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Cephalexin adsorption from aqueous solutions by biochar prepared from plantain wood: equilibrium and kinetics studies

Dariush Naghipour[a,b], Abdoliman Amouei[c,d,*] Mehdi Estaji[a], Kamran Taghavi[a,b], Ahmad Allahabadi[e]

[a]*Research Center of Health and Environment, Guilan University of Medical Sciences, Rasht, Iran, emails: dr.naghipour@gmail.com (D. Naghipour), abtinestaji@yahoo.com (M. Estaji), k.taghavi@gums.ac.ir (K. Taghavi)*
[b]*Department of Environmental Health, Guilan University of Medical Sciences, Rasht, Iran*
[c]*Environmental Health Research Center (EHRC), Health Research Institute, Babol University of Medical Sciences, Babol, I.R. Iran, Tel. +98 22344366; Fax: +98 22334367; email: iamouei1966@gmail.com (A. Amouei)*
[d]*Social Determinants of Health Research Center, Health Research Institute, Babol University of Medical Sciences, Babol, Iran*
[e]*Department of Environmental Health, Sabzevar University of Medical Sciences, Sabzevar, Iran, email: allahabadya@medsab.ac.ir*

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ABSTRACT

The biochar prepared from plantain wood was used to remove Cephalexin antibiotic from aqueous solutions. The effect of some operational parameters such as pH (1–10), contact time (0–120 min), Cephalexin concentration (10, 50, and 100 mg/L), adsorbent dose (0.2–4 g/L), and temperature (10°C–60°C) was evaluated and optimized. The micropore surface area and micropore volume of the biochar were determined to be 896 m^2/g and 0.472 cm^3/g, respectively. In the optimum conditions (pH = 6.7, initial concentration of Cephalexin = 50 mg/L, contact time = 60 min, and adsorbent dose = 2 g/L), the removal efficiency was 88.5%. The adsorption isotherm of Cephalexin follows the Langmuir model. Thermodynamic results revealed that the process was endothermic, and the kinetics study confirmed that the adsorption followed the pseudo-second-order reaction. The results of this study indicate that the biochar prepared from the plantain wood can be used as a suitable and cost-effective technology for the removal of Cephalexin from aqueous solutions with high removal efficiency.

Keywords: Plantain wood; Adsorption; Cephalexin; Wastewater treatment; Biochar

1. Introduction

Antibiotics are widely used in the treatment of diseases in humans, animals, and plants [1,2]. These compounds are the most widely used pharmaceutical compounds in different countries of the world. According to European Union research, the annual consumption of antibiotics in Europe in the early 2000s was over 10,000 tons [3]. However, this amount is only the consumption of antibiotics in the medical sector and in the treatment of diseases in humans; if the antibiotics consumption in the veterinary and agricultural sector is added; the amount of these compounds will increase dramatically [4,5]. Approximately 30%–90% of the antibiotics consumed in the human body and animals are not completely metabolized and enter the environment as metabolites through the urine and stool [6]. Today, antibiotics are found in several environments such as urban and hospital wastewater, pharmaceutical wastewater, soils, surface water, underground waters, and even in drinking waters [7,8]. These compounds are non-biodegradable and toxic materials [5]. Some of the mutagenic and carcinogenic effects of the antibiotics have been reported in different studies [9,10]. On the other hand,

* Corresponding author.

research shows that the conventional wastewater treatment systems can eliminate only 60%–90% of antibiotics [11,12].

In recent decades, the phenomenon of the resistance of pathogenic bacteria to the antibiotics has also been increasing. Studies show that more than 70% of bacteria are resistant to at least one antibiotic. This phenomenon can lead to the resistance of the pathogenic bacteria in the human body causing undesirable effects on human health through to the inability of antibiotics in the treatment of diseases [13,14].

Cephalexin (CPX) is a major antibiotic of Cephalosporin, which is used for the treatment of a variety of human infections. The chemical formula of this drug is $C_{16}H_{17}N_3O_4S.H_2O$ and its molecular weight is 347.4 g/mol (Fig. 1). Due to reduced solubility and biodegradability of antibiotics, removal of these compounds by conventional biological treatment methods is not feasible [15,16].

