Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.940391

56 (2015) 779–791
October

Taylor & Francis
Taylor & Francis Group

Kinetics modeling in liquid phase sorption of copper ions on brushite di-calcium phosphate di-hydrate $CaHPO_4{\cdot}2H_2O$ (DCPD)

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Received 27 December 2013; Accepted 22 June 2014

ABSTRACT

The sorption behavior of copper ions Cu^{2+} from aqueous solution on calcium phosphate DCPD was studied in static conditions, using batch experiments. The reaction process has shown the occurrence of two major steps. During the first interaction minutes, a rapid process occurred and led to removal of over 70% of copper ions by diffusion at the solid–solute interface. In the second step, the equilibrium was reached slowly after 300–400 min of reaction. Using the surface kinetic modeling, the experimental data was found to follow the pseudo-first-order model, which suggests the predominance of the chemisorption-type process, corresponding to a cation-exchange reaction between Cu^{2+} in solution and Ca^{2+} present in the phosphate structure. The sorption isotherm study has shown a well fit of the experimental data with the Sips model, with parameters indicating a single surface layer sorption mechanism and a maximum retention capacity of 309 mg/g when using low concentrations of reactants. At higher concentrations of Cu^{2+}, the pH of solutions decreases and the system becomes heterogeneous due to the partial dissolution of calcium phosphate DCPD.

Keywords: Calcium phosphate brushite; Kinetic modeling; Copper; Isotherm models

1. Introduction

Sorption processes in solid–liquid phase, including adsorption and ion exchange, are simple, effective and attractive methods for removing metal pollutants from water. Many sorbents have been examined and tested in different aspects for a long time. Among them, activated carbon is the most widely known due to its high capacity for trapping and holding a large variety of organic and inorganic contaminants in different media. In recent years, the development of low-cost sorbents such as agricultural by-products, biomass, chitosan, natural zeolite, clay, and others has led to the rapid growth of research interests in this field [1,2]. Some ion exchangers like zeolites, doped zeolites, and cation exchangers with different functional groupings also exhibit selective sorption capacities for wide range of dissolved pollutants [3,4]. The use of ion exchangers is strongly recommended for water purification and generally coupled with biological or other physical treatment.

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Copper is widely used in many industries such as metal finishing, electroplating, fertilizer, pigment, and wood manufacturing. However, chemical contamination of water by copper and some other heavy metals pose serious threats to environmental and public health because of their non-biodegradability and bioaccumulation properties [5]. The removal of Cu^{2+} ions from industrial effluents or decreasing its concentration to permissible level before discharge is becoming important and necessary to prevent environmental pollution.

For that purpose, removal of metallic pollutants from aqueous solutions or water by calcium phosphate compounds has been the subject of many studies in the literature. Some authors reported that the dissolution-precipitation mechanism is one of the responsible processes for removing the metal by $\beta\text{-}Ca_3(PO_4)_2$; $CaHPO_4{\cdot}2H_2O$; $Ca(H_2PO_4)_2{\cdot}H_2O$ and $\beta\text{-}Ca_3(PO_4)_2{\cdot}xH_2O$ [6,7], while others predicted that the interaction between Cu^{2+} and hydroxyapatite or phosphate rock is a complex mechanism including ion exchange, surface dissolution, surface adsorption and precipitation [8,9].

In our previous paper, a mixed Copper-calcium phosphate brushite type $[Ca_{1-x}Cu_xHPO_4{\cdot}2H_2O]$ has been synthesized and characterized. The structural study shows that the incorporation of divalent copper ions in the phosphate matrix is limited at 25% and depends on the pH of the medium [10]. Removal kinetics and isotherm studies of Cu(II) on calcium phosphate DCPD have also been performed by comparing linear and non-linear regression simulation techniques. A single surface layer sorption was found as being an appropriate isotherm and a non-linear regression as the most reliable technique for simulating the sorption data [11]. The purpose of the present work is to extend our previous research on copper interaction with calcium phosphate DCPD by treating in more detail the kinetic and isotherm studies. The different steps involved during the displacement of Cu^{2+} ions from solution towards the active sites of calcium phosphate $CaHPO_4{\cdot}2H_2O$ were also examined.

2. Experimental procedure

2.1. Chemicals

The dicalcium phosphate dihydrate $CaHPO_4{\cdot}2H_2O$ (brushite, DCPD) used as sorbent in this work was supplied by Riedel-de Haën (≥98%), without any prior treatment. The source of divalent copper ions were purchased from Merck as nitrate salt $Cu(NO_3)_2{\cdot}3H_2O$ (≥98.2%), because of low chelating capacity of NO_3^- with respect to the metal ion, in aqueous solution. Standard solutions at appropriate copper (II) concentrations were prepared at room temperature from known stock solutions by dilution in purified water.

2.2. Procedures

2.2.1. Kinetic study

The sorption potentials of calcium phosphate DCPD powder has been carried out at room temperature by batch technique on a mechanical shaker using two different experimental procedures:

(a) A fixed amount of sorbent (1 g/l) was suspended and thoroughly shaken with series of 100 ml of copper ion solutions of concentration ranging from 50 to 280 mg/l.

(b) Different sorbent doses (3–15 g/l) were mixed with 100 ml of 280 mg/l of copper solutions.

