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Kinetic and thermodynamic studies of Cu(II) adsorption onto calcium phosphate

Özlem Dogan*, Büsra Bodur, Gözde Inan

Yildiz Technical University, Chemical Engineering Department, Davutpasa, 34210 Istanbul, Turkey,
Tel. +90 2123834760, Fax +90 212 3834725, email: dogano@yildiz.edu.tr (Ö. Dogan), busra_bdr@yahoo.com (B. Bodur),
gozdetekirdag_59@hotmail.com (G. Inan)

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ABSTRACT

Adsorption of Cu(II) from aqueous solutions by calcium phosphate powders, which were produced by wet chemical synthesis has been studied. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. It was determined that the Langmuir isotherm fitted well the adsorption isotherm of Cu(II). As a result of the experiments performed, the maximum adsorption capacities of powders increased from 13.76 mg/g to 19.92 mg/g when the adsorbent production temperature decreased from 70°C to 25°C. Thermodynamic data revealed that the adsorption process was spontaneous and endothermic. Adsorption kinetics data were tested using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-second-order model is the most convenient model to represent the adsorption kinetic.

Keywords: Adsorption isotherm; Kinetics; Thermodynamics; Heavy metals; Calcium phosphate ; Copper

1. Introduction

The contamination of water by toxic heavy metals has created major environmental pollution problems. Heavy metal (e.g. Cu, Cd, Zn, Ni, Pb, Hg and Cr) containing wastewaters have originated from metal plating, mining operations, battery manufacture, petroleum refining, pigment manufacture, etc. [1,2]. These heavy metals are non-biodegradable, tend to accumulate in living tissues, and cause various diseases. Therefore, it is essential to remove them from wastewater before discharge [3,4].

There are several methods for the removal of heavy metals from aqueous solutions, including chemical precipitation [5], ion exchange [6], electrodialysis [7], membrane separation [8], adsorption [9,10] etc. However, most of these processes may not be preferred due to high operation costs, low efficiency and disposal problem. Among these processes, adsorption process is a very effective alternative for the removal of heavy metals from aqueous solutions [11,12]. A large variety of adsorbents such as activated carbons [13], silicas [14,15], plant wastes [2], zeolites [16], calcite [17], and polymers [18,19], have been used for the removal of heavy metals.

In recent years, several investigations have been carried out for removal of heavy metals from aqueous solution using the calcium phosphate salts, especially hydroxyapatite. It is reported that apatite minerals can be used for purification of wastewaters by adsorption, ion exchange, precipitation and surface complexation due to their excellent surface characteristics and the properties of ion adsorption and exchange. These type of material gain great scientific and economic significance as they have the advantages wide sources, simple process, low cost and easy application [20–22].

The aim of this study was to evaluate removal of Cu(II) from aqueous solutions by calcium phosphate powders, which were produced by wet chemical synthesis at different temperatures. The effects of contact time, initial Cu(II) concentration and adsorbent production temperature were investigated on the Cu(II) adsorption. Langmuir and Freundlich adsorption isotherm models were used to describe the adsorption mechanism of Cu(II) at the studied conditions. The adsorption kinetics was analyzed using pseudo first order, pseudo second order and intraparticle diffusion models.

2. Experimental

2.1. Materials

All chemicals used in this work were analytical grade. Cu(II) solutions were prepared from Cu(II) chloride

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*Corresponding author.

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dihydrate and distilled water. Calcium phosphate powders were synthesized by wet chemical precipitation at different temperature (Table 1). The synthesized calcium phosphate powders were sintered by thermal treatment in air at a heating rate of 10°C/min at 650°C for 3 h. The main structure of the powders were identified as hydroxyapatite by X-Ray Diffraction (XRD) analysis (Panalytical X'ert Pro, CuKα radiation) and FT-IR spectral analysis (Bruker Alpha P). The specific surface area of powders was determined by BET method (Quantachrome Instruments Autosorb 1). The procedure of the production and the characterization of calcium phosphate powders was reported in our previous study [23]. X-ray powder diffraction patterns of calcium phosphate powders (Fig. 1) show that the crystallinity of adsorbents increased when the production temperature was increased from 25°C to 70°C. FT-IR spectrum of CP50 and CP70 powders have shown characteristic bands for hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Fig. 2). The bands of CP70 and CP50 powders were assigned as 3570 cm^{-1} and 630 cm^{-1} stretching in OH$^-$ groups; 1090-1021, 961, 600, 560, 473 cm^{-1} vibrations of the PO_4^{3-} groups [24]. As seen in Fig. 2, the peaks at 3570 cm^{-1} and 630 cm^{-1} (due to OH$^-$ groups) and the first peaks at 1090 cm^{-1} (due to PO_4^{3-} groups) were observed for CP25 powder which indicates that amorphous calcium phosphate was formed in the structure.

