

REMOVAL OF ANTIBIOTIC CIPROFLOXACIN HYDROCHLORIDE FROM WATER BY KANDIRA STONE: KINETIC MODELS AND THERMODYNAMIC

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ABSTRACT

In this study, Kandira stone, extensively used as a cladding material for building stone has been examined for the removal of an antibiotic Ciprofloxacin hydrochloride (CIP) from its aqueous solution. Batch experiments were performed to investigate the adsorption kinetics, equilibrium and thermodynamics between the adsorbent surfaces and CIP. The sorption data follows Freundlich isotherm. A chemical adsorption was dominant. The adsorption behaviour of CIP onto Kandira stone followed the pseudo-second-order kinetic model, indicating that the adsorption process can be expressed with the chemisorption mechanism. The intraparticle diffusion process is a rate-controlling step. The adsorption thermodynamic parameters of the free energy change (ΔG°), the isosteric enthalpy change (ΔH°) and the entropy change (ΔS°) were calculated. The negative ΔH° values indicated that sorption of CIP was the exothermic process. The positive value of ΔG° indicates non-spontaneous nature of CIP adsorption.

Keywords Ciprofloxacin, adsorption, kinetic models, thermodynamic, Kandira stone

1. Introduction

Ciprofloxacin hydrochloride (CIP) is globally used an important fluoroquinolone antibiotics for treatment of both human and animal diseases. Due to the excret in unmetabolized form from the human and animal bodies, CIP was frequently detected in a variety of natural environments. CIP can exit the target organisms unaltered with up to 72% of the nonmetabolized form being excreted (Daughton and Ternes, 1999). Concentrations of CIP in wastewater effluents and surface water have been found at concentrations typically $<1 \mu\text{g l}^{-1}$ (Bhandari *et al.*, 2008; Carmosini and Lee, 2009). Higher concentrations were reported in effluents from hospital (up to $150 \mu\text{g l}^{-1}$) and drug manufacturing plants (31 mg l^{-1}) (El-Shafey *et al.*, 2012). Antibiotics fluoroquinolones become highly accumulated in sewage sludge (concentrations ranging from 1.4 to 2.42 mg/kg of dry matter) (Golet *et al.*, 2002).

Antibiotics can be removed effectively from the environment by adsorption on sludge, soils, and pure minerals (Wu *et al.*, 2010). Low-cost adsorption method has attracted many researchers because of not requires complicated regeneration process (Kumar, 2014). Natural adsorbents are evaluated as an appropriate adsorbents due to its low cost and high removal efficiency.

In the literature, several studies related to the adsorption of CIP to natural materials or components of natural materials have been published (activated carbon (Carabineiro *et al.*, 2012); activated charcoal and talc (Ibezim *et al.*, 1999); montmorillonite (Wu *et al.*, 2010; Wu *et al.*, 2012); soil (Carrasquillo *et al.*, 2008; Vasudevan *et al.*, 2009; Conkle *et al.*, 2010); 2:1 dioctahedral clay minerals (Wang *et al.*, 2011); kaolinite (Li *et al.*, 2011); modified coal fly ash (Zhang *et al.*, 2011); aerobically digested biosolid (Wu *et al.*, 2009); sawdust (Bajpai *et al.*, 2012); date palm leaflets (El-Shafey *et al.*, 2012); birnessite, a layered manganese oxide (Jiang *et al.*, 2013); (Fe₃O₄/C) a new magnetic mesoporous carbon composite (Shi *et al.*, 2013); Chitosan-Zn (II), Chitosan-Fe (III), Chitosan-Fe(II) microparticles (Reynaud *et al.*, 2011); aluminum and hydrous oxides (Gu and Karthikeyan, 2005); nano-sized magnetite (Rakshit *et al.*, 2013).

The objective of this research is to investigate the capability of Kandira stone for the adsorption of CIP from aqueous solution. On the basis of batch adsorption experiments, kinetic models to predict the CIP removal efficiency of a low cost and natural adsorbent used is applied. Thermodynamic studies were also performed in order to explain the adsorption mechanism.

2. Materials and Methods

2.1 Materials

Kandira stone was used as adsorbent. Kandira stone, extensively used as a cladding material for building stone in northwest Turkey, consists of approximately 91% calcium carbonate and 9% clay minerals (Arman *et al.*, 2007). Kandira stone was dried at air, passed through a 0.1mm sieve to ensure the material uniformity.

