

## Evaluation of the efficiency of the biochar prepared from the pine bark in removing diclofenac from aqueous solutions

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### ABSTRACT

**Background and objective:** In recent years, there has been a great deal of concern related to drug pollutants in water resources. The aim of this study was to evaluate the efficacy of the biochar obtained from the pine bark in removing of diclofenac from aqueous solutions.

**Methods:** In this batch study, the effect of various variables such as pH (2-12), adsorbent dose (0.1- 2 gr), initial concentration of diclofenac (50- 500 mg/L), contact time (10-120 min) and temperature (10- 50°C), as well as characterization of the biochar were investigated with BET, FTIR and FESEM techniques. The isotherm, kinetics and thermodynamics of the adsorption process were evaluated.

**Findings:** The highest removal of diclofenac (80.4%) was at pH 6.2. In this study, the adsorption efficiency of diclofenac increased with increasing the adsorbent dose and decreased with increasing the initial concentration of diclofenac. The adsorption isotherm of diclofenac fitted to Langmuir model with maximum adsorption capacity was 54.64 mg/g. The kinetics of the adsorption process followed by the pseudo-second-order kinetic model and thermodynamic parameters showed the diclofenac adsorption onto the biochar was exothermic and spontaneous.

**Conclusion:** Based on the results, the adsorption efficiency of diclofenac by the biochar of the pine bark is suitable and it can be efficient for removal of diclofenac from hospital and other pharmaceutical compounds producers' wastewaters.

**Keywords:** Diclofenac, Adsorption, Pine bark, Isotherm, Kinetic, Thermodynamic

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## Introduction

In recent years, there has been a great deal of concern and attention to the potential problems related to emerging pollutants in industrial and municipal wastewater [1, 2]. Since many of the pollutant compounds (PCs) are resistant to biodegradation and the effect of these pollutants on the environment and humans is not known, so special attention is paid to them as a new pollutant with high risk [3]. Also, most of these pollutants are not part of the conventional wastewater treatment systems and the maximum allowable of these pollutants in water and wastewater sources have not been approved [4, 5]. A significant portion of these drug compounds are excreted from the human or animal body without any metabolism or deformation and enter the wastewater and eventually into water resources.

Antibiotic compounds are the most widely used groups of drugs in Iran, as they make up about 15% of all drugs in the country [6, 7]. Due to the high consumption of antibiotics, their concentration in water increases and reduces water resources quality. Numerous studies are available that confirm the concentration of antibiotics from 1-100 micrograms per liter in surface and groundwater sources [8-10]. On the other hand, the pharmaceutical industries wastewater, especially the antibiotics production industries have a high concentration of these compounds (2-300 mg/L) [11-14].

Diclofenac under the brand name Dicloramine is also used to reduce pain, irritation, swelling and joint dryness in arthritis, gout and other rheumatic diseases, as well as to remedy other types of pain such as headache and muscle aches, menstrual cramps, and postoperative pain and childbirth. Its chemical formula is  $C_{14}H_{10}Cl_2N_2NaO_2$  and its molecular weight is 318.1 gr/mol [15].

*Figure 1. Molecular structural of Diclofenac*

Diclofenac is also a drug found in aqueous environments. The removal rate of diclofenac in conventional wastewater treatment systems is between 21-40% and the rest enters into the water resources [16, 17]. Diclofenac along with the synthetic hormone 17-alpha-ethinyl estradiol is one of the few drugs that have a negative effect on both aquatic and arid ecosystems [18,19].

Various physical, biological and chemical methods such as advanced oxidation processes [20, 21], biodegradation [22], membrane filtration [23], coagulation and flocculation [24] and adsorption [25] are used to remove PCs from contaminated water and wastewater. Although the advanced oxidation processes are highly efficient at removing PCs, they are complex and costly and often cause secondary contaminants. Biological processes although is the selective treatment method for the removal of biodegradable contaminants and environmental friendly, it requires complex operation and is not capable of complete decomposition of these compounds [26, 27].

Among of these methods, the adsorption process can be considered as one of the proposed technologies for removing PCs. Biochar is the most widely used material among various adsorbents in water and wastewater treatment. High efficiency and non-production of by-products are the most important benefits of biochar for the elimination of pharmaceutical compounds from wastewater and other aqueous solutions. The benefits are doubled if the biochar is produced from waste materials such as food and agricultural waste [28-30]. The main reason for using food and agricultural wastes as an adsorbent in the removal of pharmaceutical compounds is their cheapness and efficiency in the adsorption process [31, 32].

Agricultural wastes such as rice husk, corn stalks, peach wood and other agricultural and horticultural wastes have a major advantage over food wastes, which include easier availability and independence from the consumer. They are long-term maintenance. Materials such as banana peel can only be stored and stored for a short period of time to make carbon, while agricultural wastes such as wood can be stored for long periods of time [33, 34]. Agricultural wastes such as rice husk, corn stalks, peach wood and other agricultural and horticultural wastes have a major advantage over food wastes which include easier availability, independence of the consumer and long-term storage [20].

