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Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic from aqueous solution: adsorption isotherm study

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ABSTRACT

Antibiotics are considered among the major pollutants in water environments. The antibiotics along with the sewage, pharmaceutical industries water waste, veterinary clinics and hospital sewages noticeably enter into the water resources and the environment. The objective of this study was to investigate ciprofloxacin removal efficiency from aqueous solutions by using cupric oxide nanoparticles. The effects of pH (3–11), CuO nanoparticles dosage (0.01, 0.03, 0.05, 0.07, 0.09 and 0.1 g/L), contact time (15, 30, 45, 60, 75, 90 and 120 min) and the initial antibiotic concentration (10, 25, 50, 100, 150 and 200 mg/L) were assessed on ciprofloxacin removal efficiency in laboratory. Under optimal conditions of concentration 10 mg/L, pH = 7, CuO nanoparticles dosage 0.1 g/L and contact time 60 min, the removal efficiency was 77% and q_m of the CuO nanoparticles was 105 mg/g. The process of ciprofloxacin adsorption on CuO nanoparticles was depended on Freundlich adsorption isotherm more than other isotherms (Langmuir, Temkin and Harkins–Jura). On the basis of the obtained results, it can be concluded that CuO nanoparticles adsorption process can be used as a novel method for treating wastewater contaminated with drug sources.

Keywords: CuO; Adsorption; Ciprofloxacin; Isotherm

1. Introduction

Drugs are used in the treatment and prevention of bacterial infections [1]. They may either kill or inhibit the growth of bacteria. Unused therapeutic drugs are sometimes disposed of into the sewage system [1,2]. If the drugs are not degraded or eliminated during sewage treatment, in soil or in other environmental compartments, they will reach surface water and groundwater, and, potentially, drinking water [2]. The antibiotics along with the sewage, pharmaceutical industries water waste, veterinary clinics and hospital sewages and the agricultural products noticeably enter into the water resources and the environment [2,3].

Fluoroquinolones are important class of irresolvable antibiotics used for human beings and animals [2]. Because of non-degradability in ecosystem, fluoroquinolones are generally known as a pollutant in the environment [2,4].

The ciprofloxacin is one of the antibiotics of fluoroquinolone class used widely in the treatment of urinary, digestive and respiratory systems with good results [5]. The presence of fluoride atoms in composition of these antibiotics causes their bacterial resistance [6]. Its density in sewage and surface water is 1 μg/L and in hospital sewage more than 150 μg/L [7]. One of the main reasons for antibiotics purification is bacterial resistance and chromosomal mutation which is a major threat to human health [8]. Considering to riskiness and importance of antibiotics, especially ciprofloxacin; it should be reached to allowable discharge level before disposal to the environment [6,9]. So far, the methods applied for ciprofloxacin and other

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antibiotics elimination are: ozonation [8], oxidation [10], photocatalytic degradation [11] and adsorption [4]. The adsorption method is widely used due to simplicity, low cost and adsorption recovery to remove pollutant [12,13]. Different carbon adsorbers like activated carbon have been used to remove organic and mineral pollutant while nanoparticles are new adsorbents [12]. The adsorbents in nanoscale with greater size and mass form have more adsorbing capacity in pollutant elimination, in comparison with the aforesaid absorbents [14].

The nanoparticles of CuO are used as a catalyst with high efficiency, because of their specific surface area and more effects of its quantum size [14,15]. Two common forms of copper oxide are copper(I) oxide (cuprous oxide, Cu_2O) and copper(II) oxide (cupric oxide, CuO). Cupric oxide, the nanoparticles considered in this study, is a semiconductor of type P with a 1 mm (monoclinic) structure, having 1.2–1.7 eV band energy in room temperature [14,16].

The main purpose of this study was to assess the proper operating parameters, initial pH of solution, adsorbent dosage, and initial ciprofloxacin concentration and contact time on the adsorption capacity. Finally, adsorption isotherm models have been studied.

