Equilibrium and Kenitic Modeling of Cd(II) Adsorption from Aqueous Solution using Tricalcium Phosphate

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Abstract

The performance of adsorption of Cd(II) from aqueous solutions onto tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) have been determined and studied with kinetic and isotherm models. The effect of contact time, concentration of Cd(II) was studied. Extraction kinetics is very fast, Indeed t=5 mn. The amount of TCP sorbed per gram of Cd(II) *qt* (mg/g) increased with increasing initial Cd(II) concentration. The adsorption of Cd(II) by TCP followed pseudo-second order kinetics. Diffusion intraparticle is the only rate-controlling step. Adsorption equilibrium data were analyzed by Langmuir, Frendlich and Temkin isotherm equation using regression analysis. Langmuir found to best represent the data for Cd(II) adsorption onto TCP. The negative value of change in Gibbs free energy ($\Delta G°$=-4.249 Kj/mol) indicates the feasible and spontaneous adsorption. The positive value of the variation of adsorption energy ΔQ=31.48 Kj/mol indicate that the adsorption reaction is exothermic.

Keywords: Cd(II) adsorption, Isotherm, Kenitic, Tricalcium phosphate

1. Introduction

Content in wastewater and waste toxic metals can diffuse through leaching in soils and sediments then into groundwater. The control of these metals in the environment is becoming increasingly important. If certain metals consumed in small quantities are essential to health, others, such as cadmium, chromium, copper, nickel, lead and zinc, are dangerous if exposed too much.

The main difficulty is that the bioavailability and mobility of metals depends on their chemical structure, each metal having properties which are peculiar. The solubility, for example, is very variable.

In recent years great importance has been attached to the liquid-solid extraction for the removal of heavy metals from industrial effluents [1-5]. The extractant can also be a matrix ion [6] or apatite supports based calcium phosphates exchange resin, and more particularly hydroxyapatite, tricalcium phosphate and dicalcium phosphate, are designed to store and sequester heavy metals contained in solid waste or liquid effluents [7-11]. These minerals are, in fact, many properties of particular interest for these applications:

- The ability to accommodate a large number of ions,
- Chemical stability
- The thermal stability

In addition, they play an important role in various fields, in industry, the apatite minerals are the main source of phosphate fertilizer and used to prepare different phosphoric acid and phosphate derivatives [12]. Calcium phosphates, with a chemical composition similar to the mineral phase of bone tissue, are used as synthetic bone substitute's surgery [13]. In addition to their biological importance, the apatite compounds are studied for their electronic properties used in fluorescent lamps phosphorus [14] or laser materials [15]. A lesser scale, they are also used in pharmacy and chromatography (column) [16, 17].

In recent years, new applications in the field of environment have emerged. Are especially apatites studied as an electrolyte for fuel cell solid oxide (SOFC), [18] as a template to stabilize conditioning radioactive waste [19], or as decontaminating water or soil contaminated with heavy metals [20-23].

The focus of this research was to explore the feasibility of tricalcium phosphate for the adsorption of cadmium with the application of adsorption isotherms and kinetics models.

2. Materials and methods

2.1 Material used

The anhydrous chemical formula of tricalcium phosphate $Ca_3(PO_4)_2$ was used as the extractant in the matrix work. This material was synthesized in the Laboratory of Electrochemistry and Surface Treatment of the Faculty of Sciences Eljadida-Morocco.

2.2. Preparation of the aqueous solution of cadmium

We prepared different solutions of known concentrations of cadmium metal from salt of cadmium nitrate ($Cd(NO_3)_2$, $4H_2O$; M = 236.4g/mol) 99 mass% purity. The pH of each solution was adjusted by adding nitric acid or sodium hydroxide (pH = 5).

2.3. Experimental Protocol

Beakers of 200 ml capacity is placed 100 ml of solution of known concentration of metal with a mass of 0.015 g of the TCP. The support was previously introduced into a small bag prepared in the laboratory. This technique has two advantages, it helps to avoid breaking the grains of the materials during the agitation of the supernatant solution, it also allows us to easily make withdrawals in the aqueous solution without a problem driving grains of the material in the test samples.

Each solution was stirred vigorously at room temperature. The stirring speed is 100 tr/min. the pH of the mixture was adjusted to 5 by adding drops of HCl or NaCl.

