين (TC) من المحلول المائي. تمت دراسة متغيرات مختلفة لإظهار تأثيرها على كفاءة امتصاص TC. هذه المتغيرات هي: التركيز الأولي لـ TC ، ودرجة حموضة المحلول pH ، ووقت الامتزاز، وكمية المادة الممتزة . تم تشخيص الكربون النشط المحضر باستخدام التحليل الطيفي للأشعة تحت الحمراء لتحويل فورير (FTIR) ، والفحص المجهري الإلكتروني (SEM) ، وحيود الأشعة السينية (XRD) ، و (BET) Brunauer-Emmett-Teller. تم تمثيل عملية امتصاص TC على الكربون المنشط TAC بشكل فعال بواسطة نموذج Langmuir. تؤدي زيادة درجة الحرارة إلى زيادة قدرة امتصاص TC القصوى المحددة باستخدام نموذج Langmuir. وجد ان اقصى امتصاص التتراسيكلين على الكربون النشط المحضر تبلغ 45.662 ملي غرام/ غرام. لوحظ ان حركيات الامتزاز تتمثل بشكل جيد من خلال الدرجة الثانية الزائفة. توضح دراسة الديناميكا الحرارية للامتصاص، أن امتصاص TC على TAC ماص للحرارة وتلقائي.