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# Study of the Adsorption Mechanisms of Cephalexin on to Azolla Filiculoides

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**ABSTRACT**

*This study is focused on the application of Azolla Filiculoides (AF) as adsorbents for the removal of the cephalexin (CFX) antibiotic from aqueous solution. Several adsorption parameters including the adsorbent dosage, the initial CFX concentration, contact time and temperature were studied. The kinetic data revealed that the equilibrium time for CFX adsorption was achieved within 75 min. Several kinetic models, i.e., pseudo-first order, pseudo-second order, Weber Morris intraparticle diffusion, were applied, finding that the pseudo-second order model was the most suitable for the fitting of the experimental kinetic data. Thermodynamic parameters such as Gibb's free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were calculated. The negative values of $\Delta H^0$ and $\Delta G^0$ indicates that the CFX adsorption process is endothermic and spontaneous in nature. The study showed that AF can be used as a more efficient adsorbent for the adsorption of CFX From water solution.*

**Keywords:** Adsorption, Cephalexin, Azolla Filiculoides, Kinetics, Thermodynamic

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## INTRODUCTION

Environmental problems, including water, air and soil pollution and climate change, have attracted more global attention in the 21st century[1, 2]. Drugs are synthetic or natural substance that provides significant advantages to society[3, 4]. The occurrence of pharmaceuticals and their metabolites and transformation products in the environment is becoming a matter of concern because these compounds, which may have advers effects on living organisms, are extensively and increasingly used in human and veterinary medicine and are released continuously into the environment [5-7]. The entrance of drugs into the environment occur through various waste streams such as households, hospitals, and pharmaceutical companies, constitutes an emerging environmental issue that needs to be effectively addressed[8, 9]. However, conventional wastewater treatment plants (WWTPs) were designed without consideration of antibiotic removal[10, 11]. Thus these chemicals are only partially eliminated in WWTPs, and residual amounts can therefore reach the aquatic environment[12]. Numerous methods are being used to remove antibiotics: biological treatment, chlorination, advanced oxidation technology, electrochemical treatment, coagulation–flocculation, the membrane process, ion exchange, and the ultrasonic cavitation effect method[13-15].

However, these treatment processes present a number of drawbacks in terms of low efficiency, usually produce large amounts of sludge and cannot effectively be used to treat a wide Among the numerous techniques of antibiotic removal, the adsorption technique has been found to be superior to other techniques as it can be used to remove antibiotics from wastewater, due to its simple design, easy operation, and relatively simple regeneration[16-18]. Various adsorbents also have been developed for the removal of organic pollutants[19-22].

The numbers of non-conventional, low-cost agricultural materials are used as adsorbents for removal of pollutants from wastewater[23, 24]. Azolla Filiculoides (AF) is a floating water fern which it can grows rapidly on the water surface and can form a dense mat, therefore it can lead to many negative effects to aquatic life[25-27]. Recently, dried and modified AF has been used as a proper biosorbent for the removing of heavy metal, phenol compounds and dyes effluent[28, 29]. The present work investigates the potential use of AF biomass as adsorbent for the biosorption of cephalexin (CFX) from aqueous solutions. The effects of biosorbent dosage, contact time, initial CFX concentration on the biosorption of CFX onto AF were investigated. Furthermore, the isotherms data were evaluated.

## MATERIALS AND METHODS

Cephalexin (CFX) (formula mass 347.6 g/mol) with purity higher than 99.6% was supplied by Sigma–Aldrich. The chemical molecular formulae and structure of the CFX are $C_{16}H_{17}N_3O_3S$ is given in Fig. 1 . The CFX stock solutions were prepared by dissolving accurately weighted CFX in distilled water to the concentration of 1000 mg/L and the experimental solutions concentrations were obtained by dilution.

In this study, the AF was used as low cost natural or agricultural wastes for CFX removal from aqueous solutions. AF was collected from Anzali wetland, Iran. The AF were washed several times with water to remove the contaminant, dried in the oven at 105℃ for 5 h. The biomass was then treated with 0.5 M H2SO4 for 2 h followed by the washing with distilled water and then was oven dried at 105℃ for 5 h. After drying, ground and screened through a sieve with 110 mesh to obtain particle sizes less than 0.135 mm.

The morphological features and surface characteristics AF before and after use were examined using an environmental scanning electron microscopy (ESEM) instrument (Philips XL30). The specific surface area of adsorbent was determined by the BET method using the Gemini 2357 of micrometrics Co.