The aim of this study was to investigate the effectiveness of biochar obtained from the pine bark in the removal of diclofenac from aqueous solution. The effect of various variables such as pH, adsorbent dose, initial concentration of diclofenac, contact time and temperature on the removal of diclofenac were investigated. The kinetics, isotherm and thermodynamics of diclofenac adsorption on the biochar of the pine bark were also evaluated.

## Methods

### Preparation of the biochar

The adsorbent used in this study was the pine bark. Pieces of the pine wood as garden waste, were collected and washed with distilled water. Then it was dried in an oven for 24 hours and then was carbonized for 2 hours at 400 °C and It was sized using a laboratory mesh (12-16, 16-25 and 25). Then they were located in a vacuum furnace with CO<sub>2</sub> gas flow at 800 °C to be activated.

### The biosorbent characteristics

The pore size distribution and specific surface area of the biochar were evaluated by the Brunauer–Emmet–Teller (BET) technique. The adsorbent surface function was identified by Fourier transform infrared spectroscopy (FT-IR, Vertex 70, Bruker, Germany) in the range of 400– 3900 cm<sup>-1</sup>. The surface morphology of the biochar was studied by field emission scanning electron microscopy (FESEM; MiRA3 TESCAN, Czech Republic).

## Materials

Pure diclofenac powder with chemical formula C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>NaO<sub>2</sub> and molecular weight 318.1 g/mol was purchased from Behvarzan Pharmaceutical Company. 1 gr of diclofenac was dissolved in 1 liter of distilled water (1000 mg/L) and stock solution was provided. 0.1N hydrochloric acid and 0.1N sodium hydroxide were used to adjust the pH of the solutions.

### Adsorption experiments

The batch adsorption experiments were done to study of the effective parameters on the removal of diclofenac from aqueous solutions by modified pine bark biochar. These parameters contain adsorbent dosage (0.2–2 gr), contact time (0–140 min), pH (2–12), adsorbate concentration (50–500 mg/L) and temperature (10–50°C). Total experiments were conducted at 25°C. The diclofenac stock solution was prepared by dissolving the diclofenac solute into distilled water. Then, a certain amount of the biochar was added to 50 mL diclofenac solution with specific concentration and pH. The solutions were shaken on the

shaker-incubator at a constant rotating speed at room temperature. After shaking, the samples were centrifuged in 2800 rpm for 15 min and diclofenac concentration was measured by Hack DR5000 spectrophotometer at 292 nm.

The adsorption capacity ( $q_e$ ) of diclofenac on the biochar and the removal efficiency (RE) percentages were deliberate with the following formulas:

$$RE = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (2)$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of diclofenac (mg/L), respectively,  $V$  is the volume of solution (L), and  $W$  is the weight of the adsorbent as gram in solution.

### Determination of the adsorbent $pH_{pzc}$

The electrical charge in an adsorbent depends on the types of ions present ( $H^+$  and  $OH^-$ ) on the adsorbent surface and solution. In different pH of a solution, the surface charge of a biosorbent in terms of electrical charge it can come in many forms (negative, positive and neutral forms).  $pH_{pzc}$  of an adsorbent is determined by the state of electrical charge distribution at the adsorbent surface. In order to study of the adsorbent  $pH_{pzc}$ , 30 mL of 0.1 M NaCl solution was poured into several laboratory containers. The initial pH of diclofenac solutions ( $pH_i$ ) was adjusted between 2 to 12. The optimal dose of the biosorbent was added to each container and stirred for 24 h. In the last step, the final pH ( $pH_f$ ) of the solutions was measured. The  $pH_{pzc}$  of the pine bark adsorbent was determined by plotting  $pH_f$  versus  $pH_i$  (Figure 2).