The concentration of the metal solution after extraction of Cd^{2+} ions for each time interval was determined by flame atomic absorption (air/acetylene) at 240.7 nm on a spectrometer type Unicam 929 AA spectrometer.

The amount of adsorbed cadmium (q_e) (mg/g) by the apatite support is determined by the following literal:

$$q_e = \frac{(C_0 - C_e)}{m} . V \qquad (1)$$

With: q_e : Adsorbed amount of TCP at equilibrium ($mg.g^{-1}$),
C_o : Initial concentration of cadmium in solution ($mg.L^{-1}$),
C_e : Concentration of cadmium in solution at equilibrium ($mg.L^{-1}$),
V : Volume of solution (L),
m : Mass of TCP (g).

3. Results and discussion

3.1. Effect of time contact

The effect of contact time for the adsorption of cadmium by tricalcium phosphate was studied for a period of 70 mn for initial cadmium concentration of 10.34 mg/L at 25°C. The effect of contact time on removal of cadmium is shown in Fig. 1.

The absorption of cadmium is very fast in the early stages of the contact period, and thereafter, it becomes slower near the equilibrium. After two stages of absorption, adsorption speed is constant. This is evident from the fact that a large number of sites surface area are vacant available for adsorption during the initial stage, and after a period of time, the surface sites remaining voids are difficult to be occupied because of repulsion forces between the molecules of the solute in the solid phase.

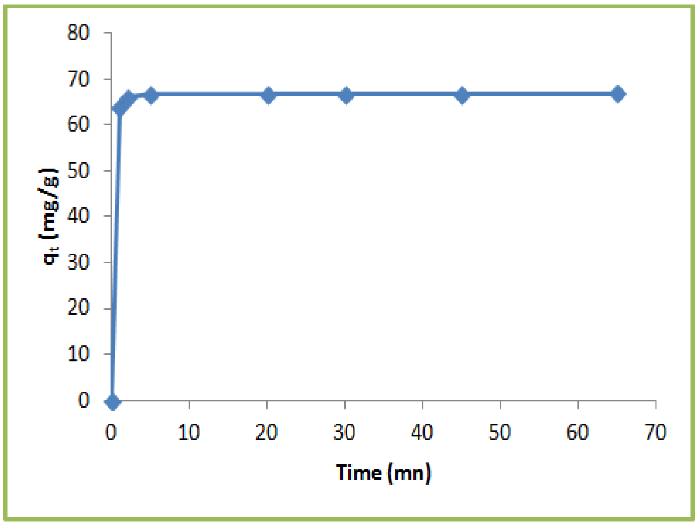

Figure 1. Effect of time contact to the sorption of cadmium into TCP

3.2. Effect of initial cadmium concentration

Adsorption of cadmium at different initial concentrations (10.34 – 144.3 mg/L) was studied. The effect of the initial concentration of cadmium on the adsorption capacity of the TCP is shown in Fig. 2. At higher concentrations of the ratio of the cadmium concentration of the adsorbent in adsorbate sites is high, which causes an increase in the adsorption capacity of cadmium into TCP. Starting from an initial concentration of Cd(II) equal to 100 mg/l a bearing is obtained, which the adsorption capacity becomes independent of the initial concentration. A higher removal of cadmium concentration is constant due to the saturation of TCP sites.

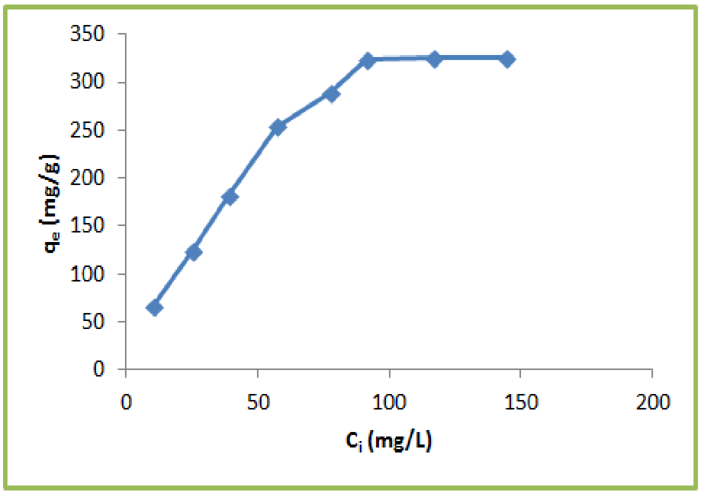

Figure 2. Effect of cadmium concentration

3.3. Modeling of the kinetics of adsorption

To investigate the adsorption kinetics of tricalcium phosphate, four simple kinetic models were used, which are: Pseudo-first order, Pseudo second order, intraparticular difusion and Bangham model. Table 1 shows the various expressions of the main kinetic models.