The initial and final pH of all mixing solutions were continuously controlled and found in between 4.75 and 6. This pH range provides optimum conditions in which the sorbent is quasi insoluble and the copper ions are globally in the divalent form Cu^{2+} [12]. The contact time intervals of sorption process were chosen between 5 and 400 min.

2.2.1. Equilibrium isotherm study

In these experiments, two different masses of calcium phosphate DCPD were added to two separate series of 100 ml of the copper solutions at various concentrations. The first experiments were performed using 0.1 g of the sorbent with concentrations of Cu^{2+} ranging from 45 to 513 mg/l, while the second experiments were conducted on 1 g of the sorbent with initial Cu^{2+} of 176 to 2,972 mg/l. The stirring time required to reach equilibrium was 300 and 400 min for 0.1 and 1 g of sorbents, respectively.

2.3. Analysis

Once the sorption reaches equilibrium, the mixture was centrifuged and the concentration of Cu^{2+} in the supernatant was evaluated by the inductively coupled plasma atomic emission spectroscopy ICP-AES (Jobin Yvon, Ultima 2). The copper ion which could integrate the phosphate structure was controlled by XRD using a Brucker D8 Advance diffractometer equipped with a copper anticathode and chemical analysis (ICP) by dissolving the sample in nitric acid (2 M). The values of the pH were measured by a pH-meter Hanna pH-211R equipped with an electrode of glass combined HI1131B.

2.4. Sorption modeling

The kinetic and equilibrium isotherm equations were used to describe the experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of the models often provide some insight into the sorption mechanism, the surface properties, and the affinity between reactants. The fitting of kinetic and isotherm models to the experimental data was performed using "Microsoft Excel 2007" software. The choice of the correct model was determined by minimizing the error function (ERRSQ) or by using the correlation coefficient R^2 for non-linear and linear regression methods, respectively [13]. The ERRSQ function used in non-linear regression technique has been optimized by the "Solver" tool. It is expressed as follows:

$$\mathrm{ERRSQ} = \sum_{i=1}^{n} (q_{\mathrm{exp}} - q_{\mathrm{cal}})_i^2. \tag{1}$$

3. Results and discussion

3.1. Kinetic study

The sorption behavior of copper ions on calcium phosphate DCPD was examined at room temperature vs. time at a controlled solution pH. Fig. 1 illustrates the progress in amount of Cu^{2+} uptake per unit mass of sorbent for various initial concentrations of copper ions.

The kinetic sorption curves q_t (mg/g) vs. time have similar shapes and show a gradual increase at the beginning of the process to reach finally a steady state after 150 min for 50 mg/l of Cu^{2+} and extended up 400 min for high copper concentrations. Concomitantly, the pH shows a slight decrease during the first 30 min of stirring before rising again until equilibrium. As seen in Fig. 1, the sorption of metal ion has taken place in two stages. The first one, wherein the removal process presents high efficiency, is due to the large number of sorption sites available on the sorbent surface and the rapid diffusion process of metal ions from the solution toward active sites. This phenomenon can be confirmed with the slope of sorption line that has the highest value. The second stage represents the equilibrium state in which the surface of the sorbent is saturated with copper species. The q_t value at equilibrium increases with the initial concentration of copper ions. This is related to the driving forces needed to overcome the resistance of mass transfer between the liquid and solid phase. Similar findings were reported for the sorption of metals onto other various sorbents [14].

The fluctuation of pH at the beginning of the process is probably due to the limited buffer effect of calcium phosphate DCPD. This result has also been observed in calcium apatite, when interacting with Cu^{2+}, Zn^{2+}, and Pb^{2+} ions [15].

On the other hand, the effect of varying the sorbent dose using an initial copper concentration of 280 mg/l is shown in Fig. 2. It can be seen that the sorption rate of copper ions increased with increase in sorbent dosage. This could be because at higher dose of sorbent more active sites are available due to increased surface area or adsorption sites. As the sites are gradually filled up, the sorption proceeds slower and the kinetic becomes more independent on the rate [16]. The equilibrium sorbent capacity q_e, decreases with increasing the sorbent mass which could be due to insufficiency of metal ions in solution with respect to the available binding sites [17]. The addition of extra sorbent offers more active sites which are not fully utilized or saturated. Therefore, the unutilized mass of sorbent is accounted during the calculation of removal capacity leading to reduction of q_e values [18].

3.2. Kinetic modeling

3.2.1. External diffusion

The external diffusion of a solute from liquid to solid phases may be modeled according to the following equation [19]:

$$-\frac{\mathrm{d}C_t}{\mathrm{d}t} = k\frac{A}{V}(C_t - C_e) \tag{2}$$

The integral form can be written:

$$\ln\left[\frac{(C_0 - C_e)}{(C_t - C_e)}\right] = k\frac{A}{V}t = k't \tag{3}$$

where C_e: equilibrium concentration of solute in solution (mg/l), C_t: solute concentration at time t (mg/l),

