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ORIGINAL ARTICLE

Adsorption of diclofenac from aqueous solution using *Cyclamen persicum* tubers based activated carbon (CTAC)

Shehdeh Jodeh [a,*], Fatima Abdelwahab [a], Nidal Jaradat [b], Ismail Warad [a], Wade Jodeh [c]

[a] *Department of Chemistry, An-Najah National University, P.O. Box 7, Nablus, Palestine*
[b] *Department of Pharmacy, An-Najah National University, P.O. Box 7, Nablus, Palestine*
[c] *Department of Medicine, An-Najah National University, P.O. Box 7, Nablus, Palestine*

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KEYWORDS

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Abstract This study aims to use the tissues of *Cyclamen persicum* tubers to prepare activated carbon (CTAC) by different methods then to set up a thermodynamic study of the pharmaceutical diclofenac sodium (DCF) adsorption from aqueous solution onto this activated carbon. Optimum percent of DCF removal was 72% when CTAC dosage was 0.25 g and DCF concentration 50 mg/L. Percentage removal of DCF increases when the concentration of DCF increases as the maximum percentage removal reached 81% when DCF concentration was 70 mg/L and 0.7 g CTAC and pH ranging from 6 to 2.

Freundlich model describes efficiently adsorption isotherm of DCF onto CTAC with n equal to 1.398 whose value indicates a favorable adsorption. This finding validates the assumption of multilayer physical adsorption process of DCF. The results showed that DCF was physically adsorbed onto CTAC, as confirmed by the values of $\Delta H°$ minor than 40 kJ/mol. As $\Delta G°$ had negative charge, the adsorption process is exothermic, and the adsorption process of the DCF onto CTAC is spontaneous, depending on temperature.

1. Introduction

Activated carbon (AC) is defined as a solid, porous, black, that is reacted with gases during carbonization which helps in increasing porosity (Calo and Hall, 2004). AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface. The main feature common to all AC is a basic structure referred to that of graphite: other definition is that AC is an amorphous solid with a large internal surface area and pore volume (de Yuso et al., 2014). For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and

* Corresponding author. Tel.: +972 92342735; fax: +972 92345982.
E-mail address: sjodeh@najah.edu (S. Jodeh).

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metal ions of environmental or economic concern from air, gases, potable water and wastewater (Ding et al., 2014).

Production of activated carbon involves the two main steps, which are pyrolysis where the carbonaceous source materials are heated, decomposed and converted to carbonized material in the absence of air (Yusof and Ismail, 2012). Then, the process is continued by activation step which will increase the surface area of the carbonized material. Activated carbon efficiency for removing a given substance depends on both its surface chemistry and its adsorption capacity (Lo et al., 2012). The AC adsorption capacity is usually attributed to its internal pore volume that may be distributed throughout the solid as pores ranging in width from micro pores to macropores. Adsorption process depends on the pore size and the type of activation of carbon. When the pollutant size equals the pore size of activated carbon the adsorption efficiency increased (Huang et al., 2014).

Activated carbon can be used for removing heavy metals from wastewater by surface complexation between metals and the acidic functional group of AC (Chen and Lin, 2001). The removal efficiency depends on different factors like solution concentration, temperature, dosage concentration, surface area and other factors including porosity (Kairvelu et al., 2001).

The most frequently used isotherms in describing the nonlinear equilibrium are: Langmuir isotherm, Freundlich isotherm and Brunauer Emmett and Teller (BET) isotherm (Liu et al., 2010). Diclofenac sodium 2-(2-2,6-dichlorophenylamino)phenyl)acetate is a white or slightly yellowish, crystalline powder, which has low solubility in water, and soluble in alcohol. It melts at about 280 °C, with decomposition. It is a nonsteroidal anti-inflammatory drug (NSAID) which is widely used in human medical care as analgesic, antipyretic, anti arthritic and anti rheumatic compound (Ku et al., 1985).

Carbamazepine and diclofenac removal was studied in waste water treatment plants and occurrence in water bodies leading to that they do not cause acute environmental toxicity but their chronic effects needs attention (Karaman et al., 2012).

Karaman et al. studied removal of diclofenac from waste water using clay-micelle complex which is positively charged, has large surface area and includes large hydrophobic domains so it was an efficient method for adsorption (Wolf et al., 2002).