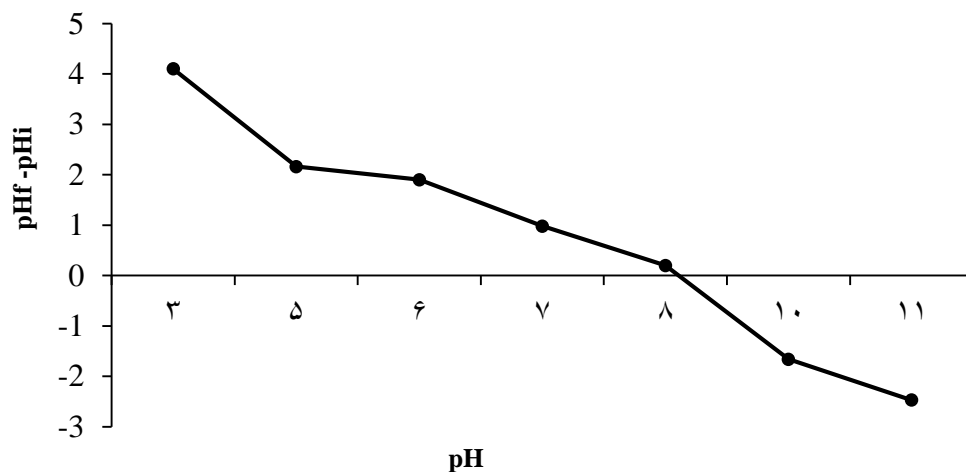


Figure 2. The point of zero charge determine in the pine bark biochar

## Results

### Characterization of the pine bark biochar

The physical structures of the biochar such as specific surface area ( $a_s$ , BET), total pore volume ( $V_T$ ), and mean pore diameters ( $D_p$ ) were determined 683.33 m<sup>2</sup>/g, 0.4179 cm<sup>3</sup>/g and 2.45 nm respectively. The FTIR spectrum of the biosorbent was shown in Figure 3. Adsorption peaks in 3400 cm<sup>-1</sup> wavenumber confirms the presence of hydroxyl ions (OH<sup>-</sup>) on the adsorbent surface. Move to down and low intensity by band and change in peak intensity in 1700 cm<sup>-1</sup> wavenumber is associated with the presence of carbonyl group (CO<sup>-</sup>) in carboxylic acids and the peak of 1000-1300 cm<sup>-1</sup> is related to C-O groups in carboxylic acids and alcohols. At peak 1900 it indicates the presence of amine groups on the biosorbent surface.

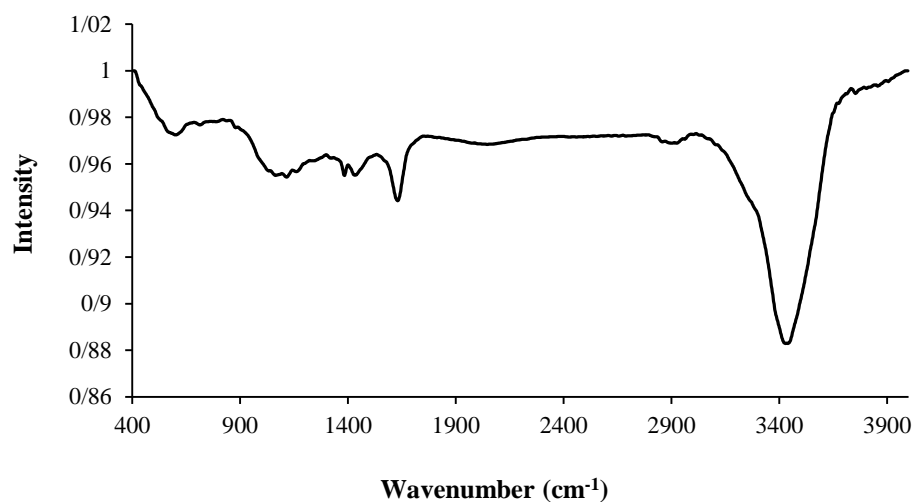


Figure 3. FTIR image of the pine bark biochar

FESEM images in the pine bark biosorbent after the diclofenac adsorption were illustrated in Figure 4. In accordance with this figure, diclofenac molecules are located inside the adsorbent pores.

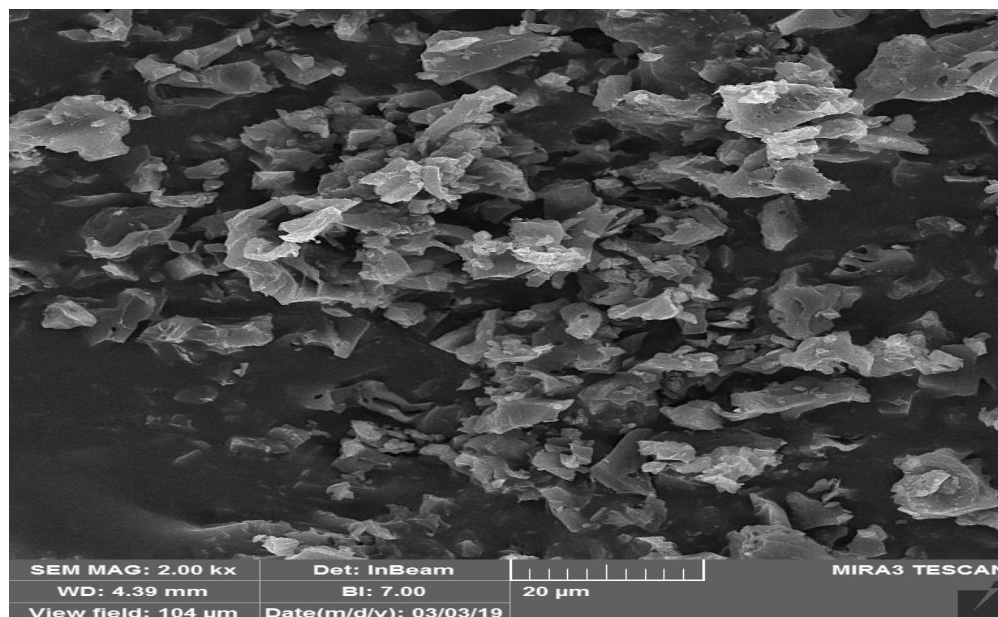


Figure 4. FESEM image of the pine bark biochar after diclofenac adsorption

### Effect of pH on diclofenac adsorption on the pine bark biochar

The effect of pH on diclofenac removal in adsorption process by the pine bark biosorbent was presented in figure 5. In according to the figure, The highest and lowest removal efficiency of diclofenac was 80.4% at pH 6.2 and 56.4% at pH 2, respectively.

