



Use of Novel Hydrochar from Co-carbonization of Hazelnut and Pistachio Shells for Tetracycline Removal from Aqueous Solution

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Abstract

In present study, the use of a new hydrochar (HSPSHC) produced by the combined hydrothermal carbonization (co-HTC) of hazelnut and pistachio shells (HS and PS) as a sorbent material in tetracycline (TC) antibiotic removal from water was investigated. It was obtained from hydrothermal carbonization of HSPSHC, hazelnut and pistachio shells by mixing 1:1 by mass at 220 oC for 6 h. Mass yield, energy density and higher heating value parameters were calculated for HSPSHC, and the surface chemistry was characterised using Fourier transform infrared spectroscopy (FTIR). TC adsorption on HSPSHC was carried out by kinetic and isotherm studies using batch method. The experimental kinetic results were qualified in pseudo first-order (PFO) and second-order (PSO) kinetic equations and it was observed that the adsorption complied with the PSO kinetics. The experimentally obtained results were applied to Langmuir and Freundlich model equations and isotherm modeling was performed. The adsorption isotherm of TC on the prepared hydrochar was well fitted by the Langmuir equation, which yielded a maximum monolayer adsorption capacity of TC of q_m : 137.06 mg/g at 323 K and pH 4.0 on the HSPSHC hydrochar. In addition, thermodynamic studies revealed that the adsorption of TC by HSPSHC is spontaneous and is an endothermic process.

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1 INTRODUCTION

Hydrothermal carbonization (HTC) is a thermochemical conversion process applied for energy production from biomass, the product of which is a valuable carbon-rich material (hydrochar) [1]. With this environmentally friendly process, hydrocarbonization of biomass takes place in an aquatic environment and at moderate temperatures (150-260°C) under an autogenic pressure. Unlike other conventional carbonization techniques, greenhouse gas emissions during the HTC process are minimal. This environmentally friendly process can also be applied to wet raw materials such as sewage sludge, animal manure and municipal waste, eliminating excessive energy consumption for the drying step [2]. Therefore, HTC technology, has been used to evaluate different types of waste such as avocado seeds [3], waste paper sludge [4], wet domestic waste [5], orange peels [1], date palm kernel [6].

Today, the co-hydrothermal carbonization (co-HTC) technique, in which more than one raw material is processed at the same time, attracts the attention of scientists. This advanced process offers some advantages over HTC of a single raw material, namely, it is applied to improve hydrochar properties such as an increase in carbon content and fuel quality or a decrease in ash content [7]. Many researchers have studied with various waste mixtures to understand and elucidate the co-HTC treatment and have studied synergistic and antagonistic impacts of different factors such as temperature, reaction time and mixing ratio on the co-HTC process. Polyvinylchloride (PVC)-bamboo powder [8], graphene oxide-tobacco waste [9], rice bran-sludge sludge [10], pineapple-watermelon peels [11], pig-chicken manures [12], banana peels-sludge sludge [13] can be given as an example of co-HTC application. Although carbon-based adsorbent materials obtained by the thermal conversion of a single biomass were used in previous tetracycline removal studies, relatively quantitative information on the contribution of the adsorbent obtained by the co-hydrothermal conversion of two different biomass to tetracycline removal is still lacking.

Therefore, in the current work, a novel kind of carbonaceous material was produced from the combined hydrocarbonization of hazelnut and pistachio shells, which has not been used in the co-HTC process until now. HSPSHC was characterized by spectroscopic techniques such as FTIR and SEM in order to define its surface properties and was used as an adsorbing agent in tetracycline removal from aqueous solution. The adsorption of TC was investigated with kinetic and isotherm studies, and the influences of pH, equilibrium-contact time and temperature over sorption were investigated.

2 MATERIALS AND METHODS

2.1 Biomass and chemical reagents

HS and PS were obtained from the hazelnut processing factory in Ordu and the peanut processing factory in Gaziantep, respectively. Both raw materials were thoroughly washed with DI water and dried at 80 °C. The dried samples were pulverised to 149 µm grain size. The chemicals used in this study are TC (chemical formula: C₂₂H₂₄N₂O₈, molecular weight: 444.43 g/mol), NaOH, HCl and C₂H₅OH analytical grade and were supplied by Sigma-Aldrich.