Today, various methods are used to purify and remove pharmaceutical compounds, especially antibiotics. These methods include advanced oxidation processes, membrane technologies, biological treatment methods, and adsorption processes [17–19]. Biological purification methods are not able to eliminate antibiotics due to the inability to degrade and eliminate complex and non-degradable organic compounds [20,21]. On the other hand, the use of membrane and advanced oxidation techniques on a large scale is costly [21,22]. Currently, the adsorption process has been dramatically applied for the removal of drug compounds, especially antibiotics. Adsorption techniques have the highest efficiency among the physical methods for the removal of organic compounds from industrial wastewater [23–25]. The design and operation of the adsorption method are very simple and do not have any effect on the production of toxic materials [26]. Therefore, adsorption is used as an effective and economical method in a wide dimension and causes the separation of organic compounds from water sources [27,28]. So far, several materials such as biochar prepared from waste materials have been tested for organic matter adsorption [29,30]. Biochar, due to high porosity, specific surface area and high adsorption capacity, is the most widely used adsorbents for the removal of organic pollutants from contaminated water and wastewater [31]. The performance of adsorption depends on the properties of the adsorbent material, the properties of the pollutant, and the environmental conditions of the wastewater and other aqueous solutions [32]. Therefore, the adsorption of each pollutant by any adsorbent needs to evaluate the parameters affecting the adsorption.

Plantain tree is one of the native trees of Iran, which is cultivated in different places in Iran. Therefore, in this study, the wood of the plantain tree was used for the preparation of biochar, and finally, the prepared biochar was used as a natural and local adsorbent to remove CPX from aqueous solutions and wastewaters. Additionally, the effects of the most critical operational parameters were tested and optimized.

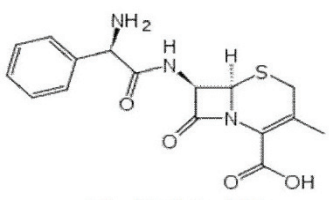

Fig. 1. Cephalexin molecular structure (pK_{a1} = 2.56; pK_{a2} = 6.88) [17].

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical grade. All solutions were prepared with distilled waters. The pH of the solutions was adjusted using hydrochloric acid and sodium hydroxide 0.1 N. CPX (99.7%, standard grade) was purchased from Merck Company Ltd., Iran.

2.2. Preparation of the plantain wood biochar

In this study, the plantain woods were obtained from Sabzevar County (Razavi Khorasan province, Iran) and used as raw material for the preparation of the biochar adsorbent. The wood was washed with distilled water several times to remove dust and other inorganic impurities and dried, crushed, and sieved to achieve a particle size of 120–250 nm. Then, the samples were placed in a vertical stainless-steel reactor under high purity nitrogen (99.99%) at a flow rate of 350 cm^3/min to a final temperature of 460°C at a heating rate of 8°C/min and were located at this temperature for 1 h to be activated. After elapsing of the required time, the temperature of the samples gradually decreased and reached room temperature. After carbonization, the samples were washed with distilled water and then dried at 105° C for 12 h, and were used as adsorbent [17,32].

2.3. Determination of physical characteristics of the plantain wood biochar

The surface morphology of the plantain wood biochar was determined by scanning electron microscopy (SEM). The specific surface area, volume, and size of the pores were calculated from adsorption–desorption isotherms using the standard Brunauer–Emmett–Teller equation. Fourier-transform infrared (FTIR) spectra were recorded in the range of 600–3800 cm^{-1} using an FTIR spectrometry.

2.4. Determination of point of zero charge (pH_{pzc})

The determination of pH_{pzc} of the adsorbent was performed by pH titration method [17,20]. 50 mL of NaCl 0.01 M solution was poured into several Erlenmeyer flasks. The pH of the solution within each flask was adjusted to a value between 2 and 10 by the addition of HCl 0.1 M or NaOH 0.1. Then, 2 g of plantain wood biochar was added to each flask, and the suspensions were shaken for 24 h and allowed to reach equilibrium for 1 h. The final pH values (pH_f) of the supernatant liquid were noted. The difference between the initial and final pH values was plotted vs. the pH_i. The point of intersection of the resulting curve with the axis of abscissas resulted in the pH_{pzc}.