2. Materials and methods

2.1. The characteristics of chemicals

Ciprofloxacin (molecular weight 367.8 g/mol, purity higher than 99.6%, molecular formula $C_{17}H_{18}FN_3O_3$ and pK_a = 5.7) was supplied by Sigma-Aldrich, USA. Stock of ciprofloxacin with concentration of 1,000 mg/L was prepared in double distilled water. The chemical structure ciprofloxacin is provided in Fig. 1.

2.2. Structure characterization of CuO

Cupric oxide nanoparticle (purity of 99% and molecular weight of 79.55 g/mol) was purchased from Sigma Company (USA). The specific surface area is one of the parameters, determining the adsorbing capability of absorbent substance and when the specific surface area of absorbent substance is high, the absorbent will have more pores, causing the higher level of contact. In this study, the morphology of CuO nanoparticles was determined by scanning electron microscope (SEM; Hitachi Model S-3000H). Fig. 2 shows SEM image of CuO nanoparticles. The specific surface areas of CuO nanoparticles were determined in size of 20 m^2/g, the sizes of CuO nanoparticles are 50 nm length.

2.3. Batch adsorption experiments

The effect of different parameters such as pH (3, 5, 7, 9 and 11), contact time (15, 30, 45, 60, 75, 90 and 120 min), pollutant concentration (10, 25, 50, 100, 150 and 200 mg/L) and adsorbent dose (0.01, 0.03, 0.05, 0.07, 0.09 and 0.1 g/L) was studied in adsorption process. To create optimal conditions a shaker with 150 rpm was used. The adsorbent was added to each 1 L of water sample containing various concentrations of ciprofloxacin. The pH of the water sample was adjusted by adding 0.1 N HCl or 0.1 N NaOH solutions in each bottle. The initial and final ciprofloxacin concentrations remaining in solutions were analyzed by a UV–visible recording spectrophotometer (Shimadzu Model: LUV-100A) construction Japan and the ciprofloxacin was determined at a wavelength of maximum absorbance (λ_{max}) 276 nm. The pH was measured using a MIT65 pH meter [16,17]. The removal, R (%) and the amount of adsorbed, q_e (mg/g) of the studied parameters from ciprofloxacin was calculated based on the following formula [18,19]:

$$\%\ \text{Removal} = \frac{C_i - C_f}{C_0} \times 100 \tag{1}$$

where C_i and C_f are the initial and final ciprofloxacin concentration, respectively.

$$q_e = \left(\frac{C_0 - C_e}{M}\right) V \tag{2}$$

where M is the weight of adsorbent (g) and V is the volume of the solution (L). C_0 and C_e are the initial and final

