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# Novel biosorbent (Canola Wastes) and Ciprofloxacin antibiotics removal ability at different temperatures

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**Abstract :** In this study, a novel biosorbent (Canola Wastes) was used as an effective adsorbent for ciprofloxacin (CIP) removal from wastewater. The adsorption performance, mechanism and effect of CIP ion on sorption were investigated. Adsorption capacity reached a maximum (45.31 mg/g) when the pH value was 7. The intraparticle diffusion, pseudo-first order and peseudo-second order kinetic models were examined to evaluate the kinetic data and the rate constants were calculated. Thermodynamic parameters such as free energy, enthalpy and entropy of dye adsorption were obtained. Adsorption kinetic of CIP followed pseudo-second order kinetics. The thermodynamic studies showed that the antibiotic adsorption onto Canola biomass is spontaneous, endothermic and physical reaction. The result indicated that Canola wastes could be used as a noval natural biosorbent for the removal of antibiotics.

**Keywords :** Canola Wastes, Ciprfloxacin, Kinetics, Thermodynamics, Antibiotics.

## Introduction:

Industrialization in the modern world has brought about the development of new products, but has likewise generated novel contaminants, which could profoundly harm our environment (1-4). The crisis of freshwater in many developing countries has been further aggravated by pollutants from chemical and biological species, which have serious effects on human health (5-6). Pharmaceutical antibiotics, one of the most heavily used classes of drugs in medical therapy and the farming industry, have frequently been detected in soil, surface water, ground water, and drinking water (7-9). Most antibiotics cannot be fully absorbed and metabolized by humans and animals (10-11).Ciprofloxacin (CIP), a synthetic antibiotic, is a typical kind of fluoroquinolone (FQ) (12). It is utilized for the inhibition of some diseases for humans and animals. In pharmaceutical wastewater, the concentrations of CIP are as high as 28–31 mg/L (13).

Various technologies and methods have been reported for antibiotics removal, including advanced oxidation, adsorption, photo degradation, and biodegradation. Compared to other technologies, the adsorption process promises convenience, ease of operation, and simple design, and has been used for antibiotics removal (14-16).

It is now recognized that adsorption using low-cost adsorbents has been proved to be an effective and economic method to treateffluents, offering advantages over conventional process such as simplicity of design, low cost, availability and ability to treat dyes in more concentrated form, especially from the environmental point of view (17-19). However, low-cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dosage and minimize disposal problems (20-21). An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little processing (22-24). Agricultural waste biosorbents generally used in biosorption studies are also inexhaustible, low-cost and non-hazardous materials, which are specifically selective for antibiotics and easily disposed by incineration (25, 26).

One of these low-cost sorbents particularly suited to biosorption is Canola straw, a by-product of the oil industry, which exhibits a large capacity to bind pollutant (27). This material is very cheap and is mainly used as animal feed. There are some reports of antibiotics biosorption by Canola wastes, but little attention has been paid to the investigation of temperature dependence of biosorption process and evaluating equilibrium, kinetic and thermodynamic parameters of the system, which are important in the design of treatment systems (28-30). This paper presents the study of biosorption characteristics of dried Canola wastes for removing CIP from aqueous solutions using batch adsorption studies. The effects of various factors such as contact time, temperature and initial CIP concentration on the removal efficiency of CIP onto Canola biomass were also studied. The kinetic and thermodynamics data were analyzed so that we can understand the adsorption mechanism and different models were applied to fit the experimental data.

## Materials and Methods

Ciprofloxacin (CIP) antibiotics, ($C_{17}H_{18}FN_3O_3{\cdot}HCl$, purity >98%) with a molecular weight of 696.6 g/mol was purchased from Sigma-Aldrich and used without further purification, the molecular structure of Ciprofloxacin is given in Figure 1.

Canola wastes were obtained from farm lands in Rasht city. These shells were washed with deionized water and dried in hot air oven at 120 $^0$C for 3 hours and then grounded into fine particles and resultant biomass was subsequently used in thesorption experiments (31).

### Removal experiments

All the adsorption experiments were carried out in 250 ml Erlenmeyer flasks with 3.5 g biomass, and 100 mL CIP solution was added. pH value was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl. The mixtures were shaken at 180 rpm at different temperatures for 90 min. Adsorption experiments were carried out by batch method at room temperature. The time-dependent behavior of antibiotic adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 10-180 min. The concentration of CIP was kept at 10 to 200 mg/L, while the dose of canola biomass was 3.5 g/L. At the end of each adsorption experiment, the solution and solid phase were separated by centrifugation at 3600 rpm for 10 min. The residual dye concentration in the supernatant part was analyzed using a UV–Vis spectrophotometer at the maximum absorption wavelength of 275 nm. The adsorption capacity of CIP on adsorbent was calculated using the following equation (32-34):

$$q_e=\frac{\left(Co-Ce\right)\times v}{W}$$

Where $C_0$ and $C_e$ are the CIP concentrations in mg/L initially and at a given time t, respectively, V is the volume of CIP solution in L, and W is the weight of sorbent in g.