Table 1
Production temperature of calcium phosphate powders

Calcium phosphate powders	Production temperature (°C)
CP25	25
CP50	50
CP70	70

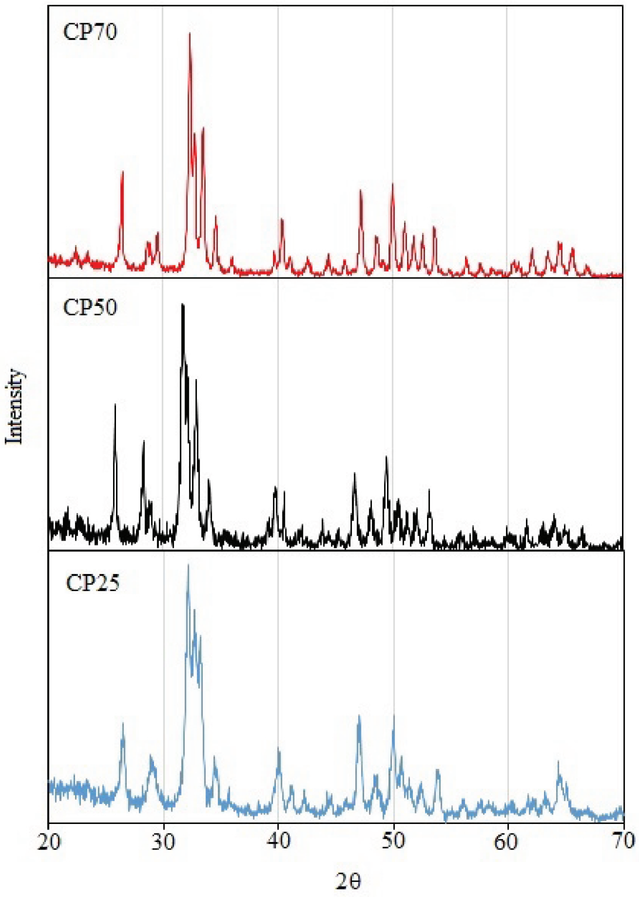

Fig. 1. X-ray diffraction patterns of calcium phosphate powders.

The specific surface areas of CP25, CP50 and CP70 were found as 19.16, 23.78 and 23.04 m^2/g, respectively. The production temperature did not significantly affect the specific surface area [23].

2.2. Equilibrium adsorption experiments

Adsorption experiments were carried out in the batch process. The Erlenmeyer flasks containing 25 mL of Cu(II) solution of different initial concentrations (2–50 mg/L) were prepared, and then 5–80 mg of adsorbent was added into the solution. During the adsorption period, solution pHs were measured (Eutech Instruments Alpha pH 1000), and no pH change has been observed. The solution pH value is one of important parameters controlling the heavy metal ions adsorption because the degree of ionization of the metal ions and the solubility of the adsorbent depends on it. Previous studies show that the optimum solution pH value for adsorption of Cu(II) from aqueous solutions onto calcium-based adsorbent is between 5 and 6 [22,25]. Initial pHs of the Cu(II) solutions were measured as 5.6, and all experiments were carried out at pH 5.6. After agitating these suspensions for 75 min at constant temperature in a thermostated bath with a shaker, the mixed liquors were centrifuged for 15 min at 5000 rpm. Initial and equilibrium Cu(II) concentrations were determined by using Perkin-Elmer Analyst 200 AAS. The equilibrium experiments were carried out at 25°C, 35°C and 45°C. Cu(II) adsorption capacity was calculated using the following equation:

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

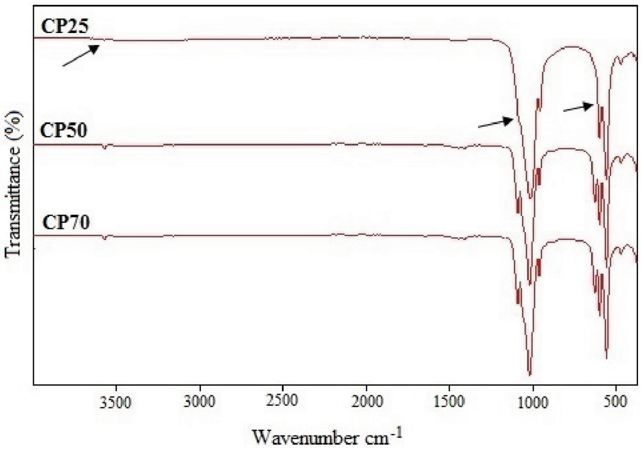

Fig. 2. FT-IR spectrums of calcium phosphate powders.

where C_0 and C_e are the initial and equilibrium Cu(II) concentrations (mg/L) respectively, V is the Cu(II) solution volume (L) and M is the mass of the adsorbent (g). Adsorption isotherms were obtained by using the equilibrium data.

2.3. Adsorption isotherms

Adsorption isotherms are very important to determine the equilibrium adsorption capacity of the adsorbent at constant temperature. There are several adsorption isotherm models to explain the adsorption equilibrium. However, the most commonly used isotherm models in the application of the adsorption of metal ions onto adsorbent are Langmuir and Freundlich. In this study Langmuir and Freundlich adsorption isotherms models were used to explain the adsorption equilibrium.

The Langmuir equation is one of the best known empirical equations based on the saturated monolayer adsorption. It is given as follows [26]:

$$q_e = \frac{bC_e q_{max}}{1 + bC_e} \tag{2}$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium metal ion concentration in aqueous solution (mg/L), q_{max} and b are the Langmuir adsorption constant related to maximum adsorption capacity (mg/g) and the free energy of adsorption (L/mg), respectively. The Langmuir constants, q_{max} and b, can be determined by using the linear form of Eq. (2).

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

The slope and intercept of the plot of C_e/q_e vs. C_e (Eq. (3)) were used to calculate the constants q_{max} and b.

Langmuir isotherm model can be expressed by a dimensionless constant termed as separation factor, R_L, which is defined by Eq. (4);

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_0 is the initial concentration of metal ion (mg/L). The magnitude of R_L determines the feasibility of the sorption process. If $0 < R_L < 1$, it indicates favorable adsorption. If $R_L = 1$, the adsorption is linear, if $R_L = 0$, the adsorption is irreversible [27,28].

The Freundlich equation is based on multilayer adsorption onto heterogeneous surface, and adsorption heat. It is expressed as follows [27,29]:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F and n are Freundlich constants related to the adsorption capacity of adsorbent (mg/g) and adsorption intensity, respectively. Eq. (5) can be linearized as follows:

$$ln\, q_e = ln\, K_F + \left(\frac{1}{n}\right) ln\, C_e \tag{6}$$

The slope and intercept of Eq. (6) were used to calculate the Freundlich constants, K_F and n.

2.4. Adsorption kinetics

Kinetic adsorption experiments were carried out to determine the adsorption rate of Cu(II). 250 mL of 20 mg/L Cu(II) solution was added to the reaction vessel, which was thermostated at 25°C. Initial pH was measured and then a given amount of the adsorbent was added into the solution. Solution pH was measured during the experiments. Solution was stirred at 300 rpm for 120 min at 25°C. At certain time intervals, a little amount of samples were taken and immediately centrifuged during the 120 min of reaction period. The Cu(II) concentration in the supernatant was analyzed by atomic absorption spectrophotometer. The Cu(II) adsorption kinetics were examined by pseudo-first order and pseudo-second order kinetic models and intraparticle diffusion model.

The pseudo-first-order kinetic model can be expressed as [30]:

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t\right) \tag{7}$$

where k_1 is the pseudo-first-order rate constant (1/min), q_e and q_t are the amount of adsorption (mg/g) at equilibrium and time t, respectively. If Eq. (7) is integrated for the boundary conditions of $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$ the kinetic expression becomes:

$$ln\left(q_e - q_t\right) = ln\, q_e - k_1 t \tag{8}$$

The values of k_1 and q_e were calculated from the slope and intercept of the plot of $ln(q_e - q_t)$ vs. t, respectively.