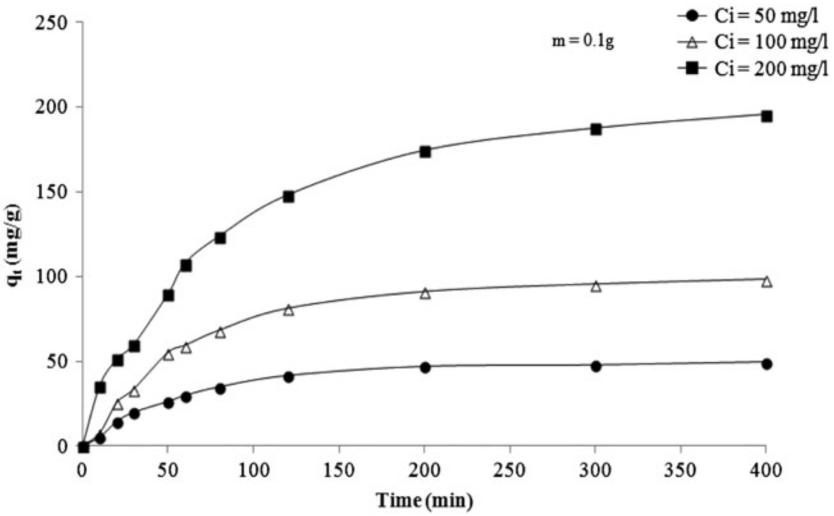

Fig. 1. Effect of contact time for different initial concentrations of copper ions.

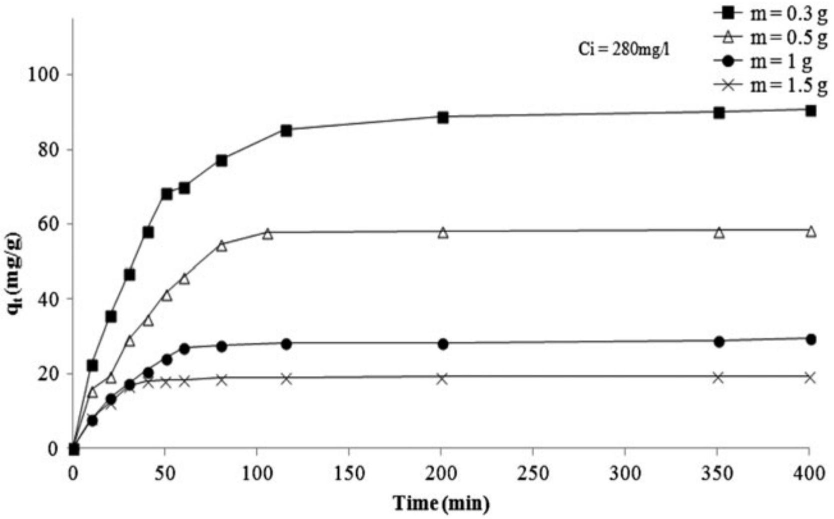

Fig. 2. Removal kinetics of copper ions at different masses of DCPD sorbents.

A: area of the solid/liquid interface (m^2), V: volume of solution (l), k: reaction constant (m/min).

The plotting of Eq. (3) using the linear regression leads to straight line with slope equal to k'.

For porous materials, Furusawa and Smith [20] and Mckay [21] have proposed another external diffusion equation which is written as:

$$\frac{C_t}{C_0} = \frac{1}{1 + m_s K_L} + B \times \exp\left[-\frac{k_f \times S_s \times t}{B}\right] \quad (4)$$

where C_0: initial concentration of solute (mg/l), B: constant equal to $\frac{m_s K_L}{1+m_s K_L}$, m_s: sorbent concentration (g/l), K_L: langmuir constant (l/g), S_s: surface area of sorbent (m^2/l), k_f: coefficient of external mass transfer (m/min).

The plotting of Eq. (4) is obtained with non-linear regression by minimizing the error function ERRSQ.

The classical external diffusion and Furusawa and Smith's models were applied to experimental data in order to evaluate the importance of this step on the sorption processes. Table 1 and Figs. 3 and 4 illustrate the modeling results.

Table 1
Kinetic parameters using external diffusion models

		Classical diffusion model		Furusawa and Smith model		
m (g)	C_i (mg/l)	k' (min^{-1})	R^2	k_L (l/g)	$k_f{\cdot}S_s$ (min^{-1})	ERRSQ
0.1	50	0.0166	0.9906	38.8011	0.0158	0.0194
0.1	100	0.0135	0.9952	35.1423	0.0158	0.0231
0.1	200	0.0108	0.9978	56.9926	0.0103	0.0255
0.3	280	0.0258	0.9966	8.3019	0.0245	0.0138
0.5	280	0.0248	0.9950	7.5336	0.0241	0.0387
1	280	0.0304	0.9999	5.8474	0.0331	0.0244
1.5	280	0.0629	0.9895	2.3519	0.0575	0.0229

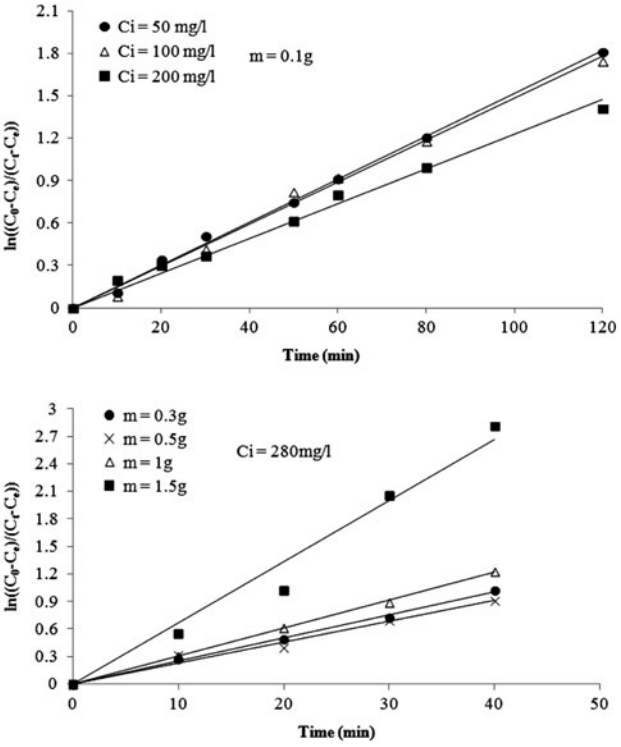

Fig. 3. External diffusion simulation using the classical model.

