Kinetic, Isotherm and Thermodynamic Studies on the Ciprofloxacin Adsorption from Aqueous Solution Using Aleppo bentonite

Abazli Hicham[1]   *Jneidi Hussein[2]*   *Hatem Siba[3]**

[1] Chemistry Department, College of Science, Tishreen University, Latakia, Syria.
[2] Environmental Systems Engineering Department, High Institute for Environment Research, Tishreen University, Latakia, Syria.
[3] Environmental Chemistry Department, High Institute for Environment Research, Tishreen University, Latakia, Syria.
Corresponding author: hishamabazli@gmail.com, juniedih@gmail.com, sibahatem@gmail.com
ORCID ID: https://orcid.org/0000-0001-7146-6017 , https://orcid.org/0000-0003-4385-5589, https://orcid.org/0000-0002-1735-090X

Abstract:

Aleppo bentonite was investigated to remove ciprofloxacin hydrochloride from aqueous solution. Batch adsorption experiments were conducted to study the several factors affecting the removal process, including contact time, pH of solution, bentonite dosage, ion strength, and temperature. The optimum contact time, pH of solution and bentonite dosage were determined to be 60 minutes, 6 and 0.15 g/50 ml, respectively. The bentonite efficiency in removing CIP decreased from 89.9% to 53.21% with increasing Ionic strength from 0 to 500mM, and it increased from 89% to 96.9% when the temperature increased from 298 to 318 K. Kinetic studies showed that the pseudo second-order model was the best in describing the adsorption system. The adsorption equilibrium data is better represented by the Langmuir isotherm, and the maximum adsorption capacities of CIP were defined as 243.9, 270.27, 285.71 mg/g at 298, 308 and 318 K, respectively. Thermodynamic parameters were figured out showing that the adsorption was spontaneous and endothermic according to the negative values of ΔG° and positive value of ΔH° respectively. Based on these results, Aleppo bentonite seems to be an effective raw material for CIP adsorption and removal from aqueous solutions.

Keywords: Adsorption, Aleppo Bentonite, Ciprofloxacin, Isotherm, Kinetic Studies

Introduction:

Antibiotics have been accounted as pollutants that were getting more and more important since the last twenty years [1, 2]. They constituted of -critical compounds within the environmental pollutants that are difficult to remove in the water systems [2, 3]. These compounds can be found in the environment mostly as a result of their use in human and veterinary medicine, and the incompetence of wastewater treatment units in removing them. They have been grouped as pollutants with priority risk due to their toxicological influence on aquatic organisms even at low concentrations, in addition to their effect on inducing resistance in some strains of bacteria [3, 4].

Ciprofloxacin (**CIP; $C_{17}H_{18}O_3N_3F$**) is a synthetic compound that belongs to a group of antibiotics called fluoroquinolones (FQs), and widely used of human health in many countries [5]. It can be discharged into aquatic systems coming from municipal or hospital wastewater because of its deficient metabolism in humans, or from discharges of pharmaceutical industries, as conventional water treatments cannot remove CIP [6]. CIP has been found at concentrations within range of 0.01–0.03 mg/L in wastewater effluents[7]. Higher concentrations (up to 50 mg/L and 150 μg/L) were observed in wastewater from industrial effluent and hospital effluent respectively [8, 9].

The occurrence of CIP in the environment in considerable concentrations with its characteristics including persistency and potency to induce antibiotic resistance like other antibiotic compounds pushed hard to treat CIP in aquatic bodies [10].

Among different methods investigated to remove CIP from contaminated water including oxidation [11], ozonation, oxidation by chlorination

and biological treatment [9], adsorption stands out as a very desirable and promising method because of its efficiency, affordability and ease of implementation [5, 12, 13] with remarkable ease of design and operation compared to others. Moreover, there are abundant adsorbents with various characteristics [14].

Among adsorbents, bentonite, has gained great important because it is an effective, low-cost and eco-friendly adsorbent [14].

The objective of this research is to investigate the capability of Aleppo bentonite, for the CIP adsorption from aqueous solution.

Materials and Methods:
Materials
Aleppo Bentonite used as adsorbent was crushed and passed through a sieve to get a homogeneous material. It is mainly constituted of montmorillionite [15]. Some specifications of Aleppo bentonite is shown in Table 1.

**Table 1. Characteristics of adsorbent /Aleppo bentonite [15]**

Cation exchange capacity/CEC (Sodium acetate method)	Specific Surface Area SSA (EGME[1] method)	point of zero charge /PZC (Drift Method)	Bentonite Suspensin pH
87meq/100g	291 m^2/g	8.7	7.8

[1]Ethylene Glycol Monoethyl Ether

Ciprofloxacin hydrochloride with purity (98.9%) was obtained from (ZHEJIANG GUOBANG PHARMACEUTICAL CO,LTD). The molecular structure and characteristics of ciprofloxacin hydrochloride quoted from PubChem, the world's largest collection of freely accessible chemical information, are shown in Fig.1 and Table 2 respectively. The protonable groups in the CIP structure create two acid dissociation constants / pKa values (6.1 and 8.7), which conform to the carboxylic acid group and the amine group in the piperazine moiety, respectively.

Table 2. Some properties of CIP HCl (PubChem)

HCl Ciprofloxacin Hydrocloride/ CIP	
Molecular formula	$C_{17}H_{19}ClFN_3O_3$
Molar mass	367.8 g/mol
Physical form	Light yellow crystalline powder
CAS Number	86483-48-9
Dissociation Constants	pKa$_1$= 6.1 (carboxylic group) pKa$_2$= 8.7 (nitrogen on piperazinyl)
Solubility in water (at 20 C°)	30 mg/ml
Drug class	Fluoroquinolone antibiotic
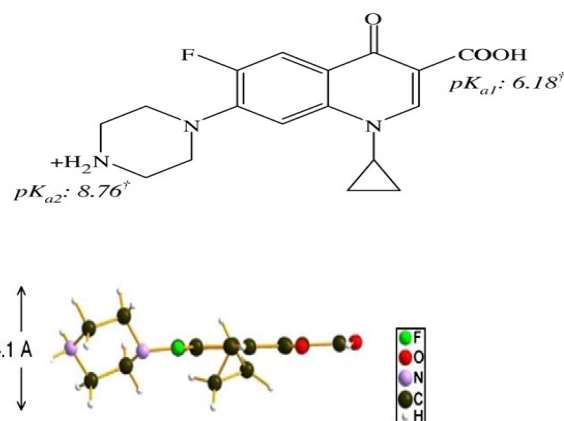
Figure 1.The CIP molecular structure (PubChem)

Batch Adsorption Studies
The adsorption studies were conducted in various conditions including different contact times, pH, bentonite dosages, ionic strengths, initial CIP concentrations, and temperatures.

For all experiments, 0.15 g bentonite was scattered in 50 mL CIP solution with a flask of 100 mL wrapped with aluminum foil to avoid photodegradation. The solutions were shaken at 200 rpm for one hour, filtered using buchner funnel with 0.45 μm mesh size filters and analyzed for equilibrium CIP concentration. All experiments were performed twice and the average value was used.

For a kinetic study, 0.15 g of bentonite was put into 50 ml of CIP solution at concentration of 500 mg/L without adjusting the startup (pH=5.5). The adsorption was carried out at 298 K with steady agitation (200 rpm). The contact times for kinetic studies were 5, 15, 20, 30, 45, 60, 90, 120, 180,and 240 min.

For the pH experiments, the initial concentration was 110 mg/L. The pH value was changed in the range of (3 -10) using 1 M HCl or 1 M NaOH for pH adjusting.