2.2 HSPSHC production

The co-HTC process of HS and PS was conducted using a 100 mL batch reactor at an autogenous pressure of 1.8 MPa (Fytronix, FYHT-8000, Turkey). A mixture of 50 mL ultrapure water and 5 g biomass (2.5 g of HS and 2.5 g of PS) was added to the HTC reactor to keep the biomass /water ratio 1:10. The biomass-water mixture was kept in an autoclave at 220 °C for 6 h and obtained final sample was collected by filtration, washed with DI water, and dried at 80 °C for 12 h.

2.3 Characterization of HSPSHC

The mass yield (*MY*), higher heating value (*HHV*) and energy yield (*EY*) of HSPSHC were calculated according to the following formulas:

$$MY (\%) = \frac{\text{mass of hydrochar}}{\text{mass of feedstock}} \times 100 \quad (1)$$

$$HHV = 0.3491 C\% + 1.1783 H\% + 0.1005 S\% - 0.1034 O\% - 0.015 N\% - 0.021 ash\% \quad (2)$$

$$EY = MY \times \frac{HHV_{hydrochar}}{HHV_{feedstock}} \quad (3)$$

Fourier transform infrared (FTIR) spectrum (Perkin-Elmer Spectrum 100) was recorded to perform the qualitative analysis of the surface functional groups of HSPSHC. To obtain information about the surface morphology of HSPSHC, SEM (Scanning Electron Microscope, Jeol/jsm-6335F, USA) images of the surface were taken. The ultimate analysis (CHNS) were detect instrumentally (LECO 932 CHNS), and oxygen contents were determined by calculating C, H, N and S contents. Fixed carbon, volatile matter, moisture and ash content analyzes of hazelnut and pistachio shells and HSPSHC were made according to China GB/T212-2008 standard test.

2.4 Adsorption studies

Batch experimental works were performed to investigate the sorption of TC on HSPSHC. All experimental studies were carried out with 0.1 g of HSPSHC, each experiment was repeated twice and calculations and models were made with average values. TC sorbed by hydrochar (q (mg/g)) was calculated with the help of Eq. (4) given below:

$$q = \frac{(C_0 - C_e)V}{m} \quad (4)$$

where C_0 and C_e are the initial and the residual concentration of TC, respectively. m (g) is the mass of sorbent and V (L) is the solution volume. The influence of pH was studied at different pH levels (2- 11), constant initial concentration (100 mg/L) and temperature (293 K). The solutions pHs were adjusted using HCl and NaOH (0.1 M). Adsorption kinetics were investigated at temperature of 293-323 K and within a period from 5 to 200 minutes at a concentration of 100 mg/L. Isotherm studies were performed using a series of TC solutions (20-400 mg/L) at 293, 308 and 323 K for 12 h. The concentration of TC was measured using an ultraviolet spectrometer (Perkin Elmer-Lambda 25, USA) at a wavelength of 360 nm. The rate constants for the HSPSHC-TC system were calculated by evaluating the kinetic data in pseudo first-order [14] (PFO) (Eq. (5)) and pseudo second-order [15] (PSO) (Eq. (6)) kinetic equations:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads,1}}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_{ads,2}q_e^2} + \frac{t}{q_e} \quad (6)$$

In these equations, q_e (mg/g) is the equilibrium sorption uptake, q_t (mg/g) is the removed amount at t time, and $k_{ads,1}$ (1/min) with $k_{ads,2}$ (g/mg.min) denotes rate constants of the PFO and PSO, respectively.