CIP with purity higher than 99% was obtained from SANOVEL. This commercially available product contains no more than 0.2% by weight of the by-product contaminant fluoroquinolonic acid. CIP used in the experiments is the commercial product, with a molecular weight of 367.80. The solubility of CIP is pH-dependent, ranging from 6.19 g l⁻¹ at pH 5 to 0.15 g l⁻¹ at pH 7 at 37 °C (Wu *et al.*, 2010).

2.2 Batch CIP Adsorption Experiments

Batch adsorption experiments were conducted by CIP solution at concentration of 30 mg l⁻¹. For a kinetic study, 0.6 g of Kandira stone was put into 50 mL of CIP solution. The initial pH values of the CIP solutions were not adjusted. The adsorption was carried out in the flask containing both Kandira stone and CIP solution at 20 °C and constant agitation (125 rpm). The concentrations of CIP in solution were analyzed with 5 - 60 min time intervals after the solids were separated by filtration.

For the isotherm study, Kandira stone and CIP solution at initial concentrations ranging from 3 to 30 mg l⁻¹ were combined and mixed on a shaker at 125 rpm, 20°C and initial pH for 30 min. For the thermodynamic analysis, Kandira stone and CIP solution at initial concentration of 10, 20, 30, 40 mg l⁻¹ were combined and mixed at 20, 30, 40, 50 °C at 125 rpm for 30 min under initial pH condition. After mixing, samples were analyzed for equilibrium CIP concentration.

2.3 Analysis

The concentrations of CIP in the filtered supernatant were measured by means of the UV spectrometer (Hach-Lange DR 5000). The concentration of CIP was analyzed at the maximum wavelength. The calibration curve was established with 17 standards between 0 and 50 mg l⁻¹ with the coefficient of determination (R²= 0.9992). The amount of CIP adsorbed at equilibrium was calculated according to Eq (1):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e and C_e are the amount of CIP was adsorbed per unit weight of the adsorbent (mg g^{-1}) and the equilibrium concentration of CIP in solution (mg l^{-1}) at equilibrium, respectively; C_0 is the initial concentration of CIP (mg l^{-1}); V and m are the volume of CIP solution (l) and the mass of adsorbent used (g), respectively.

3. Results and Discussion

3.1 Effect of adsorbent dosage

Effect of adsorbent dose on removal of CIP investigated with adsorbent dose in the range of 2-24 g l^{-1} at initial pH and CIP concentration of 30 mg l^{-1} (Fig. 1a). From Fig., it is obvious that, the amount of CIP adsorbed increased from around 18.1% to 68.5% when Kandira stone was increased from 2 to 12 g l^{-1} . 12 g l^{-1} was selected as optimum dose. The removal of CIP increases sharply with increase in adsorbent dose due to the availability of more binding sites on adsorbent surface. After that, removal becomes in less significant rate. Percent removal increased to 77.4% up to dose of 24 g l^{-1} . It may be due to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area.

3.2 Effect of contact time on the removal of CIP

The equilibrium time is the most important design parameters in an economical wastewater treatment system. The adsorption capacity of Kandira stone was determined by varying the contact time in the range of 5-60 min (Fig. 1b). Optimum contact time is the amount of time required for maximum adsorption at minimum contact time. It is shown in Fig.1 that there was a rapid uptake within the first 30 min. The initial adsorption rate is rapid and gradually decrease with raising the time and reach equilibrium at about 30 min of contact time. Therefore, 30 min of contact time was chosen as the optimum contact time for Kandira stone. The amounts of CIP adsorbed increased from 48.1 % to 63.9 % when contact time increased from 5 min to 30 min. Percent removal increased to 79.8% up to 60 min.

3.3 The effect of pH on the removal of CIP

For investigating the pH dependence of CIP sorption, 30 mg l^{-1} CIP solution was shaken with 12 g l^{-1} Kandira stone and equilibrated for 30 min at pH values ranging from 1.0 to 12. Comparison of removal efficiency at different values of pH shows that adsorbed CIP percentage is decreased by increasing of pH (Fig.1c). The pKa values for CIP are 6.1 (for the carboxylic acid group) and 8.7 (for the amine group on the piperazine moiety). The cationic form due to protonation of the amine group in the piperazine moiety predominates when solution pH is below 6.1. CIP is the zwitterionic form of CIP dominates at pH 6.1-8.7. As the solution pH is above 8.7, the anionic form due to loss of a proton from the carboxylic group prevails (Wu *et al.*, 2010). At $\text{pH} < 6.0$, removal of CIP increased because of the electrostatic attraction improved due to the opposite charge between CIP and Kandira stone. As can be seen, the removal percentage significantly decreased at higher pH values. This behavior may be attributed to the zwitterionic properties of CIP. In acidic solutions, high ionic interactions occur between the cationic CIP^+ and adsorbents' surface. Because of these interactions, high removal of CIP is accomplished.