For the effect of bentonite dosage on the CIP adsorption, dosage was varied from 1 to 20 g/L.

The effect of temperature was studied at three temperature values (298, 308, and 318 K) by using a water shaker bath. The experimental procedures were the same as those mentioned above and the temperature was controlled.

UV spectrophotometer (UV-1700, SHIMADZU) was used for following CIP concentrations in the residual solutions at 279 nm wavelength. The amount of antibiotic adsorbed on the bentonite (q_t) was calculated from the equation (1) [12]:

$$q_t = \frac{C_0 - C_t}{m} \times V \ldots (1)$$

Where q_t (mg/g) and C_t (mg/L) are the CIP amount adsorbed and the CIP concentration in solution at

specific time, respectively; C_0 (mg/L) is the initial concentration of CIP; V (L) is the volume of CIP solution and m (g) is the mass of adsorbent/bentonite. The removal percentage (R) was calculated using equation (2) [12]:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \ldots(2)$$

Error Analysis

For the purpose of assessing and comparing the performance of isotherm models, root-mean-square error (RMSE) was also assessed from the equation (3) [16]:

$$RMSE\% = \sqrt{\frac{1}{n}\sum_{i=0}^{n}(\frac{q_{exp}-q_{calc}}{q_{exp}} \times 100)^2} \quad \ldots(3)$$

Where q_{exp} is the value of q_e observed in the experiment, q_{calc} is the value of q_e predicted by the model and n is number of data.

Results and Discussion:

Effect of Contact Time

Adsorption kinetic studies are considered as one of the substantial methods for clarifying the efficiency of an adsorption process and assessing
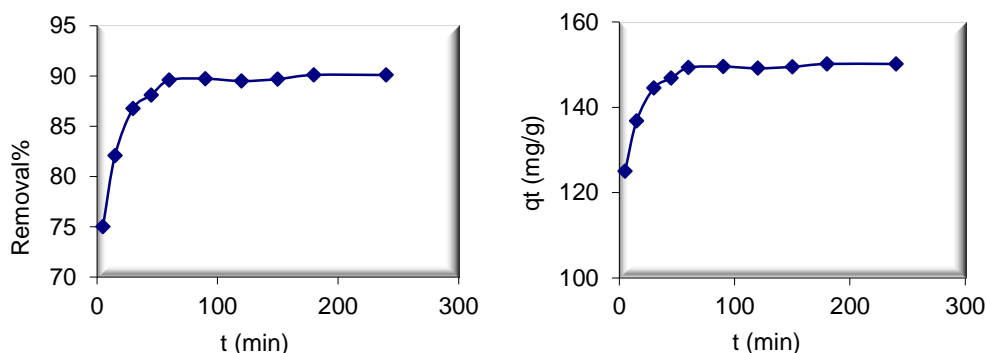
the time required for the complete process. The contact time was changed in the range of (5-240 min). It can be noticed from Fig.2, which shows the effect of time on the removal of CIP, that the initial adsorption rate was rapid and gradually decreased as a result of the reduced number of active sites along the time. The adsorption amount of CIP increased quickly to achieve a maximum adsorption at about one hour of contact time. Therefore, one hour was chosen as the optimum contact time or equilibrium time at which the adsorbed CIP amount is the maximum adsorption capacity of bentonite under the same conditions mentioned above [17]. The removal percentage of CIP increased from 75.01% to 89.5 % when contact time increased from 5 min to 60 min, and stayed unchanged for 24 hours.

The comparatively high removal of CIP is explained by the abundant number of vacant adsorption sites for CIP adsorption on bentonite. At certain point, no more CIP is removed from solution, as the desorbed CIP amount is in equilibrium with that being adsorbed.

Figure 2. Effect of contact time [at pH 5.5, V= 50 ml, m= 0.15 g, CIP$_{initial}$= 500 mg/L, particle size (53-100μm), T= 298 K]

Adsorption Kinetics Models

For the purpose of more evaluation of the CIP adsorption kinetics on the bentonite and characterizing the adsorption process, pseudo-first-order, pseudo-second-order kinetic models, were employed to fit the experimental data [10].

Lagergren Pseudo-first-order Kinetics

The pseudo-first order equation has the following linear form (equation 4) [5, 12, 18]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \ldots(4)$$

Where k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption, q_e and q_t (mg/g) are the amount of adsorbed CIP on adsorbent at equilibrium and at time t, respectively. The validity of the pseudo-first-order model is determined by comparing the calculated adsorption capacity ($q_{e,calc}$) with the experimental value ($q_{e,exp}$). The k_1

and ($q_{e,calc}$) values can be obtained from the slope and intercept of the linear plot of ln $(q_e - q_t)$ vs.t, respectively [5, 19].

Pseudo-second-order Model

The pseudo-second order equation has the following linear form (equation 5) [5, 12, 18]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots(5)$$

$$h = k_2 q_e^2 \ldots(6)$$

Where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption, h (mg/g min) is the initial adsorption rate, q_e and q_t (mg/g) are the amount of adsorbed CIP on adsorbent at equilibrium and at time t, respectively. The linear plot of t/q_t vs. t enables to obtain k_2 and ($q_{e,calc}$). The pseudo-second-order model suggests that the rate-limiting step may be chemical adsorption with

sharing or exchange of electrons between adsorbent and adsorbate [20-22].

The parameters for mentioned models are listed in Table 3. The pseudo-second-order model had a higher value of correlation coefficient (Fig.3). Furthermore, the theoretical value of q_e was very close to the experimental q_e in the pseudo-second-order model, unlike the first-order model where the two values were significantly different, so it can be concluded that the reaction was not a first-order one despite of the high correlation coefficient [19, 23]. In conclusion, the above results suggested that the adsorption process was well represented by the pseudo-second-order model, which signified that chemisorption might be the main rate-limiting step of the adsorption process.
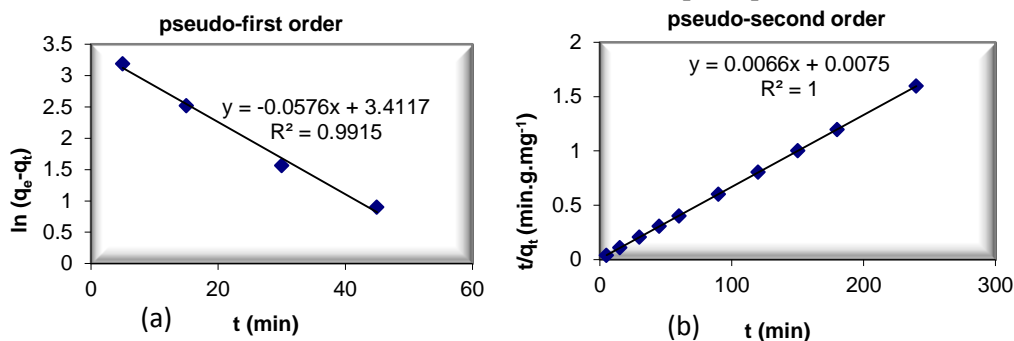

Figure 3. (a) pseudo-first-order, (b) pseudo-second-order kinetic models for the CIP adsorption on Aleppo bentonite surface

Table 3. the kinetic parameters for pseudo-first-order and pseudo-second-order models

Models	Parameters	Value
pseudo-first-order	$q_{e,calc}$ (mg/g)	**33.075**
	k_1 (min^{-1})	**0.0644**
	R^2	**0.99**
pseudo-second-order	$q_{e,calc}$ (mg/g)	**151.5**
	k_2 (g/mg min)	**0.0058**
	R^2	**1**
	h= (mg/g min)	**133.33**

Effect of pH

Among the most critical factors, pH is affecting the adsorption process due to its effect on both the properties of the adsorbent surface and ionic forms of adsorptive in solution. The influence of pH on CIP adsorption onto Aleppo bentonite was assessed at different pH values (3-10) with an initial CIP concentration (110 mg/L). According to the solubility results in previous studies, the CIP does not precipitate at all pH values [24].