Table 1. Adsorption kinetic models

Model	Linear expression	Plot
Pseudo first-ordre [24]	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$ (2)	$\log(q_e - q_t)$ vs. t
Pseudo second-ordre [25]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$ (3)	$\frac{t}{q_t}$ vs. t
Intraparticular diffusion [26]	$q_t = k_i . t^{1/2} + X_i$ (4)	q_t vs. $t^{1/2}$
Bangham [27]	$\log \log \left(\frac{C_o}{C_o - q_t . m}\right) = \log\left(\frac{K_B}{2.303.V}\right) + \alpha \log t$ (5)	$\log \log \left(\frac{C_o}{C_o - q_t . m}\right)$ vs. $\log(t)$

Where k_1 is the rate constant of Pseudo first-order model, k_2 is the equilibrium rate constant (g/mg.min) of Pseudo-second-order chemical sorption, q_t (mg/g) is the amount of adsorbed cadmium at any time t(min), X_i is the value of the thickness of the boundary layer and K_i is the speed constant of diffusion intraparticular, V is volume of the solution (mL), *m* is weight of the adsorbent (g), α and K_B are the constant of Bangham model. The parameters of each model are given in Table 2.

Applying these kinetic models is shown in Figures 3, 4, 5 and 6. The parameters of kinetic models: pseudo-first order, pseudo-second order, intraparticular diffusion and Bangham are grouped in Table 2.

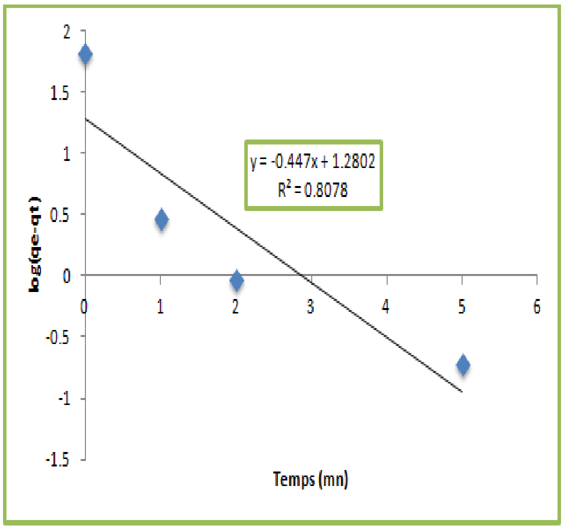

Figure 3. Pseudo first-order kinetic model

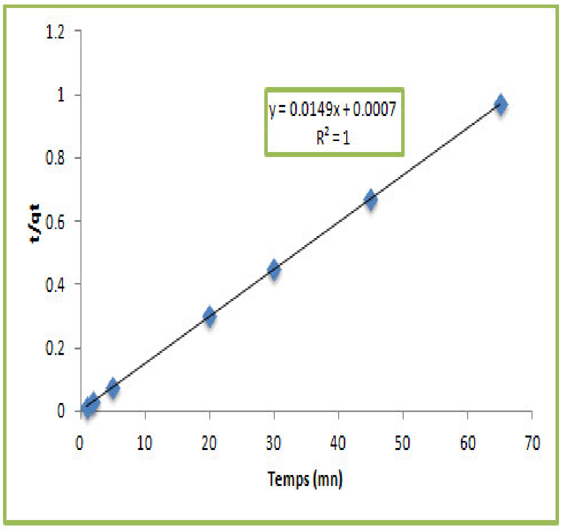

Figure 4. Pseudo second-order kinetic model

The correlation coefficient (R^2) value for pseudo second-order adsorption model is equal to unity (R^2=1), this value is higher than that of pseudo first-order model (R^2=0.8078). Moreover, $q_{e,theo}$ was quite similar to $q_{e,exp}$. Therefore, the adsorption kinetics of cadmium onto TCP can be better described by pseudo second order model. These results imply that chemisorption mechanism may play an important role for the adsorption of cadmium on TCP. Similar phenomenon has observed in the literature for the adsorption of copper and silver on various adsorbents [28-31].