3.4 Adsorption isotherms

Equilibrium data, also known as adsorption isotherms, describe how the adsorbate' surface interaction between adsorbed molecules and give a comprehensive understanding of the nature of interaction (Moradi *et al.*, 2013). In this study, several isotherm equations are applied.

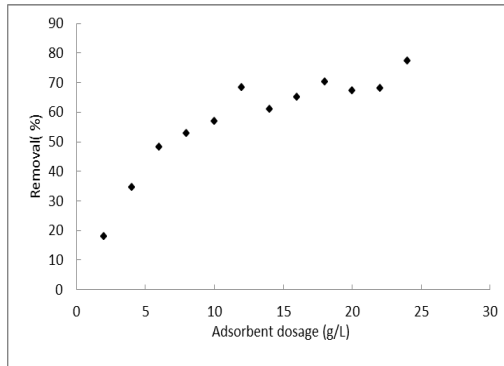
3.4.1 Langmuir isotherm

Langmuir isotherm models the single coating layer on adsorption surface. Moreover, the adsorbent surface is homogeneous so, adsorption energy is constant over all sites. Langmuir isotherm can be defined as:

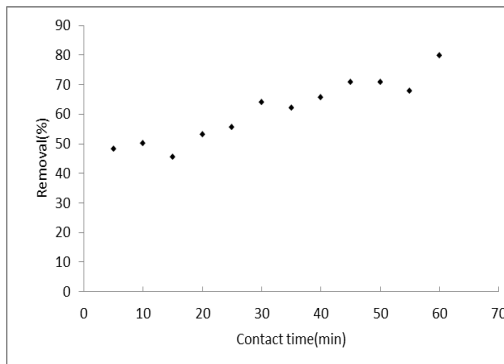
$$\frac{C_e}{q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m} \quad (2)$$

where V_m is the monolayer capacity, k is the equilibrium constant. These constants can be determined from the intercept and the slope of the linear plot of experimental data of C_e/q_e vs. C_e . The linear form of Langmuir equation for CIP adsorption on Kandira stone is given by the following expression (correlation coefficient, $R^2=0.6311$):

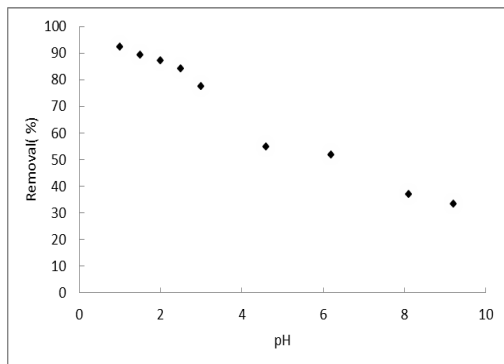
$$\frac{C_e}{q_e} = 117.85 - 8.2534 C_e \quad (3)$$



(a)



(b)



(c)

Figure 1. Effect of adsorbent dose (a), contact time (b), and pH (c) on the adsorption of CIP

3.4.2 Freundlich isotherm

Freundlich isotherm is used for modelling the adsorption on heterogeneous surfaces. The linear form of Freundlich isotherm is written as the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f is taken as a relative indicator of adsorption capacity, and $1/n$ indicates the favorable adsorption, K_f and n were calculated from the slope and intercept of the plot $\log q_e$ vs. $\log C_e$. n value indicates the degree of nonlinearity as follows: when $n=1$, adsorption is linear; $n<1$, adsorption is a chemical process; $n>1$, adsorption is a physical process (Kumar, 2014). According to the Freundlich theory, $n>1$ indicates the favorable adsorption (Hai-Ling *et al.*, 2007). The linear form of the Freundlich isotherm from experimental data is given with the following formulas ($R^2= 0.8368$).

$$\log q_e = -3.5387 + 3.1845 \log C_e \quad (5)$$

Results from this study showed that the n value (0.314) was less than 1, which suggests that a chemical rather than a physical adsorption was dominant. The value of n lying confirm the unfavorable conditions for adsorption

It was shown that Freundlich isotherm fits better most of the adsorption data, since the line corresponding to the model fitting is closer to the experimental points than that from Langmuir isotherm. R^2 values are higher in the case of Freundlich isotherm.