2.5. Adsorption experiments

The parametric experiments were carried out in the Erlenmeyer flask of 150 mL. In each test, 50 mL of the CPX with different concentrations (10, 50, and 100 mg/L) was transferred into the Erlenmeyer flasks. The pH of the solution

was adjusted using hydrochloric acid or sodium hydroxide 0.1 N. The certain doses of the plantain wood biochar (0.2, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 g/L) were added into the solution and mixed at 150 rpm. After completely mixing at a specific time, the solution was centrifuged at 5,000 rpm, and the CPX concentration in the solution was analyzed by a UV–visible spectrophotometer, PG-instrument model, at the wavelength 258 nm and measured using a standard curve. The variables of this study included pH, the initial concentration of CPX, adsorbent dosage, the temperature of the solution, and reaction time. All experiments were repeated three times in order to obtain accurate results. The amount of CPX adsorbed on the adsorbent, as an adsorption capacity in equilibrium conditions (q_e [mg/g]) and CPX removal efficiency were calculated using the following equations, respectively:

$$q_e = \frac{\left(C_o - C_e\right) \times V}{M} \tag{1}$$

$$\text{CPX removal } \% = \frac{\left(C_o - C_e\right)}{C_o} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of CPX (mg/L), respectively. V is the volume of the CPX solution (L), and M is the mass of the adsorbent used (g).

2.6. Determination of the adsorption kinetics models and equilibrium isotherm

The effect of contact time and kinetics of the adsorption was conducted by adding 2 g of biochar to the Erlenmeyer flasks containing various concentrations of CPX (10, 50, and 100 mg/L). At specific time intervals, samples were taken from the solution and analyzed. The other variables were kept constant in their optimum values. The same procedure was also used to evaluate adsorption isotherms. In order to determine the adsorption equilibrium time, 50 mL of CPX solution with different concentrations (50, 100, 200, 300, 400, and 500 mg/L) was added to each Erlenmeyer flask at pH = 7, as an optimum pH, and the constant temperature of 25°C for 6 h. The flasks were shacked at 400 rpm until reaching equilibrium. After reaching equilibrium, the solutions were centrifuged at 5,000 rpm for 15 min to separate the adsorbent. The concentrations of CPX in the supernatants were analyzed using the PG-instrument spectrophotometer. The pseudo-first-order (PFO), pseudo-second-order (PSO) models, and intraparticle diffusion model were employed to fit the kinetics of CPX adsorption. The results of the equilibrium study for the adsorption of CPX on the plantain wood biochar were evaluated by the Langmuir and Freundlich isotherm models.

3. Results and discussion

3.1. Physical characteristics of the adsorbent

The micropore specific surface area, micropore volume, and diameters of the produced biochar were 896 m^2/g, 0.472 m^3/g, and 2.18 nm, respectively (Table 1), which indicate that the prepared biochar adsorbent has an appropriate surface and porosity.

The FTIR spectrum of the plantain wood biochar is shown in Fig. 2. The most significant bands of the biochar are in the position of 1,091.83, 2,929.26, and 3,413.34 cm^{-1}. The bands in the 1,000–1,300 cm^{-1} range can be attributed to the C–C and C–O vibrations in acids, alcohols, phenols, ethers, and esters [18]. The broad peak at 3,413.34 cm^{-1} is from the O–H strength for carboxyl and phenol functional groups or adsorbed water, and the asymmetric peak shape is characteristic of hydrogen bonding [34]. The peak at 1,091 cm^{-1} indicates the presence of amine functional group on the adsorbent surface.

The morphologies (SEM images) of the biochar prepared from the plantain wood before and after CPX adsorption are presented in Figs. 3 and 4, respectively. According to Fig. 3, the prepared biochar has a shape such as compressed parallel fibers. High hollow fibers of this substance indicate the presence of large micropores and the suitability of this adsorbent for its use in the adsorption process [19].