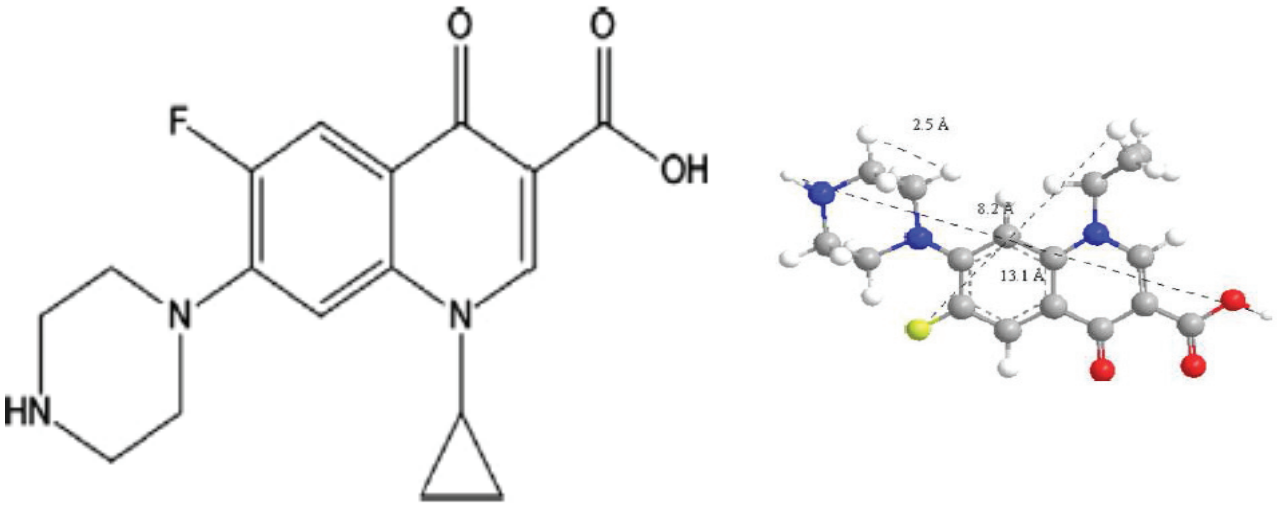

Fig. 1. The chemical structure of ciprofloxacin.

equilibrium liquid phase concentration of ciprofloxacin (mg/g), respectively.

3. Results and discussion

3.1. Effect of initial pH on the CuO adsorption

Effect of different pH (3–11) in absorption of ciprofloxacin on CuO nanoparticles (contact time: 60 min, ciprofloxacin concentration: 50 mg/L and dosage: 0.05 g/L) was shown in Fig. 3. By increasing the pH from 3 to 7, the removal efficiency ciprofloxacin increased; while pH higher than 7 reduced the removal efficiency. The removal percentage increased with pH (from 3 to 7) up to 50%–75% at biosorbent dosage of 0.05 g/L. The amount of adsorbed ciprofloxacin also increased from 5 to 7.5 mg/g, respectively.

The increase and decrease of ciprofloxacin deletion efficiency, in acidic and alkaline pH depends on pH_{zpc} and pK_a parameters. The pK_a for ciprofloxacin was 5.7 and the pH_{zpc} of CuO nanoparticles of copper oxide was 9.4 [16,20]. In other words, ciprofloxacin at pH less than 5.7 and nanoparticles of copper at pH less than 9.4 have a positive alloy and at higher values they have negative alloy and near to these levels, the inclination of ciprofloxacin and cupric oxide nanoparticle, because of the neutral alloy of one of these two will be decreased [16]. At pH 8–12, the concentration of OH^- ions increased, therefore, competition between them and anions increased. In this situation, efficiency is reduced due to electrostatic disposal. The efficiency of removal decreased because of repulsive force of negative charges of catalyst and ciprofloxacin anions [20,21].

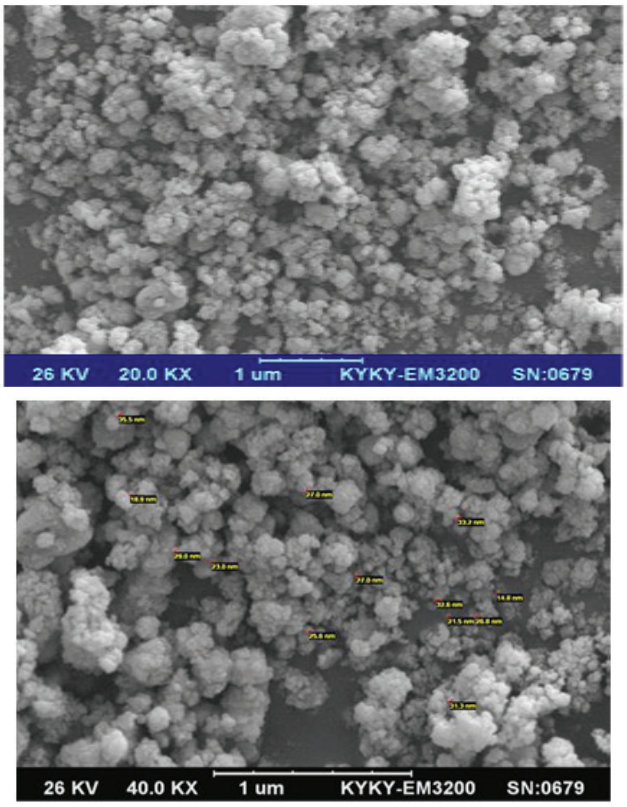

Fig. 2. SEM image of CuO nanoparticles.