3.5 Sorption kinetics

In order to predict the adsorption behavior, kinetic models were employed to the experimental data. In this study, several kinetic models are applied.

The pseudo-first order equation has the following formulation (Eq 6) (Plazinski *et al.*, 2009):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t (mg CIP/ g adsorbent) is the concentration of CIP adsorbed in the solid phase at t time, k_1 (1/min) is the observed rate constant of the pseudo-first-order model and t (min) is time. The values of q_e and k_1 parameters are usually determined by applying the commonly accepted linear regression procedure. In the first-order kinetic model, by plotting the values of $\ln(q_e - q_t)$ vs. t may give a linear relationship that k_1 and q_e values can be determined from the slope and intercept of the obtained line, respectively (Ghaedi and Kokhdan, 2012).

The most commonly-applied form of the pseudo-second order equation can be written in Eq (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 (g adsorbent/ mg CIP. min) is a constant.

The two most commonly used kinetic models were not able to explain the diffusion mechanism and the rate determining step. This is explain by the intraparticle diffusion model and Body kinetic equations (Kumar, 2014).

Intraparticle diffusion model based on diffusive mass transfer that adsorption rate expressed in terms of the square root of time is given (Eq. 8) (Ghaedi and Kokhdan, 2012).

$$q_t = k_{\text{diff}} t^{0.5} + C \quad (8)$$

k_{diff} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intraparticle diffusion rate constant and C is a constant related to the thickness of the boundary layer, which is in direct ratio to the effect of the boundary layer. The value of k_{diff} and C were calculated from the slope and intercept of the plot of q_t vs. $t^{0.5}$. Generally, the plot of q_t against $t^{0.5}$ may show a multilinearity, and this indicated that the adsorption processes contained two or more steps. The adsorption of a solute from solution by porous adsorbents is essentially relevant to three consecutive steps. Steps were the external surface adsorption or the instantaneous adsorption, gradual adsorption stage and the final equilibrium stage. If the line passed through the origin, the intraparticle diffusion would be the sole rate-limiting step. If the line did not pass through the origin, it implied that intraparticle diffusion was not the sole rate control step, and other processes may control the adsorption rate (Zou *et al.*, 2012).

The mass transfer effect on the adsorption kinetics can be analyzed by the Body kinetic equation. Equation was applied identify the slowest step in the adsorption process which is expressed as: (Kumar, 2014; Hai-Ling *et al.*, 2007).

$$\ln(1-F) = -R^e t \quad (9)$$

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (10)$$

$$\text{when } F > 0.85, Bt = -\ln(1-F) - 0.4977 \quad (11)$$

where F is the fractional attainment of equilibrium, R^e and B are the mass coefficients (1/min). The linearity of the plot of $\ln(1-F)$ and t indicates the role of the external mass transfer in the adsorption process. The linearity of the plot of Bt against t would show the role of the intraparticle mass transfer (Hai-Ling *et al.*, 2007).

Calculated pseudo-first-order, pseudo-second-order, intraparticle, and Body kinetic parameters and coefficient for adsorption of CIP on Kandira stone are listed in Table 1.

Table 1. Comparison of the kinetic parameters for pseudo-first-order and pseudo-second-order, intraparticle, and Body kinetic models

Parameters	Adsorption kinetic equation			Mass transfer equation	
	Intraparticle diffusion	First-order	Second-order	External mass transfer	Intraparticle mass transfer
Rate constant	$k_{\text{diff}}=0.1479$ ($\text{mg/g. min}^{0.5}$)	$k_1=0.086$ (1/min)	$k_2=0.049$ ($\text{g mg}^{-1} \text{min}^{-1}$)	$R_e=0.0825$ (1/min)	$B=0.0649$ (1/min)
q_e	-	1.74	2.17	-	-
R^2	0.8717	0.1282	0.9647	0.7242	0.8131

Comparison of correlation coefficients values showed that the fit of the experimental data by the pseudo-second-order kinetic model gave higher correlation coefficients. Hence, the adsorption behaviour of CIP onto Kandira stone followed the pseudo-second-order kinetic model, indicating that the adsorption process can be expressed with the chemisorption mechanism. The intraparticle diffusion process is a rate-controlling step because of its larger correlation coefficients. k_2 value from the present study was compared with other adsorbents in previous studies (Table 2). Kandira stone is effective than many adsorbents.