3.2. Determination of pH_{pzc}

In this study, pH_{pzc} of the surface of the plantain wood biochar was determined to be 6.8 (Fig. 5). The pH_{pzc} in any

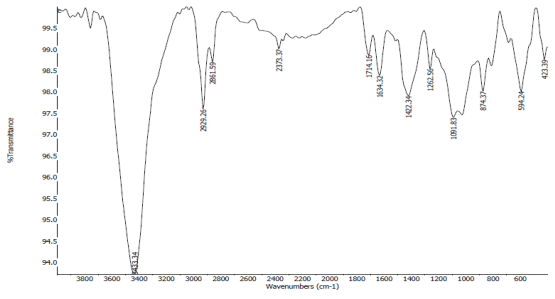

Fig. 2. FTIR spectrum of the plantain wood biochar.

Table 1
Structural features of the biochar prepared from some materials

Parameter	Merc carbon (a)	Plantain wood (this study)	Paulownia wood (b)	Walnut wood (c)	Puplar wood (d)
Surface area, m^2/g	1,024	896	2,736	1,184	1,029
Pore volume, cm^3/g	0.572	0.47	1.387	0.50	0.63
Mono layer volume, cm^3/g	235	198	–	–	236.4
Average pore diameter, nm	2.23	2.18	2.92	1.69	2.64

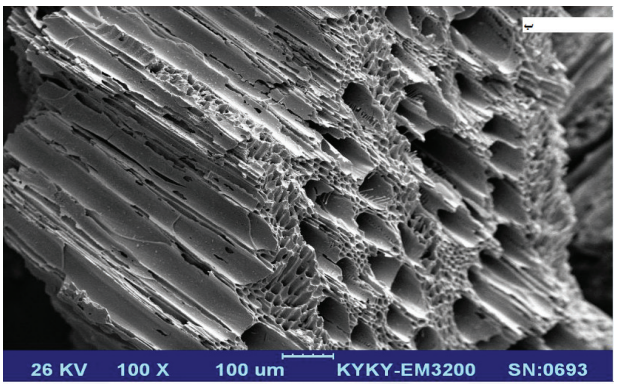

Fig. 3. SEM image of the plantain wood biochar before CPX adsorption.

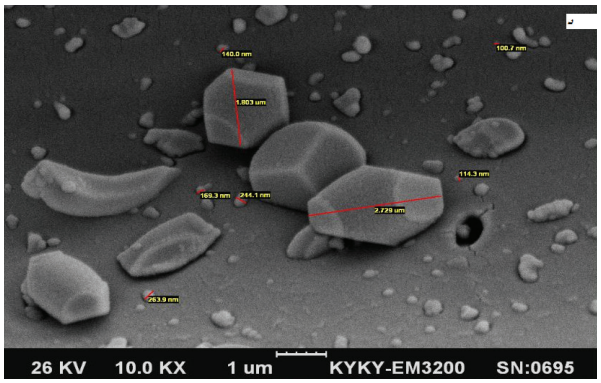

Fig. 4. SEM image of the plantain wood biochar after CPX adsorption.

adsorbent is a point at which an adsorbent has zero potential charge on its surface [17]. The pH_{pzc} can be used to evaluate the quality of the relation between pH and CPX adsorption value [19]. The presence of H^+ and OH^- ions in the solution may affect the potential surface charges of adsorbents [20]. When the pH of the solution is lower than the pH_{pzc}, the solution donates more protons to adsorbent than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions). Conversely, if the pH of the solution is above pH_{pzc}, the surface functional groups of the adsorbent is negatively charged (attracting cations) [33].

3.3. Effect of pH on CPX adsorption

In this study, the effect of initial pH on the adsorption of CPX was investigated. CPX can exist in three forms (cationic, anionic, and zwitterion) in aqueous solutions depending on the pH. At $pK_{a1} \leq 2.56$, CPX is mostly cationic, in $pK_{a2} \geq 6.88$, anionic CPX dominates and at pH = 2.56–6.88, zwitterionic CPX is dominant [10,20]. According to Fig. 6, the maximum removal of CPX is obtained (90%) at a pH value of 6.7. In this case, the CPX solution is in the zwitterionic form, in which, the negative functional groups in the solution (OH^-) is predominant.