The isotherm data were analyzed using Langmuir [16] (Eq. (7)) and Freundlich [17] (Eq. (8)) isotherm models and the equilibrium parameters of the system were calculated:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (7)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

In Eq. (7), C_e (mg/L) is the aqueous TC concentration at equilibrium, b (L/mg) is Langmuir sorption energy and q_m (mg/g) represents the maximal sorption capacity. K_F in Eq. (8) [(mg/g) (L mg)^{1/n}] is the Freundlich sorption constant. $1/n$ symbolizes the adsorption density. In addition, Langmuir constant b is used in Eq. (8) to calculate the equilibrium parameter R_L , which gives information about whether the adsorption is spontaneous or not:

$$R_L = \frac{1}{1 + b C_0} \quad (9)$$

In this equation, C_0 was adsorbate concentration (ppm) before sorption. The isotherm parameter R_L is an adsorption. It reflects whether the process is favorable ($R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

3 RESULTS AND DISCUSSION

3.1 Characterization of HSPSHC

3.1.1 Elemental analysis, fuel properties and proximate analysis

Elemental analyzes of the raw materials (HS and PS) and HSPSHC hydrochar produced by the co-HTC technique were carried out to evaluate the change in elemental compositions and the data obtained are listed in Table 1. From the table, the elemental carbon content of HSPSHC is higher than that of HS and PS, which is due to the carbonization and hydrolysis reactions that occur through the co-hydrothermal operation. Also, the reduction in H and O content compared to HS and PS is owing to the decarboxylation, dehydration and condensation reactions that occur through the co-hydrothermal operation [18]. In addition, the fact that the H/C and O/C atom ratios of HSPSHC are lower than the raw materials show that the co-HTC process increases the aromatization in the structure. Ash, volatile matter and fixed carbon contents of HS and PS shells and HSPSHC are also presented in Table 1. The ash values of HS and PS decreased by 52% and 60%, respectively, during the co-HTC treatment. During the HTC process, ash as an inorganic component is mostly inactive, so the reaction and decomposition of the biomass components allows the inorganic structures to easily pass into the liquid phase [19]. When the volatile matter content and fixed carbon values are examined, a decrease in volatile matter and an increase in fixed carbon content are observed after co-HTC for both biomasses. The decrease in volatile matter and the increase in fixed carbon are attributed to the polymerization and condensation reactions that occur during the HTC process [20]. In accordance with Table 1, the HHVs of the HS and PS increased after co-HTC treatment and reached 20.12 MJ/kg. In addition, fuel ratios increased by 64% and 87%, respectively, to 0.84 for HS and PS. The increase in HHVs is due to both the increase in carbon content and degradation of cellulose and hemicellulose. That is, after HTC stage, the ash and volatile matter content decrease, and hemicellulose and cellulose, which have HHVs ranging from 16.81 to 18.6 MJ/kg, are decomposed at temperatures around 180°C and 220-230°C. As a result, components with higher HHV remain in the structure of the hydrochar and increase HHV [21]. Considering the mass and energy yield values, it was calculated as MY: 75.45% and EY: 81.24%, respectively.

Table 1. Physicochemical characteristics of HS, PS and HSPSHC

Sample ID	HS	PS	HPSHC
%C	48.46	44.75	51.85
%H	5.661	5.705	5.404
%N	0.458	0.292	0.362
%S	-	0.068	-
%O	44.37	47.93	41.88
H/C	1.40	1.53	1.25
O/C	0.69	0.84	0.61
HHV (MJ/kg)	18.97	17.36	20.12
Moisture (%)	10.62	4.73	4.93
Ash (%)	1.05	1.26	0.50
Volatile matter (%)	57.64	64.62	51.29
Fixed carbon (%)	30.69	29.39	43.28
Fuel ratio (%)	0.53	0.45	0.84

3.1.2 SEM analysis

Figure 1 includes SEM images of HSPSHC showing the surface morphologies before and after adsorption. From Figure 1a, HSPSHC surface has some unevenly distributed cavities and pores. This facilitates the attachment of TC molecules to the HSPSHC surface. As seen in Figure 1b, these pores and cavities disappeared after adsorption and the surface of HSPSHC was covered with TC molecules.

3.1.3 FTIR analysis

Figure 2 shows the FTIR spectrum of the HPSHC. The absorption bands observed at 3500 and 3000 cm^{-1} corresponds to O–H stretching vibrations [22]. The bands between 3000 and 2500 cm^{-1} belong to aliphatic $-\text{CH}_x$ vibrations [23]. The absorption bands between 1750 and 1500 cm^{-1} belong to $-\text{C}=\text{O}$ groups originating from ketone and amide structures in the structure. The peak observed at 1650 cm^{-1} indicates the presence of $-\text{C}=\text{N}$ groups on the surface. The peaks at 1000 and 950 cm^{-1} are due to the aromatic C–H out-of-plane bending vibrations. In

addition, the peaks observed at 1500 and 1450 cm^{-1} confirm the existence of carboxylic groups on hydrochar surface.