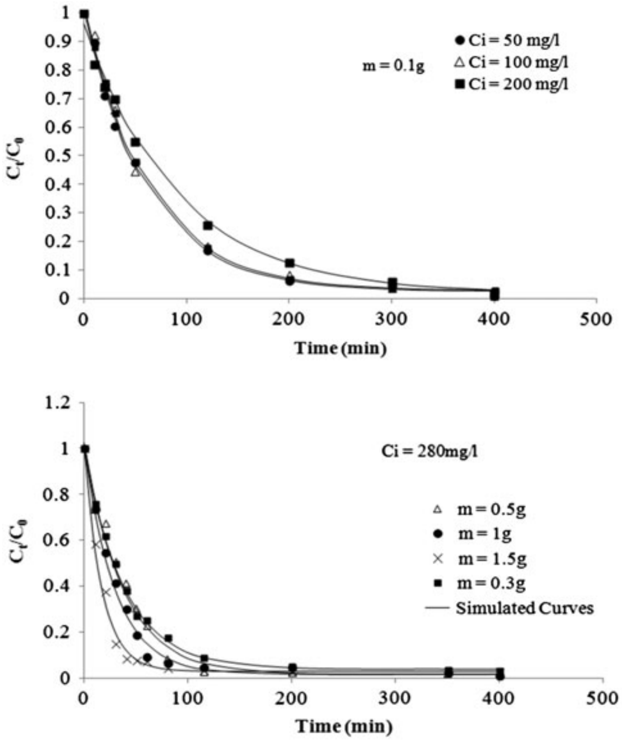

Fig. 4. External diffusion simulation using the model of Furusawa and Smith.

For all experiments, the plotting of Eq. (3) leads to a straight lines with better values of the linear regression factor R^2 (Table 1 and Fig. 3). Similarly, the plotting of Eq. (4) using nonlinear regression shows decreasing curves with minimizing values of error functions ERRSQ quite acceptable (Table 1 and Fig. 4). These results demonstrate that the external diffusion step is present during the sorption process. The resulting mechanism seems to depend on the initial copper concentration but also on the sorbent dose. Since the particle size is constant, the surface area from Eq. (4) will directly be proportional to the mass of the sorbent [22]. According to Table 1, the mass-transfer coefficient k_f increases with increasing sorbent dose and the initial copper concentration decreases. This effect can be explained by the large amount of active sites available to the metal ions for high mass of sorbent, thereby reducing the driving force in solid–liquid interface which consequently enhances the rate of diffusion process [22]. Otherwise, increasing the sorbent dose improves the driving force for mass transfer which reduces the diffusion rate.

3.3.2. Intra-particle diffusion

Weber and Morris observed that the plot of the adsorption capacity (q_t) vs. the square root of time ($t^{1/2}$) results in a straight line when the intra-particle diffusion is the controlling factor in the sorption process [23]. The model's equation is thus expressed as follows:

$$q_t = k_{dif} \cdot t^{1/2} + C \tag{5}$$

where q_t: quantity sorbed at a given time, expressed by $q_t = (C_0 - C_t)V/m$ (mg/g), k_{dif}: constant diffusion rate (mg/g min$^{1/2}$), C: double-layer thickness (mg/g).

The plots of Eq. (5) for different experiments show multi-linearity in the process (Fig. 5). According to recent works, similar lines have indicated the existence of three steps during sorption process [24,25]. The first can be attributed to diffusion of sorbate from solution to the external surface of the sorbent. The second stage may describe the intra-particle diffusion process and the final one corresponds to the equilibrium state wherein the intra-particle diffusion becomes ineffective due to low concentration of sorbate in the solution [22,26]. On the other hand, if the lines of the second stage pass through the origin the intra-particle diffusion becomes the controlling step. Otherwise, the larger the intercept C (Eq. (5)), which reflects the boundary layer thickness, the greater the contribution of the boundary layer can be [27]. The determination of intra-particle diffusion coefficients using a linear regression analysis are shown in Table 2.