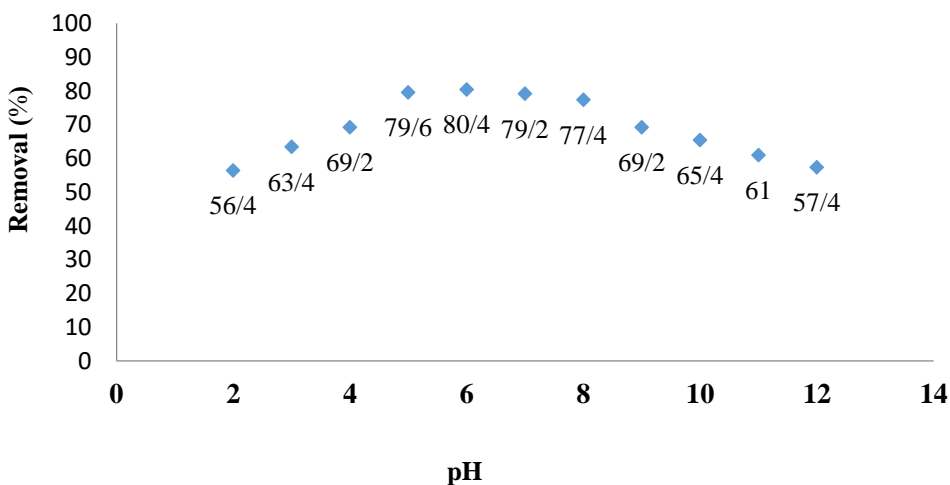


Figure 5. Effect of pH on diclofenac removal efficiency ( $C=50$  mg/L; adsorbent dose= 0.8 gr; time= 15 min;  $T= 25$  °C)

### Effect of biochar dose on diclofenac adsorption

The adsorbent dose is an important parameter in the adsorption process. In this study, diclofenac removal efficiency increased with increasing biochar dose. For this reason, diclofenac molecules have been completely removed at 1.6 gr and in 15 minutes. Although the removal of diclofenac increased from 10.8% to 100% with increasing adsorbent content, but the adsorption capacity of the biochar decreased from 54 to 31.25 mg/gr (Figure 6).

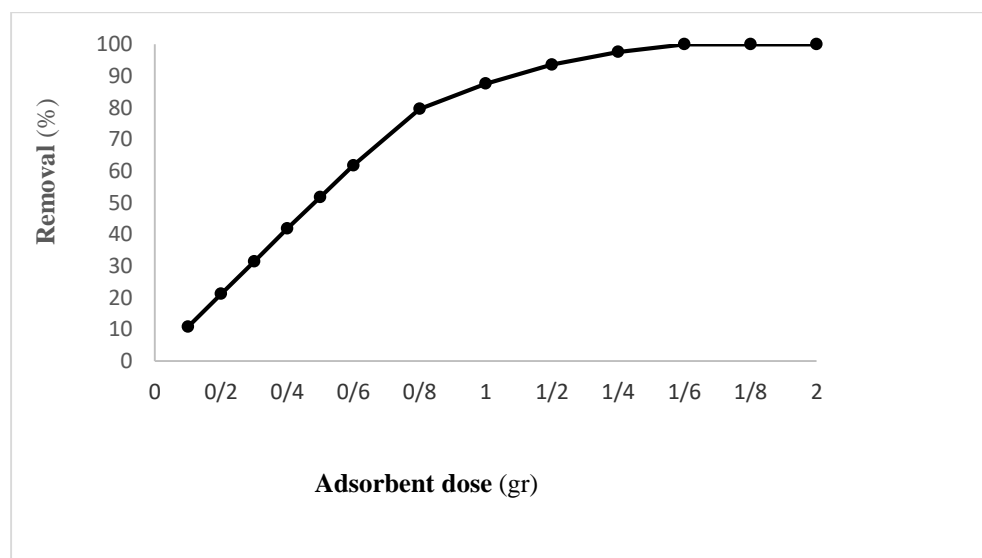


Figure 6. Effect of adsorbent dose on diclofenac removal ( $C=50$  mg/L;  $pH=6.2$ ;  $time=15$  min;  $T=25$  °C)

### Effect of initial concentration of diclofenac on the adsorption process

The concentration of solute or adsorbate is an effective factor in the adsorption process. In figure 7, removal efficiency of diclofenac by the biosorbent at different concentrations of diclofenac was presented. By increasing diclofenac concentration from 50 to 500 mg/L, the removal efficiency was reduced from 100% to 86.46% within 140 minutes, but the adsorbent capacity of this biochar increased from 62.5 to 540.38 mg/gr.