On the other hand, the surface of the plantain wood biochar at pH values lower than the pH_{pzc} is positively charged (pH_{pzc} > pH). In this condition, attracting force between the

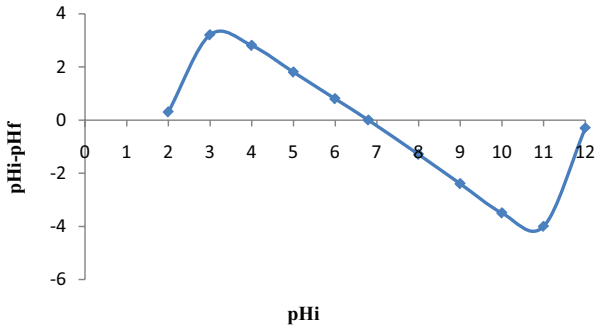

Fig. 5. Determination of the point of zero charge of the plantain wood biochar.

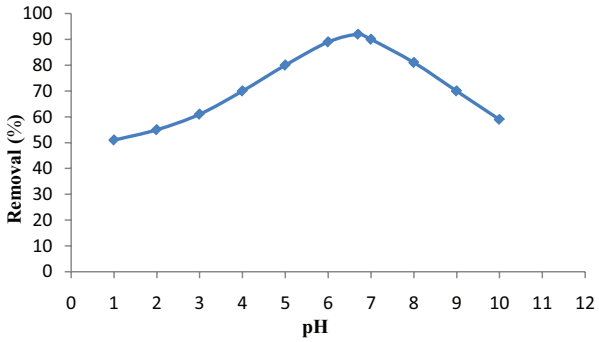

Fig. 6. Effect of pH of solution on CPX (C = 50 mg/L; adsorbent dose = 2 g; time = 60 min; T = 25°C).

negative functional groups of CPX and the positive charge of the adsorbent surface increases, resulting in the maximum adsorption capacity of CPX in pH = 6.7. At acidic (pH = 1) and alkaline (pH = 10) conditions, the CPX removal was minimum. It can be attributed to the fact that at pH = 1, the positive functional groups on the surface of the adsorbent and the CPX dominate, leading to an increase in the repulsive forces between the positive charges of the adsorbent surface and the solution [17,20]. At pH = 10, the negative functional groups of the CPX are predominant and the negative charges on the surface of the plantain wood biochar due to the deprotonation (or obtaining OH^-) increase, resulting in repulsive forces between the negative charges. As a result, the adsorption of CPX decreased. It is notable that some negative and positive functional groups can simultaneously exist on the surface of the adsorbent while the surface charge of the adsorbent may be predominantly positive or negative [20,34].

3.4. Effect of adsorbent dose on CPX adsorption

The influence of adsorbent dosage on the CPX removal efficiency from aqueous solution is presented in Fig. 7. It shows that the removal of CPX increases with the increase in the adsorbent dosage up to a certain amount (2 g) and then it remains constant. The increase of the removal efficiency of the CPX with increasing the adsorbent dose can be ascribed to an increase in the surface area of the adsorbent and the existence of more adsorption sites [17,35]. In this study, with increasing the adsorbent dose, the adsorption capacity decreased

significantly. This phenomenon can be attributed to two aspects: first, at a fixed concentration and volume of CPX, the increase in the adsorbent dosage resulted in unsaturation of adsorption sites, and second, the aggregation of the adsorbent particles, due to higher mass of the adsorbent, could lead to a reduction in the adsorbent capacity [20].

