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Effect of activated carbon produced from biochar on removal of 2, 4-dichlorophenoxy acetic acid from aqueous solutions

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The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment. Therefore, the removal of pesticides from water is one of the major environmental concerns these days. 2,4-Dichlorophenoxy acetic acid (2,4-D) belonging to the herbicide group, which is among the numerous pesticides used today, is widely used to control weeds due to its low cost and good selectivity. In order to offer an alternative to this environmental problem, the effect of activated carbon obtained by chemical activation from pyrolysis biochar on 2,4-dichlorophenoxy acetic acid removal from aqueous solutions has been investigated. The adsorption mechanism is explained by analyzing the effect of adsorption parameters. It is determined that the equilibrium data are suitable for Langmuir isotherm model among the applied isotherm models and the monolayer adsorption capacity is 344.83 mg g^{-1} at 318 K. The adsorption kinetics data of 2,4-D on activated carbon is better defined by the pseudo-second-order model. Thermodynamic calculations reveal that the adsorption process is spontaneous and endothermic. The activated carbon obtained from biochar has been observed to have a high adsorption capacity compared to adsorbent materials obtained from many other raw materials for the removal of 2,4-Dichlorophenoxy acetic acid.

Keywords: Activated carbon, Adsorption, Biochar, Herbicide, Potassium hydroxide

The herbicides began to be used in agriculture in the middle of the twentieth century and their intensive use still continues in many parts of the world. The toxicity of herbicides and degradation products makes these chemicals a potential hazard[1-4]. Due to its low cost and good selectivity, herbicide of 2, 4-dichlorophenoxyacetic acid (2,4-D), is used extensively to control broadleaf weeds in agricultural and non-agricultural areas. The maximum permissible concentration in the 2,4-D drinking water, a biodegradable contaminant, is 100 µg L^{-1}and is considered to be moderately toxic[5-6].The problem of soil and groundwater pollution caused by the application of these herbicides leads to increased research on alternative solutions. In this context, adsorption method is much more preferred with its ease of use, design simplicity and low cost compared too many other methods that ensure the removal of hazardous compounds in wastewater[7-10].

The activated carbon is an effective adsorbent used in adsorption processes to remove organic compounds even at low concentrations due to its large surface area and high porous structure[11-14]. However, the high cost of activated carbon in large-scale adsorption applications limits the use of activated carbon. Therefore, much research has been done on the production of cheap and efficient activated carbon from low-cost materials[15-18]. Activated carbons can be produced from raw materials with high carbon content and low inorganic content by physical or chemical activation. Chemical activation is more preferred than physical activation due to its application at lower temperatures, lower activation time and much larger surface area and porous structure formation[19-21]. In the chemical activation process, many chemical reagents can be used that provide the porous structure and wide surface area of the activated carbon. Among the various chemical reagents, many studies with alkaline hydroxides such as KOH and NaOH have shown that the activated carbons obtained have very high specific surface areas and a well-defined pore size distribution[22-25].

It is well known that activated carbons can be prepared from various precursors with high carbon content and low inorganic compounds. Biochar is a high carbon content product obtained as a solid product as a result of thermal decomposition (pyrolysis) of organic compounds. However, the most important problem affecting the adsorption performance of the biochar is the poorly developed pores and low surface area. It has been determined in many studies that this problem can be solved by physical or chemical activation of the biochar, and an adsorbent with a high surface area and pore structure can be produced[26-30].

In this study, the effect of activated carbon obtained by chemical activation (KOH) of the biochar obtained as a result of pyrolysis of safflower press cake, which is a biomass source, on herbicide removal (2,4-D) from aqueous solutions was investigated. For this purpose, the effect of adsorption parameters such as initial pH value, adsorbent dosage, initial concentration, contact time and solution temperature on the adsorption process was investigated using activated carbon obtained under optimum conditions. The adsorption data were analyzed using the pseudo-first order and pseudo-second order kinetic models. In addition, the suitability of isotherm models such as Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin have been checked for the adsorption of 2,4-D to activated carbon.