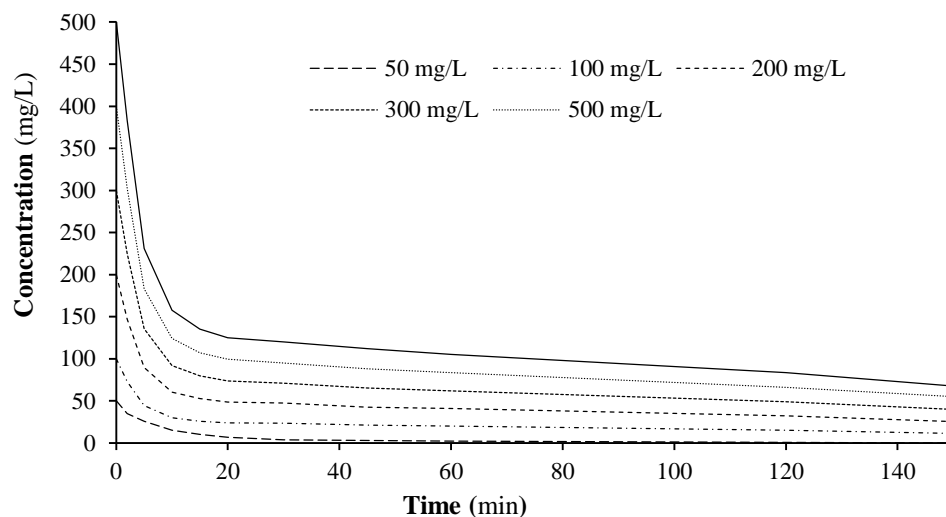


Figure 7. Effect of the initial concentrations and contact time on diclofenac removal (adsorbent dose= 0.8 gr; pH=6.2; T= 25 °C)

### The effect of temperature on the adsorption removal of diclofenac

Temperature is one of the most important parameter in the adsorption process. According to Figure 8, the removal efficiency of diclofenac was increased from 77.8% to 83.4% .with increasing temperature from 10 to 50 °C.

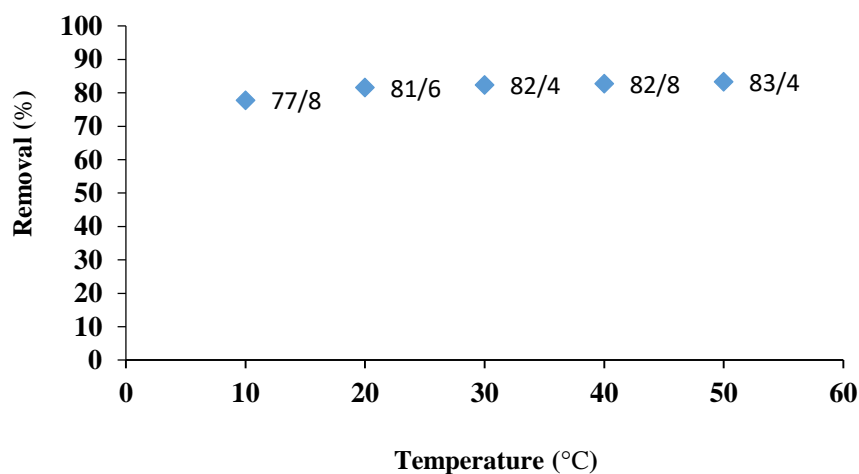
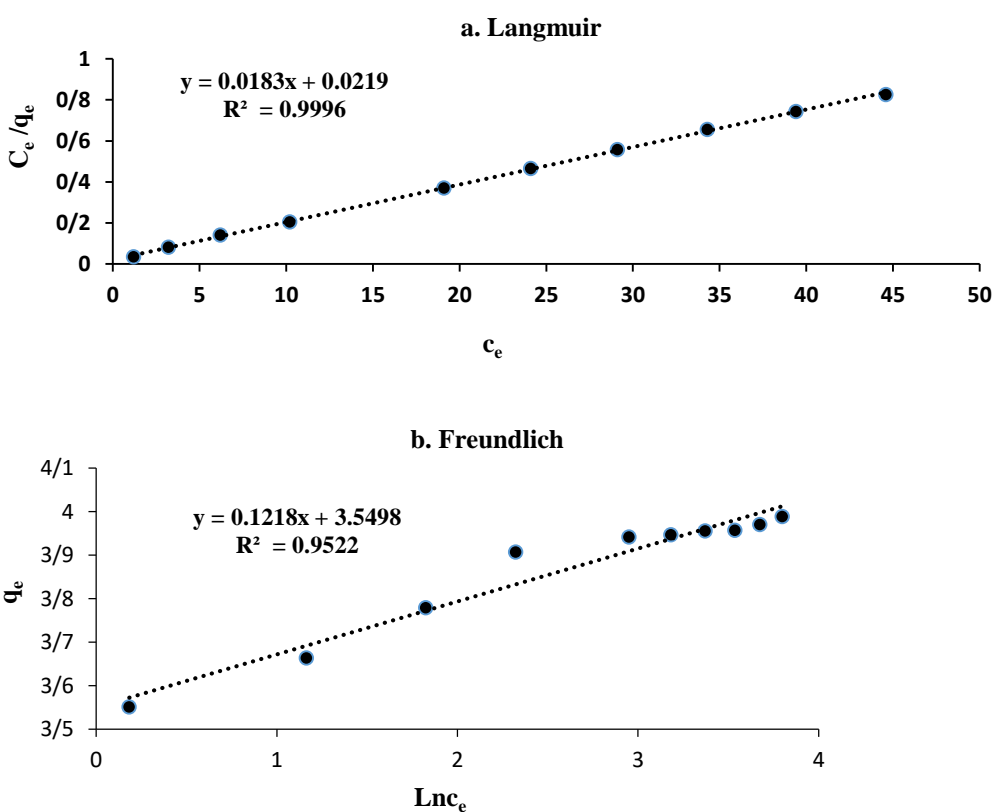


Figure 8. Effect of temperature on diclofenac removal (C=50 mg/L; pH=6.2; adsorbent dose= 0.8 gr; time= 15 min)



### Adsorption isotherms of diclofenac on the pine bark biochar

Diclofenac adsorption isotherms on the pine bark biosorbent was illustrated in Figure 9. Based on the stoadied isotherms, the correlation coefficients ( $R^2$ ) for the Langmuir, Freundlich and Temkin isotherm models are  $R^2 = 0.999$ , 0.952 and 0.960. In Table 1, the Langmuir isotherm data such as  $b$  (y-intercept),  $q_{\max}$  and  $R_L$  (Langmuir equilibrium constant) was presented.