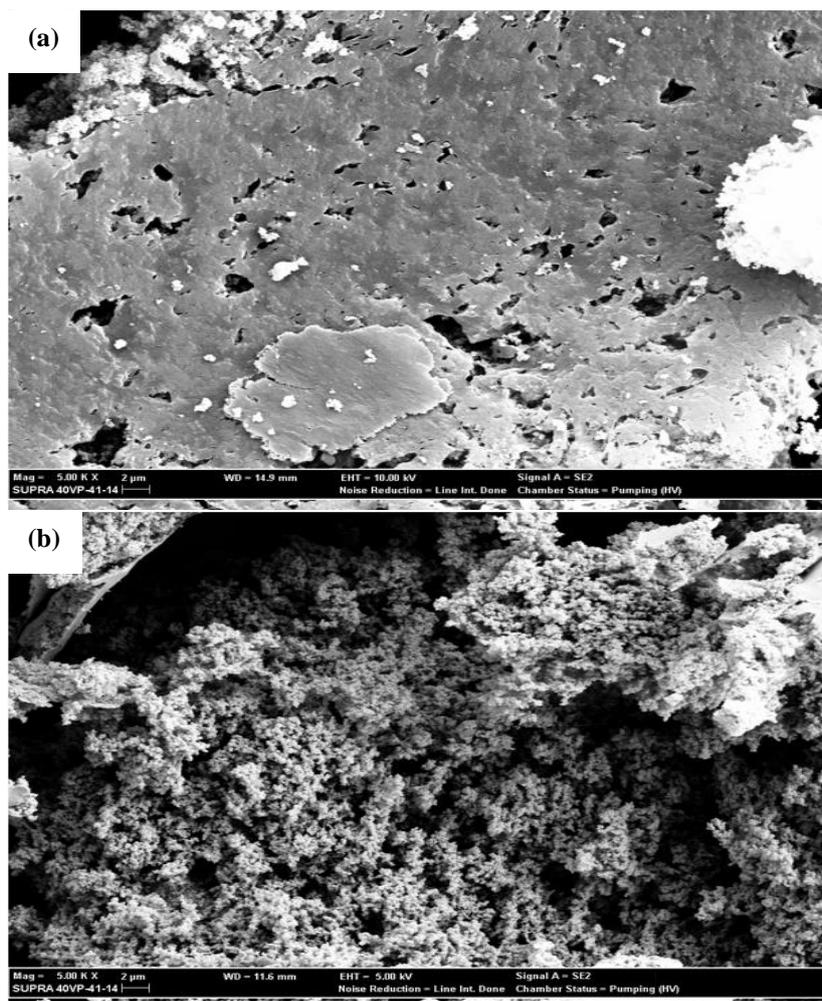


Figure 1. Micrographs of hydrochar (a) and TC loaded hydrochar (b)