Experimental Section

Materials

The biochar, which is used as precursor material in the production of activated carbon, was obtained as a solid product as a result of pyrolysis of safflower seed press cake[31]. All chemical reagents used in this study were of analytical grade. 2,4-dichlorophenoxyacetic acid (2,4-D) with high purity (≥98%) was supplied from Sigma-Aldrich.

Production and characterization of activated carbon

In this study, potassium hydroxide (KOH) with an impregnation (KOH:biochar) ratio of 1:1 was utilized for the chemical activation of biochar. Carbonization was carried out in the tubular reactor (Protherm PTF 12) at an activation temperature of 800°C and under inert nitrogen gas (100 cm^3 min^{-1}). The solid product obtained after carbonization was washed with 1 N HCl solution, then with hot distilled water until the pH value was 6-7 and dried at 105±3°C[32,33]. The elemental analysis and surface properties of precursor material and activated carbon were determined by using CARLO ERBA Elemental Analyzer and Quantachrome, Autosorb-1C instruments.

Adsorption studies

In adsorption experiments of 2,4-dichlorophenoxyacetic acid (2,4-D) on activated carbon, 0.1 g of activated carbon and 100 mL of herbicide solution (100 mg L^{-1}) were used as adsorbent. Adsorption experiments were carried out in a temperature controlled water bath for 24 h at 120 rpm agitation rate. After the adsorption, the solution was filtered and then the concentration of 2,4-D in the solution was measured using spectrophotometer (Shimadzu UV-Vis 1240) at 220 nm wavelength. Adsorption experiments were carried out to determine the 2,4-D adsorption capacity of the activated carbon obtained by examining the effect of adsorption parameters such as initial pH, adsorbent dosage, contact time, solution temperature and initial concentration. In order to investigate the effect of initial *p*H value on the removal of 2,4-D, adsorption experiments were carried out at different *p*H values (2; 4; 6; 8.55; 10 and 12), 100 mg L^{-1} initial concentration using 100 mL solution containing 0.1 g activated carbon at 298 K solution temperature. The *p*H was measured with pH-meter (Mettler-Toledo). After determining the optimum *p*H value, the effect of adsorbent amount was investigated. For this purpose, adsorption experiments were carried out by shaking for 24 h at a solution temperature of 298 K using different dosages of adsorbents in the range of 0.05 g/100 mL to 0.8 g/100 mL. As a result of the experiments, 2,4-D removal percentage was determined by the following equation:

As a result of the experiments, 2,4-D removal percentage was determined by the following equation:

$$Removal\ (\%) = \frac{C_0 - C_e}{C_0} x100 \qquad \dots (1)$$

where C_0 is initial concentration and C_e is equilibrium concentration (mg L^{-1}) of the herbicide (2,4-D), respectively[1,34-37].

The amount of 2,4-D adsorbed in equilibrium (q_e) was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad \ldots (2)$$

where C_0 and C_e(mg L^{-1}) represent the solution concentrations of 2,4-D at the initial and equilibrium, respectively, V (L) is the volume of 2,4-D solution, and w (g) is the weight of activated carbon used[2,36,38].

Results and Discussion

Characterization of biochar and activated carbon

The results of elemental analysis and surface properties of the biochar and activated carbon are given in Table 1[32]. Considering the elemental analysis results of biochar and activated carbon, the C content of the char used as precursor increased from 62.5% to 72.1% in activated carbon obtained by chemical activation. Similarly, H content increased from 1.85% to 2.68% also. Nitrogen and oxygen content decreased from 4.07% to 2.77% and 31.63% to 22.46% for biochar and activated carbon, respectively. Sulfur was not detected in the raw material (biochar) and accordingly in the activated carbon. These changes are an expected result due to the removal of volatile substances and non-carbon compounds in the process of chemical activation and carbonization. The surface and micropore area of the activated carbon were determined as 1277 m^2 g^{-1} and 1133 m^2 g^{-1}, respectively. It is observed that the micro pore area accounts for about 89% of the total surface area and the activated carbon is predominantly composed of micro pores. Similar results have been obtained in many studies[26,39,40].