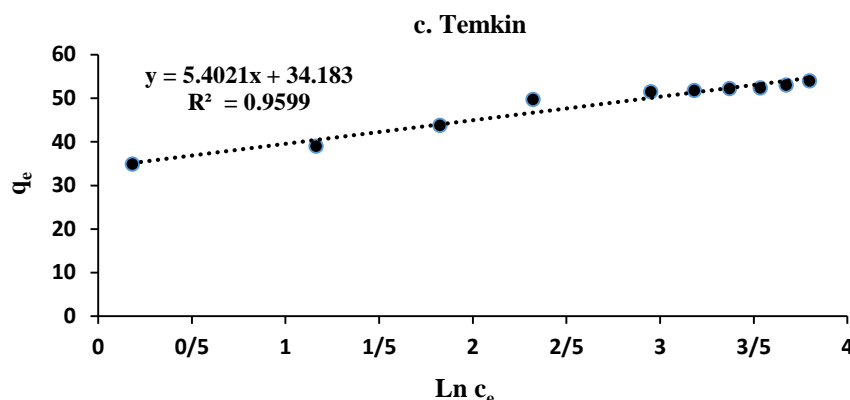


Figure 9. Diclofenac adsorption isotherms (a: Langmuir; b: Freundlich; c: Temkin)

Isotherm models					
Langmuir		Freundlich		Temkin	
<b>R<sup>2</sup></b>	<b>0.999</b>	<b>R<sup>2</sup></b>	<b>0.952</b>	<b>R<sup>2</sup></b>	<b>0.960</b>
<b>b (L/mg)</b>	<b>0.84</b>	<b>n</b>	<b>8.2</b>	<b>b</b>	<b>5.4</b>
<b>q<sub>max</sub> (mg/gr)</b>	<b>54.64</b>	<b>K<sub>F</sub></b>	<b>34.80</b>	<b>K<sub>T</sub> (L/gr)</b>	<b>561.2</b>
<b>R<sub>L</sub></b>	<b>0.02</b>	<b>[(mg/gr)/(L/mg)<sup>n</sup>]</b>			

Table 1. Diclofenac adsorption isotherm data

### The kinetic of diclofenac adsorption on the pine bark biochar

Kinetic studies for controlling the adsorption process, such as reaction speed, chemical reaction and diffusion mechanisms is essential. There are some kinetic models for investigating of an adsorption process. The most important models contain pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models. Considering to Table 2, correlation factors ( $R^2$ ) and  $q_{e-model}$  in PFO kinetic model are 0.860 and 22.97 mg/gr and in PSO kinetic models are 0.999 and 64, respectively, which adsorption capacity obtained from PSO kinetic model (64 mg/gr) was consistent with the adsorption capacity obtained from experiments (62.44 mg/gr).

Kinetic models	
<b>pseudo-first-order (PFO)</b>	<b>pseudo- second order (PSO)</b>

<b>R<sup>2</sup></b>	<b>0.860</b>	<b>R<sup>2</sup></b>	<b>0.999</b>
<b>k<sub>1</sub> (min<sup>-1</sup>)</b>	<b>0.013</b>	<b>k<sub>2</sub> × 10<sup>-3</sup> (mg/L.min)</b>	<b>0.0067</b>
<b>q<sub>e-model</sub> (mg/gr)</b>	<b>22.97</b>	<b>q<sub>e-model</sub> (mg/gr)</b>	<b>64</b>
<b>q<sub>e-test</sub> (mg/gr)</b>	<b>62.44</b>	<b>q<sub>e-test</sub> (mg/gr)</b>	<b>62.44</b>

Table 2. Diclofenac adsorption kinetics data in concentration of 50 mg/L

### Thermodynamics of diclofenac adsorption process on the biochar

The effect of temperature on the removal efficiency of diclofenac in the adsorption process was determined (Figure 8). Thermodynamic parameters including Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) were illustrated by Eqs. (3) and (4):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

Where R is the universal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>), T is the absolute temperature (K) and K<sub>L</sub> is the thermodynamic equilibrium constant, determined from  $\frac{q_e}{C_e}$ .  $\Delta S^\circ$  and  $\Delta H^\circ$  values of the adsorption process were obtained from the slope and intercept of plotting  $\ln \frac{q_e}{C_e}$  versus 1/T, respectively (Figure 10). The thermodynamic parameters were summarized in Table 4. Considering to this table,  $\Delta H^\circ$  and  $\Delta S^\circ$  values are 6.2 kJ/mol and 34.79 J/mol.K, respectively and  $\Delta G^\circ$  value is negative.