In this study the tissues of *Cyclamen persicum* were used to prepare activated carbon by different methods then to set up a thermodynamic and kinetic study of diclofenac sodium (DCF) adsorption from aqueous solution onto this activated carbon. Another objective is to compare this activated carbon with Eucarbon the one sold in pharmacies in terms of adsorption, thermodynamics and other physical properties.

2. Materials and methods

2.1. Materials

The residual *C. persicum* tubers tissues remained after extraction of saponin glycosides and were used as the precursor for the preparation of activated carbon by the physical activation method. This powder was washed many times with distilled water, dried at 110 °C in oven and then sieved through mesh # 18 to #30 to get rid of the remaining pulp and skin. The saponin glycosides were extracted using the method by Sharma and Palliwal and used for other studies (Sharma and Palliwal, 2013).

2.2. Adsorbate and chemicals

Diclofenac sodium (DCF) (molecular weight = 318.1 g/mol; chemical formula = $C_{14}H_{10}C_{l2}NNaO_2$; pK_a = 4.2) was purchased from Jerusalem pharmaceutical company in Ramallah – Palestine. All other chemicals used such as hydrochloric acid, sodium thiosulfate, iodine and sodium hydroxide, phosphoric acid, zinc chloride and potassium hydroxide were of analytical grades.

2.3. Activation process

2.3.1. Physical activation

In this process, the char produced from carbonization step is activated using N_2 gas as carbon activating agent. Oxidation reaction takes place between the carbon atom and the gas, which is increasing the number of pores in the carbonaceous structure. This process is environmentally friendly as no chemical polluting agents are engaged in the process; still it has several drawbacks represented in the low carbon yield and high energy consumption. Longer carbonization/activation time and higher temperature are required to produce activated carbon with the same characteristics obtained in the chemical activation. An amount of 30 g of dried cyclamen is placed in a flat crucible and inserted in the center of calibrated furnace. The carbonization/activation temperature was 550 °C with a heating rate of 20 °C/min. The holding time was 70 min with 0.2 L/min flow rate of nitrogen.

2.3.2. Chemical activation

Chemical activation produces highly porous activated carbon by impregnation of the precursor with the following chemical activating agents; potassium hydroxide (KOH), phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$). These chemical agents have dehydrating properties that influence the pyrolytic decomposition and prevent the formation of tars and volatile organic compounds during activation at high temperature producing high activated carbon.

2.4. Adsorption and thermodynamic of diclofenac sodium onto (CTAC) experiment

2.4.1. Diclofenac sodium standard solution preparation

Diclofenac sodium stock solution (1000 mg/L) was prepared by dissolving 1.02 g in 100 ml distilled water then diluted to 1.00 L with distilled water. This intermediate solution was used to prepare different calibration standard solutions with concentrations in the range of 0.0–50 mg/L diclofenac sodium. Calibration curve was constructed by plotting value of net absorbance vs. concentration of standard (DCF) solutions. For comparison purposes, adsorption behaviors of activated carbons prepared here and Eucarbon drug were studied.

The initial and final concentrations of DCF were measured. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by Eq. (1).

$$q_e = (C_0 - C_e)V/W \quad (1)$$

Table 1 Surface areas of different AC according to iodine number test.

Sample	Surface area (mg/g)
$ZnCl_2$	606.78
H_3PO_4	423.3
KOH	493.85
Physical activation	522.07
Eucarbon	592.62

The removal percentage of diclofenac sodium (DCF) was calculated using Eq. (2).

$$PR(\%) = (C_0 - C_e)100/C_0 \quad (2)$$

where V is the volume of the solution (L) and W is the weight of activated carbon (mg), the C_0 and C_e are initial and equilibrium DCF concentration respectively.

3. Results and discussion

3.1. Iodine number surface area

As shown in Table 1 the best surface area of the produced activated carbon samples following the iodine number test was obtained using zinc chloride as chemical activating agent, which produced 606.78 mg/g followed by physical activation process that gave 522.07 mg/g as surface area. For comparison Eucarbon drug had 592.62 mg/ g using this iodine number test.

Table 2 Percentage yield of prepared activated carbon.