Table 1 — Characteristics of the biochar and activated carbon[32].

	Biochar	Activated carbon
Ultimate analysis (wt.%)		
Carbon	62.45	72.09
Hydrogen	1.85	2.68
Nitrogen	4.07	2.77
Sulfur	Not detection	Not detection
Oxygen (by difference)	31.63	22.46
Surface properties		
BET surface area (m^2/g)	14.14	1277
Micropore area (m^2/g)	---	1133
Total pore volume (cm^3/g)	---	0.6628
Micropore volume (cm^3/g)	---	0.4952
Average pore diameter (nm)	---	2.08

Effect of initial *p*H value

The initial *p*H of the solution is of great importance in adsorption processes, as it affects not only the types of contaminants in the solution, but also the surface load properties of the adsorbent[1,34,41]. The effect of the initial *p*H value is given in Fig. 1. As seen in the Fig. 1, 2,4-D removal efficiency decreased with the increase in the *p*H value of the solution. While the *p*H value increased from 2 to 12, the removal percentage of 2,4-D decreased from 96.71wt% to 49.55wt%, respectively. It has 2,4-D anionic character and the separation of hydrogen ion from molecules largely depends on the *p*H level of the solution. Since more protons were present in the solution at low *p*H values, it increased the electrostatic attraction of the 2,4-D between molecular species and positively charged adsorption zones, thereby causing an increase in the adsorption of 2,4-D. Also, as a result of the electrostatic repulsion between negatively charged functional groups on the adsorbent (activated carbon) surface and the anionic 2,4-Dichlorophenoxy acetic acid molecules, the adsorption capacity decreased as the solution *p*H value increased. Similar changes were observed in studies with different adsorbents for removal of 2,4-D from aqueous solutions[1,3,34,41]. The adsorption studies below were carried out at *p*H 2 value, where the maximum 2,4-D removal was achieved.

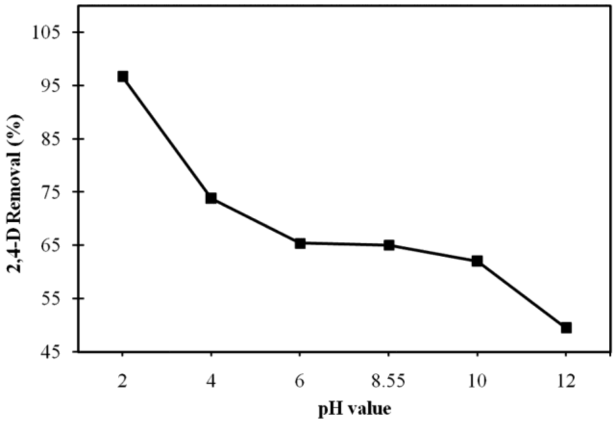

Fig. 1 — Effect of initial *p*H on the adsorption of 2,4-D.

Effect of activated carbon dosage

The effect of the dosage of adsorbent on the herbicide (2,4-D) removal and adsorption capacity from aqueous solutions is given in Fig. 2. It is seen that 2,4-D removal increases rapidly with the dosage of adsorbent. It is apparent that the removal percentage of 2,4-D increased from 84.67% to 96.50% with increasing dosage from 0.05 to 0.1 g/100 mL, then remaining almost constant (98.10%) but the amount of herbicide adsorbed per unit was decreased. As the amount of adsorbent increases, the free absorption surface and adsorption zones also increase, and as seen in experimental results, more 2,4-D molecules are adsorbed[38,42]. However, increasing the adsorbent dosage amount despite the constant percentage of 2.4-D removal reduces the total surface area as a result of the accumulation of high amounts of activated carbon particles, and accordingly, the amount of 2.4-D adsorbed per unit adsorbent has decreased[41,43,44]. Therefore, the adsorbent dose of 0.1 g/100 mL (96.50 mg g^{-1}) was used in the following experimental studies.