3.5. Effect of initial concentration and contact time on CPX adsorption

As shown in Fig. 8, at the initial concentration of 10 mg/L, adsorbent dose = 2 g, pH = 7, and temperature = 25°C, the maximum removal rate of CPX obtained was 98% at the first 10 min. The cause of this phenomenon can be attributed to the presence of more adsorptive sites on the adsorbent surface at lower CPX concentration, and as a result, more CPX molecules can be adsorbed on the adsorbent surface [35]. At concentrations of 10, 50, and 100 mg/L CPX at 60 min, the CPX removal rate was 99.6%, 90%, and 78.2%, respectively. In this case, with increasing the initial concentration to 50 and 100 mg/L, the adsorptive sites present on the surface of the adsorbent are entirely occupied by CPX molecules [34,36]. For this reason, CPX removal rate was significantly reduced at a concentration of 100 mg/L. In the study of Mohseni et al. [32] regarding the removal of dexamethasone from aqueous solutions by clinoptilolite adsorbent, it was found that by increasing the initial concentration of dexamethasone from 5 to 40 mg/L, the removal efficiency decreased from 58% to 21%. In this study, the optimum concentration was determined as 50 mg/L with the effective removal of 88.5% at a contact time of 60 min.

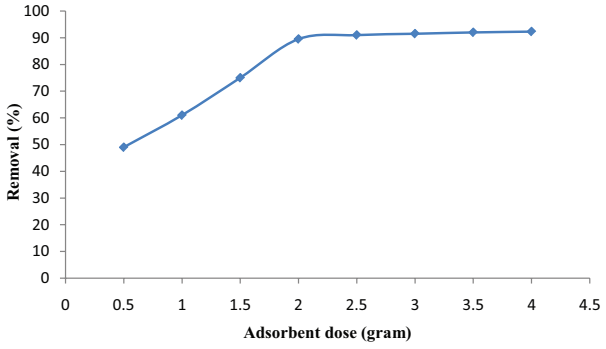

Fig. 7. Effect of adsorbent dose on CPX removal (C = 50 mg/L; pH = 7; time = 60 min; T = 25°C).

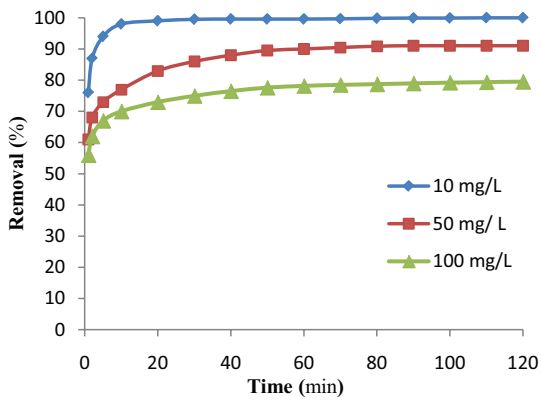

Fig. 8. Effect of the initial concentrations and contact time on CPX removal (adsorbent dose = 2 g; pH = 7; T = 25°C).

3.6. The effect of temperature and thermodynamics on CPX adsorption

In Fig. 9, the rate of the adsorption of CPX on the plantain wood biochar adsorbent at different temperatures (5°C–60°C) under certain conditions was investigated. In addition, the highest CPX adsorption (97%) was obtained at 40°C (Fig. 9). Increasing the optimum solution temperature until 40°C causes the increased adsorption of CPX molecules onto the adsorbent cavities [20]. Therefore, the removal percentage of CPX increased, and the adsorption process is an endothermic reaction [12]. A decrease in the removal of CPX with increasing of the temperature above the equilibrium temperature can be related to the CPX desorption and the entrance of the CPX molecules into the solution, showing that CPX adsorption at higher temperatures (more than 40°C) is an exothermic reaction [18].

3.7. The equilibrium of CPX adsorption on the plantain wood biochar

The results of the equilibrium of CPX adsorption in the batch scale in different concentrations of CPX on the plantain wood biochar are shown in Fig. 10.

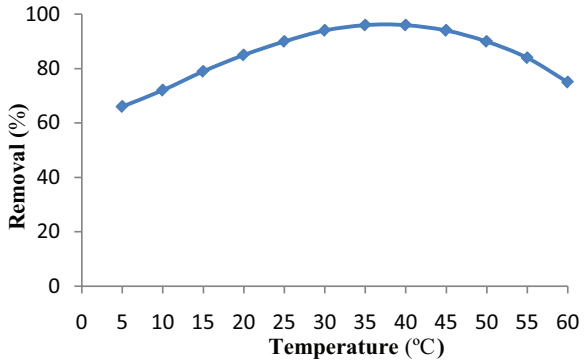

Fig. 9. Effect of temperature on CPX removal (C = 50 mg/L; pH = 7; adsorbent dose = 2 g; contact time = 60 min).