3.6 Thermodynamics of CIP Adsorption

Changes of temperature can affect sorption behavior of CIP on Kandira stone, thus sorption of CIP at 20, 30, 40, 50 °C were investigated. The removal of CIP decreased from 51% to 45% on increasing the temperature from 20 to 50 °C for CIP concentration of 30 mg l^{-1} . CIP removal from aqueous solution is difficult at higher temperatures. For all CIP concentration, the maximum removal of CIP was obtained at 20 °C (Fig. 2).

The nature of adsorption was ascertained by the thermodynamic analysis of the process. To discuss about thermodynamic behavior of the adsorption of CIP, thermodynamic parameters were calculated.

The relationship between the CIP distribution coefficient (K_d) and free energy (ΔG° J/mol) of adsorption (Eq. 12) is:

$$\Delta G^\circ = -RT \ln K_d \quad (12)$$

Table 2. k_2 value of different adsorbents used for removal of CIP

Adsorbent	k_2 (g mg ⁻¹ min ⁻¹)	Reference
kaolinite	855×10^{-3}	(Li <i>et al.</i> , 2011)
montmorillonite	133.3×10^{-3} 2.33×10^{-3}	(Wang <i>et al.</i> , 2011; Wu <i>et al.</i> , 2010)
rectorite	3.33×10^{-3}	(Wang <i>et al.</i> , 2011)
illite	5×10^{-3}	(Wang <i>et al.</i> , 2011)
modified coal fly ash	2.07	(Zhang <i>et al.</i> , 2011)
chemically prepared wet and dry carbon	0.2×10^{-3} and 0.18×10^{-3}	(El-Shafey <i>et al.</i> , 2012)
birnessite	322×10^{-3}	(Jiang <i>et al.</i> , 2013)
molecularly imprinted polymer and non-imprinted polymer	1.381 and 0.472	(Zhang <i>et al.</i> , 2012)
bentonite	7.33×10^{-3}	(Genç and Doğan, 2015)
zeolite	7.70×10^{-3}	
pumice	30.76×10^{-3}	
Kandira stone	49×10^{-3}	This study

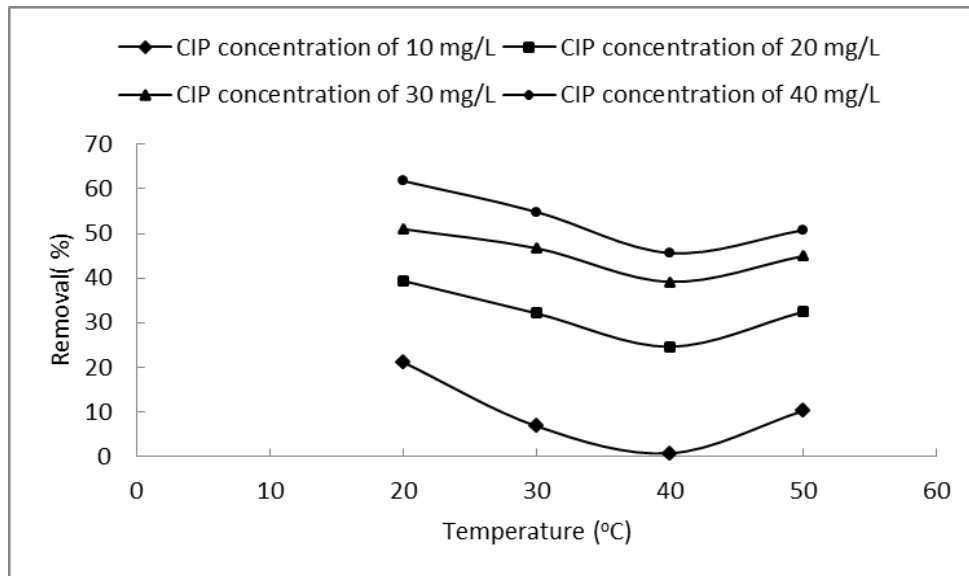


Figure 2. Effect of temperature on the adsorption of CIP

where ΔG° is the standard free energy change, R ($8.314 \text{ J mol}^{-1} \text{ }^\circ\text{K}^{-1}$) is the gas constant and T is the reaction temperature ($^\circ\text{K}$). The distribution coefficient for the adsorption process (K_d) was calculated with Eq. (13) (Li *et al.*, 2014).

$$K_d = \frac{q_e}{C_e} \quad (13)$$

ΔH° (J mol⁻¹) and ΔS° (J mol⁻¹ °K⁻¹) according to Eq. (14) are calculated (Hai-Ling *et al.*, 2007).