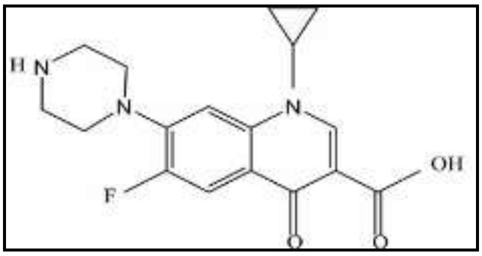

**Fig.1. the structure of Ciprofloxacin**

## Results and Discussion

### Adsorption thermodynamics

The thermodynamics for CIP ion removal by sesame was investigated in temperature range of 273-318 K, and the influence of temperature on the adsorption capacity is shown in Fig. 2. It can be found that there is an increase in the adsorption capacity of sesame with the temperature increase. Thermodynamic parameters such as change in Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were determined using the following equation (35-37):

$$K = \frac{q_e}{C_e}$$

$$\Delta G^0 = -RT \ Ln \ K$$

$$Ln \ K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Table 1 summarizes the thermodynamic parameters associated the adsorption process. Values of $\Delta G^0$ were calculated from the values of adsorption equilibrium constant (K) using above thermodynamic equations. The negative values of $\Delta G^0$ at the four temperatures show that the adsorption process is spontaneous and the degree of spontaneity increases with increasing the temperature.

The values of $\Delta H^0$ and $\Delta S^0$ are calculated from the slope and the intercept of the linear plot of Ln K vs. 1/T (Fig. 3). The overall adsorption process seems to be endothermic ($\Delta H^0$= 8.412 KJ/mol). This result also supports the suggestion that the adsorption capacity of increases with increasing temperature. Table 1 also shows that the $\Delta S^0$ value is positive (entropy increases as a result of adsorption). A positive $\Delta S^0$ value reflects the affinity of the adsorbent to the CIP ions, as a result of redistribution of energy between the adsorbate and adsorbent (38). Before adsorption occurs, the CIP ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free CIP ions to ions interacting with the adsorbent will; be higher in the adsorbed state (39-40).