The CIP molecule, as mentioned above (Fig.1), has two acid dissociation constants / pKa (6.1 and 8.7) and therefore, there are three potential ion forms in solution at different pH values [21], as the protonation-deprotonation reactions that take place controling these forms. So, CIP can be present as cation (CIP$^+$), zwiterion (CIP$^\pm$), or anion (CIP$^-$) under various pH values (Fig. 4a) [14, 24]. In an acidic solution with pH < 6.1, the protonation of the amine group will allow CIP molecules to exist mainly as cations (CIP$^+$) [25]. At pH > 8.7, CIP molecules are found as anions (CIP$^-$) as a result of the carboxylic group deprotonation. When the pH is in the range of 6.1 - 8.7, zwitterions forms of CIP molecules prevail in the aqueous solution, which were confirmed by many studies [25-27], due to the balance between the charges of the two groups; the negatively charged carboxylate with the protonated positively charged amine group. The obtained results showed, as can be noticed from Fig.4b, that CIP adsorption was very high at low pH values, which can be interpreted by the presence of CIP species in their cationic form preferring the adsorption on negative charged surface of bentonite. Many studies have reported cation exchange as a likely mechanism for CIP adsorption onto montmorillonites [24, 28]. The highest adsorbed amount was obtained at pH=6, due to presence of CIP$^+$. Indeed, these cationic forms are existed in high concentration at low pH value, but apparently the competition between CIP$^+$ and the H$^+$ for the adsorption sites on the bentonite, made the adsorption lower than the one obtained at pH 6 [24]. The decrease in CIP adsorption after a pH of 6 could be explained by the presence of the zwiterionic and anionic forms of CIP which resulted in repulsive interactions with the bentonite negative surface. At pH=10, there were mainly CPX$^-$ anions in the solution which showed the lowest adsorption.

It is worth mentioning that the major constituent of adsorbent/ Aleppo bentonite (montmorillonite), has two charges, permanent negative charge exhibited by faces (basal planes) which arises from the isomorphic substitution within the adsorbent particles, and variable pH-dependent charge exhibited by the amphoteric edge surfaces [29]. There is a specific pH at which the net charge on these amphoteric surfaces is zero, which is called "point of zero net proton charge". This point was measured

for Aleppo bentonite in previous study, [15] and found to be 8.7 (Table 1). In fact, these edge surfaces constitute a small fraction of the whole surface area and the relative magnitude of this charge is low and of little importance for cation exchange which is the

proposed mechanism by many researchers for CIP sorption onto montmorillonite [25, 30]. Accordingly, the different CIP species at different pH values would be the dominant factor affecting CIP removal.
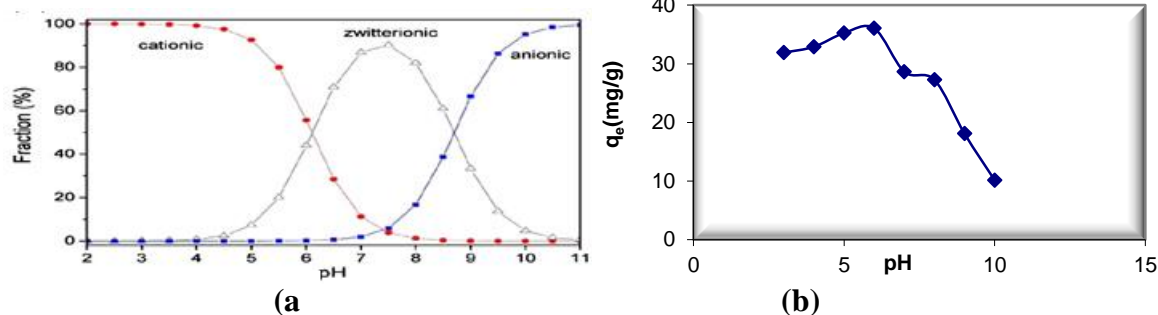

(a) **(b)**

Figure 4. (a) CIP ionic forms at different pH values (b) Effect of pH [V= 50 ml, m= 0.15 g, CIP$_{initial}$= 110 mg/L, particle size (53-100µm), T= 298 K]

Effect of Adsorbent Dosage

The effect of bentonite dosage on CIP adsorption was investigated at various bentonite doses [0.05, 0.1, 0.125, 0.15, 0.2, 0.25, 0.3, 0.5, 0.75, and 1g/50ml] under the same experimental conditions [at pH 5.5, V= 50 ml, CIP$_{initial}$= 500 mg/L, particle size (53-100µm), T= 298 K], in order to find the optimum amount of adsorbent bentonite needed to attain the maximum CIP adsorption. The results indicated that the removal percentage increased gradually with increase in the adsorbent dose (Fig. 5). This may be due to the increasing the surface area of Aleppo bentonite leading to get availability of more active sites on its surface [9, 31, 32]. It was also

noticed that the adsorption amount (mg/g) decreased with increase in adsorbent dosage [13], simply because they have an inverse relationship as can be seen in the equation (1) as mentioned above, and the adsorption sites of bentonite at higher dosage was not fully employed in comparison to lower dosage. The better adsorption efficiency was obtained at adsorbent dosage 0.15 g /50 ml. Any significant increase in CIP removal wasn't noticed with the further increase in adsorbent dosage, this may be explained by the overcrowded adsorbent particles, which may cause packed adsorption sites[33].
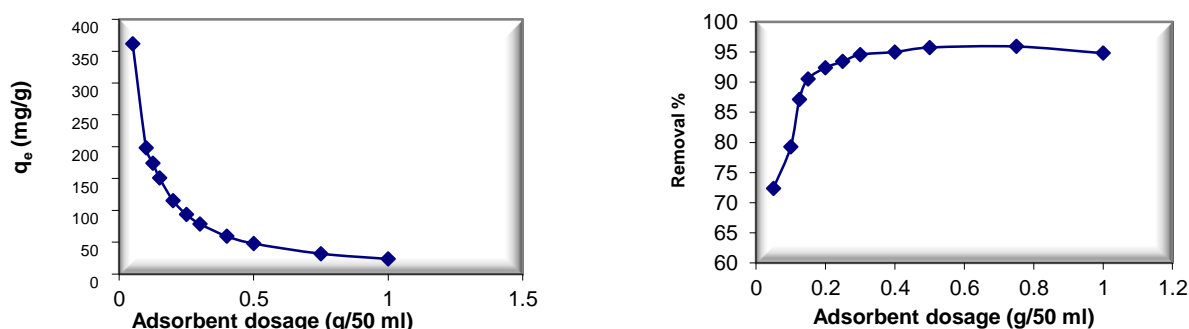