CTAC sample	% Yield
$ZnCl_2$	45
H_3PO_4	53
KOH	40
Physically activated	26.50

For comparison the BET surface area for zinc chloride activated sample was 880.936 m^2/g and for physically activated sample was 799.028 m^2/g, this result indicated that iodine value was a good method for comparing the prepared samples of CTAC (Table. 1).

3.2. Scanning electron microscopy (SEM) of AC

In Fig. 1 differential scanning electron microscopy for activated carbon samples is shown to indicate the effect of each method in activation process.

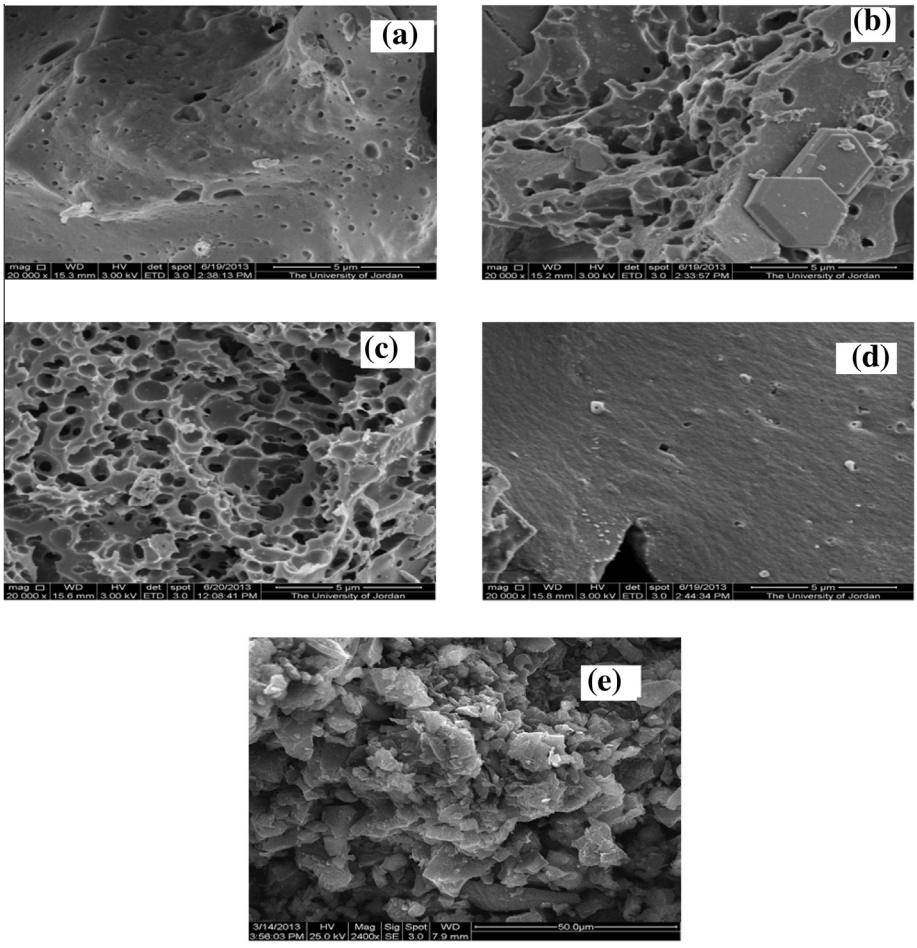

Figure 1 SEM micrographs of several types of the produced activated carbon: (a) ($ZnCl_2$/CTAC), (b) (H_3PO_4/CTAC), (c) (KOH/CTAC), (d) (physically CTAC), (e) (Eucarbon).