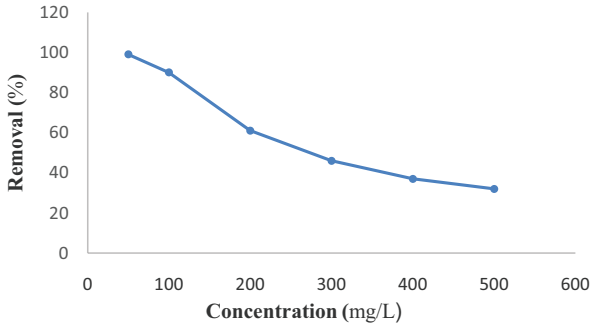

Fig. 10. Adsorption efficiency of 6-h equilibrium of CPX on the plantain wood biochar.

Removal of CPX by the plantain wood biochar at a concentration of 100 mg/L after 6 h was 99% and when the CPX concentration was 500 mg/L, the removal efficiency decreased to 32% (Fig. 10). In contrast, the adsorption capacity increased by increasing the concentration of CPX from 10 to 500 mg/L (Fig. 11). Because the conditions of the equilibrium experiments are similar in different concentrations, the decreasing of the adsorption efficiency of CPX with increasing its concentration is due to the restriction of the adsorbent sites and the significant number of CPX molecules in the solution [35]. It can be justified in this way that increasing the concentration of CPX leads to an increase in the mass transfer of the CPX molecules on the adsorbent, and therefore, the adsorption capacity increases [15,17].

3.8. Adsorption isotherms of CPX on the plantain wood biochar

An adsorption isotherm explains the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. The Langmuir, Freundlich, and Temkin isotherms are used to describe the equilibrium adsorption [32,36]. Langmuir model is valid for single-layer adsorption on the adsorbent surface with limited and homogeneous adsorption sites. Langmuir isotherm defined by the following equation:

$$q_e = \frac{q_{\max} \times K_L \times C_e}{1 + K_L \times C_e} \tag{3}$$

where $q_{\max}$ (mg g^{-1}) is the maximum adsorption capacity; C_e (mg L^{-1}) is the equilibrium concentration; q_e (mg g^{-1}) is the equilibrium adsorption capacity, and K_L (L mg^{-1}) is the Langmuir equilibrium constant.

The Freundlich isotherm model is an empirical equation, and the model is valid for adsorption that occurs on heterogeneous surfaces. The Freundlich isotherm can be represented by Eq. (4):

$$q_e = K_F \times C_e^{1/n_F} \tag{4}$$

where K_F is the Freundlich equilibrium constant (mg g^{-1} × [mg L^{-1}]$^{-1/n_F}$) and n_F is the dimensionless exponent of the Freundlich model. The results of the CPX adsorption isotherm are presented in Figs. 12 and 13. Based on these figures, the correlation coefficient (R^2) for the Langmuir isotherm model (R^2 = 0.992) is higher than the Freundlich isotherm (R^2 = 0.979). The maximum CPX adsorption capacity on the plantain wood biochar was 84 mg/g according to the Langmuir model.

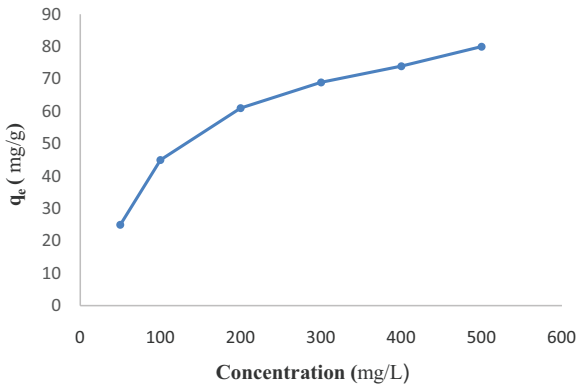

Fig. 11. Adsorption capacity (q_e) of 6-h equilibrium of CPX on the plantain wood biochar.