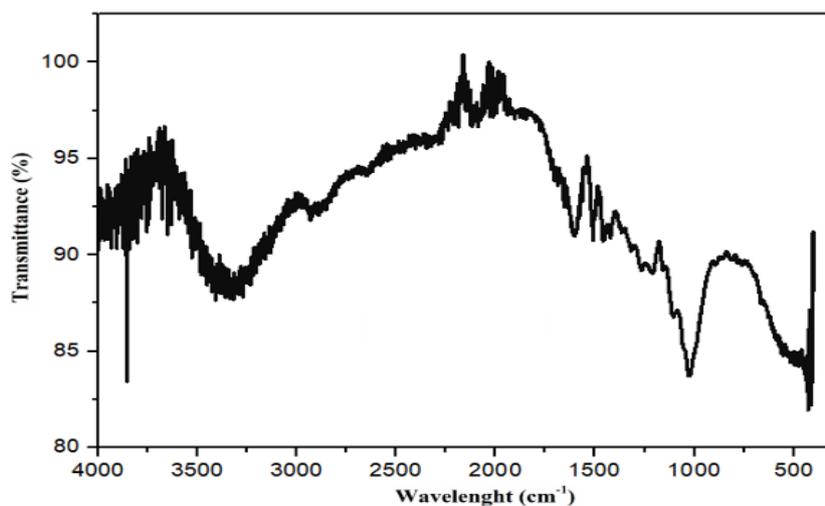


Figure 2. FT-IR spectra of HPSHC

3.2 Adsorption studies

3.2.1 Effect of pH on TC adsorption

The influence of pH was worked at different pH levels between 2-11 and the results obtained are shown in Figure 3. TC is an amphoteric molecule with multiple ionizable functional groups. TC has three different pK_a values: 3.30, 7.68 and 9.68. At pH values lower than pH 3.30, TC is cationic (TCH_3^+) in the medium due to the protonation of the dimethylammonium group. Between pH 3.30 and 7.68, TC exists in the form of zwitter ions (TCH_2) in the medium with the removal of protons from the phenolic diketone groups. At pH values higher than 7.68, TC is in an anionic position (TCH^- or TC_2^-) owing to the loss of protons from diketone and tricarbonyl groups [24]. From Figure 3, the maximal sorption of TC on the HSPSHC surface has occurred at pH 4, and as the pH increases, the amount adsorbed decreases. TC exists in the form of zwitter ions (TCH_2) at pH 4, which is also the most abundant state of TC in natural waters. With the increase in pH, TC transforms from a cation in a strongly acidic solution to an anion under basic conditions, and with this, the functional groups on the HSPSHC surface are dissociated and cause an increase in the negative charge density on the surface. As a result, as the pH increased, the repulsive forces between the TC and the HSPSHC surface increased and the TC adsorption on the adsorbent surface is decreased [25].

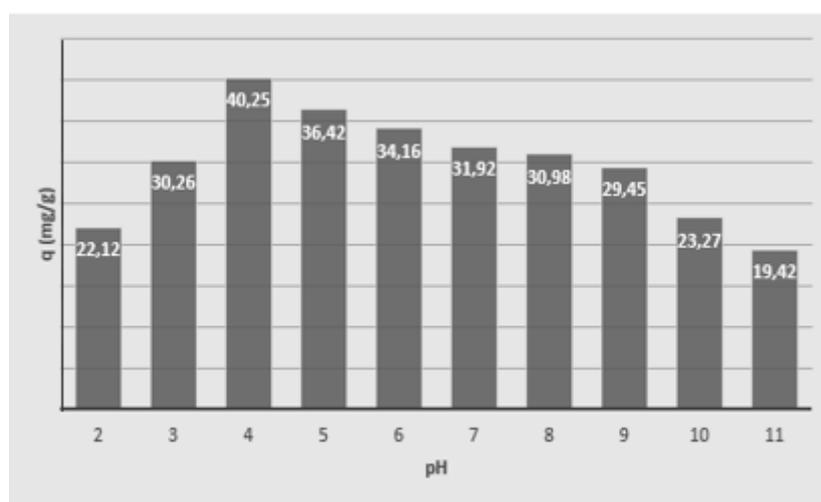


Figure 3. The effect of solution pH on TC adsorption performance

3.2.2 Kinetic modeling

In order to make kinetic modeling, the experimental data were evaluated in Eq. (5) and Eq. (6), and plots of PFO and PSO models were obtained (Figure 4 (a-b)). PFO and PSO rate parameters were determined from slope values of these linear graphs ($k_{ads,1}$ and $k_{ads,2}$) and $q_{e,cal}$ values were determined from intercepts of these plots. The suitability of the models were investigated by comparing $q_{e,cal}$ and experimental q_e values ($q_{e,exp}$). The parameters and correlation coefficients (R^2) determined for both kinetic models are listed in Table 2. From the Table 2, considering R^2 values, TC sorption on HSPSHC complies with the PSO kinetics. Also, for the PSO model, the closeness of $q_{e,exp}$ and $q_{e,cal}$ values with each other confirms this suitability.