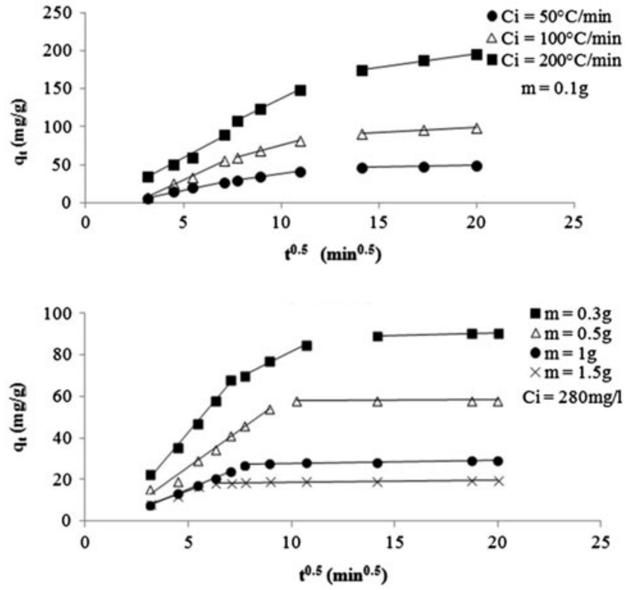

Fig. 5. Kinetic modeling using intra-particle diffusion model.

From Fig. 5, it is clear that the intra-particle diffusion step exists only at low doses of the sorbent ($m \leq$ 0.3 g). For high doses of sorbent, this intermediate process practically disappears and equilibrium is reached so fast. The parameter C increases with the concentration of Cu^{2+}, as it has been reported by some authors, this behavior may be attributed to the growing effect of the double layer on sorption [27,28]. Accordingly, the intra-particle diffusion phase may occur rather at low concentrations of sorbent and sorbate but does not constitute the determining step because the curves do not intercept the origin. It is evident that beside the intra-particle diffusion, other sorption processes may exist.

3.3.3. Surface sorption

To provide a suitable model for the surface reaction step, the experimental data were fitted by non-linear regression techniques using the most known equations: the pseudo-first-order model of Lagergren, the pseudo-second-order, the Adam–Bohart–Thomas, and the Elovich models (Table 3).

The results of modeling using the equations mentioned above are shown in Fig. 6 and the calculated kinetic parameters are summarized in Table 4.

The ERRSQ error function values obtained from non-linear regression analysis were the lowest for the Lagergren pseudo-first-order kinetic model, which indicate the relative good adequacy of this model with

Table 2
Intra-particle diffusion coefficients for Cu^{2+} ions sorption onto calcium phosphate DCPD

m (g)	C_i (mg/l)	k_{dif} (mg/g min$^{1/2}$)	C (mg/g)	R^2
0.1	50	3.62	1.90	0.996
0.1	100	6.79	7.24	0.999
0.1	200	12.53	11.05	0.999
0.3	280	5.05	15.14	0.993

Table 3
Surface sorption kinetic models

Model	Equation
Pseudo-first-order	$q_t = q_e(1 - \exp(-k_1 t))$
Pseudo-second-order	$q_t = \dfrac{q_e^2 k_2 t}{1 + q_e k_2 t}$
Adam–Bohart–Thomas	$q_t = \dfrac{C_0}{m_S} \cdot \dfrac{1 - \exp[k_{ads} m_S (\frac{C_0}{m_S} - q_e).t]}{1 - \frac{1}{q_e}\frac{C_0}{m_S}\exp[k_{ads} m_S (\frac{C_0}{m_S} - q_e).t]}$
Elovich	$q_t = \dfrac{1}{b_E}.\ln(1 + a_E.b_E.t)$

the experimental data. Therefore, the removal of Cu^{2+} ions by calcium phosphate DCPD was performed by chemisorption process preceded by diffusion through a boundary [26,29]. As we have seen above, the diffusion mechanism includes both external and intra-particle diffusions. On the other hand, the chemisorption reaction corresponds probably to a cation exchange process between calcium ions available in calcium phosphate DCPD and copper ions present in solution as it have been demonstrated in our previous work [10]. The constant k_1 of the pseudo-first-order model was found to increase from 0.0127 to 0.0157 min^{-1} with decreasing concentration of copper ions and from 0.0259 to 0.0580 min^{-1} with the increase in mass of sorbent. This effect can be explained by the fact that the removal process was faster at low concentrations of Cu^{2+} and at high mass of DCPD due to the increase in active sites quantity per amount of solute present in solution [21,26].

When the concentration of Cu^{2+} ions was low and the pH of solution was slightly acidic, the removal process seems to follow the cation exchange reaction according to scheme:

$$\begin{aligned} &CaHPO_4 \cdot 2H_2O + xCu^{2+} \\ &\quad \longrightarrow Ca_{1-x}Cu_xHPO_4 \cdot 2H_2O + xCa^{2+} \end{aligned} \tag{6}$$

At higher concentrations of Cu^{2+} ions and at low solution pH, another parallel phenomenon appears with the exchange reaction which is the dissolution/precipitation process [10]. It can be written as follows:

$$\begin{aligned} &yCaHPO_4 \cdot 2H_2O + yH^+ \\ &\quad \longrightarrow yCa^{2+} + yPO_4{}^{3-} + 2yH^+ + 2yH_2O \end{aligned} \tag{7}$$

$$3y/2Cu^{2+} + yPO_4^{3-} + yH_2O \longrightarrow y/2Cu_3(PO_4)_2 \cdot 2H_2O \tag{8}$$

The formation of a new copper phosphate $Cu_3(PO_4)_2{\cdot}2H_2O$ strongly depends on pH of the medium and it was previously identified by XRD and FTIR analysis [10].

3.3. Adsorption isotherm studies

The effect of initial concentration on the amount of Cu^{2+} sorbed per unit mass of the calcium phosphate DCPD was obtained by studying the sorption process at equilibrium and at room temperature (20°C). The adsorption isotherms are presented in Fig. 7.