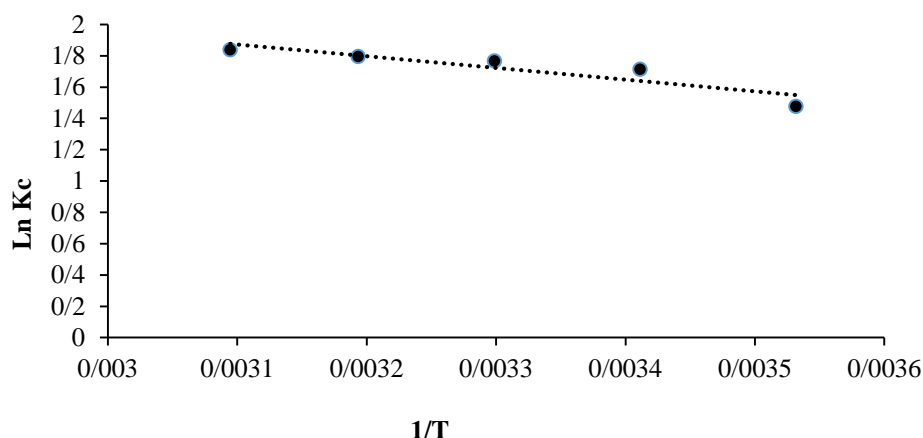


Figure 10. Thermodynamic diagram of diclofenac adsorption

)°K( Temperature	)kJ/mol( $\Delta H^\circ$	)kJ/mol( $\Delta G^\circ$	$\Delta S^\circ$ (J/mol.K)
283	6.2	- 3.40	34.79
293	-----	- 4	-----
303	-----	- 4.36	-----
313	-----	- 4.57	-----
323	-----	- 4.38	-----

Table 3. Data on the thermodynamics of diclofenac adsorption

## Discussion

In this study, the physical structure of the biosorbent including specific surface area, volume and average diameter of pores in the biochar were determined 683.33 m<sup>2</sup>/g, 0.4179 m<sup>3</sup>/g and 2.45 nm, respectively which confirms the prepared biochar is appropriate adsorbent. FTIR image shows that carboxyl, hydroxyl and amine functional groups are present in the biosorbent surface and these functional groups are effective on the adsorption efficiency increasing of diclofenac [19]. The FESEM image illustrates that the prepared biosorbent has a surface with pores in different sizes due to the separation of hydrogen and carbon groups from the biosorbent surface at a temperature of 800 °C. This indicates that the biosorbent is well activated and has appropriate pores. The difference between this absorbent and others can be due to the activation method [30]. In addition to the produced biosorbent made of pine tree is inexpensive and efficient and can be used to remove water and wastewater contaminated with diclofenac.

pH is very effective on the activity of ions in solution and functional groups at the adsorbent surface. Acid-ionization constant (pKa) in diclofenac is 4.15 and it means that diclofenac is molecular form at pH

below 4.15 and ionized form with negatively charge at pH above 4.15 [24, 30]. According to the results of this study, the  $pH_{pzc}$  of the biochar is 8.2. In this case, the adsorbent surface at pH below and above 8.2 has positive and negative electrical charge, respectively. In pH range 4.15 to 8.2, the adsorbent surface and diclofenac solution have positive and negative electrical charges, respectively. This phenomenon can be the reason of the high removal efficiency of diclofenac removal by the biochar in this area. Outside this area, the electrostatic repulsion force between diclofenac negative ions in solution and negative charges on the biosorbent surface leads to adsorption efficiency reduction [32].

In this study, with increasing the adsorbent dose, the removal efficiency of diclofenac increased and the adsorbent capacity of the biosorbent decreased. As the amount of adsorbent increases, the active site numbers of the biosorbent increases [30]. Increasing the removal efficiency with adsorbent dosage can be related to increase in the surface area and the availability of more adsorption sites [15, 29]. However, with increasing of adsorbent dose, adsorption capacity of the biosorbent decreased considerably. The decrease in the diclofenac adsorption capacity with increasing dosage of the adsorbent is essentially due to remain unsaturated sites during the adsorption process [28].

The removal efficiency of diclofenac decreased with increasing diclofenac concentration at the constant amount of the biosorbent. Due to the constant dose and active site numbers of the biochar, solute concentration increasing at a time, cause the removal efficiency reduction [15, 18]. On the other hand, with increasing the concentration of diclofenac at constant adsorbent dose, the solute molecules competition to occupy the active sites of the adsorbent increases and leads to higher adsorption capacity of the adsorbent [20, 24]. In this study, the removal efficiency of diclofenac was increased with increasing contact time. It is noted that, in the early times, the removal efficiency speed of diclofenac was very fast, so that with increasing time, the removal speed was decreased.