The pseudo-second-order kinetic model is given as the following equation [31]:

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \tag{9}$$

where k_2 is the pseudo-second-order rate constant (g/mg·min), q_e and q_t are the amount of adsorption (mg/g) at equilibrium and time t, respectively. Integrating Eq. (9) with the same boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, Eq. (9) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

The slope and intercept of the plot of t/q_t vs. t were used to calculate the values of k_2 and q_e. At $t = 0$, initial adsorption rate, h (mg/g min), is defined as follows:

$$h = k_2 q_e^2 \tag{11}$$

The intraparticle diffusion model that is used to identify the rate limiting step is given as follows:

$$q_t = k_{id} t^{1/2} + c \tag{12}$$

where k_{id} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), q_t is the amount of adsorption (mg/g) at time t, respectively [32]. According to Eq. (12), a plot of q_t vs. $t^{1/2}$ should be a straight line with a slope k_{id} when the intraparticle diffusion is rate-limiting step. The adsorption kinetics is controlled only by intraparticle diffusion when the plot go through the origin. If the plot is not linear or the intercept is not zero then the adsorption kinetics may be controlled by two or more steps [33,34].

3. Results and discussion

3.1. Effect of initial Cu(II) concentration

Initial ion concentration is one of the process parameters that affect the adsorption capacity. Effect of initial Cu(II) concentration on adsorption was given for CP70 in Fig. 3. It can be seen from Fig. 3 that percentage Cu(II) removal decreased while the adsorption capacities increased with increasing initial Cu(II) concentrations. When the initial Cu(II) concentration has been increased from 5 mg/L to 50 mg/L, the adsorption capacities increased from 2.48 mg/g to 10.48 mg/g and the percentage Cu(II) removal decreased from 99.3% to 41.9%. The adsorption capacity increased with the increase of Cu(II) concentration as the mass transfer driving force increased. The decrease in the percentage Cu(II) removal with increasing Cu(II) concentration might be caused by the saturation of the binding sites on the adsorbent surface [33,35].

3.2. Adsorption isotherms studies

Determining the equilibrium adsorption capacity of the adsorbent and the adsorption mechanism are important for defining the adsorption processes. In the present work, convenience of the experimental data and theoretical (Freundlich and Langmuir) adsorption isotherm models has been investigated at different temperatures (Fig. 4). The values of the maximum Cu(II) adsorption capacity of CP50 adsorbent calculated for 25°C, 35°C and 45°C were obtained as 17.12 mg/g, 17.15 mg/g and 21.32 mg/g, respectively.

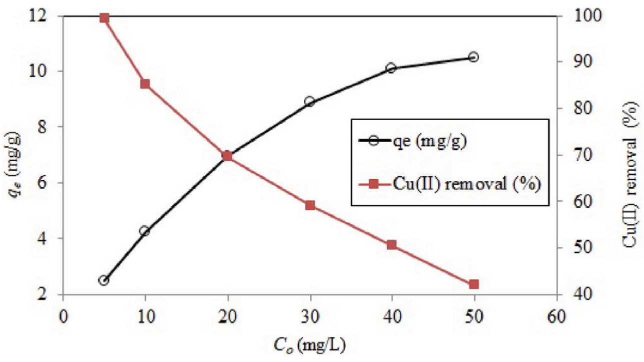

Fig. 3. Effect of initial Cu(II) concentration on adsorption (adsorbent (CP70) concentration: 2 g/L, pH = 5.6, T = 25°C, contact time = 120 min).

The effect of production temperature of calcium phosphate powders on the Cu(II) adsorption capacity has also been examined. Experimental and theoretical Cu(II) adsorption isotherms of CP25, CP50 and CP70 adsorbents are shown in Fig. 5. The experimental adsorption data were obtained at 25°C. Cu(II) adsorption capacity of calcium phosphate powders increased from 13.76 mg/g to 19.92 mg/g when the adsorbent production temperature decreased from 70°C to 25°C. The maximum adsorption capacity has been obtained with CP25, which has low crystallinity. Researchers reported also that the ion adsorption capacity of hydroxyapatite increased with decreasing crystallinity [21].