According to the classification proposed by Giles and Limousin [30,31], the experimental isotherm curves are of type H, which means that there is a strong affinity between solute and sorbent. The maximum uptake of Cu^{2+} ions was equal to 258 and 309 mg/g for initial DCPD masses of 1 and 0.1 g, respectively.

3.4. Isotherm modeling

To understand the sorption mechanism of Cu^{2+} ions on the calcium phosphate DCPD, the experimental data were analyzed and fitted by sorption isothermal models using the nonlinear regression. Here, Langmuir, Freundlich, and Sips models were used to describe the equilibrium state between sorbed Cu^{2+} on calcium phosphate DCPD and Cu^{2+} ions in solution (C_e) at a constant temperature (Table 5).

Where C_e is the equilibrium concentration (mg/l), q_e is the amount of Cu^{2+} sorbed at equilibrium (mg/g), K_F is the Freundlich equilibrium constant (mg l/g), n is the parameter characterizing the system's heterogeneity, q_{max} is the sorption capacity (mg/g), K_L is the Langmuir equilibrium constant (l/mg), and a_{LF} is the sips isotherm constant (l/mg).

The modeling results are shown in Fig. 8 and summarized in Table 6.

The sorption isotherm data obtained from the interaction of Cu^{2+} ions onto calcium phosphate DCPD at equilibrium (Fig. 8) showed a best fit with the Sips isotherm model based on the lowest values of error functions (Table 6), and led to the calculated q_{max} values very close to the experimental results. The Sips model parameter n is observed close to 1 for the lowest mass of sorbent (0.1 g). In this case, the isotherm model can be simplified and becomes comparable to the Langmuir model.

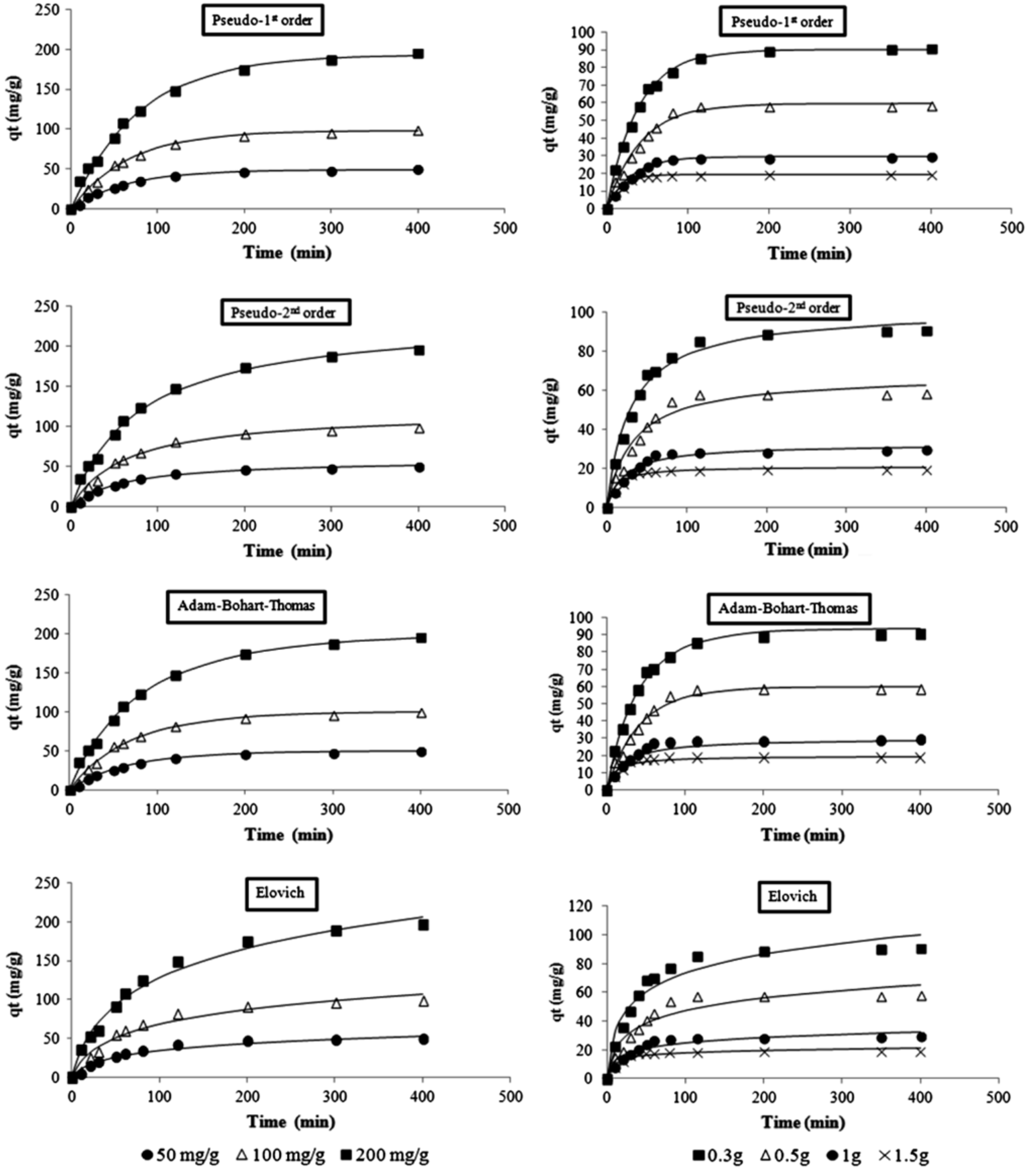

Fig. 6. Surface sorption modeling for different initial concentrations of Cu^{2+} and masses of calcium phosphate DCPD.