**Batch adsorption studies**

The adsorption of CFX on AF adsorbent was studied using the batch adsorption technique. The adsorption experiments have been conducted using 50 mL of CFX solution of different initial concentrations (10 to 100 mg/L). The solutions were mixed with 0.3 g AF in 100 mL Erlenmeyer flasks. All experiments were performed at the optimum pH (pH 7) by adding 0.1 M HCL and NaOH solutions. The flasks were placed in a shaker at a constant speed of 200 rpm and 30 °C for 90 min to reach equilibrium. Then, the samples were placed in a centrifuge for 10 min at 3600 rpm. The concentrations of CFX at equilibrium ($C_e$) were determined by DR-5000 spectrometer at a wavelength of 263 nm. The amount of CFX adsorbed onto AF ($q_e$) and removal percent can be calculated as below[30, 31]:

$$q_e = \frac{(C0 - Ce)V}{W}$$

$$R = \frac{C0 - Ce}{C0} \times 100$$

Where $C_0$ and $C_e$ (mg/L) are the initial and the equilibrium concentrations of CFX, respectively. V (L) is the volume of the solution and W (g) is the mass of the adsorbent. The optimum amount of the adsorbent dosage was investigated using different amounts of the adsorbent (0.05–0.5 g) at a concentration of 100 mg/L.

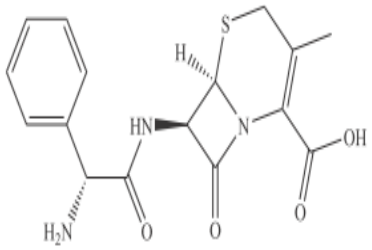


**Fig 1. Molecular structure of CFX**

## RESULTS AND DISCUSSION

The specific surface area is related to the number of active adsorption sites of dried AF. The specific surface area of the modified AF was determined in the size of 36 $m^2$/g.

AF biomass was also examined before and after use using environmental scanning electron microscopy. Fig. 2(a) clearly shows the pore textural structure of AF biomass before use. However, as shown in Fig. 2(b), clear pore textural structure is not observed on the surface of AF biomass after use which could be due to either agglomeration on the surface or the incursion of CFX into the pores of dried AF.

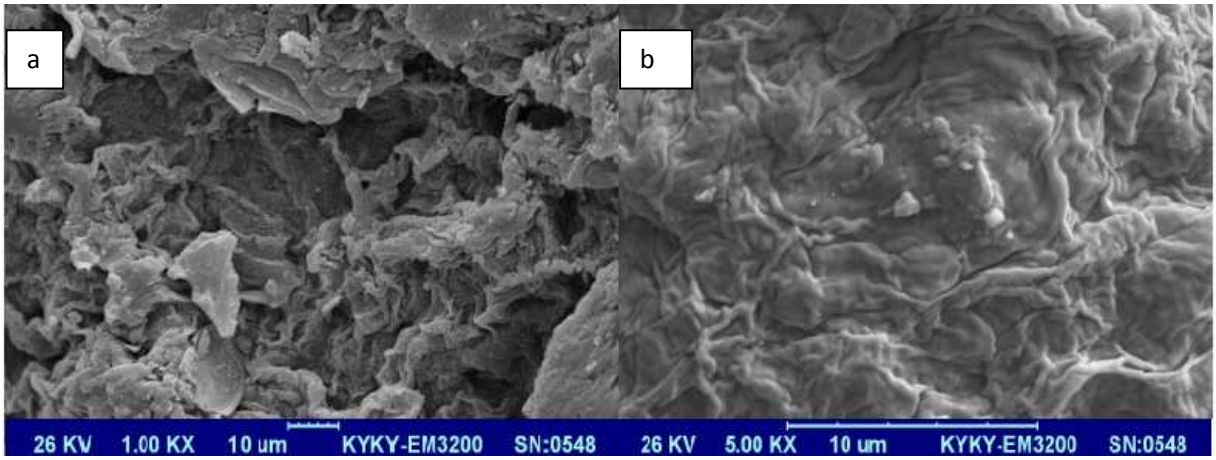


**Fig 2: SEM image of Azolla Filiculoides a: before used b: after used**

**Effect of Contact time and Initial CFX Concentration**

In order to study the effect of contact time on the removal of CFX, experiment were conducted at different contact times (from 10 to 150 min. The variation of the percentage removal of CFX by AF biomass with contact time was shown in Figure 3. The extent removal of CFX increases sharply initially and found to be constant after the optimum contact time. The optimum contact time was found to be 75 minutes with the effective adsorption of 98.2% for Initial CFX Concentration 10 mg/L. The percentage removal of CFX was rapid in the beginning due tolarger surface area available of adsorbent but it gradually decreased with time until it reached equilibrium[32, 33].