3.2.3 Isotherm modeling

Adsorption equilibrium results were investigated by the Langmuir (Eq. (7)) and Freundlich (Eq. (8)). Langmuir and Freundlich isotherm constants were calculated from the slope and intercept values of these plots (Figure 5a-b) and gathered in Table 3. From Table 3, R^2 correlation coefficients of Langmuir model are higher than the R^2 correlation coefficients of the Freundlich model. It shows that TC adsorption on HSPSHC fits the Langmuir model. This compatibility shows that the sorption active centers on the HSPSHC surface show a homogeneous distribution. Obtained maximum sorption uptake fitted with the Langmuir model was found as q_m : 137.06 mg/g at 323 K. From this result, it can be concluded that the TC adsorption process is associated with monolayer formation.

The mechanism of adsorption of TC onto HSPSHC may include physical adsorption, electrostatic interactions, hydrogen bonds, and π - π interactions. The FTIR result supports that this is due to the presence of oxygen-rich functional groups on the HSPSHC surface.

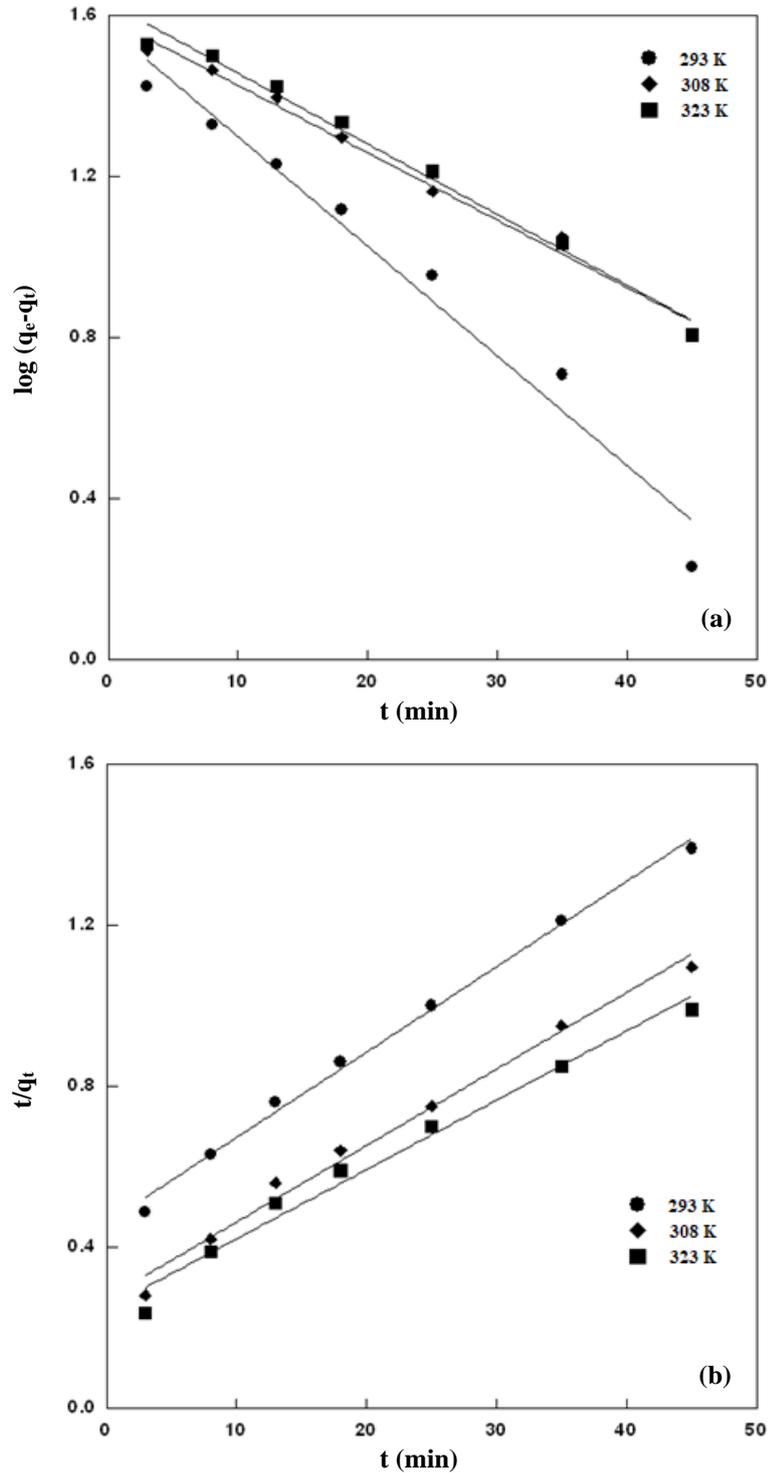


Figure 4. Sorption kinetic fitting results for TC uptake onto HPSHC; Linear fitting curves from PFO (a) and PSO (b) models