Adsorption isotherms

When the adsorption process reaches equilibrium, adsorption isotherms explaining how molecules are distributed between liquid and solid phases provide the necessary information for the design of adsorption systems. Therefore, it is important to evaluate equilibrium data using different theoretical or empirical isotherm equations to interpret adsorption[11,44,45]. In this study, Langmuir, Freundlich, Dubinin-Radushkevich (D–R) and Temkin isotherm models were used to evaluate the balance data. To obtain adsorption equilibrium data the solutions with different initial concentrations (100, 150, 200, 250, 300 and 400 mg L^{-1}) were used. In adsorption experiments, using 100 ml of herbicide solution and 0.1 g of activated carbon, the studies were conducted at optimum pH value for 2,4-D. Adsorption was carried out for 24 hours in a water bath at a shaking rate of 120 rpm at 298 K, 308 K and 318 K temperatures. The amount of 2,4-D adsorbed in equilibrium (q_e) was calculated by using Eq. (2). The corresponding equations of the isotherm models used in the study and the isotherm constants obtained are given in Table 2. Also, comparison of isotherm models for different solution temperatures is shown in Fig. 3.

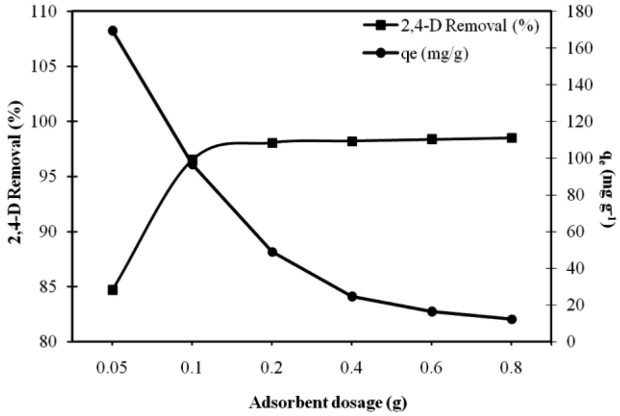

Fig. 2 — Effect of adsorbent dosage on the adsorption of 2,4-D.

The Langmuir isotherm model is the most widely used isotherm in theory for the adsorption of pollutants from liquid solutions. This isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of molecules on adsorbate surface with a constant energy, and that no transmigration of adsorbate occurs in the plane of the adsorbate surface[45-46]. Important properties of Langmuir isotherm can be explained with R_L, which is a dimensionless constant separation factor. The value of R_L indicates that the isotherm type is

Table 2 — Adsorption isotherm constants for adsorption of 2,4-D onto activated carbon at different solution temperatures.

Isotherms	Temperature (K)	Parameters			
Langmuir		Q_0 (mg g^{-1})	K_L(L mg^{-1})	R_L	R^2
$\frac{q_e}{C_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0}$	298	312.50	0.077	0.010-0.038	0.9895
	308	333.33	0.136	0.018-0.068	0.9938
$R_L = \frac{1}{1 + K_L . C_0}$	318	344.83	0.25	0.031-0.115	0.9926
Freundlich			$1/n$(L mg^{-1})	K_F (mg/g).(L/mg)$^{1/n}$	R^2
$\log q_e = \log K_F + \frac{1}{n} \log C_e$	298		0.3661	63.62	0.9347
	308		0.2960	88.33	0.8673
	318		0.2077	124.57	0.9598
D – R		q_s(mg g^{-1})	B (mol^2 kj^{-2})	E(kj mol^{-1})	R^2
$ln q_e = \ln q_s - B\varepsilon^2$	298	234.86	0.1	2.236	0.7766
$\varepsilon = \mathrm{RT} \ln \left[1 + \frac{1}{C_e}\right]$	308	250.49	4.0	0.354	0.8842
$E = \frac{1}{\sqrt{2B}}$	318	258.53	2.0	0.500	0.9169
Temkin			A (L g^{-1})	B_1	R^2
$q_e = B_1 \ln \mathrm{A} + B_1 \ln C_\mathrm{e}$	298		24.825	38.775	0.9779
$B_1 = RT/b$	308		2.740	56.661	0.9452
	318		1.057	66.526	0.9789