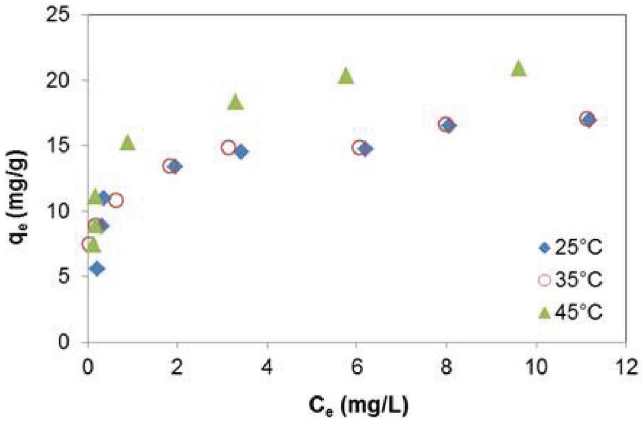

Fig. 4. Experimental Cu(II) adsorption isotherms of CP50 at different temperatures (C_0 = 20 mg/L, adsorbent concentration: 2 g/L, pH = 5.6, contact time = 75 min).

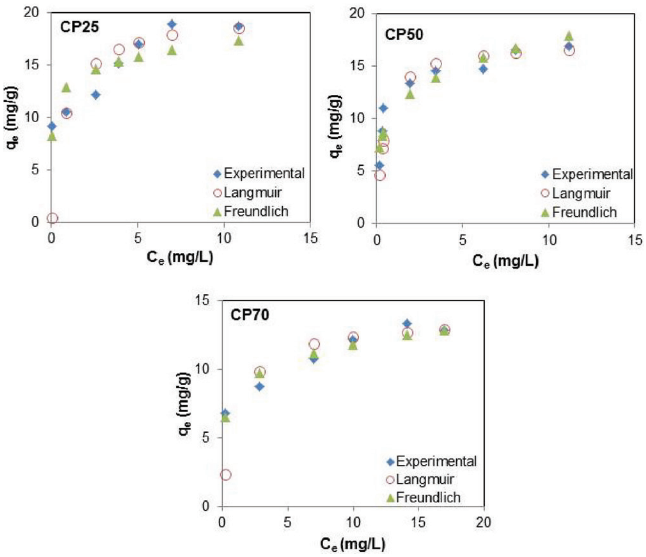

Fig. 5. Experimental and theoretical Cu(II) adsorption isotherms (C_0 = 20 mg/L, adsorbent concentration: 2 g/L, pH = 5.6, T = 25°C, contact time = 75 min).

Langmuir and Freundlich adsorption isotherm parameters, evaluated from the linear plots, are presented in Table 2. Evaluating R^2 values, it is clear that Langmuir model fit well with the experimental data. The theoretical maximum monolayer adsorption capacities of CP25, CP50 and CP70 were found to be 19.92, 17.12 and 13.76 mg/g, respectively. The adsorption capacity of Cu(II) on different adsorbents used in the literature are presented in Table 3. Separation factor, R_L, values are in the range of 0 and 1, which indicates that the Cu (II) adsorption onto CP25, CP50 and CP70 are favorable [28].

Thermodynamic parameters of Cu(II) adsorption such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) are calculated by using following equations [34]:

$$\Delta G^o = RT \ln K_C \tag{13}$$

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{14}$$

where R is the universal gas constant (8.314 J/mole K), T is the absolute temperature (K), and K_c is the adsorption equilibrium constant. K_c values were determined from Langmuir adsorption isotherms.

Thermodynamic data which were obtained at different temperature are given in Table 4. Negative values of ΔG^0 indicate the feasibility and spontaneity of adsorption process for all adsorbent at a given temperature. Positive values of ΔH^0 indicate the endothermic nature of adsorption process.

Table 3
Comparison of the adsorption capacity of Cu(II) with different adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
Rubber wood sawdust	5.73	34
Hazelnut husk	6.65	36
Activated clay	13.20	10
Acid-activated palygorskite	32.24	37
Tamarind fruit shell	64.10	38
CP25	19.92	This study
CP50	17.12	This study
CP70	13.76	This study

Table 4
Thermodynamic parameters for the adsorption of Cu(II).

Adsorbent	T (°C)	K × 10³	ΔG⁰ (kJ/mole)	ΔH⁰ (kJ/mole)	ΔS⁰ (kJ/mole K)
CP25	25	3.40	–20.15	24.65	0.15
	35	4.04	–21.26		
	45	6.39	–23.17		
CP50	25	4.45	–20.82	55.16	0.25
	35	7.73	–22.93		
	45	18.13	–25.92		
CP70	25	1.24	–17.66	31.55	0.17
	35	1.63	–18.93		
	45	2.78	–20.97		

3.3. Adsorption kinetics studies

The effect of contact time was investigated at 25°C. Plots of the adsorption of Cu(II) onto adsorbents, as a function of time are shown in Fig. 6. It can be seen that the adsorption of Cu(II) increased with increasing contact time and more than 50% of Cu(II) was adsorbed within 5 min. Although the equilibrium was reached at around 40 min contact time for CP70 and CP50 adsorbents, it was required 70 min in order to obtain equilibrium for CP25 sample.