3.2. Effect of absorbent dose on the CuO adsorption

From Fig. 4, it is evident that adsorbent dose significantly influences the amount of adsorbed. The effect of adsorbent dose on removal of ciprofloxacin was studied by varying the dose of adsorbent from 0.01 to 0.1 g/L. When the adsorbent concentration increased from 0.01 to 0.1 g/L for improved concentration 50 mg/L ciprofloxacin, the efficiency increased from 65% to 83%, while the biosorption capacity (q_e) of ciprofloxacin on CuO nanoparticle decreased from 15 to 4.15 mg/g when CuO nanoparticle dosage increased from 0.01 to 0.1 g/L. In fact the level of deletion significantly depends on active places and by increasing the dosage of nanoparticles to an appropriate level, the number of available adsorption sites will increase as a result of increased adsorption capacity [22,23]. However, as the study shows, if the level of nanoparticles be higher than an extent, it will has no more an effect on deletion and it even may result to the decrease of efficiency [23].

3.3. Effects of contact time and initial antibiotic concentration

Effects of contact time and initial antibiotic concentration were the parameter that was studied in adsorption process. Fig. 5 shows the ciprofloxacin adsorption vs. contact time and different ciprofloxacin concentrations of CuO nanoparticles adsorbent. The experiments were done in solution with

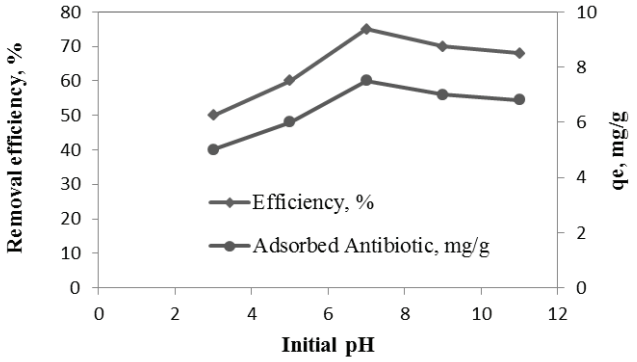

Fig. 3. Effect of initial pH on ciprofloxacin adsorption onto CuO nanoparticles (time: 60 min, dosage: 0.05 g/L and ciprofloxacin concentration: 50 mg/L).

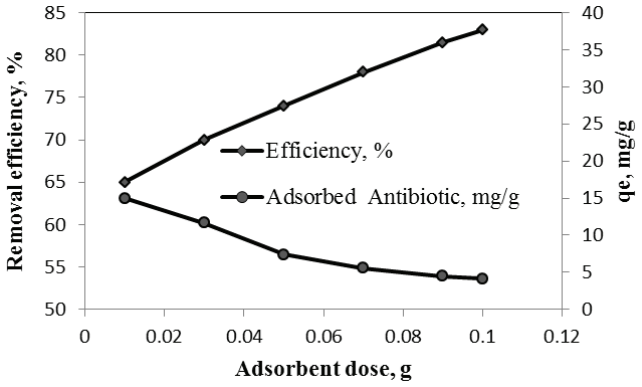

Fig. 4. Effect of adsorbent dose on ciprofloxacin adsorption onto CuO nanoparticles (contact time: 60 min, pH: 7 and ciprofloxacin concentration: 50 mg/L).

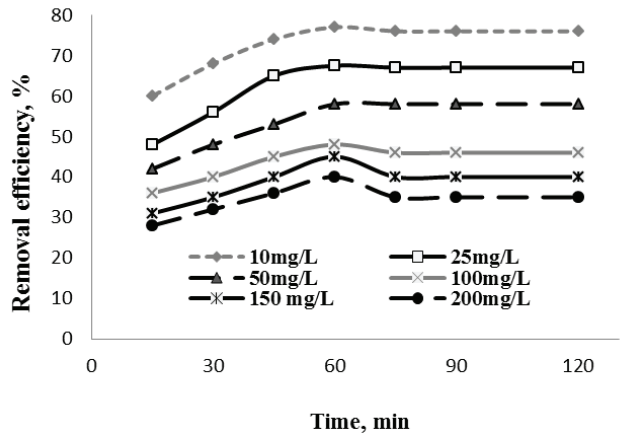

Fig. 5. Effect of contact time on percentage removal of ciprofloxacin (pH: 7 and dosage: 0.1 g/L).