Figure 5. Effect of adsorbent/Aleppo bentonite dosage [at pH 5.5, V= 50 ml, CIP$_{initial}$= 500 mg/L, particle size (53-100µm), T= 298 K]
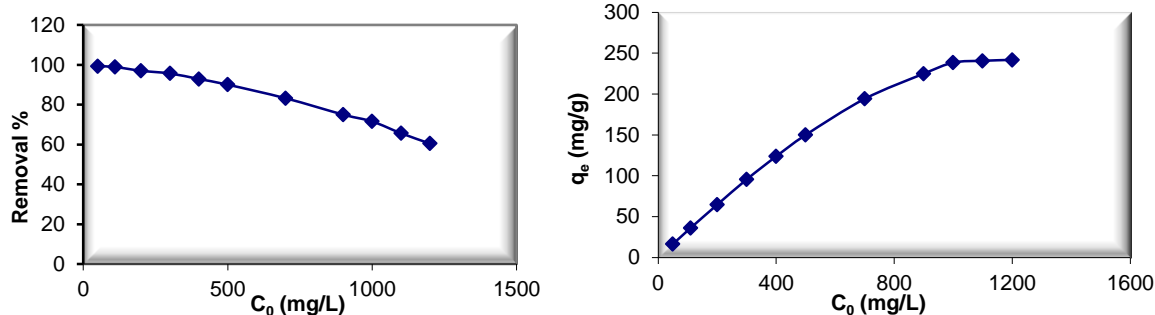
Effect of Initial CIP Concentration

The effect of initial CIP concentration on the removal of CIP was studied in the concentration range (50–1200 mg/L), with similar other experimental conditions. The achieved results showed that CIP removal percentage decreased with increase in CIP concentrations, whereas the adsorption capacities increased (Fig. 6). The removal percentage was 99.3% for initial concentration 50 mg/l and decreased to 74.99%

when the initial concentration was increased to 900 mg/L, according to the equilibrium adsorption amount, q$_e$, increased from 16.55 to 224.97 mg/g. At low initial concentration, there were abundant binding sites on the bentonite surface, and CIP molecules were easily adsorbed on the highly available adsorption sites, whereas at higher initial concentration, the adsorption sites were less available as more binding sites were occupied causing a decrease in CIP removal [34-35]. It was

noticed that q_e values stayed almost unchanged when the initial concentration was greater than 900 mg/L, as the residual binding sites on bentonite

were almost completely occupied [35]. Similar findings were obtained in previous studies [9, 20, 35, 36].

Figure 6. Effect of Initial CIP concentration [at pH 5.5, V= 50 ml, m= 0.15 g, particle size (53-100μm), T= 298 K]

Effect of Ionic Strength

The process of CIP adsorption on montmorillonite (the main component of Aleppo bentonite), seems to be dependent on cation exchange according to previous studies [24, 28, 37]. The effect of ionic strength on CIP adsorption was investigated using electrolyte solution (NaCl) at different concentrations (0-500mM). The effect of NaCl concentrations on CIP adsorption onto Aleppo bentonite is shown in Fig.7.

The results showed that the presence of NaCl electrolyte reduced Aleppo bentonite efficiency in removing CIP, which could be explained by the competition between the cationic form of CIP, which was present in solution at pH< 6.1, and cations from NaCl, for adsorption sites on Aleppo bentonite [36]. The removal percentage of CIP decreased from 89.9% (0 M NaCl) to 53% (at 0.5 M NaCl). The decreased affinity between bentonite and CIP molecules noticed in the presence of NaCl might be influenced by ion exchange or outer-sphere surface complexation mechanism, as these cations (Na^+) are more favorable for adsorption due to their small size compared to CIP molecules [18]. Similar results were reported in other studies [9, 38-40].
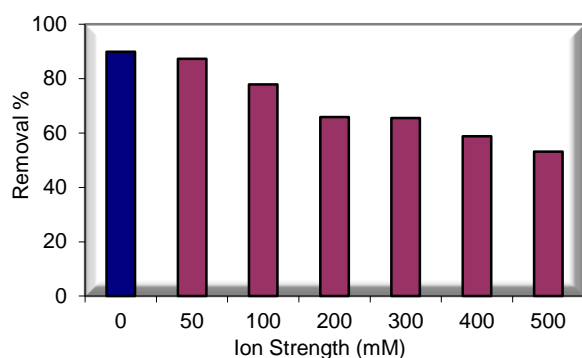
Figure 7. Effect of Ionic Strength [at pH 5.5, V= 50 ml, m= 0.15 g, CIP$_{initial}$= 500 mg/L, particle size (53-100μm), T= 298 K]

Effect of Temperature

The effect of temperature on CIP adsorption onto Aleppo bentonite was studied by choosing three temperature values (298, 308 and 318 K). The adsorption capacities at each temperature value were calculated, and the results listed in Fig.8, showed that there was no considerable influence of temperature on CIP removal for lower initial concentrations (between 50-500 mg/L), but the CIP removal might be facilitated at higher temperature for higher initial concentrations, and maximum removal was attained at 318 K, indicating the endothermic nature of CIP adsorption. This behavior may be interpreted by the increase in kinetic energy of CIP molecules which causes increasing the frequency of interfere between the bentonite and CIP molecules that promoting its adsorption on bentonite surface [41].
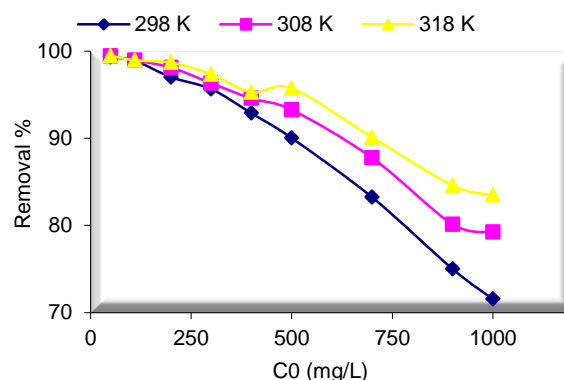
Figure 8. The effect of temperature [at pH 5.5, V= 50 ml, m=0.15 g, particle size (53-100μm)]

CIP Adsorption Isotherms

There are various kinds of attractive forces, act in harmony, between adsorbent and adsorbate molecules in the adsorption process, but one may be more prevalent in a special case [42]. An adsorption isotherm is to describe the relationship between the equilibrium concentration of the adsorptive and the

amount of adsorbate on the adsorbent surface at steady temperature [29]. It can be noticed from Fig.9 that adsorption isotherm of CIP on bentonite is L-shaped isotherm perceived by high affinity between the adsorbent and the adsorptive molecules at low concentrations, which then decreases with increase in concentration [29].

Experimental isotherm is a useful tool for characterizing the adsorption capacity of different adsorbents and assessing their efficiencies for a given application [43]. The isotherm experimental data were fitted to the linear forms of the most well-known isotherms, Langumair and Freundlich models to understand the possible mechanisms of CIP adsorption on bentonite, and the nature of interaction.
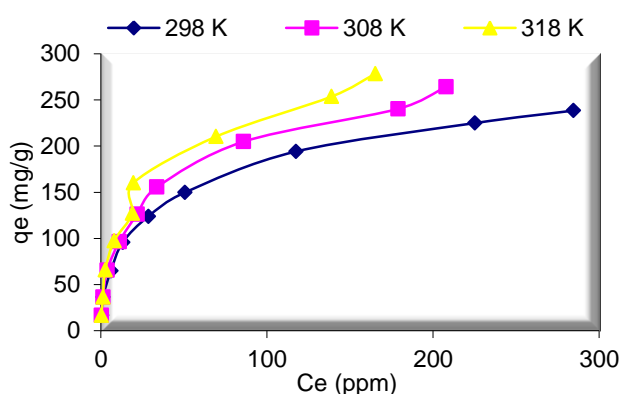
Figure 9. Adsorption Isotherm of CIP on Aleppo bentonite at different temperatures (298. 308 and 318 K) [at pH 5.5, V= 50 ml, m=0.15 g, particle size (53-100μm)]

The Langmuir Model

The Langmuir model assumes homogeneous adsorption with monolayer coverage and uniform energetic adsorption sites. The linear form of Langumair model is presented by (equation 7)[44-47]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad \dots (7)$$

Where q_e (mg/g) is the amount of the CIP adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium CIP concentration in the solution, q_{max} (mg/g) is the constant related to the maximum monolayer adsorption capacity, and K_L (L/mg) is the Langumair constant related to the free energy or net enthalpy of adsorption. The constants q_{max} and K_L are obtained from the slope and intercept of the linear plot of C_e/q_e versus C_e, respectively.