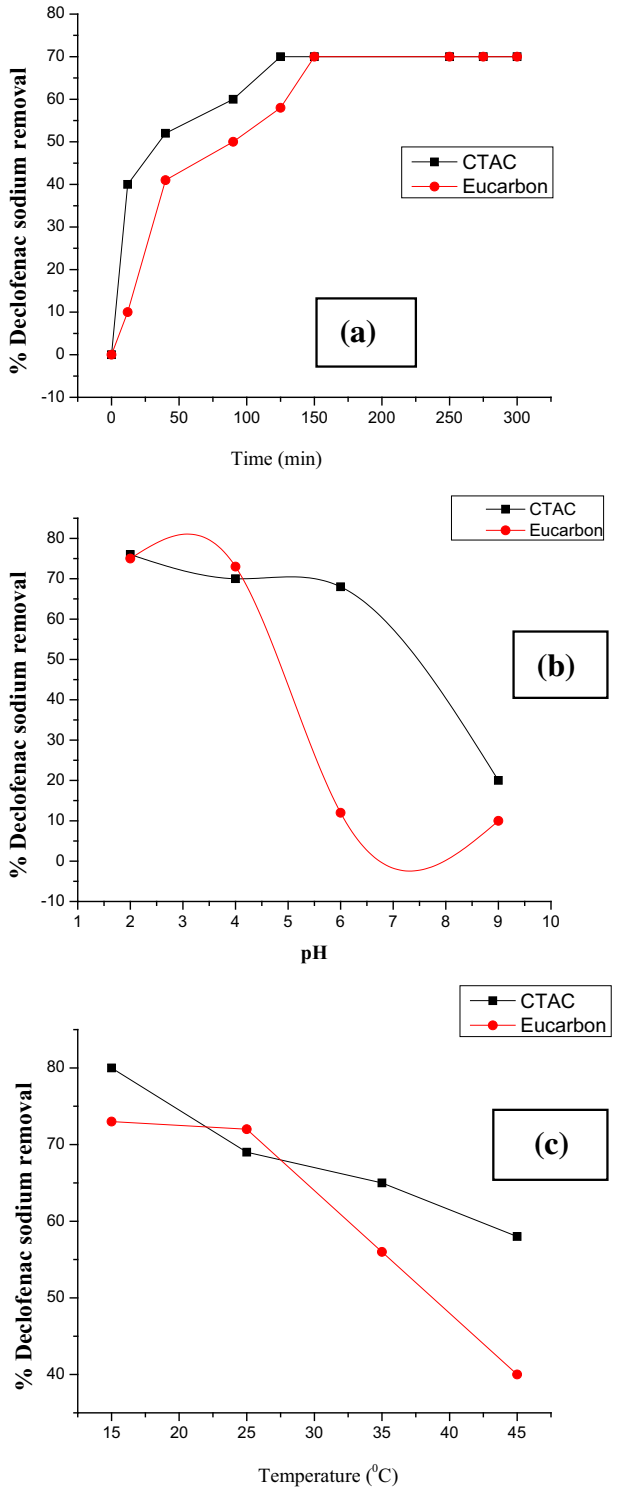

Figure 2 Effect of contact time (a), pH (b) and temperature (c) on diclofenac sodium removal by CTAC and Eucarbon at initial conc. 50 mg/L.

The external surface showed the best porous structure in chemically activated carbon by potassium hydroxide (KOH) reagent as this surface was rich in pores, whereas the surface of the carbon activated physically had no porous structure except for some occasional cracks. The porous structure of the activated carbon prepared by zinc chloride ($ZnCL_2$) and

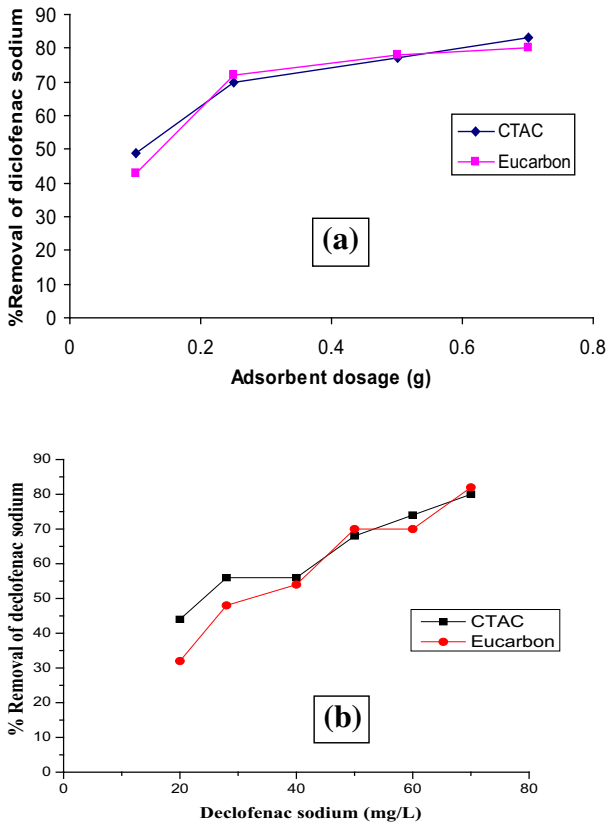

Figure 3 Effect of adsorbent dosage (a) and diclofenac sodium concentration (b) on diclofenac sodium removal by at pH: 4, temperature: 25 °C and contact time: 120 min).