Adsorption isotherm models describe the relationship between the amount of the solute adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Many isotherm models such as Langmuir, Freundlich and Temkin isotherms are used to explain the equilibrium adsorption [29]. Langmuir isotherm is appropriate for single-layer adsorption on the adsorbent surface with homogeneous adsorption sites. Langmuir isotherm is defined by the below equation:

$$q_e = \frac{q_{\max} \times K_L \times C_e}{1 + K_L \times C_e} \quad (5)$$

Where  $q_{\max}$  (mg/gr) is the maximum adsorption capacity;  $C_e$  (mg/L) is the equilibrium concentration;  $q_e$  (mg/gr) is the equilibrium adsorption capacity, and  $R_L$  (L/mg) is the Langmuir equilibrium constant. The Freundlich isotherm model is an empirical equation, and the model is consistent with adsorption process on heterogeneous surfaces. The Freundlich isotherm was represented by Eq. (6):

$$q_e = K_F \times C_e^{1/n_F} \quad (6)$$

Where  $K_F$  is the Freundlich equilibrium constant [ $\text{mg/gr} \times (\text{mg/L})^{-1/n_F}$ ] and  $n_F$  is the dimensionless exponent of the Freundlich model. Another isotherm model in the adsorption system is Temkin isotherm. According to this model, the adsorption heat of all molecules in the layer decreases linearly due to adsorbent and adsorbate interaction. The equation is illustrated as follows:

$$q_e = \frac{RT}{B_T} \ln A_T + \frac{RT}{B_T} \ln C_e \quad (7)$$

Where  $C_e$  is the concentration of diclofenac in equilibrium,  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the universal gas constant,  $T$  ( $^{\circ} \text{K}$ ) is the absolute temperature,  $B_T$  ( $\text{J/mol}$ ) is the Temkin constant and  $A_T$  ( $\text{L/gr}$ ) is the equilibrium binding constant. The  $A_T$  and  $B_T$  are obtained by plotting  $q_e$  versus  $\ln C_e$ .

According to the results of diclofenac adsorption isotherm were shown in table 2, the correlation coefficient for the Langmuir isotherm ( $R^2 = 0.999$ ) is higher than the Freundlich ( $R^2 = 0.952$ ) and Temkin ( $R^2 = 0.960$ ) isotherm models. Therefore, the experimental data adsorption in this study consistent with the Langmuir model. This means that the adsorption mechanism is monolayer and adsorption is probably done by hydrogen bonding and pi-pi interactions [25]. According to Table 2,  $R_L$  value is 0.02, which indicates that the adsorption process is desirable.

The kinetic studies are useful for the identifying of the dynamic and speed of the reaction in the adsorption process [27]. The kinetic parameters are important agents to designing and modeling of the adsorption process. The evaluation of adsorption kinetic models are necessary to obtain some valuable information on the effective factors on the reaction pathways, as well as on adsorption process control mechanisms such as surface adsorption, chemical reactions and diffusion mechanisms [30]. In this study, the kinetics of the adsorption process was evaluated by PFO and PSO models. If the adsorption process due to the boundary layer diffusion, the adsorption kinetics usually follow a PFO model, so that the adsorption rate are related to the unoccupied sites numbers at the adsorbent surface. In the PSO model, a type of chemical adsorption controls the adsorption process and the occupancy rate of adsorption sites is proportional to the square of the number of unoccupied sites [24].

The liner form of the PFO and PSO kinetic models was presented by Eqs. (7) and (8):

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (8)$$

In this study, the correlation coefficients for the PFO and PSO kinetic models at the diclofenac concentration of 50 mg/L were 0.860 and 0.999, respectively. Due to the higher correlation coefficient in PSO model than PFO model, the kinetics of diclofenac adsorption follows the PSO model.

Based on the results of this study, the negative values of  $\Delta G^\circ$  confirm that the sorption process is thermodynamically feasible and spontaneous [26, 36]. In the exothermic and endothermic reactions,  $\Delta H^\circ$  values is negative and positive, respectively [37]. Due to the positive value of  $\Delta H^\circ$  in the present study, the reaction is endothermic process which confirms that with increasing temperature, the removal efficiency of diclofenac in the adsorption process increases. Additionally, the negative entropy ( $\Delta S^\circ$ ) represents the randomness decreasing at the solid/liquid interface during the diclofenac adsorption on to the modified pine bark as biochar.

## Conclusion

In this study, the biochar prepared from pine barks was used as a natural adsorbent for removal of diclofenac from aqueous solutions. The characteristics of the biochar includes specific surface= 683.33 m<sup>2</sup>/gr; total pore volume= 0.4180 cm<sup>3</sup>/gr; mean diameter= 2.45 nm and pH<sub>pzc</sub>= 8.2. At pH= 6.2, contact time= 15 min, adsorbent dose= 0.8 gr and temperature= 25°C, the removal efficiency of diclofenac was obtained 80.4%. In this study, with increasing adsorbent dose, the removal efficiency of diclofenac increased, and the adsorption capacity decreased. The experimental data in diclofenac adsorption fitted to the Langmuir isotherm (R= 0.999) with maximum adsorption capacity of 54.64 mg/gr. The PSO kinetic model was better than the PFO kinetic model to assessing of the diclofenac adsorption kinetics. Recovery study of the pine bark biochar is so important that this study was not performed. Therefore, this matter should be considered by investigators. According to the results, diclofenac as a drug compound could be removed from aqueous solutions by the biochar prepared from the pine bark and can be used as an efficient and inexpensive biosorbent for the purifying of wastewater containing diclofenac in hospitals and other health care facilities.

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## Conflict of interest

The authors declare that they have no conflict of interests.



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