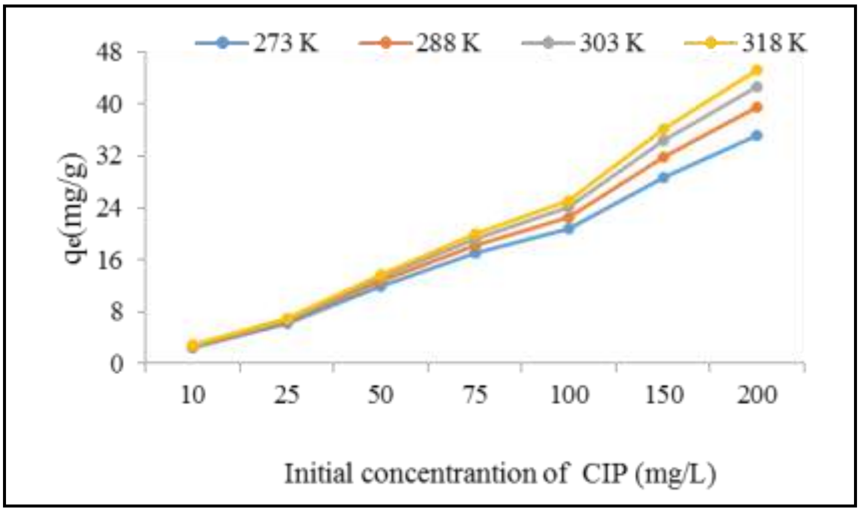

**Fig 2. Effect of temperature on adsorption capacity at initial concentration of CIP**

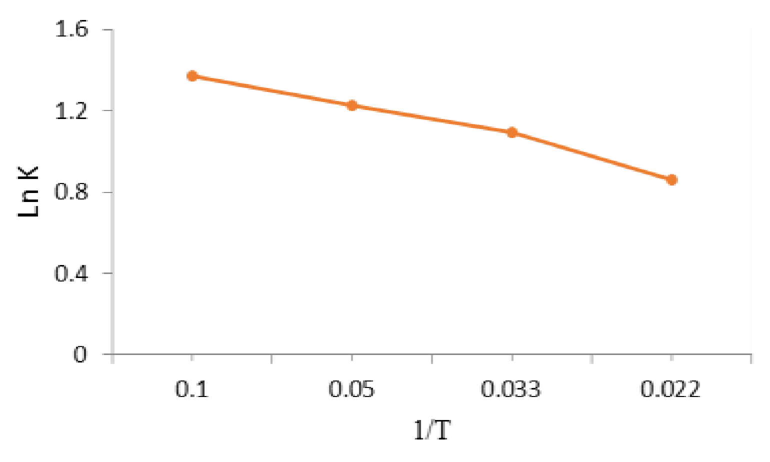

**Figure 3. Plot of Ln K vs. 1/T for CIP ion removal by Canola**

**Table 1. Thermodynamic parameters for CIP ion adsorption by Canola biomass**

| Temp (K) | $\Delta G^0$ (KJ/mol) | $\Delta H^0$ (KJ/mol) | $\Delta S^0$ (KJ/mol) |
|---|---|---|---|
| 273 | -2.47 | 4.71 | 0.212 |
| 288 | -2.96 | | |
| 303 | -3.25 | | |
| 318 | -3.78 | | |

## Adsorption Kinetics

In the removal of antibiotics from wastewater, it is important for design purposes to study the adsorption mechanism and potential rate controlling steps which control the adsorption rate (41). In order to find the contribution of rate controlling steps such as external mass transfer, intraparticle diffusion, and adsorption process and also, mass transfer and kinetic models have been used to test the experimental data.

In order to investigate the adsorption mechanism, characteristic constants of adsorption were determined using intraparticle diffusion, pseudo-first order and pseudo-second order kinetics. The adsorption process required a multi-step involving the transport of solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, rate-determining step. The intraparticle diffusion model is explored using the following equation (42-43):

$$q = K_t^{1/2} + C$$

Where $q_t$, $K_t$ and C are amount of CIP adsorbed (mg/g) at time t (min), the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and the intercept, respectively. When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first-order rate. The pseudo-first-order rate expression of Lagergren based on the sorption capacity of adsorbent is generally expressed as follows (44-46):

$$\mathrm{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2}.303\ t$$

Where $q_e$ and $K_1$ are the amount of CIP adsorbed at equilibrium (mg/g) and the equilibrium rate constant of pseudo-first order kinetics (1/min), respectively.

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It has the following advantage: the adsorption capacity, the pseudo-second-order rate constant, and the initial adsorption rate can be determined from the equation without knowing any parameters beforehand. A linear form of pseudo-second order model for the CIP adsorption onto Canola biomass was as follows (47-48):

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$$

Where $K_2$ is the equilibrium rate constant of pseudo-second order (g/mg min).

To understand the applicability of the intraparticle diffusion, pseudo-first-order and pseudo-second-order models for the CIP adsorption onto Canola biomass, linear plots of qt against $t^{1/2}$, $\log(q_e-q_t)$ versus contact time (t) and $t/q_t$ versus contact time (t) are ploted and shown in Figs. 4–6, respectively. The values of $K_1$, C, $K_2$, $R^2$ and the calculated q are shown in Table 2. The linearity of the plots ($R^2$) demonstrates that intraparticle diffusion and pseudo-first order kinetic models do not play a significant role in the uptake of the dye by biomass (Table 2). The plot of qt against $t^{1/2}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process (Fig. 4). The linear fit between the $t/q_t$ versus contact time (t) and calculated correlation coefficients ($R^2$) for pseudo-second order kinetics model show that the CIP antibiotics removal kinetics can be approximated as pseudo-second order kinetics (Table 2). Inaddition, the experimental qe ($q_e$ exp) values agree with the calculated ones ($q_e$ Cal.), obtained from the linear plots of pseudo-second order kinetics. Balarak et al, (44) studied the adsorption kinetics and isotherms of antibiotics by using different adsorbent such as Azolla and Carbon nanotubes and results of their study showed that adsorption using this biosorbent complies with pseudo-second-order kinetics (49-51).