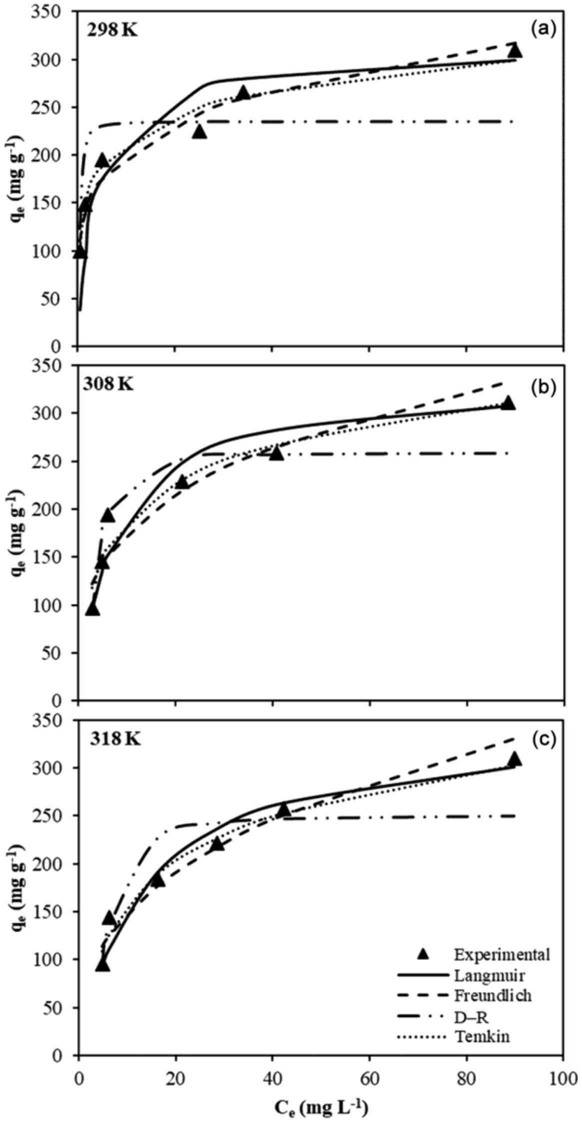

Fig. 3 — Comparison of different isotherm models for the adsorption of 2,4-D onto activated carbon at different solution temperatures.

irreversible ($R_L = 0$), positive ($0 < R_L<1$), linear ($R_L = 1$), or negative ($R_L> 1$). The R_L values between 0 and 1 indicate favorable adsorption[2,5,8].

The R_L values in the current research have been found to be between 0.010-0.068 at different solution temperatures, and have shown that 2,4-D adsorption on activated carbon is favorable. The Q_0 and K_L Langmuir isotherm constants represent the maximum adsorption capacity and adsorbate/adsorbent interaction constant, respectively. These parameters increased with the increase of temperature. The Q_0 value increased from 312.50 mg g^{-1} to 344.83 mg g^{-1} when the temperature rose from 298 K to 318 K, suggesting that the adsorption process is endothermic.

The Freundlich isotherm model is an empirical equation commonly used to determine the adsorption intensity of adsorbate surfaces with non-uniform energy distribution and to define reversible adsorption[1,8,34,47]. Freundlich constant K_F is defined as the adsorption coefficient and represents the amount of herbicide adsorbed to the activated carbon adsorbent for a unit equilibrium concentration. A high K_F value is an indication of high adsorption capacity, and it was observed in this study that the K_F value increased with increasing temperature. 1/n is a measure of adsorption density or surface heterogeneity, and it's indicates that the heterogeneity increases as its value approaches zero. The 1/n value calculated from the Freundlich isotherm equation was found between 0 and 1 for all temperatures. This result indicates that 2,4-D adsorption to activated carbon is suitable and there are minimal interactions between the adsorbed molecules[7,11,48].