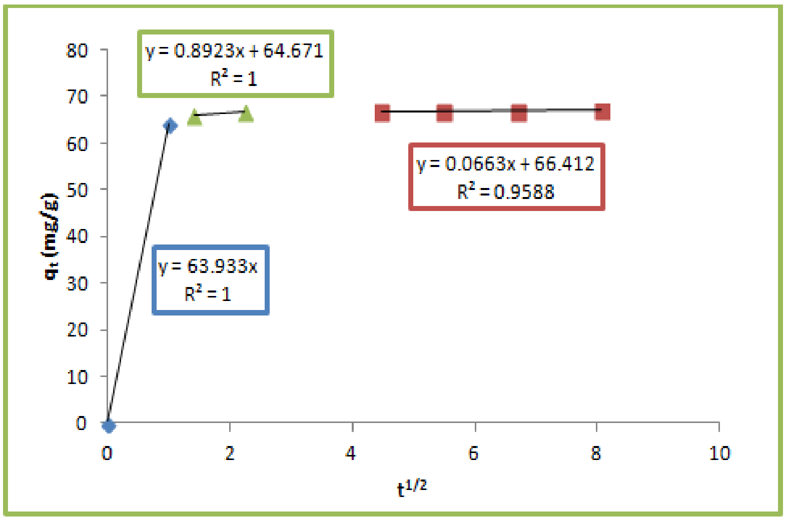

Figure 5. Intraparticular diffusion model

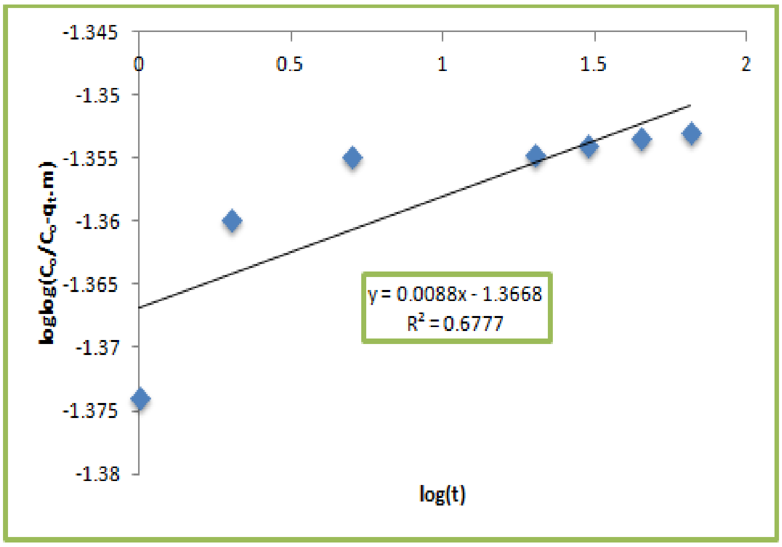

Figure 6. Bangham kinetic model

The double logarithmic plot, according to eq. (5) of Bangham model did not yield satisfactory linear curves for the cadmium removal by the TCP. This shows that the diffusion of adsorbate into the pores of the sorbent was not the only rate-controlling step. The film and pore diffusion both were important to different extents in the removal process.

The curves presented the intraparticle model (Fig.5) has multi-linearities implying the existence of several steps in the adsorption process, indicating that the diffusion of Cd (II) ions to the surface of TCP is performed in three steps. The first step corresponds to a limitation of the adsorption by the external diffusion (R^2=1). The second is the progressive adsorption of the solute, then the phenomenon is limited by intraparticular diffusion (R^2=1). The third stage corresponds to an equilibrium state where no further evolution of the adsorption capacity (R^2=0.9588). We concluded that only the intraparticular diffusion is involved in the adsorption process of Cd^{2+} ions on TCP because the straight line passes through the origin.