Table 2. Kinetic parameters related to TC adsorption on HPSHC surface at different temperatures

Temperature (K)	PFO				PSO		
	$q_{e,exp}$	$q_{e,cal}$	$k_{ads,1}$	R^2	$q_{e,cal}$	$k_{ads,2} \cdot 10^3$	R^2
293	32.20	35.14	0.0526	0.9756	34.10	0.298	0.9942
308	46.50	37.61	0.0482	0.9882	48.08	0.174	0.9905
323	50.80	45.16	0.0570	0.9816	51.92	0.158	0.9956

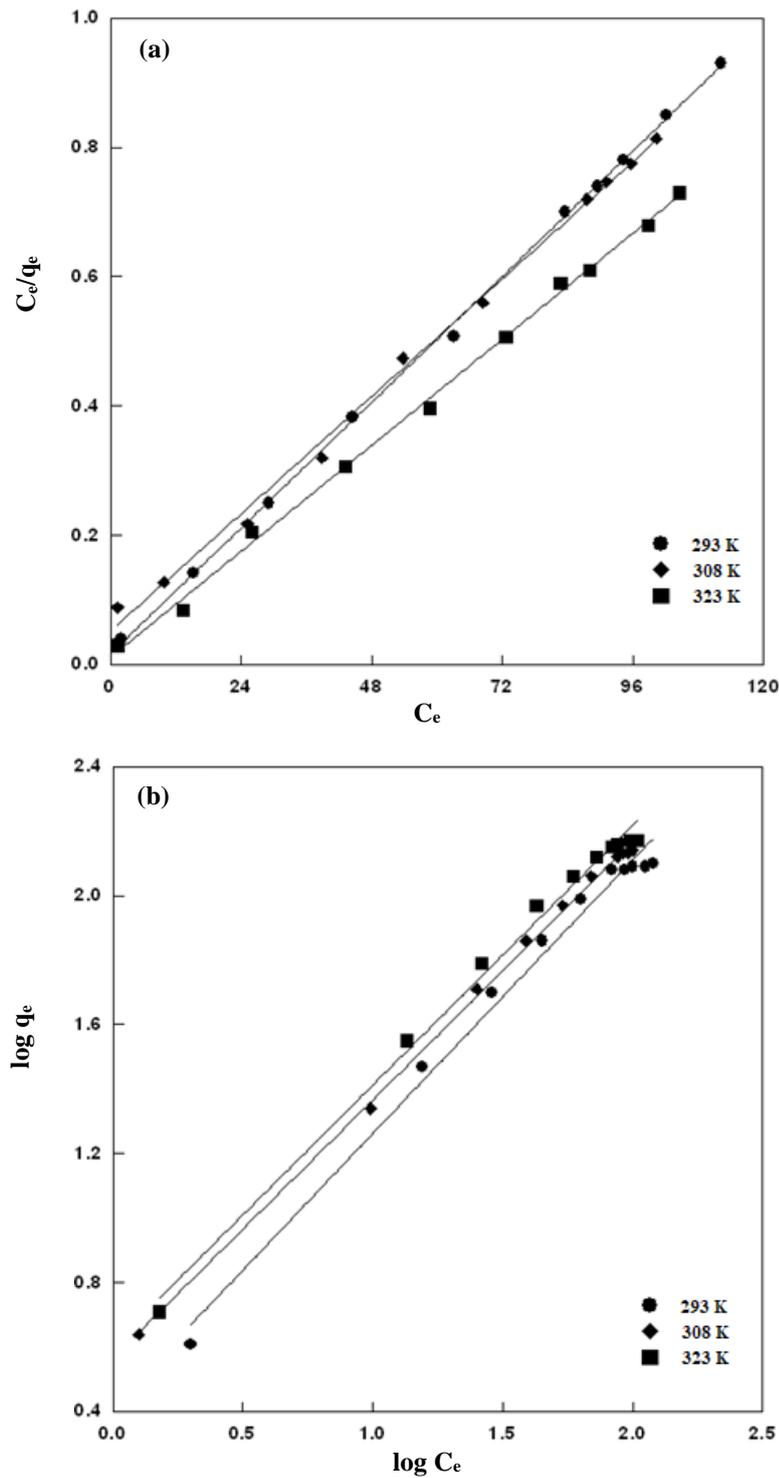


Figure 5. Isotherms of adsorbing TC onto HPSHC with the fitting curves by Langmuir (a) and Freundlich (b) models

Table 3. Parameters of isotherms for TC adsorption onto HPSHC

Temperature (K)	Langmuir				Freundlich		
	q_m	b	R_L	R^2	K_F	$1/n$	R^2
293	13.95	0.1042	0.0640	0.9989	1.97	0.58	0.9647
308	128.18	0.5254	0.0507	0.9967	3.30	0.83	0.9755
323	137.06	0.6712	0.0480	0.9956	4.64	0.87	0.9716

3.2.4 Adsorption thermodynamics

Thermodynamic analysis of the adsorption process was carried out to reveal whether TC adsorption is spontaneous on the HSPSHC surface and whether adsorption is an endothermic or exothermic process. Thermodynamic functions determined from Van't Hoff given by Eq. (10) below:

$$\ln K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (10)$$

Here K_C is the apparent sorption equilibrium constant, T is temperature (K) and R (8.314 J/mol K) is the gas constant. Thermodynamic metrics, including the enthalpy (ΔH^0 , kJ/mol), entropy (ΔS^0 , kJ/molK) and free energy (ΔG^0 , kJ/mol) were calculated by the following Eqs. (10) and (11), respectively.

$$\Delta G^0 = -RT \ln K_C \quad (11)$$

The negative ΔG^0 values display that sorption process is spontaneous and positive ΔH^0 value reveals the endothermicity of removal process. Also, positive value of ΔS^0 confirms the affinity of TC molecules to the HSPSHC surface (Table 4).

Table 4. Thermodynamic parameters for the uptake of TC onto HSPSHC surface

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/molK)	ΔS^0 (J/molK)	R^2
293	-5.2045			