Dubinin and Radushkevich (D–R) isotherm model, which defines the liquid phase adsorption, is used to determine whether adsorption occurs by a physical or chemical process. According to this isotherm model, it is assumed that adsorption in micropores is limited to one layer[1,36,49]. The mean sorption energy (E) is the free energy transfer of one mole of solute from infinity to the surface of the adsorbent and according to the magnitude of E the adsorption process is defined as physical (below 8 kJ mol^{-1}) or chemical (8-16 kJ mol^{-1}) adsorption[1,43]. It was determined that the adsorption of herbicide (2,4-D) on activated carbon is physical adsorption according to calculated free energy values (0.50–2.236 kJ mol^{-1}). On the other hand, the correlation coefficient values (R^2) showed that D–R isotherm model cannot sufficiently explain the adsorption process (Table 2).

The Temkin isotherm model suggested that the adsorption heat of all molecules in the layer will decrease linearly with the coverage area due to the adsorbent-adsorbate interactions and is characterized by the distribution of the binding energies of the adsorption process[1,43,50]. In the Temkin isotherm model, B is the isotherm constant related to the heat of sorption and it was observed that it increases with increasing temperature for the adsorption of the 2,4-D herbicide on activated carbon (Table 2). This trend indicates the endothermic reaction, as noted in the Langmuir isotherm model.

The Langmuir isotherm model was found to be highly compatible with experimental data compared to other isotherm models according to the regression coefficients. Comparison of Langmuir adsorption capacities obtained from 2,4-D adsorption from aqueous solutions using activated carbons from different raw materials is given in Table 3. According to the data in the table, the activated carbon obtained from biochar was observed to have a high adsorption capacity for 2,4-D compared to adsorbent materials obtained from other raw materials.

Adsorption kinetics

The mass transfer and adsorption rate expressed by adsorption kinetics is one of the most important factors in the design of the adsorption process[39,51]. In order to investigate the effect of contact time on the removal of 2,4-D herbicide, the kinetic studies were performed by using 0.1 g activated carbon with 100 mL herbicide (2,4-D) solution (100 mg L^{-1}) at 298, 308, 318 K solution temperatures. The contact times were chosen in the range of 30-420 minutes. The adsorption mechanism has been tried to be determined by using fake first order and fake second order models, which are frequently preferred in the adsorption of organic and inorganic pollutants to solid adsorbents. This kinetic model can be expressed in a linear form as follows;

Pseudo-first-order equation:

$$\log(q_e - \mathrm{q_t}) = \log q_e - \frac{\mathrm{k_1 t}}{2.303} \qquad \dots (3)$$

Pseudo-second-order equation:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{\mathrm{k_2 q_e}} + \frac{t}{q_e} \qquad \dots (4)$$

Where q_t and q_e (mg g^{-1}) are amounts of 2,4-D adsorbed over a given period of time t and at equilibrium, respectively; t is the adsorption time (min); k_1 (min^{-1}) and k_2 (g $mg^{-1}min^{-1}$) are the adsorption rate constants[7,38-39].

For the adsorption of 2,4-D on activated carbon at different temperatures, pseudo-first-order and pseudo-second-order kinetic plots are given in Fig. 4. In Table 4, rate constants, calculated equilibrium intakes and correlation coefficients are given for both kinetic models. The adsorption data of 2,4-D was found to be more suitable for the pseudo-second-order kinetic model for biochar activated carbon with its high correlation coefficient (R^2 = 0.999). This result suggests that the number of effective adsorption sites of activated carbon prepared from biochar is related to the adsorption rate[51]. Also, the experimental and theoretical values of equilibrium adsorption capacity (q_e) were found to be quite close to each other for the pseudo-second-order kinetic model.