concentration of 10, 25, 50, 100, 150 and 200 mg/L in contact time 15, 30, 45, 60, 75, 90 and 120 min. The contact time of equilibrium was very short. After 45 min, high amount of ciprofloxacin was adsorbed and after it, no significant changes were observed. The maximum efficiency of the removal of different ciprofloxacin concentrations was at time of 60 min. By increasing the contact time, the efficiency of antibiotic deletion will be increased. The reason for increasing the removal efficiency at the early hours is that by passing the time the access of ciprofloxacin molecules to active sites on the surface of adsorbent. In the early stages (60 min) is more accessible of active sites on the surface of the absorbent but over time (90 min) these empty sites filled by ciprofloxacin molecules [24,25]. The equilibrium can be reached within 90 min, and thus, further adsorption experiments were carried out for a contact time of 90 min.

The effect of initial ciprofloxacin concentration (10–200 mg/L) on its the removal of is shown in Fig. 5. The highest removal efficiency is related to the ciprofloxacin concentration of 10 mg/L. The efficiency of removal in this concentration and in time 60 min was 77%. This may be owing to the finite number of active sites on the adsorbent that becomes saturated at high concentration of ciprofloxacin. In other words, at low concentrations, the availability of ciprofloxacin molecules to adsorption sites is more than high concentrations [23,24].

3.4. Adsorption isotherms

The isotherms of equilibrium adsorption will be stated by drawing ciprofloxacin concentration in solid state against the concentration of such compounds in solution phase. The distribution of ciprofloxacin compound molecule between solution and absorption phase is a criterion of equilibrium situation on adsorption process and is generally stated by one or more adsorption isotherm models. There are many isotherm models for experimental data analysis and description of equilibrium in adsorption such as Langmuir, Freundlich, Harkins–Jura and Temkin. The Langmuir isotherm model is presented in Eq. (3) [26,27]:

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

where q_e is the metal uptake (mg/g) by CuO nanoparticles (mg/g), maximum adsorption capacity (q_m) is monolayer adsorption capacity (mg/g), K_L is Langmuir isotherm constant related to the affinity of the binding sites and energy of adsorption (L/mg). The essential specifications of a Langmuir isotherm can be expressed in idiom of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by Eq. (4) [26]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

The R_L values indicate the kind of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$) or favorable ($0 < R_L < 1$).

The Freundlich isotherm is shown in Eq. (5) [28]:

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \tag{5}$$

where q_e is the amount of ciprofloxacin adsorbed (mg/g), C_e is the equilibrium concentration of ciprofloxacin in solution (mg/L) and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively.

The Temkin isotherm has been expressed by the following Eq. (6) [26,28]:

$$q_e = B_1 \ln(A_T) + B_1 \ln(C_e) \tag{6}$$

A plot of q_e vs. lnC_e enables the determination of the constants A_T and B_1. B corresponds to the heat of sorption and A is the equilibrium binding constant; where $B = RT/b$, T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K).

The Harkins–Jura [13,28] is given by the following equation:

$$\frac{1}{q_e^2} = \left[\frac{B_{HJ}}{A_{HJ}}\right] - \left[\frac{1}{A_{HJ}}\right] \log C_e \tag{7}$$

The values of constants B_{HJ} and A_{HJ} were obtained from linear plot of $1/q_e^2$ and logC_e at 303 K. The values of constants A_{HJ} and B_{HJ} along with regression coefficient are listed in Table 1.

According to the obtained results (Table 1 and Figs. 6–9), this study is more compatible with Freundlich isotherm. The basis for choosing the appropriate isotherm is R^2; concerning Freundlich isotherm ($R^2 = 0.994$) adsorption, this parameter is higher than other adsorption isotherms. In this study, K_f is more than 1, showing ciprofloxacin favorable absorption by nanoparticles. In general, increase of K lead to increase of adsorbent capacity in Freundlich isotherm. Moreover, if the variable $1/n$ be between 0 and 1, it indicates the heterogeneity of level and the adsorption will be desirable [13]. Therefore, when $n > 1$, the adsorption process was acceptable [29].