The favorability of adsorption can be determined by the dimensionless parameter 'R_L' which is calculated using Langmuir constant by the (equation 8)[44, 48]:

$$R_L = \frac{1}{1 + K_L C_0} \dots (8)$$

Where C_0 (mg/L) is the initial concentration of adsorbate and K_L (L/mg) is the Langmuir constant described above. The R_L parameter is considered as more dependable indicator of the adsorption process. It indicates favorable adsorption $(0<R_L<1)$, unfavorable adsorption $(R_L>1)$, linear adsorption $(R_L=1)$ and irreversible adsorption $(R_L= 0)$ [36, 44].

The Freundlich Model

The Freundlich isotherm model is proper for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption. The Freundlich model in linear form is presented by (equation 9) [44, 47, 49]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (9)$$

Where K_f (mg/g) is the constant related to the adsorption capacity and n is the experimental parameter related to the intensity of adsorption. The 1/n value suggests favorable isotherm $(0 <1/n< 1)$, unfavorable $(1/n>1)$, or irreversible $(1/n=0)$. The values of K_f and 1/n can be determined from the intercept and slope of linear plot of log q_e versus log C_e, respectively.

The results in Table 4 and, Figs. 10 and 11, revealed the applicability of both the Langmuir and Freundlich models with a high correlation coefficients (0.99 and 0.98 respectively), indicating that the CIP adsorption on Aleppo bentonite may be complex interactions [50-52]. But there is a preference for Langmuir model which represented the adsorption process better than the Freundlich model as the RMSE value for the Langmuir model (1.34) is much lower than that for Freundlich model (11.766). The favorability of the adsorption process according to Langmuir model was assessed by R_L parameter which was found to be in the range of (0.01-0.27) that suggesting a favorable adsorption process and strong binding between CIP molecules and Aleppo bentonite [29, 34], and the maximum monolayer adsorption capacity was (q_{max}= 243.9 mg/g) at 298 K. Furthermore, by applying the Freundlich isotherm, it can be observed that the slope (1/n) values were (0 <0.39 - 0.42< 1), confirming the favorable adsorption process, and the high value of Freundlich constant K_f indicated the high adsorption capacity for the bentonite adsorbent.
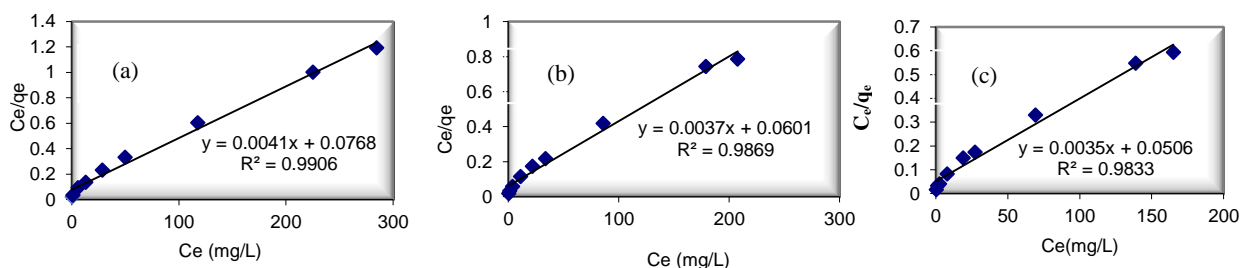
Figure 10. Linearized Langmuir isotherm model for CIP adsorption on Aleppo bentonite surface at (a) 298 K, (b) 308 K and (c) 318 K
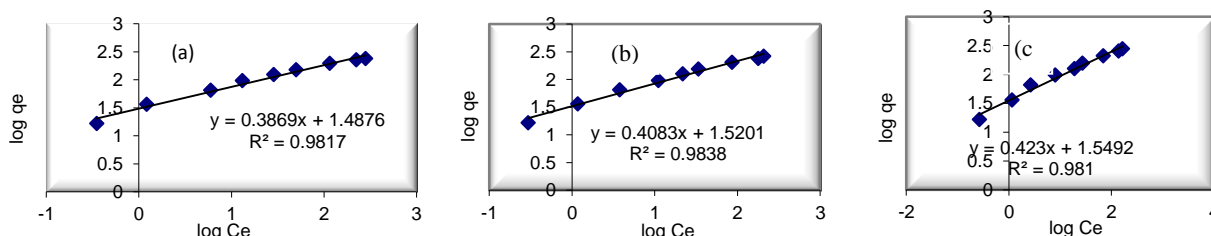

Figure 11. Linearized Freundlich isotherm model for CIP adsorption on Aleppo bentonite surface at (a) 298 K, (b) 308 K and (c) 318 K

Table 4. Parameters of Langmuir and Freundlich adsorption isotherm models for CIP adsorption on Aleppo bentonite at different temperatures

T (K)	Langmuir				Freundlich			
	q_{max}	K_L	R^2	RMSE	K_f	n	R^2	RMSE
	(mg/g)	(L/mg)		%				%
298	243.9	0.053	0.99		30.732	2.58	0.98	
308	270.27	0.0615	0.986	1.34	33.12	2.449	0.983	11.766
318	285.71	0.0691	0.983		35.416	2.364	0.981	

Thermodynamics of CIP Adsorption

Thermodynamic parameters are important guide in adsorption process. All of Gibbs free energy ($\Delta G°$ J/mol), enthalpy change ($\Delta H°$ J/mol) and the entropy change ($\Delta S°$ J/mol K) are calculated in this study. The free energy of adsorption ($\Delta G°$) is calculated according to (equation 10) [11, 35]:

$$\Delta G° = -RT \ln K \quad … (10)$$

Where R is the gas constant (8.314 J/mol.K), T is the reaction temperature in Kelvin, K is the adsorption Langmuir constant. The relation of $\Delta G°$ to The enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) of adsorption is given in (equation 11):

$$\Delta G° = \Delta H° - T\Delta S° \quad ….(11)$$

By substituting Eq. 10 into Eq.11, Vant Hoff equation (Eq 12) is resulted [53]:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad ….(12)$$

$\Delta H°$ and $\Delta S°$ can be calculated from the slope and the intercept of the plots of ln K vs. 1/T (Fig. 12) [35, 54].