phosphoric acid (H_3PO_4) had a lesser extent of porous structure compared with potassium hydroxide; this can be explained as the evaporation of KOH during the carbonization process would leave empty spaces on the carbon surface more than other chemical reagents. Eucarbon sample showed a multilayered structure that forms sites for adsorption process.

3.3. Percentage yield of the prepared CTAC samples

The %Yield of the prepared activated carbon from cyclamen tubers is summarized in Table 2.

3.4. Adsorption of diclofenac sodium on AC from C. persicum tubers

UV–Vis spectrophotometry was chosen and preferred over many other methods. That is due to its low pollution effects, simplicity, speed and suitability to indicate the kinetic change of the diclofenac sodium concentration. A typical calibration curve for diclofenac sodium at 276 nm was made with a good correlation of fitting of $R = 0.995$.

3.5. Effect of contact time

The effect of contact time on removal percentage of diclofenac sodium is shown in Fig. 2a.

The adsorbed amount of DCF onto CTAC and Eucarbon increases with the increase of contact time, as shown in Fig. 2a, and the DCF adsorption reached equilibrium in about 120 min for CTAC and 150 min for Eucarbon. Adsorption capacity for DCF showed a rapid increase in adsorption amount during the first 15 min, while Eucarbon® showed this increase during 30 min. This fast adsorption capacity at the initial stage by CTAC indicated higher driving force that made fast transfer of DCF to the surface of CTAC particles compared with Eucarbon, this result indicated a significant effectiveness in using CTAC as an adsorbent rather than Eucarbon. From Fig. 2a the% removal of DCF using CTAC was 72% while using Eucarbon it was 70%.

3.6. Effect of adsorbent dosage

The effect of CTAC and Eucarbon dosage on diclofenac sodium removal was studied using 0.1–0.7 g adsorbent dosage at an adsorption time of 120 min to reach equilibrium. The results are summarized in Fig. 3a. The percent of DCF removal increased by increasing dosage for each type of adsorbents.

Adsorption increases up to 82% with an adsorbent dosage of 0.7 g/50 mL of CTAC and 76% with Eucarbon, because increasing adsorbent dosage at fixed DCF concentration provided more available adsorption sites and thus increased the extent of DCF removal.

3.7. Effect of pH

The variation of adsorption onto CTAC and Eucarbon was investigated in the pH range 2–12 using sulfuric acid and sodium hydroxide to control pH. The effect of pH on diclofenac sodium removal was studied, using 0.25 g of CTAC and Eucarbon at an adsorption time of 150 min to reach equilibrium, Fig. 2b summarizes these results.

For each adsorbent, the optimal pH for the adsorption of diclofenac sodium was 2, this result indicated a pH less than the pK_a of this pharmaceutical (pK_a = 4.20), as DCF is present in its neutral form, and its solubility in water decreases. So as pH decreases the 'van der Waal' interaction between DCF and the adsorbent surface increased by physical adsorption process.

3.8. Effect of temperature

The effect of temperature on adsorption onto CTAC and Eucarbon was investigated in the range of 15–45 °C. The results are shown in Fig. 2c.

In this figure, diclofenac sodium adsorption decreased with increasing temperature. The highest percentage of adsorption performance was at 15 °C which reached 83.58% by CTAC and 74% by Eucarbon.

Increasing temperature will cause an increase in solubility of water and this will decrease the adsorption process and decrease the attraction forces between DCF and the pharmaceuticals.

3.9. Effect of diclofenac sodium concentration

In Fig. 3b the effect of the initial concentration of diclofenac sodium on the% removal at equilibrium is shown. This figure shows that the increase of concentration increases the percentage of DCF removal, by CTAC and Eucarbon.