Table 4
Surface sorption kinetic parameters for Cu^{2+} sorption onto calcium phosphate DCPD

Experiment			Pseudo-first order			Pseudo-second order			Adam–Bohart–Thomas model			Elovich model		
m_i (g)	C_i (mg/l)	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	q_e (mg/g)	ERRSQ	k_2 ($g\,mg^{-1}\,min^{-1}$)	q_e (mg/g)	ERRSQ	k_{ads} ($g\,l\,mg^{-2}\,min^{-1}$)	q_e (mg/g)	ERRSQ	a_E (mg/min g)	b_E (g/mg)	ERRSQ
0.1	50	49.49	$1.57.10^{-02}$	48.83	0.8983	$2.89.10^{-04}$	58.58	1.4963	$8.42.10^{-05}$	195.85	0.9459	1.5066	0.0705	2.7862
0.1	100	98.77	$1.51.10^{-02}$	97.63	2.3522	$1.33.10^{-04}$	118.41	3.7440	$3.39.10^{-05}$	457.16	2.6042	2.6961	0.0338	6.2248
0.1	200	195.88	$1.27.10^{-02}$	192.86	5.9952	$5.36.10^{-05}$	238.10	5.6421	$3.16.10^{-05}$	442.13	5.3743	4.3792	0.0165	7.7427
0.3	280	90.63	$2.59.10^{-02}$	89.96	1.3038	$3.26.10^{-04}$	101.66	3.3904	$3.52.10^{-05}$	261.55	2.0506	8.2688	0.0515	6.9617
0.5	280	58.34	$2.40.10^{-02}$	59.51	1.9974	$4.49.10^{-04}$	67.47	3.6512	$1.73.10^{-05}$	59.76	2.2219	4.6998	0.0758	5.6840
1	280	29.44	$3.26.10^{-02}$	29.31	0.7390	$1.37.10^{-03}$	32.63	1.7103	$1.59.10^{-04}$	30.00	2.3973	4.8564	0.1787	2.9733
1.5	280	19.33	$5.80.10^{-02}$	19.31	0.4581	$4.50.10^{-03}$	20.89	1.0818	$3.25.10^{-04}$	19.84	1.3296	38.3952	0.4089	1.9551

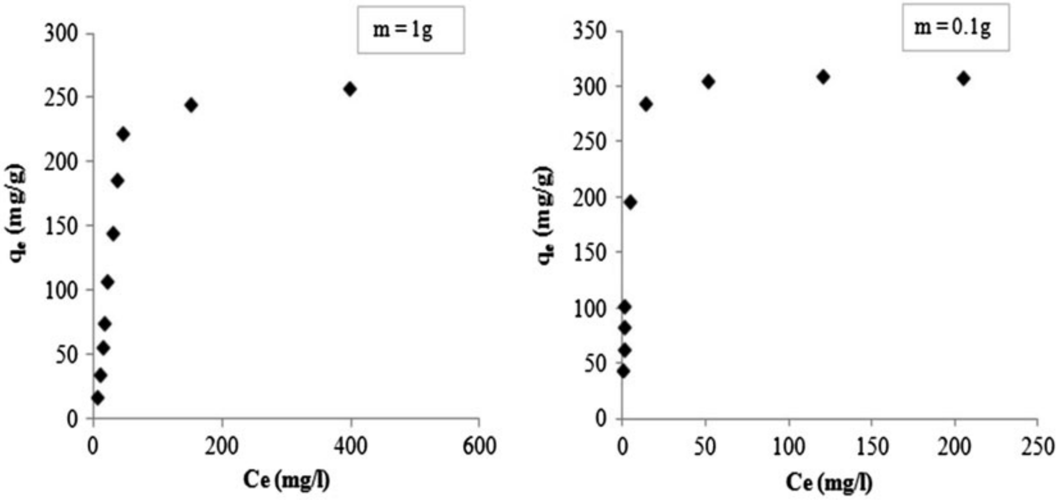

Fig. 7. Sorption isotherms of copper ions over calcium phosphate DCPD.

Table 5
Sorption isotherm equations used to model the equilibrium state

Model	Equation significances Pl
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$
Sips	$q_e = \frac{q_{max} (a_{LF} C_e)^n}{1 + (a_{LF} C_e)^n}$

Therefore, the mechanism of sorption adopts more likely the assumptions of Langmuir [32], which predicts the sorption of Cu^{2+} ions on identical sites and each site holds a single species. This approach justifies the exchange process that could be established between the calcium ions of sorbent and copper ions of solution as it has been observed and discussed in many ion exchange resins [33–35]. When the mass of sorbent is 1 g, the parameter n becomes different from unity due to the heterogeneity of the system [36] which results from the high concentrations of copper ions in solution at low pH. This causes the partial dissolution of calcium phosphate DCPD and leads to the formation of new phase of copper phosphate.