The adsorption experiment was carried out varying the concentration of CFX (10, 25,50, 75, 100 mg/L) keeping the fixed dose of AF biomass (3 g/L), pH (7) and temperature 28 ± 2°C. The variation in the percentage removal of CFX with their concentration are shown diagrammatically in Figure 3. It was observed that the percentage removal of CFX by AF is low at higher concentration and gradually increases as the concentration decreases. This is due to the fact that after the formation of mono-ionic layer at lower concentration over the adsorbent surface, further formation of layer is highly hindered at higher concentration due to interaction between CFX surface and in the solution[34, 35]. In addition to that at low concentration of the CFX, the ratio of the initial number of moles of the CFX ions to the available surface area of the adsorbent is large and subsequently, the fraction of the adsorption becomes independent of the initial concentration of the CFX ion [36, 37]. But at higher concentration, the adsorption sites available for adsorption become lesser, and hence, the percentage removal of the CFX ions at higher concentration decreases. The optimum concentration was found as 10 mg/L with the effective removal of %98.2.

**Effect of adsorbent dosage:** The effect of adsorbent dosage on the CFX removal efficiency from aqueous solution is shown in Fig. 4. It reveals that the removal of CFX increases up to a certain limit (3 g/L) and then it remains almost constant. An increase in the removal efficiency with adsorbent dosage can be attributed to increase in the surface area and the availability of more adsorption sites [38, 39]. However, with enhancement of adsorbent dose, adsorption capacity decreased considerably (Fig. 4). The decrease in the CFX adsorption capacity with increasing dosage of the adsorbent is essentially due to remaining unsaturated sites during the adsorption process [40]. For the quantitative removal of CFX, a maximum dose of 3 g/L of the adsorbent is required.

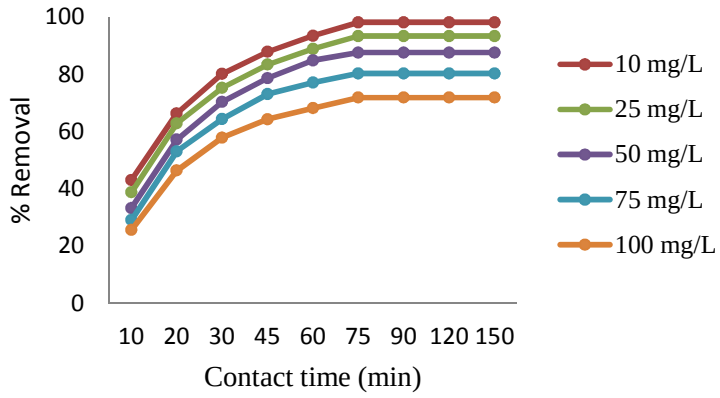


**Fig 3. Effect of contact time and concentration on CFX removal (pH =7, Dose 3 g/L and Temp = 28± 2°C)**

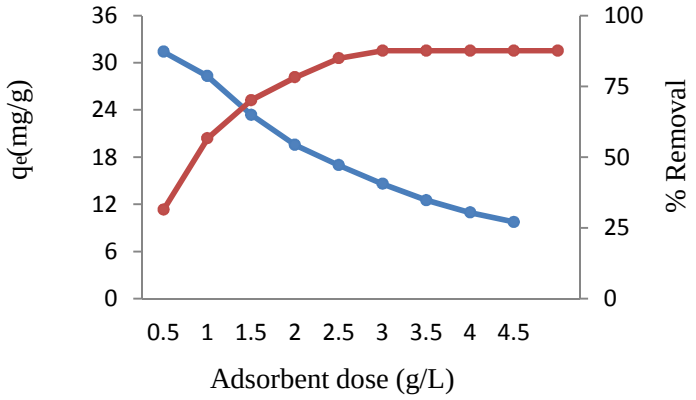


**Fig 4. Effect of adsorbent dose ($C_0$ = 50 mg/L, pH=7, Contact time=75 min and Temp: 28± 2°C)**

**Adsorption kinetics**

The adsorption rate is an important parameter used to predict the adsorption process of tested adsorbents in order to design an adsorption treatment plant. The kinetic data of CFX adsorption have been tested by the pseudo-first-order, pseudo-second-order and intraparticle diffusion models using the following equations, respectively.