Table 2. Parameters of kinetic models

<table>
<tr><th colspan="4"><i>Pseudo-first order</i></th></tr>
<tr><td>$q_{e,exp}$ (mg.g^{-1})</td><td>$q_{e,theo}$ (mg.g^{-1})</td><td>k_1 (min^{-1})</td><td>R^2</td></tr>
<tr><td>66.7</td><td>19.063</td><td>1.029</td><td>0.8078</td></tr>
</table>

<table>
<tr><th colspan="5"><i>Pseudo-second order</i></th></tr>
<tr><td>$q_{e,exp}$ (mg.g^{-1})</td><td>$q_{e,theo}$ (mg.g^{-1})</td><td><i>Relative difference (%)</i></td><td>K_2</td><td>R^2</td></tr>
<tr><td>66.7</td><td>67.114</td><td>0.61</td><td>0.32</td><td>1</td></tr>
</table>

<table>
<tr><th colspan="4"><i>Intraparticular diffusion</i></th></tr>
<tr><td><i>Temps (min)</i></td><td>K_i</td><td>X_i</td><td>R^2</td></tr>
<tr><td>t<1</td><td>63.933</td><td>0</td><td>1</td></tr>
<tr><td>1<t<20</td><td>0.8923</td><td>64.671</td><td>1</td></tr>
<tr><td>t>20</td><td>0.0663</td><td>66.412</td><td>0.9588</td></tr>
</table>

<table>
<tr><th colspan="3"><i>Bangham</i></th></tr>
<tr><td>α</td><td>K_B</td><td>R^2</td></tr>
<tr><td>0.0088</td><td>0.00989</td><td>0.6777</td></tr>
</table>

3.4. Adsorption Isotherms

The adsorption data were analyzed to see whether the isotherm obeyed the Freundlich, Langmuir and Temkin isotherm models equations. Table 3 describes the different expressions of the main models used isotherms.

Table 3. Models adsorption isotherms

Model	Model expression	Linear expression	Plot
Freundlich [32]	$q_e = K_F C_e^{\frac{1}{n}}$ (6)	$\log q_e = \log K_F + \frac{1}{n} \log C_e$ (9)	$\log q_e$ vs. $\log C_e$
Langmuir [33]	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ (7)	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ (10)	$\frac{C_e}{q_e}$ vs. C_e
Temkin [34]	$q_e = \frac{RT}{b} \ln(AC_e)$ (8)	$q_e = B \ln A + B \ln C_e$ (11)	q_e vs. $\ln C_e$

Where k_F is multilayer adsorption capacity and *n* is adsorption intensity for Freundlich isotherm, q_m is the

monolayer adsorption capacity, and K_L is the constant of the Langmuir isotherm, T is the temperature (K), R is the gas constant (8.314 $J.mol^{-1}.K^{-1}$) and the variation energy adsorption ΔQ ($B = RT / \Delta Q$), A or K_o is a constant of adsorption (L.mg-1). The parameters of each isotherm are listed in Table 4.
The Langmuir separation factor (R_L) is calculated from the Langmuir isotherm based equation as follow:

$$R_L = \frac{1}{1+K_L C_i} \qquad (12)$$

This factor was applied to estimate either the sorption system is [28]:

- Favorable ($0<R_L<1$),
- Unfavorable ($R_L>1$),
- Irreversible ($R_L=0$)
- Linear ($R_L=1$).

A temperature studied, the free energy of adsorption ΔG°_{ads} can be calculated by the following equation:

$$\Delta G^o_{ads} = -RT(\ln K_L + 4.02) \qquad (13)$$

ΔG°_{ads}, R, T and K_L represents the free energy of adsorption, the ideal gas constant, the absolute temperature and the Langmuir constant, respectively.

The experimental results for the initial concentrations of cadmium ranging from 25 to 144 mg/L provide isothermal data in Figure (7). These results indicate a form of L type according to the classification of Giles et al. [21]. This form is Langmuir isotherm types. The interpretation of this curve must be done with the adsorption isotherm models shown in Figures 8, 9, 11 and 12.