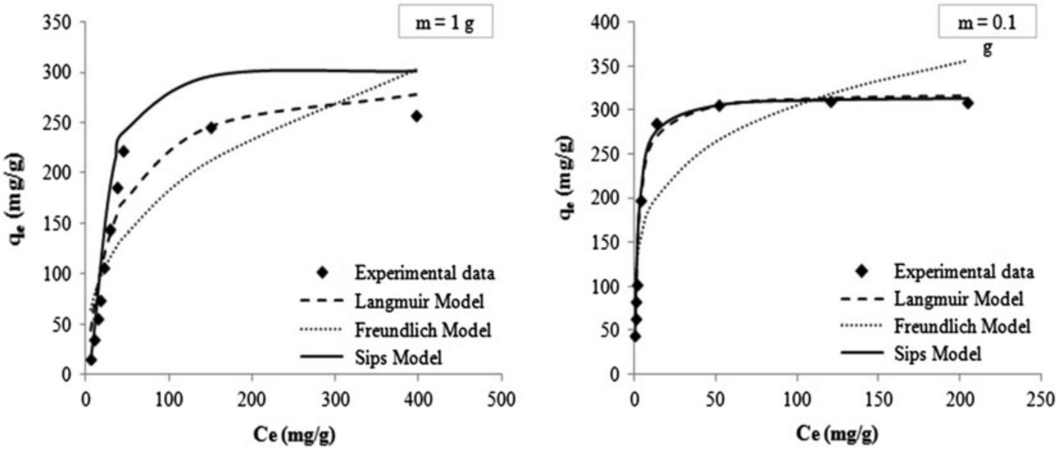

Fig. 8. Isotherm sorption modeling of Cu^{2+} ions over calcium phosphate DCPD.

Table 6
Isotherm parameters for the sorption of Cu^{2+} ions onto calcium phosphate DCPD

		Langmuir isotherm			Freundlich isotherm			Sips isotherm			
	q_{max} (exp) (mg/g)	k_L (l/mg)	q_m (mg/g)	ERRSQ	k_F (mg l/g)	$1/n$	ERRSQ	a_s (l/mg)	q_m (mg/g)	n	ERRSQ
$m = 0.1$ g	309	0.3928	320.1	6.36	114.92	0.2123	45.60	0.4225	314.8	1.1135	4.59
$m = 1$ g	258	0.0297	302.1	26.72	34.01	0.3656	45.44	0.0430	256.4	2.2659	6.76

Table 7
Comparison of maximal sorption capacity of different materials

Sorbents	q_{max} (mg/g)	References
Carbonate hydroxyapatite	143	[37]
Hydroxyapatite	125	[38]
Carbonated phosphate	29.8	[39]
Natural phosphate rock	166	[15]
Na-exchanged bentonite	30	[40]
Natural bentonite	8	[40]
Cedar sawdust	294	[41]
Chitosan	107	[42]
Banana peel	125	[43]
Present work	258–309	

4. Conclusion

Modeling the kinetic removal of Cu^{2+} ions by calcium phosphate DCPD, in aqueous solutions, showed the involvement of two major processes:

(1) During the first minutes of interaction (transitional period) and depending on mass of sorbent, the diffusion in the solid-solute interface was the predominant process. However, the kind of diffusion depended on the concentration of reactants. At low concentrations of sorbent and solute, the predominant process was primarily an external diffusion through the diffuse double-layer followed by intra-particle diffusion. At high masses of sorbent and high initial concentrations of Cu^{2+} ions in solution, the diffuse double-layer gradually thickened, thus leading to the predominance of external diffusion to the detriment of intra-particle diffusion. During this phase, between 70 and 90% of Cu^{2+} ions were removed.

(2) During the second phase (equilibrium period), the sorption process was slow and the equilibrium was reached after 300–400 min. The surface sorption reaction was predominant at this step with a chemisorption type process corresponding to a cation exchange reaction between copper ions in solution and calcium ions present in the sorbent, following a pseudo-first-order reaction with respect to active sites. The reaction rate increases when decreasing the concentration of solute and increasing the mass of sorbent.

The sorption isotherm study showed that the characteristics of the system (DCPD–Cu^{2+}) at equilibrium depended on the mass of solid. At low sorbent mass, the removal follows the assumptions of Langmuir that agree well with the cation exchange mechanism, which described the interaction between the DCPD and Cu^{2+} ions in solution as carrying the following equation:

$$\begin{aligned} &CaHPO_4 \cdot 2H_2O(s) + xCu^{2+}(aq) \\ &\longrightarrow Ca_{1-x}Cu_xHPO_4{\cdot}2H_2O(s) + xCa^{2+}(aq) \end{aligned} \qquad (9)$$

At high sorbent dose ($m = 1$ g), the system becomes heterogeneous due to the presence of large quantity of copper ions and phosphate ions produced by partial dissolution of the sorbent.

Compared with the sorbents already studied in the literature (Table 7), the maximum retention capacity of Cu^{2+} ions was equal to 309 and 258 mg/g for DCPD sorbent doses of 1 and 10 g/l, respectively. The present findings suggest that calcium phosphate DCPD is efficient and can be considered as a potential support for the removal of Cu^{2+} ions in aqueous solution because, at moderate pH, it can lead to two parallel reactions: cation exchange process between structural calcium and copper present in solution and dissolution/precipitation process.

Acknowledgment

The authors are grateful for the financial support of this project by research Grant (SCH04/09) of University of Mohammed V-Agdal, Morocco.

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