Thermodynamic parameters

Adsorption thermodynamics is important to understand the effect of temperature on the adsorption process and the mechanism of the adsorption process. For this purpose, Gibss free energy (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) can be calculated using the following equations.

$$K = \frac{C_A}{C_e} \qquad \dots (5)$$

$$\Delta G^o = -RT\ln K \qquad \dots (6)$$

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \dots (7)$$

The values of ΔH° (kJ mol^{-1}) and ΔS° (J $mol^{-1}K^{-1}$) were calculated using van`t Hoff equation and plot[7-10].

The effect of temperature for adsorption of 2,4-D on activated carbon was investigated under isothermal conditions in the temperature range of 298-318 K and calculated thermodynamic parameters are given in Table 5. The negative values of ΔG° (– 12.845, – 8.943 and –7.871 kJ mol^{-1}) obtained at 298 K, 308 K and 318 K showed that the process of the adsorption process was spontaneous and feasible. The adsorption capacity of 2,4-D on activated carbon increases with increasing temperature, indicating that the adsorption reaction is endothermic. The calculated

Table 3 — Comparison of Langmuir adsorption capacities of 2,4-D with activated carbons from various materials.

Adsorbents	BET Surface area (m^2 g^{-1})	Adsorption capacity (mg g^{-1})	Reference
Biochar activated carbon	1277	344.83	Present study
Groundnut shell activated carbon	709	250	Trivedi *et al.*, 2019
Layered Double Hhydroxide LDH	43.48	25.974	Calisto *et al.*, 2019
Orange peel activated carbon	592.47	515.46	Pandiarajan *et al.*, 2018
Commercial activated carbons (GAB)	1189	367.15	Spaltro *et al.*, 2018
Olive-waste cake activated carbon	1418	129.87	Angin and Ilci, 2017
Pumpkin seed activated carbon	737.90	260.7	Njoku *et al.*, 2013
Commercial activated carbons (SorboNorit)	1225	203.3	Ocampo-Pérez *et al.*, 2012