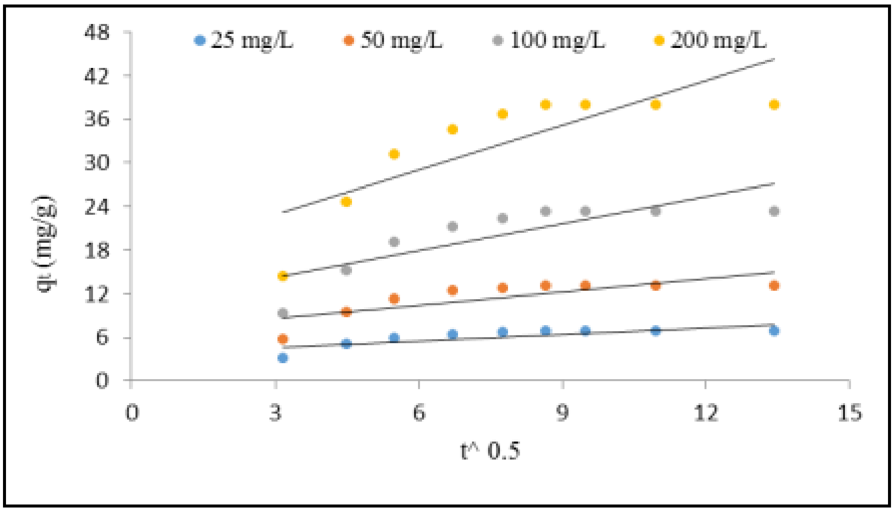

**Fig.4. Intraparticle diffusion kinetics model of CIP adsorption at different concentrations**

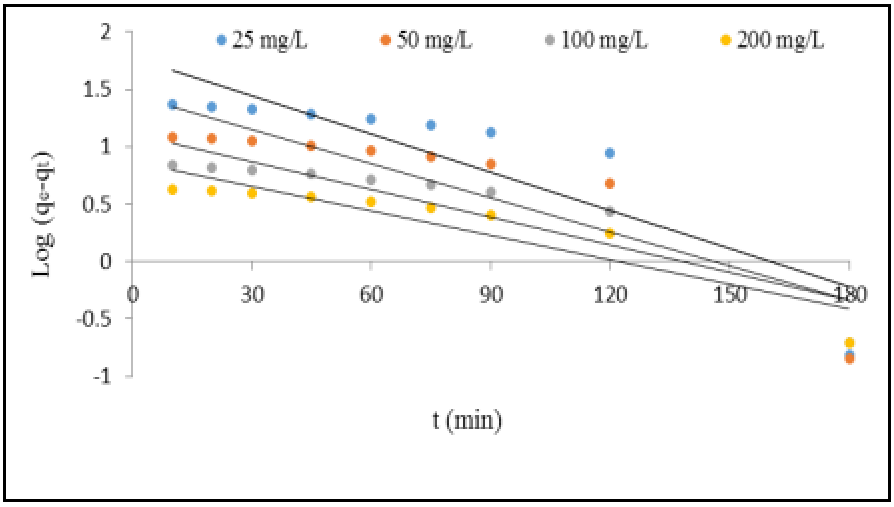

**Fig.5. Pseudo-first order kinetics of CIP adsorption onto Canola at different Concentrations**

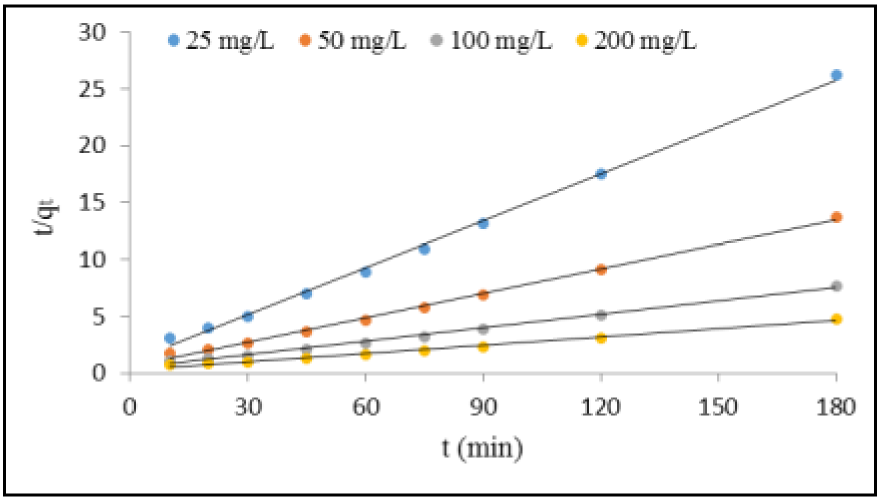

**Fig.6. Pseudo-second order kinetics of CIP adsorption onto Canola at different Concentrations**

## Conclusion:

The effective removal of antibiotics from aqueous wastewaters is among the most important issues for many industrialized countries. Removal of Ciprofloxacin antibiotics from aqueous solutions was studied using Canola wastes. The operating variables studied were initial CIP concentration of solution, temperature and contact time. The high efficiency for CIP adsorption and equilibrium can be achieved in 90 min. In order to investigate the efficiency of CIP adsorption on Canola biomass, intraparticle diffusion, pseudo-first-order and pseudo-second-order kinetic models were studied. It was observed that the pseudo-second-order kinetic model fits better than other kinetic model with good correlation coefficient.

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