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

where ΔH° is the isosteric enthalpy change, ΔS° is the entropy change. Where ΔH° and ΔS° were calculated from the slope and intercept of the linear plot of $\ln K_d$ against $1/T$ (Li *et al.*, 2014). The values of the thermodynamic parameters calculated from experimental data are presented in Table 3.

Table 3. Thermodynamic parameters for the adsorption of CIP on Kandira stone

Initial CIP concentration (mg l ⁻¹)	ΔH° (J mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (J mol ⁻¹)			
			20 °C	30 °C	40 °C	50 °C
10	*	*	10202	-	-	15437
20	-7643	-51	7092	8132	9355	8628
30	-5776.6	-40.3	5954	6589	7608	7215
40	-6908.9	-40.9	4880	5769	6921	6591

(*)Because the plot of $\ln K_d$ versus $1/T$ was not linear for initial concentration of 10 mg/L, thus the related thermodynamic parameters such as ΔH° and ΔS° are not available.

The negative ΔH° means a chemical exothermic process and support the chemisorption is the rate-determining step (Eser *et al.*, 2012). When ΔG° is positive, the reaction is going to be endothermic to go in a forward direction, but will be spontaneous in going backwards. The magnitude of ΔG° depends on temperature and distribution coefficient of adsorption. ΔG° increased by increasing of temperature and decreased by increasing of initial CIP concentration. Entropy has been defined as the degree of chaos of a system (He *et al.*, 2010). The negative entropy changes suggest that more ordered arrangement of solute molecules is shaped on the surface of the adsorbent, which are indicative of an enthalpy-driven adsorption process (Hai-Ling *et al.*, 2007). ΔS° values increase with the increase of initial CIP concentration because of the higher CIP concentration augments the randomness at the adsorbent –solution interface.

4. Conclusions

Batch adsorption experiments were carried out for the removal of CIP by adsorption from aqueous solution using Kandira stone as adsorbent. The effects of parameters adsorbent dosage, contact time, pH and temperature on the adsorption were investigated. The following conclusions may be drawn:

CIP removal percentage increased by increasing the amount of Kandira stone until 12 g l⁻¹ owing to a corresponding increase in the number of active sites, removal of CIP was 68.5% at 12 g l⁻¹. The removal percentage do not change significantly at higher value of Kandira stone due to overlapping or aggregation of adsorption sites. The equilibrium adsorption is practically achieved through a time of 30 min, removal of CIP was 63.9% at 30 min. Due to CIP exist in a cationic form in acidic solution, CIP adsorption was high. The removal percentage significantly decreased at higher pH values. At pH<6.0, removal of CIP increased because of the electrostatic attraction improved due to the opposite charge between CIP and Kandira stone. Kinetic models were used to analyze the experimental data. The kinetic study was performed based on pseudo-first-order, pseudo-second-order equations, intraparticle diffusion and Body kinetic equations. The data indicate that the adsorption kinetics follow the second-order kinetic models. The results of this study indicate that Kandira stone is efficient adsorbent for the removal CIP, although it shows a lower adsorption capacity than

those observed on other minerals. k_2 (g adsorbent/mg CIP min) value for Kandira stone was calculated as 49×10^{-3} . Also, the intraparticle diffusion process is determined as a rate controlling step because of its larger correlation coefficients. The equilibrium data have been analyzed using Freundlich and Langmuir adsorption isotherms. The sorption data follows Freundlich isotherm. The Freundlich type adsorption isotherm is an indicator of surface heterogeneity. Results from this study showed that the n value (0.314) was less than 1, which suggests that a chemical rather than a physical adsorption was dominant. The removal of CIP decreases with increase in temperature, the maximum removal of CIP was obtained at 20°C. Thermodynamic of CIP adsorption shows that adsorption is the exothermic adsorption. ΔS° values increase with the increase of initial CIP concentration because of the higher CIP concentration augments the randomness at the adsorbent – solution interface.

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