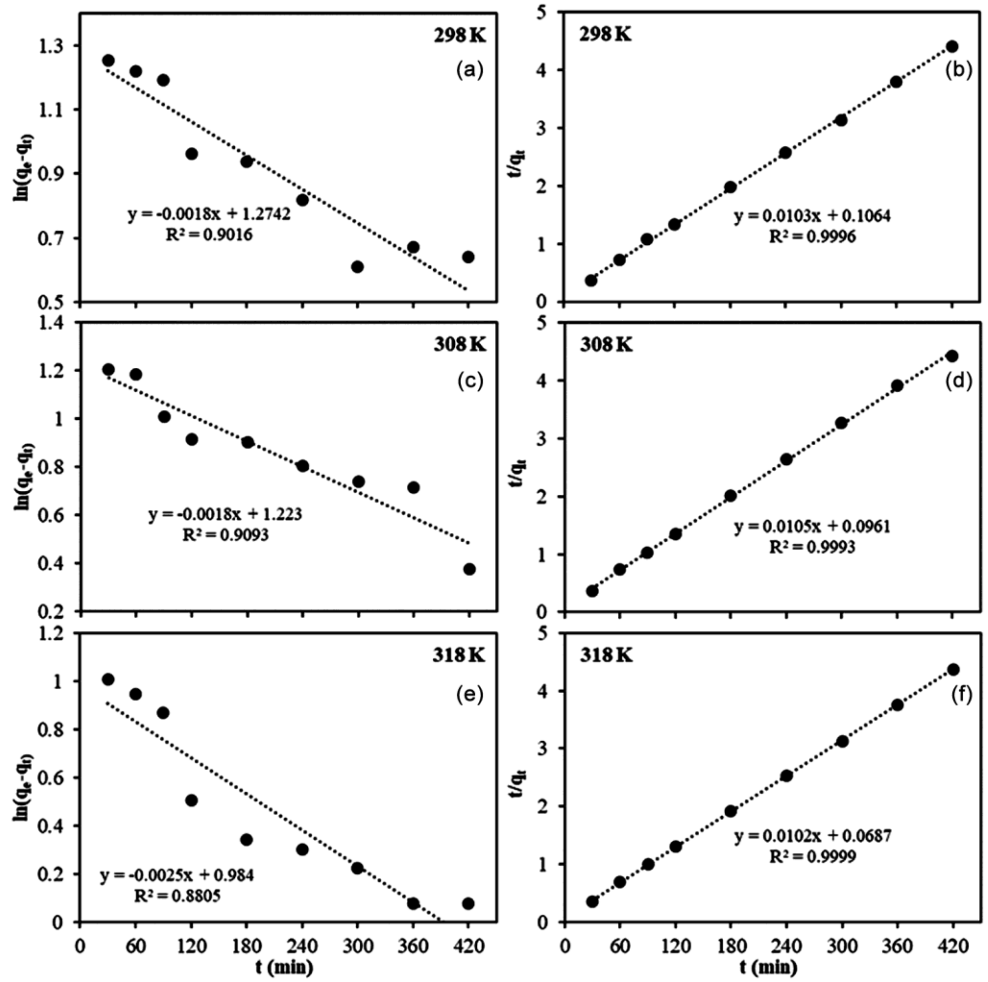

Fig. 4 — Pseudo-first-order and pseudo-second-order kinetic plots for the adsorption 2,4-D onto activated carbon at different temperatures.

Table 4 — Kinetic parameters for the adsorption of 2,4-D onto activated carbon at different solution temperatures.

Solution Temperature (K)	298	308	318
$q_{e,exp}$ (mg g^{-1})	99.443	97.047	95.153
Pseudo-first-order			
k_1 (min^{-1})	0.0041	0.0041	0.0058
$q_{e,calc}$ (mg g^{-1})	18.802	16.711	9.638
R^2	0.9016	0.9093	0.8805
Pseudo-second-order			
k_2 (g mg^{-1}min^{-1})	0.097	0.109	0.148
$q_{e,calc}$ (mg g^{-1})	97.087	95.238	98.040
R^2	0.9996	0.9993	0.9999

Table 5 — Thermodynamic parameters for the adsorption of 2, 4-D onto activated carbon.

T (K)	Δ*G*° (kJ mol^{-1})	Δ*H*° (kJ mol^{-1})	Δ*S*° (J mol^{-1}K^{-1})
298	– 12.845	87.430	251.76
308	– 8.943		
318	– 7.871		

ΔH° value (87.43 kJ mol^{-1}) was also found positive and supports this result. The ΔS° value was found as 251.76 J mol^{-1}, which showed that the randomness increased at the solid-solution interface by loading 2,4-D herbicide molecules on the inner and outer surfaces of the activated carbon.

Conclusion

In this study, it has been demonstrated that the activated carbon obtained by chemical activation from biochar that is a pyrolysis by-product and with a high carbon content is a highly effective adsorbent with high adsorption performance in the removal of 2,4-D from aqueous solutions. The rate of removal in the adsorption process is an important indicator that affects the process design. In the experimental studies conducted for this purpose, 2,4-D removal from aqueous solutions was found to be much better at acidic pH values. In adsorption studies, the highest removal rate of 2,4-D from aqueous solutions was determined as 96.50% by weight with adsorbent amount of 0.1 g/100 mL at an initial concentration of 100 mg L^{-1}. Kinetic results showed that the pseudo-second-order model was more compatible with the experimental data for all temperatures. The Langmuir adsorption isotherm model provided a better correlation for the adsorption of 2,4-D herbicide onto activated carbon from biochar, and its maximum adsorption capacity was found to be 344.83 mg g^{-1} at 318 K. The determined thermodynamic parameters (ΔG°, ΔH° and ΔS°) revealed that adsorption is spontaneous and endothermic. These results showed that activated carbon obtained by chemical activation from biochar can be effectively used for adsorption of 2,4-D herbicide from aqueous solutions.

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