3.5. Intraparticle diffusion model

Adsorption is a thermodynamic system in which different compounds are in competition to reach an equilibrium state. In an adsorption phenomenon, three separated phases

Table 1
Isotherms parameters for adsorption of ciprofloxacin onto CuO at temperatures 303 K

Langmuir isotherm		Temkin isotherm	
q_{max} (mg/g)	105	B_T (kJ/mol)	18.28
K_L (L/mg)	0.02	A_T (L/g)	1.7
R_L	0.48	B_T (kJ/mol)	0.02
R^2	0.937	R^2	0.92
Freundlich isotherm		Harkins–Jura isotherm	
n	1.68	B_{HJ}	1.8
K_f (mg$^{1-1/n}$L$^{1/n}$/g)	4.65	A_{HJ}	114.9
R^2	0.994	R^2	0.74

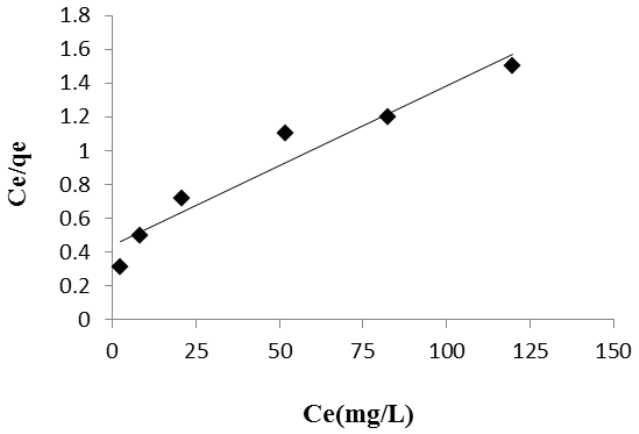

Fig. 6. Langmuir adsorption isotherms of ciprofloxacin by CuO.

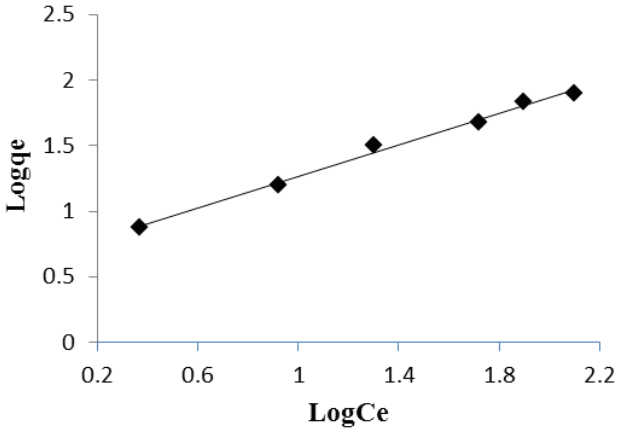

Fig. 7. Freundlich adsorption isotherms of ciprofloxacin by CuO.

should be happened, the adsorbing molecules should be transferred from solution mass phase to the level of solvent film surrounded the adsorbent particle. This phase is called film penetration process. The ciprofloxacin adsorption on CuO nanoparticles may be controlled by penetration process on film or on intraparticle penetration. Meanwhile, the R^2 = 0.956 gained by this process represents the desirable antibiotic adsorption. Its mathematical model is as follows [29,30]:

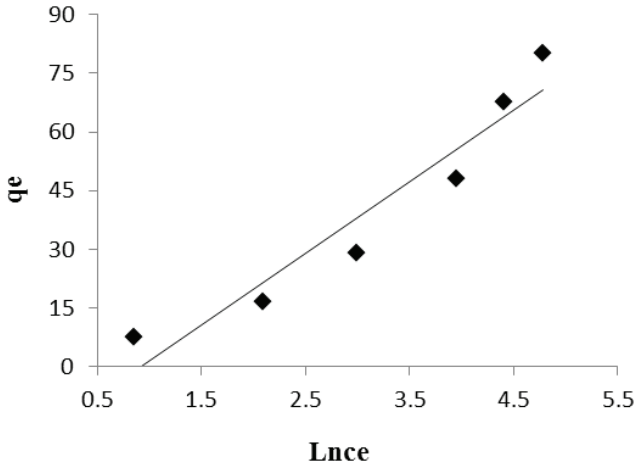

Fig. 8. Temkin adsorption isotherms of ciprofloxacin by CuO.