308	-10.2130	32.18	156.72	0.9972
323	-11.7174			

4 CONCLUSION

A new hydrochar production was carried out by processing hazelnut and peanut shells together using co-hydrothermal carbonization technique. The feedstocks mixed in equal proportion (1:1) by mass was carbonized at 220 °C for 6 h. The produced HSPSHC has a mass yield of 75.45%, an energy yield of 81.24% and a higher heating value of 20.12 MJ/kg. HSPSHC was evaluated as a sorbent for removal of TC antibiotic from water. The effects of solution pH and temperature on TC adsorption were investigated. The highest amount of adsorption occurred at pH 4, and sorbed quantity of TC decreased as solution of pH rised. Experimental data obtained by kinetic and isotherm studies based on temperature were evaluated in kinetic and isotherm equations. The kinetic path of TC sorption was consistent with the PSO kinetic model. Equilibrium data are compatible to the Langmuir model, and the maximum sorption uptake was determined as 137.06 mg/g at 323 K. Thermodynamic analysis showed spontaneous and endothermic adsorption of TC molecules. In addition, FTIR analysis showed that the HSPSHC surface is suitable for sorption of TC in terms of the functional groups. SEM images taken before and after adsorption also confirm that adsorption has taken place. This study demonstrated the potential of using low-cost HSPSHC produced with an environmentally friendly technology as an alternative adsorbent to remove TC antibiotic from aqueous media.

Author Contributions

Hasan SAYGILI: Conceptualization, Methodology, Software, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization

Gülbahar AKKAYA SAYGILI: Conceptualization, Methodology, Validation, Writing - Original Draft, Writing -Review & Editing, Supervision

All authors read and approved the final manuscript.

Conflict of interest

No conflict of interest was declared by the authors.

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