The pseudo-first-order model can be expressed as [41, 42]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$

The pseudo-second-order model based on equilibrium can be written as [43, 44]:

$$\frac{t}{q_t} = \frac{1}{k_2 . q^2} + \frac{t}{q_e}$$

where $q_e$ and $q_t$ are the amounts of CFX adsorbed (mg/g) at equilibrium and at time t (min), respectively, $k_1$ (1/h) and $k_2$ (g/mgh) are pseudo-first-order and pseudo-second-order rate constants, respectively.

The adsorption kinetic data were further processed to explore the possibility of intra-particle diffusion using the Weber–Morris equation. The model is expressed by the following equation [45, 46]:

$$q_t = k\, t^{0.5} + C$$

Where k is the intra-particle diffusion rate constant and C is the boundary layer thickness.

Also, to further justify adsorption kinetics, the normalized standard deviation ΔQ(%), which was calculated for kinetic model studies can be expressed as(47):

$$\Delta Q(\%) = \sqrt{\sum \frac{\left(\frac{q_{e\,exp} - q_{e\,cal}}{q_{e\,exp}}\right)_{\times 100}}{n-1}}$$

Where N is the number of data points, $q_e$ ,exp (mg/g) and $q_e$ ,cal (mg/g) are the experimental and calculated equilibrium adsorption capacity value, respectively.

The kinetic model parameters and the correlation coefficient values of different kinetic models are listed in Table 1. It can be observed from Table 1 and Fig. 5. The linear plot of t /$q_t$ versus t for pseudo-second order equation exhibited the highest correlation coefficients $R^2$ value and lower normalized standard deviation ΔQ. In addition, the experimental $q_e$ values of AF are in agreement with the calculated $q_e$ values generated by the pseudo-second-order, indicating the adsorption of CFX onto the AF could be best described by the pseudo-second-order kinetic model. This implied that the rate-limiting step of CFX onto the AF is controlled by chemisorption involving valence forces through the sharing or exchange of electrons between adsorbents surface and CFX.

The Weber-Morris intraparticle diffusion model was commonly used to determine the sorption data, which was used to study the diffusion mechanism during the adsorption process. A linear plot of $q_t$ versus $t^{1/2}$ at different initial concentrations is shown in Fig. 5 and the model parameters are given in Table 1. As can be seen from Fig. 6, the diffusion kinetic plots exhibited the three-stage linearity. It has a good linear correlation between $q_t$ and $t^{1/2}$ in this stage, indicating that the adsorption process was not only controlled by intra-particle diffusion but two or more steps were controlling the adsorption process. The first portion of curve has sufficient available adsorption sites on the adsorbents surface with high adsorption rate; this portion was ascribed to the diffusion of CFX molecule in mesopores. Afterwards, the second linear portion belongs to intraparticle diffusion. The CFX molecules come across much larger hindrance because of transfer in deeper inner pores. Then the third section represented final equilibrium stage where the intra-particle diffusion begins to slow down the arrival of absorption saturation, and the diffusion of CFX molecules into micropores.

**Table 1: Adsorption kinetic constants CFX adsorption onto AF**

| $C_o$ (mg/L) | $q_e$ exp (mg/g) | Pseudo-first order | | | Pseudo-second order | | | Intraparticle diffusion | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_1$ | $q_e$ | $R^2$ | $K_2$ | $q_e$ | $R^2$ | K | $_C$ | $R^2$ |
| 10 | 3.451 | 0.181 | 2.144 | 0.812 | 0.035 | 3.845 | 0.997 | 0.825 | 2.45 | 0.884 |
| 25 | 8.942 | 0.294 | 5.483 | 0.798 | 0.061 | 9.416 | 0.999 | 0.948 | 3.11 | 0.871 |
| 50 | 16.84 | 0.428 | 11.58 | 0.829 | 0.074 | 16.12 | 0.996 | 1.324 | 3.86 | 0.844 |
| 100 | 25.16 | 0.594 | 18.42 | 0.847 | 0.089 | 26.28 | 0.998 | 1.946 | 2.59 | 0.862 |