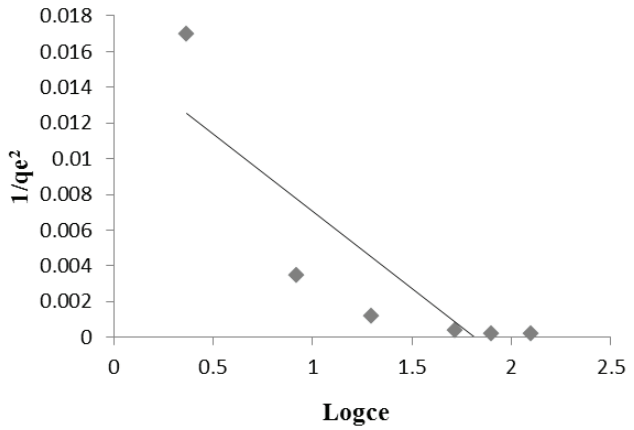

Fig. 9. Harkins–Jura adsorption isotherms of ciprofloxacin by CuO.

$$q_t = K_{pi} t^{0.5} + c \quad (8)$$

where c is constant and K_{pi} is the intraparticle diffusion rate constant (mg/g min), q_t is the amount adsorbed (mg/g) at time t (min).

The correlation coefficient in this model (Fig. 10) was also high for the nanoparticles of CuO nanoparticles;

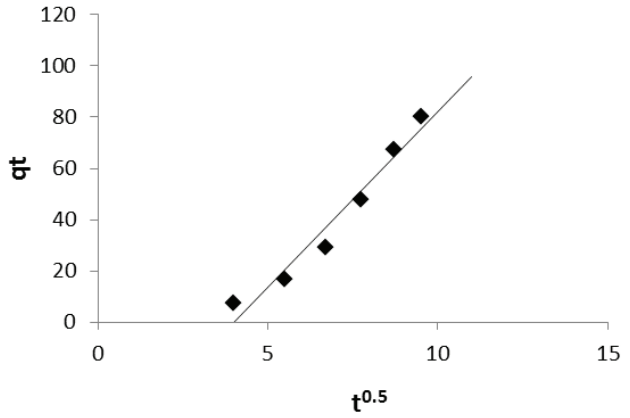

Fig. 10. Intraparticle diffusion plot of ciprofloxacin adsorption on CuO.

also the amount of *c* from the intraparticle diffusion equation was less than zero (q_t = 13.677$t^{0.5}$ – 54.599). Then, intraparticle diffusion model is a suitable controlling factor in determining the kinetics of the process (R^2 = 0.9564) [31,32].

4. Conclusions

In this study, the adsorption of ciprofloxacin onto CuO nanoparticles has been investigated. The results of this study indicate that the process of adsorbing in cupric oxide nanoparticles, in a very short time can remove ciprofloxacin; with increasing contact time and CuO nanoparticles dosage removal efficiency increases. Optimum conditions for the operation of the CuO nanoparticles with ciprofloxacin concentration of 10 mg/L, pH of 7, CuO dose 0.1 g/L and contact time of 60 min can remove a large impact on the concentration of ciprofloxacin in water. According to the results, at the best conditions of optimal the removal efficiency of 77% was observed. The process of ciprofloxacin adsorption on CuO nanoparticles was depended on Freundlich absorption isotherm more than other isotherms. CuO nanoparticles an absorber with a very high capacity is yet convenient economically to remove various contaminants from water. This method can be used as a novel method for treating wastewater contaminated with drug sources.

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