3.9. The kinetic of CPX adsorption on the plantain wood biochar

In order to investigate the information on the factors affecting the reaction speed, also the mechanisms for controlling the adsorption process, such as surface adsorption, chemical reaction, and diffusion mechanisms, the evaluation of kinetics is essential. The kinetics of the adsorption of CPX was analyzed using the PFO, PSO, and Weber–Morris intraparticle diffusion models to fit the experimental data.

The liner form of the PFO kinetic models can be presented by Eq. (5):

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{5}$$

The PSO model is based on chemisorptions on the adsorbent. The liner form of the PSO kinetic model can be expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} \tag{6}$$

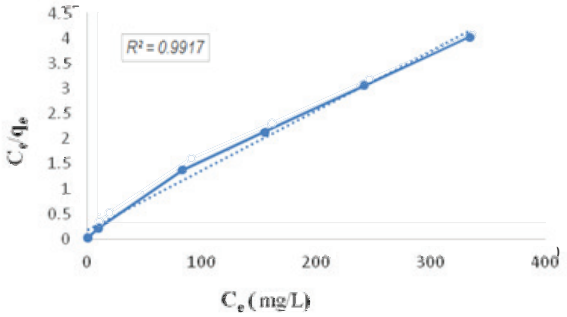

Fig. 12. Langmuir isotherm of CPX on the plantain wood biochar.

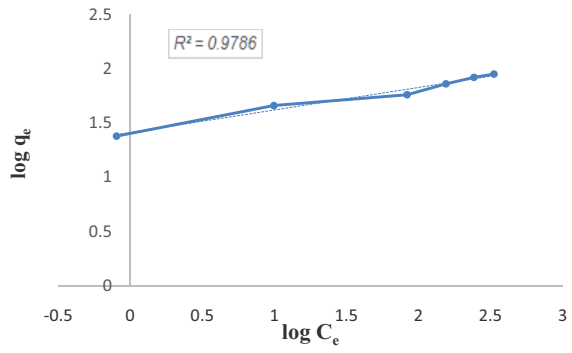

Fig. 13. Freundlich isotherm of CPX on the plantain wood biochar.

Table 2
The kinetic adsorption of CPX on the plantain wood biochar

C_0 (mg/L)	Pseudo-first order			Pseudo-second order		
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
50	15.91	0.0587	0.932	27.25	0.0054	0.994
100	22.32	0.0129	0.915	41.67	0.0029	0.987

The kinetics study is useful for the understanding of the dynamic and rate of the reaction in the adsorption process [19,20]. For this reason, kinetics parameters play an important role in designing and modeling of the adsorption process. According to Table 2, the correlation coefficients for the PSO kinetic model at the concentrations of 50 and 100 mg/L were 0.994 and 0.987, respectively, while the corresponding values for the PFO were 0.932 and 0.915, respectively.

4. Conclusion

In this study, plantain wood is used as natural raw materials to prepare biochar to remove CPX from aqueous solutions. The micropore specific surface area, micropore volume, and diameters of the produced biochar were 896 m^2/g, 0.472 cm^3/g, and 2.18 nm, respectively, which indicate that the prepared biochar adsorbent has an appropriate surface and porosity. The effects of some parameters on the removal efficiency of CPX were studied. Results showed that the optimum removal efficiency (88.5%) was found at pH 6.7 and adsorbent dose of 2 g/L. In this study, with increasing adsorbent dose, the removal efficiency increased, and the adsorption capacity decreased significantly. The PSO kinetic model better described the adsorption kinetics. The adsorption data of CPX fitted very well to the Langmuir isotherm model. The thermodynamic studies indicated that the adsorption of CPX onto the plantain wood biochar is an endothermic reaction. Finally, the results indicate that the biochar prepared from plantain wood can be used as an efficient adsorbent for the treatment of pharmaceutical wastewater containing cephalosporin compounds.

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