The rate of adsorption process depends on several parameters such as physical and chemical properties of adsorbent, adsorbate concentration, interaction between the adsorbate and adsorbent, etc. [10,34]. The kinetic adsorption data were evaluated using pseudo-first-order and pseudo-second-order kinetic models and intraparticle diffusion model. Calculated kinetic parameters from models are given in Table 5. While pseudo-first-order and pseudo-second-order kinetic models give higher correlation coefficient (R^2), the intraparticle diffusion model gives lower than 80%. As can be seen from Table 5, the highest correlation coefficient was obtained for pseudo-second-order model. In addition to this, calculated q_e values are quite close to experimental q_e values. It can be concluded that the adsorption of Cu(II) onto calcium phosphate powders was well described by the pseudo-second-order model. Similarly, several studies have also reported that pseudo-second-order kinetic model well

Table 2
Langmuir and Freundlich isotherm constants for the adsorption of Cu(II) at 25°C

Adsorbent	Langmuir				Freundlich		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	K_F (mg/g)	n	R^2
CP25	19.92	1.255	0.035	0.981	13.108	8.540	0.770
CP50	17.12	2.317	0.024	0.995	10.726	4.708	0.854
CP70	13.76	0.889	0.048	0.990	8.227	6.357	0.942

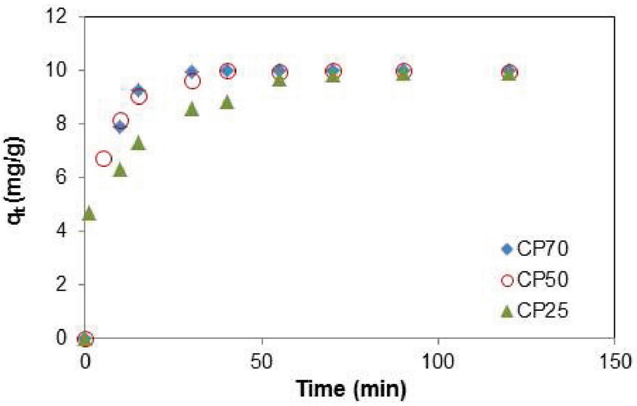

Fig. 6. Effect of contact time on the adsorption (C_0 = 20 mg/L, adsorbent concentration: 2 g/L, pH = 5.6, T = 25°C).

Table 5
Kinetic parameters for the adsorption of Cu(II)

	Adsorbent		
	CP25	CP50	CP70
$q_{e,exp}$ (mg/g)	9.897	9.985	9.996
Pseudo-first-order model			
$q_{e,cal}$ (mg/g)	7.210	4.375	7.762
k_1 (1/min)	0.063	0.089	0.169
R^2	0.959	0.969	0.917
Pseudo-second-order model			
$q_{e,cal}$ (mg/g)	10.363	10.194	10.163
k_2 (g/mg min)	0.020	0.054	0.070
h (mg/g min)	2.148	5.612	7.230
R^2	0.998	0.999	0.999
Intraparticle diffusion model			
k_{id} (mg/g min$^{1/2}$)	0.787	0.703	0.741
C	3.101	4.330	4.036
R^2	0.797	0.599	0.591

explains the adsorption kinetic of Cu(II) onto different adsorbents [39–41]. The pseudo-second-order model also suggests that chemisorption based on exchange or sharing of electrons between the adsorbate and the surface of the adsorbent might be rate-limiting step in adsorption process [31].

4. Conclusions

All calcium phosphate powders synthesized were evaluated in terms of efficiency of Cu(II) removal from aqueous solutions. Results showed that Cu(II) adsorption capacity of calcium phosphate powders increased with increasing initial Cu(II) concentration and the adsorbent production temperature. The equilibrium adsorption data fitted better to the Langmuir isotherm model than the Freundlich adsorption isotherm model. Thermodynamic data indicated that the adsorption process was spontaneous and endothermic. Cu(II) adsorption onto calcium phosphate powders followed by pseudo-second-order model.

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