The values of thermodynamic parameters obtained are listed in Table 5. The negative values of the free energy changes $\Delta G°$ indicated that the adsorption is spontaneous process [55] with a high affinity of CIP on Aleppo bentonite [5, 56]. In addition it decreased slightly with an increase in temperature showing increasing adsorption. The positive value of the enthalpy change $\Delta H°$ confirmed the endothermic process of CIP adsorption on Aleppo bentonite [21, 55]. Furthermore, the value of $\Delta H°$ indicated that CIP adsorption on bentonite is physical process, as it is less than 40 kJ/mol [21, 35]. However, there might be a conflict between thermodynamics study and kinetics one which indicated that chemisorption might be the main rate-controlling step of the adsorption process, as the adsorption was best fit by the pseudo-second-order kinetic model, but in general, adsorption is a complex multistep process, and a kinetic study provide important insights of the mechanisms, but it is not enough to describe this complex process and confirm the chemisorption mechanism, therefor, further isotherms and thermodynamics evaluations must be done. In addition. it is always remarkable that both physical and chemical forces can, and often do, occur together in the adsorption process [29]. Indeed, there are many previous studies that have faced such opposite results without mentioning any explanation of these results, but it was proposed and reported by

a few studies that pseudo-second-order model is valid for both chemical and physical process [57].

As cation exchange mechanism was previously reported for CIP adsorption on montmorillonite, It should be noticed that ion exchange is usually referred to as a chemical reaction although it is not in the usual concept [30], as it falls within electrostatic outer-sphere complexes which belong to the physical forces [29].

The entropy change (ΔS^o) is helpful in describing the randomness during adsorption at the solid/liquid interface. The positive value of the entropy change ΔS^o signified that there is an increase in the randomness in the adsorption system, confirming the favorable adsorption of CIP onto bentonite [5, 35].

Table 5. Adsorption Energies obtained from Langmuir model

T (K)	K_L (L/mg)	K_L (L/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
298	0.053	17561.073	-24.1725		
308	0.0651	20377.47	-25.3646	10.486	0.1162
318	0.0691	22895.66	-26.4942		
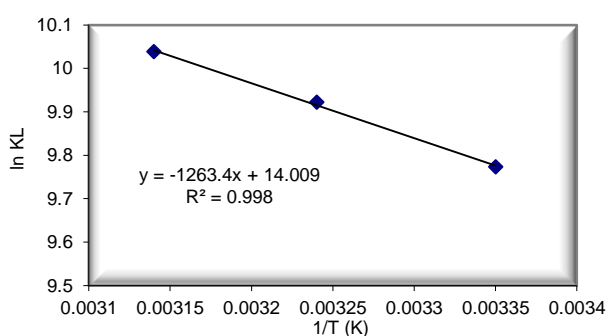
Figure 12. The fitting plot of thermodynamic model using Langmuir constant

In order to assess the efficiency and feasibility of Aleppo bentonite in CIP removal from aqueous solution, it may be appropriate to compare its maximum adsorption capacity value with those reported in previous studies for other adsorbents. A comparison between Aleppo bentonite and other adsorbents with regard to their CIP adsorption capacities is presented in Table 6. Aleppo bentonite, based on this comparison, has much higher adsorption capacity for CIP than the most of the studied adsorbents, and it can be a good choice as an efficient, low cost and eco-friendly adsorbent.

Table 6. CIP maximum adsorption capacities for different adsorbents

Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Montmorillonite	330	(25)
Modified coal fly ash	1.55	(20)
chemically prepared carbon (wet and dry)	133.3&125	(27)
Activated carbon	231±6	(26)
Carbon xerogel	112±8	(26)
Carbon nanotubes	135±2	(26)
Bentonite	147.06	(36)
Activated carbon	77	(5)
Fe_3O_4/C	90.1	(55)
Modified flax noil cellulose	238.7	(21)
Hazelnut based activated carbon	65	(44)
Bamboo charcoal	36.0	(40)
Red mud	25.2	(31)
Red mud	25.44	(32)
Activated red mud	41.5	(32)
KMS-1/L-Cystein/Fe_3O_4(KCF)	181.32	(23)
Schorl	8.5	(54)
Biochar (rice straw)	131.58	(22)
Halloysite nanotubes	25.09	(10)
SiO_2 nanoparticle	9.98	(47)
Raw oat hulls	16	(11)
Pretreated oat hulls	83	(11)
Synthesized Nanoceria	49.38	(12)
Jeriva activated carbon (40 ℃)	335.8	(53)
Aluminum-Pillared Kaolin Sodium Alginate Beads /CA-Al-CAB$_s$ (308.15 K)	68.36	(13)
Natural bentonite	126.6	(9)
Acid activated bentonite	305.2	(9)
Bentonite from Aleppo (298 K)	243.9	Present study

Conclusion:

This study revealed that Aleppo bentonite can be an efficient adsorbent for CIP removal from aqueous solution, with a relatively high adsorption capacity (up to 243 mg/g at 298 K) compared to CIP adsorption capacities for the previously studied adsorbents. Batch adsorption experiments conducted to study the various parameters affecting the removal process showed that the optimum contact time, pH of solution and bentonite dosage were 60 minutes, 6 and 0.15 g/50 ml, respectively. The bentonite efficiency in removing CIP decreased from 89.9% to 53.21% with the increase in ionic strength from 0 to 500mM. Kinetic modeling results showed that the CIP adsorption kinetics performance was best characterized by the pseudo second-order model, while the adsorption isotherm data revealed the applicability of both the Langmuir and Freundlich models to the adsorption equilibrium data with preference for the Langmuir isotherm which better represented the adsorption process and the maximum adsorption capacities of CIP were defined as 243.9, 270.27, 285.71 mg/g at 298, 308 and 318 K, respectively. Both values of R_L and 1/n parameters which were found to be in the range of (0.01-0.27) and (0.39-0.42), respectively, indicated the favorable adsorption process. The CIP removal percentages might be facilitated at higher temperature for higher initial concentrations, as the removal percentage increased from 89% to 96.9% when the temperature increased from 298 to 318 K for CIP concentration 500 mg/L. The thermodynamics study for the CIP–Aleppo bentonite system revealed that CIP adsorption process is physical in nature, as the value of $\Delta H°$ was less than 40 kJ/mol. The adsorption process was endothermic and spontaneous indicated by the positive value of $\Delta H°$ and negative values of $\Delta G°$, respectively. The positive value of the entropy change $\Delta S°$ signified an increase in the randomness in the adsorption system at the bentonite-solution interface, confirming the favorable adsorption of CIP onto Aleppo bentonite.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Tishreen University.

Authors' contributions statement:

A.H. and J.H. contributed to the conception of the the research, and supervised the findings of this work. H.S. contributed to the design and implementation of the research, analysis and interpretation of the results, and to the writing of the manuscript.

All authors discussed the results and contributed to the final manuscript

References:

1. Ashiqa A, Adassooriya NM, Sarker B, Rajapaksha AU. Municipal solid waste biochar-bentonite composite for the removal of antibiotic ciprofloxacin from aqueous media. J. Environ. Manag. 2019 April 15; 236: 428-435.
2. Kanakaraju D, Glass BD, Oelgemöller M. Advanced oxidation process-mediated removal of pharmaceuticals from water: A review. J. Environ. Manag. 2018 Aug 1; 219: 189–207.
3. Philip J M, Aravind U K, Aravindakumar CT. Emerging contaminants in Indian environmental matrices–A review. Chemosphere. 2018 Jan; 190: 307–326.
4. Huang X, Zheng J, Liu C, Liu L. Removal of antibiotics and resistance genes from swine wastewater using vertical flow constructed wetlands: Effect of hydraulic flow direction and substrate type. Chem. Eng. J. 2017 Jan 15; 308: 692–699.
5. Genç N, Dogan EC. Adsorption kinetics of the antibiotic ciprofloxacin on bentonite, activated carbon, zeolite, and pumice. Desalination Water Treat. 2015 Sep 25; 53(3): 785-793.
6. Azanu D, Styrishave B, Darko G, Weisser JJ. Occurrence and risk assessment of antibiotics in water and lettuce in Ghana. Sci. Total Environ. 2018 May 1; 622–623: 293–305.
7. Maul JD, Schuler LJ, Belden JB, Whiles MR. Effects of the antibiotic ciprofloxacin on stream microbial communities and detritivorous macro-invertebrates. Environ. Toxicol. Chem. 2006 June; 25 (6): 1598–1606.
8. GENÇ N. Removal of Antibiotic Ciprofloxacin Hydrochloride from Water by KANDIRA STONE: Kinetic Models and Thermodynamic. Global NEST Journal. 2015 June 24; 17 (3): 498-507.
9. Maged A, Kharbish S, Esmael IS, Bhatnagar A. Characterization of activated bentonite clay mineral and the mechanisms underlying its sorption for ciprofloxacin from aqueous solution. Environ Sci Pollut Res Int. 2020 June 10; 27: 32980–32997.
10. Cheng R, Li H, Liu Z, Du C. Halloysite nanotubes as an effective and recyclable adsorbent for removal of law-concentration antibiotics ciprofloxacin. Minerals. 2018 Sep 5; 8(9):387.
11. Movasaghi Z, Yan B, Niu C. Adsorption of ciprofloxacin from water by pretreated oat hulls: Equilibrium, kinetic and thermodynamic studies. Ind Crops Prod. 2019 Jan; 127: 237-250.
12. Rahdar A, Rahdar S, Ahmadi S, Fu J. Adsorption of Ciprofloxacin from Aqueous Environment by Using

Synthesized Nanoceria. ECOL CHEM ENG S. 2019 Jul 18; 26(2): 299-311.

13. Hu Y, Pan C, Zheng X, Liu S, Hu F, Xu L, et al. Removal of Ciprofloxacin with Aluminum-Pillared Kaolin Sodium Alginate Beads/CA-Al-CAB: Kinetics, Isotherms, and BBD Model. Water J. 2020; 12(3): 905.

14. Jalil ME, Baschini M, Sapag K. Removal of Ciprofloxacin from Aqueous Solutions Using Pillared Clays. Materials. 2017 Nov 23; 10 (12): 1345.

15. Hicham A, Hussein J, Siba H, Contribution in Characterization of Bentonite from Aleppo. Tishreen University Journal for Research and Scientific Studies - Basic Sciences Series TUJ-BA. 2020 June; 42(2).

16. Maheshwari M, Vyas RK, Sharma M. Kinetics, equilibrium and thermodynamics of ciprofloxacin hydrochloride removal by adsorption on coal fly ash and activated Alumina. Desalination Water Treat. 2013 Mar 28; 51 (37–39): 7241-7254.

17. Chidi O, Nnanna OU, Ifedi OP. The Use of Organophilic Bentonite in the Removal Phenol from Aqueous Solution: Effect of Preparation Techniques. Mod Chem Appl. 2018 April 30; 6(2).

18. Rizzi V, Gubitosa J, Fini P, Romita R, Agostiano A, Nuzzo S, et al. Commercial bentonite clay as low-cost and recyclable natural adsorbent for the Carbendazim removal/recover from water: overview on the adsorption process and preliminary photodegradation considerations. Colloids Surf. A Physicochem. Eng. Asp. 2020 May 29; 602: 125060.

19. Ghaedi M, Kokhdan SN. Oxidized multiwalled carbon nanotubes for the removal of methyl red (MR): Kinetics and equilibrium study. Desalin. Water Treat. 2012 Nov 21; 49 (1-3): 317–325.

20. Zhang CL, Qiao GL, Zhao F, Wang Y. Thermodynamic and kinetic parameters of ciprofloxacin adsorption onto modified coal fly ash from aqueous solution. J. Mol. Liq. 2011; 163 (1): 53–56.

21. Hu D, Wang L. Adsorption of ciprofloxacin from aqueous solutions onto cationic and anionic flax noil cellulose. Desalin Water Treat. 2016 May 9; 57 (85).

22. Zeng ZW, Tan XF, Liu YG, Tian SR, Zeng GM, Jiang LH, et al. Comprehensive Adsorption Studies of Doxycycline and Ciprofloxacin Antibiotics by Biochars Prepared at Different Temperatures. Front. Chem. 2018 Mar 27; 6:80.

23. Wang YX, Gupta K, Li JR, Yuan B. Novel Chalcogenide based magnetic adsorbent KMS-1/L-Cystein/Fe$_3$O$_4$ for the facile removal of ciprofloxacin from aqueous solution, Colloids Surf. A Physicochem. Eng. Asp. 2018 Feb 5; 538: 378-386.

24. Roca Jalil, M.E, Baschini MT, Sapag MK. Influence of pH and antibiotic solubility on the removal of ciprofloxacin from aqueous media using montmorillonite. Appl. Clay Sci. 2015 Sep; 114: 69–76.

25. Wang CJ, Li Z, Jiang WT, Jean JS, Liu CC. Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite . J Hazard Mater B. 2010 Nov 15; 183 (1-3): 309-314.

26. Carabineiro SAC, Thavorn-amornsria T, Pereiraa MFR, Serp P, Figueiredo JL. Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin. Catal. Today. 2012 June 1; 186 (1): 29-34.

27. El-Shafey SI, Al-Lawati H, Al-Sumri AS. Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets. J Environ Sci (China). 2012 Sep; 24 (9): 1579-1586.

28. Lagaly G, Ogawa M, Dékány I. Clay mineral-organic interactions. Dev. Clay Sci. 2013 Dec; 5: 437-505.

29. Sparks DL. Environmental Soil Chemistry. Second ed. USA: Academic Press; 2003.

30. McBride MB. Environmental Chemistry of Soils. Oxford: Oxford University Press; 1994.

31. Balarak D, Mostafapour FK, Joghataei A. Kinetics and mechanism of red mud in adsorption of ciprofloxacin in aqueous solution. Biosci. Biotechnol. Res. Commun. 2017; 10 (1): 243-250.

32. Balarak D, Joghataei A, Mostafapour F, Bazrafshan E. Ciprofloxacin antibiotics removal from effluent using heat-acid activated red mud. J. Pharm. Res. Int. 2018 Jan; 20(5): 1-8.

33. Gaur N, Kukrega A, Yadav M, Tiwari A. Adsorptive removal of lead and arsenic from aqueous solution using soya bean as a novel biosorbent: equilibrium isotherm and thermal stability studies. Applied water science. 2018 June 18; 8(98).

34. Wang FY, Wang H, Ma JW. Adsorption of Cadmium (II) Ions from Aqueous Solution by a New Law-Cost Adsorbent – Bamboo Charcoal. J Hazard Mater. 2010 May; 177 (1-3): 300-306.

35. Zhang JX, Zhou QX, Li W. Adsorption of enrofloxacin from aqueous solution by bentonite. Clay Miner. 2013 Sep; 48 (4): 627-637.

36. Genc N, Dogan EC, Yortsever M. Bentonite for ciprofloxacin removal from aqueous solution. Water Sci. Technol. 2013; 68 (4): 848-855.

37. Wu Q, Li Z, Hong H, Yin K. Adsorption and intercalation of ciprofloxacin on montmorillonite. Appl. Clay Sci. 2010 October; 50 (2): 204–211.

38. Akpomie KG, Fayomi OM, Ezeofor CC, Sha'Ato R. insights into the use of metal complexes of thiourea derivatives as highly efficient adsorbents for ciprofloxacin from contaminated water. Trans R Soc. 2019 Jul 12; 74 (2):180-188.