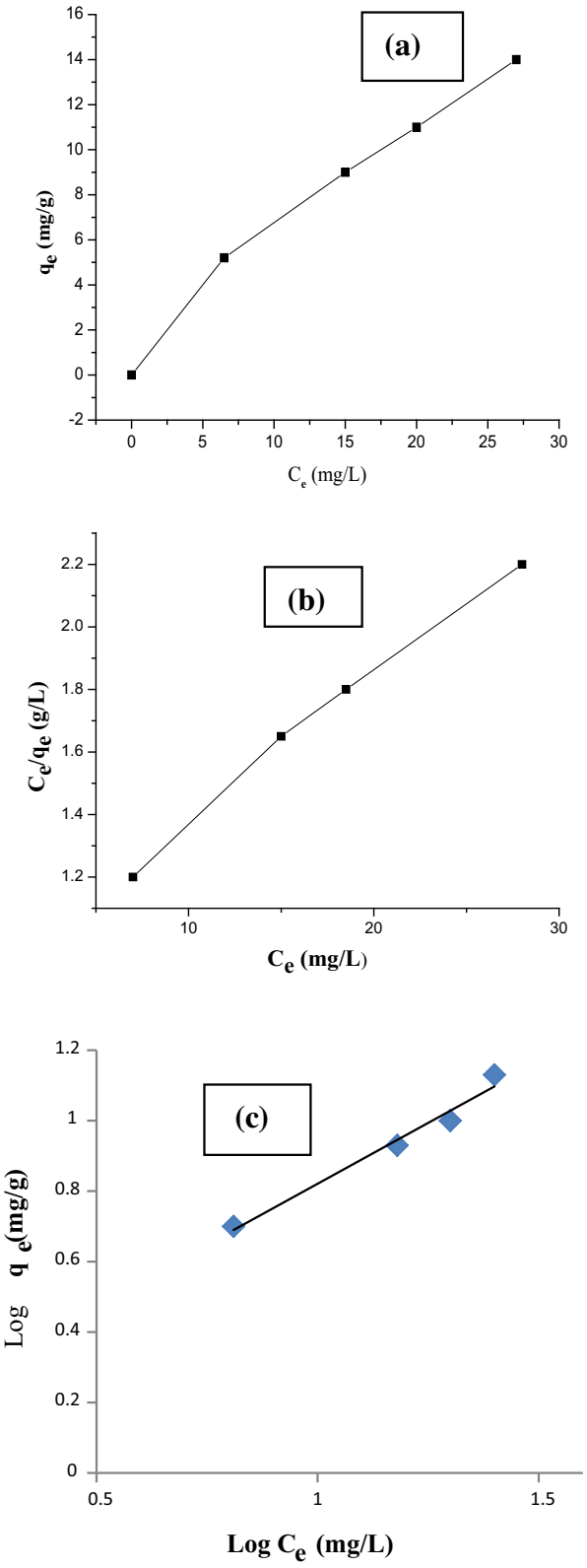

Figure 4 Equilibrium adsorption isotherm (a) Langmuir plot (b) and Freundlich plot (c) of DCF onto CTAC at (temperature: 25 °C, initial pH 4 and solid/liquid ratio 0.25 g/50 mL).

Table 3 Isotherms constants for DCF adsorption onto CTAC.

Langmuir isotherm			Freundlich isotherm		
R^2	K_L (L/mg)	Q_{max} (mg/g)	R^2	K_F ((mg/g)(L/mg)$^{1/n}$)	N
0.952	0.0467	22.22	0.9942	1.211	1.398

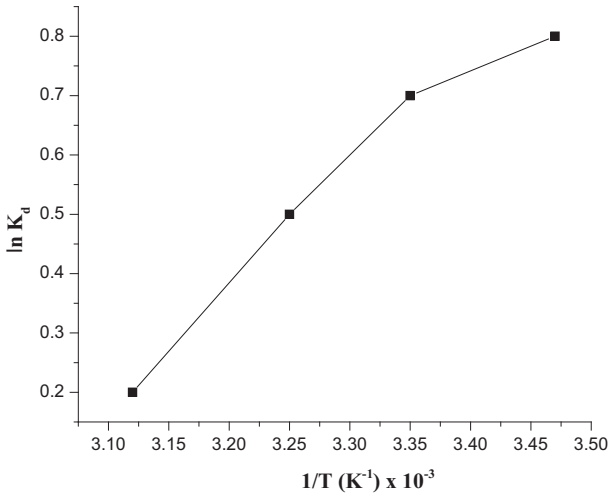

Figure 5 Thermodynamic adsorption plot of ln K_d vs. $1/T$ for 50 mg/L DCF concentration.