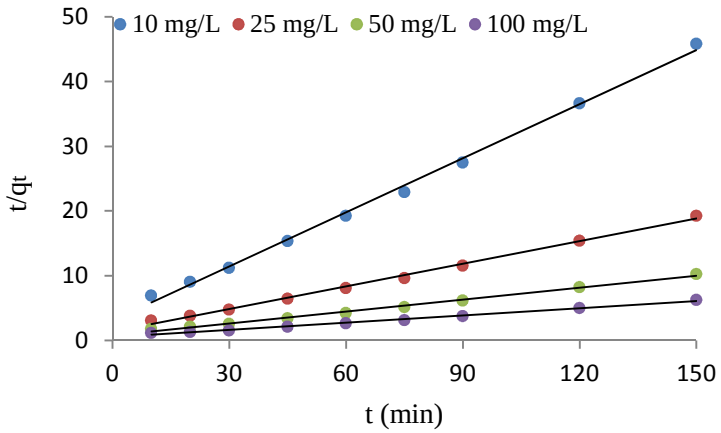


**Fig 5. Pseudo second order kinetics for CFX adsorption onto AF**

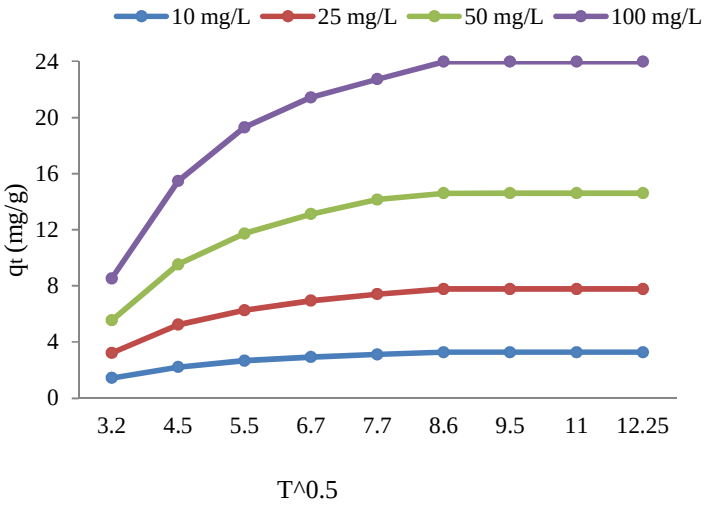


**Fig. 6. Intraparticle diffusion kinetic model for the adsorption of CFX adsorption onto AF**

**Evaluation of thermodynamic parameters**

The thermodynamic parameters such as, entropy ($\Delta S^0$), enthalpy ($\Delta H^0$) and Gibbs free energy change ($\Delta G^0$) were computed using the following equations [48-50]:

$\Delta G^0 = -RT \ln K$
$\Delta G^0 = \Delta H^0 - T \Delta S^0$

Where K is the distribution coefficient for adsorption. Table 2 shows the thermodynamic parameters at different temperatures. The ΔG° values were between -2.44 and -7.12 kJ/mol for CFX adsorption. This negative ΔG° values indicate that a spontaneous physisorption take place. The enhancement of ΔG° negative values with increase of temperature indicates a rapid and more spontaneous at higher temperature. The endothermic nature of CFX sorption by AF confirmed by the positive values of ΔH°. An adsorption proces is generally considered as physisorption if 8> ΔH° kJ/mol and as chemi-adsorption if 25<ΔH° kJ/mol. When ΔH° lied between 8 and 25 kJ/mol, both the chemisorption and physisorption is responsible for the adsorption process. Accordingly, we concluded that CFX sorption by AF (ΔH° =11.34 kJ/mol) is the both chemi and physisorption adsorption process. The positive value of ΔS° (Table 9) indicates an enhancement in the degree of freedom of irregularities at the solid/liquid interface during the adsorption of CFX on the AF. Thus, the adsorption is favored on the AF.

**Table 2: Thermodynamic parameters of adsorption of CFX onto AF**

| Tem (*K*) | $\Delta G^0$(KJ/mol) | $\Delta H^0$(kJ/mol) | $\Delta S^0$ (J/mol K) |
|---|---|---|---|
| 273 | -2.44 | | |
| 299 | -3.85 | | |
| 313 | -5.24 | 11.34 | 0.982 |
| 333 | 7.12 | | |

## CONCLUSION

The following conclusions can be drawn based on the investigation of CFX adsorption by AF biomass adsorbents. The percentage adsorption of CV CFX on AF increased with increasing AF adsorption dose and increased with increase in contact time. Higher percentage adsorption capacity of CFX on AF was observed at higher temperature. The negative value of ΔG° confirms that the feasibility of the reaction and spontaneous nature of the adsorption. Similarly the positive value of ΔH° and ΔS° suggests that the decreased disorder and randomness at the solid solution interface with endothermic adsorption. Adsorption kinetics was tested with pseudo first order, pseudo second order model and intra particle diffusion models. Kinetic studies indicate an adsorption pseudo second order reaction.

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