39. Xu X, Liu Y, Wang T, Ji H, Chen L, Li S, et al. Co-adsorption of ciprofloxacin and Cu(II) onto titanate nanotubes: speciation variation and metal-organic complexation. J Mol Liq. 2019 October 15; 292:111375.

40. Wang L, Chen G, Ling C, Zhang J. Adsorption of Ciprofloxacin onto bamboo charcoal: effects of pH, salinity, cations and phosphate. Environ. Prog. Sustain. Energy. 2017 Feb; 36 (4).

41. Hefne JA, Mekhamer WK, Alandis NM, Aldayel O. Removal of Silver (I) from aqueous Solutions by Natural Bentonite. JKAU: Sci. 2010 Jan; 22 (1): 155-176.

42. Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochem. 1999 July; 34 (5), 451-465.

43. HO YS, McKAY G. The Kinetics of Sorption of Basic Dyes from Aqueous Solution by Sphagnum Moss Peat. Can J Chem Eng. 1998 Aug;76 (4): 822-827.

44. Balarak D, Mostafapour FK, Azarpira H. Adsorption Kinetics and Equilibrium of Ciprofloxacin from Aqueous Solutions Using Corylus avellana (Hazelnut) Activated Carbon. Br. J. Pharm. Res. 2016 Sep 26; 13(3): 1-14.

45. Hameed BH. Evaluation of papaya seed as a novel non-conventional low-cost adsorbent for removal of methylene blue. J Hazard Mater. 2008 May 28; 162 (2-3):939-944.

46. Rizzi V, Romanazzi F, Gobitosa J, Fini P, Romita R, Agostiano A, et al. Chitosan Film as Eco-Friendly and Recyclable Bio-Adsorbent to Remove/Recover Diclofenac, Ketoprofen, and their Mixture from Wastewater. Biomolcules. 2019 Oct 5; 9(10): 571.

47. Mostafapour FK, Balarak D, Baniasadi M. Removal of ciprofloxacin from Pharmaceutical Wastewater by adsorption on SiO_2 nanoparticle. J. Pharm. Res. Int. 2019 Mar; 25 (6): 1-9.

48. Ponnusami V, Vikram S, Srivastava SN. Guava (Psidium guajava) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. J Hazard Mater. 2008 Mar 21; 152 (1): 276–286.

49. Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, et al. The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies. J. Colloid Interface Sci. 2015 July; 7: 16–19.

50. Wang Y, Yang B, Wang H, Song Q. Removal of ciprofloxacin from aqueous solution by a magnetic chitosan grafted graphene oxide composite. J. Mol. Liq. 2016 Oct; 222: 188-194.

51. Ziaei E, Mehdinia A, Jabbari A. A novel hierarchical nanobiocomposite of graphene oxide-magnetic CS grafted with mercapto as a solid phase extraction sorbent for the determination of mercury ions in environmental water samples. Anal. Chim. Acta. 2014 Aug; 850: 49-56.

52. Carabineiro SAC, Thavorn-Amornsri T, Pereira MFR, Figueiredo JL. Adsorption of ciprofloxacin on surface-modified carbon materials. Water Res. 2011 Oct 1; 45: 4583-4591.

53. Carvalho CO, Rodrigues DLC, Lima EC, Umpierres CS. Kinetic, equilibrium and thermodynamic studies on the adsorption of ciprofloxacin by activated carbon produced from Jeriva (Syagrus romanzoffana). Environ Sci Pollut Res Int. 2018 Dec 18; 26(6): 4690-4702.

54. Yin D, Xu Z, Shi J, Shen L. Adsorption characteristics of ciprofloxacin on the schorl: kinetics, thermodynamics, effect of metal ion and mechanisms. J. Water Reuse Desalination. 2018; 8 (3): 350-359.

55. Mao H, Wang S, Lin JY, Wang Z. Modification of a magnetic carbon composite for ciprofloxacin adsorption, J. Environ. Sci. 2016 Nov 15; 49: 179-188.

56. Moradi O, Fakhri A, Adami S, Adami S. Isotherm, thermodynamic, kinetics, and adsorption mechanism studies of Ethidium bromide by single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube. J. Colloid Interface Sci. 2013 April; 395: 224–229.

57. Baraka A. Adsorptive removal of tartrazine and methylene blue from wastewater using melamine-formaldehyde-tartaric acid resin (and a discussion about pseudo second order model). Desalin Water Treat. 2012 May 15; 44 (1-3): 128-141.

دراسات الحركية والتوازن والترموديناميك لإزالة السيبروفلوكساسين من المحلول المائي باستخدام البنتونايت الحلبي

هشام أبظلي[1]   حسين جنيدي[2]   صبا حاتم[3]

[1] قسم الكيمياء،كلية العلوم، جامعة تشرين، اللاذقية، سورية .

[2] قسم هندسة النظم البيئية، المعهد العالي لبحوث البيئة، جامعة تشرين، اللاذقية، سورية.

[3] قسم الكيمياء البيئية، المعهد العالي لبحوث البيئة، جامعة تشرين، اللاذقية، سورية.

الخلاصة:

درست الفعالية الامتزازية للبنتونايت الحلبي في إزالة السيبروفلوكساسين من محلوله المائي باستخدام تجارب الامتزاز بالطريقة الساكنة. وقد جرى تقييم تأثير عدد من العوامل على عملية الامتزاز متضمنة كلاً من زمن التماس وpH المحلول وكمية المادة المازة والشدة الأيونية ودرجة الحرارة، حيث أظهرت النتائج أن الشروط المثلى لكل من زمن التماس، pH المحلول، وكمية البنتونايت الحلبي، هي 60 دقيقة، 6، و0.15 غ/50 مل على التوالي. وقد انخفضت فعالية البنتونايت في إزالة السيبروفلوكساسين من 89.9% إلى 53.21% مع زيادة الشدة الأيونية من 0 إلى 500 ميللي مول، كما ازدادت من 89% إلى 96.9% مع ارتفاع درجة الحرارة من 298 إلى 318 كلفن. أظهرت دراسات الحركية قوة العلاقة الارتباطية في نموذج الرتبة الثانية الكاذبة، كما أظهرت دراسة إيزوثيرمات الامتزاز عبر ملاءمة نموذجي لانغمير وفريندليش مع البيانات التجريبية نتائج ملاءمة جيدة بالنظر للقيم العالية لمعاملي الارتباط (0.99 و0.98 على التوالي) مع ملاءمة أفضل لنموذج لانغمير حيث كانت قيمة الخطأ التجريبي RMSE من أجل نموذج لانغمير (1.34) أقل بكثير منها في نموذج فريندليش (11.766). وقد تم حساب الدوال الترموديناميكية لجملة البنتونايت الحلبي- السيبروفلوكساسين، حيث تشير القيمة الموجبة لتغير الأنتالبية والقيم السالبة لتغير الطاقة الحرة إلى أن الامتزاز ماص للحرارة وتلقائي على التوالي. استناداً إلى هذه النتائج، يمكن القول إن البنتونايت الحلبي يمتلك فعالية امتزاز عالية للسيبروفلوكساسين مع سعة امتزاز بلغت 243.9 مغ/غ عند درجة الحرارة 298 كلفن، لذا يمكن اعتباره خياراً جيداً كمادة مازة فاعلة، منخفضة الكلفة وصديقة للبيئة لمعالجة الدفوق الحاوية على السيبروفلوكساسين.

الكلمات المفتاحية: امتزاز، بنتونايت حلبي، سيبروفلوكساسين، إيزوثيرمات، دراسات الحركية