As diclofenac sodium concentration increases from 20mg/L to 70 mg/L, the percentage removal was increased from 42% to 81% for CTAC and from 30% to 77% for Eucarbon.

3.10. Adsorption isotherms

In this study, Langmuir and Freundlich isotherm models were used to describe the adsorption isotherm and to study the relationship between the amounts of diclofenac sodium adsorbed (q_e) and its equilibrium concentration in solution at 25 °C as shown in Fig. 4.

The adsorption isotherm parameters, which were calculated from the slope and intercept of the linear plots using the linear form of the Langmuir and Freundlich equations, together with the determination coefficient R^2 values are given in Table 3.

It is clear from the R^2 values that the Freundlich isotherm is fitted to the experimental data more than the Langmuir isotherm model. The Freundlich isotherm shows that adsorption will increase with increasing diclofenac sodium concentration and this adsorption occurred in a multilayered system rather one layered.

Table 4 Thermodynamics parameters for DCF adsorption onto CTAC at different temperatures with initial concentration of DCF of 50 mg/L.

T (K)	K_d	$\Delta H°$ (kJ/mol)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (j/mole k)
288	3.56	−17.45	−3.04	−50.08
298	2.82		−2.55	
308	2.16		−1.97	
318	1.8		−1.55	

A favorable adsorption is when Freundlich constant (n) is between 1 and 10. When n is higher than that range it implies stronger interaction between the adsorbent and the adsorbate. From Table 3, it can be seen that the (n) value was between 1 and 10 showing favorable adsorption of diclofenac sodium onto the activated carbon prepared from cyclamen tubers.

This finding validates that the assumption of multilayer physical adsorption between the adsorbate (DCF) and the adsorbent surface (CTAC) was achieved.

3.11. Thermodynamic of DCF adsorption onto CTAC

Thermodynamics parameters like ΔG^0, ΔH^0 and ΔS^0 can be calculated from the following equations: (Zhang et al., 2008) (Eq. (3)).

$$\ln K_d = -\Delta H^0_{adsb}/RT + \Delta S^0_{ads}/R \quad (3)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature, (K_d) is the distribution coefficient of the system which can be calculated as: $K_d = C_i/C_e$.

where C_i (mg) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration of DCF.

The Gibbs free energy ($\Delta G°_{ads}$) can be calculated from (Önal et al., 2007) (Eq. (4)).

$$\Delta G^{\circ}_{ads} = -RT \ln K_d \quad (4)$$

The values of $\Delta H°$ and $\Delta S°$ can be found from slopes and intercepts of plotting ln K_d vs. ($1/T$) in Fig. 5. The obtained thermodynamic values are given in Table 4.

When the temperature increased the amount of pharmaceuticals adsorbed decreased and this can be explained due to increasing the solubility in water and the energy exchanged. Also, the force of attraction decreased which caused an increase in the agitation of the dissolved chemical species, reducing its physical interaction with the adsorbent. Also, due to the exothermic process which found from the calculations implied a decrease in the adsorption due to the increase in temperature which caused heat released to the system, and the equilibrium shifted to the opposite direction of the reaction. From the value of $\Delta H°$ which was less than 40 kJ/mol, indicating a physisorption process. The change in free energy indicates spontaneous process and this depends on temperature.

4. Conclusion

Activated carbon produced from *C. persicum* tubers gave a good percentage of yield reaching 45% with highest adsorption capacity when activated by zinc chloride. Most of the studies like effect of contact time, concentration, pH and temperature gave good results which agreed with recent and previous studies. Finally Freundlich equilibrium model describes the adsorption isotherm of DCF onto CTAC more efficiently than Langmuir model and the values of thermodynamic

parameters indicated that the adsorption process was spontaneous and exothermic one.

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