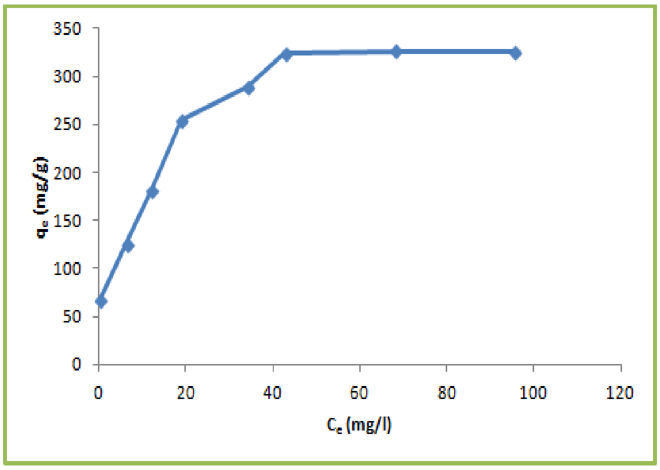

Figure 7. Adsorption isotherm of cadmium on TCP

From the results shown in Table 4 on the correlation factors, it is found that:

Adsorption isotherm of cadmium on TCP according to the model is favorable Freundlich, the value of 1/n is less than 1.

The isotherm of cadmium on the TCP is well represented by the Langmuir model, the correlation coefficient is very close to the unity $R^2=0.9937$, with a maximum value of adsorption capacity (370.37 mg/g) very close to the experimental value (325.2 mg/g) wich RD is 12 %. The R_L values are in the domain of validity ($0.065<R_L<0.49$). The results demonstrate the formation of monolayer coverage of cadmium ion at the outer surface of TCP and the value of the free energy of adsorption $\Delta G^\circ_{ads}=-4.249$ Kj/mol demonstrates the spontaneous nature of the process involved.

Temkin model can also well represent the experimental results. The correlation coefficient is close to unity $R^2=0.916$. The variation of adsorption energy, ΔQ=(-ΔH), is positive, which indicate that the adsorption reaction is exothermic.

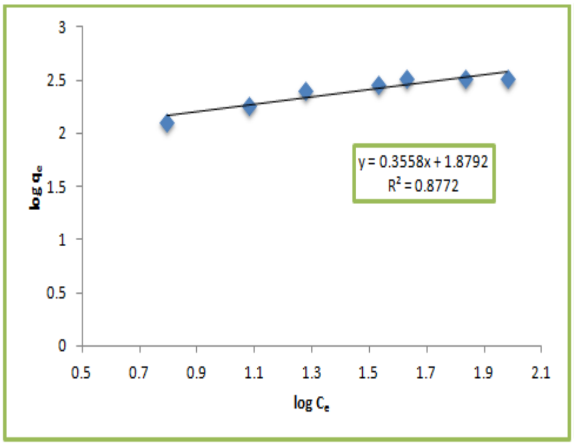

Figure 8. Freundlich isotherm model

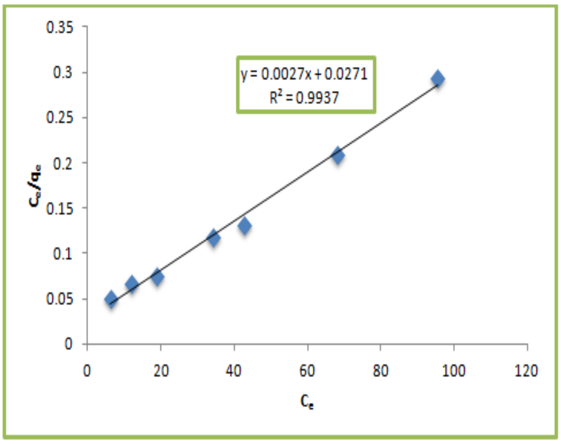

Figure 9. Langmuir isotherm model

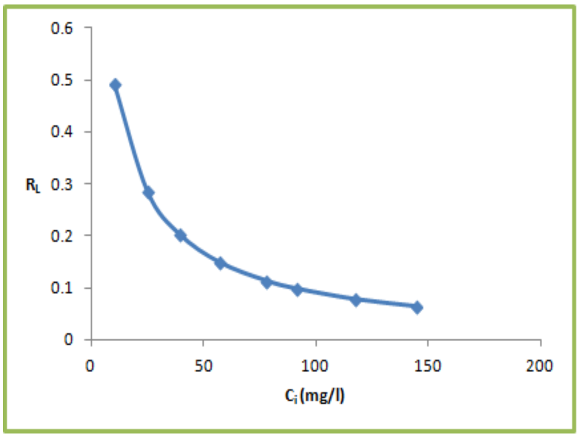

Figure 10. Evolution of the separation factor

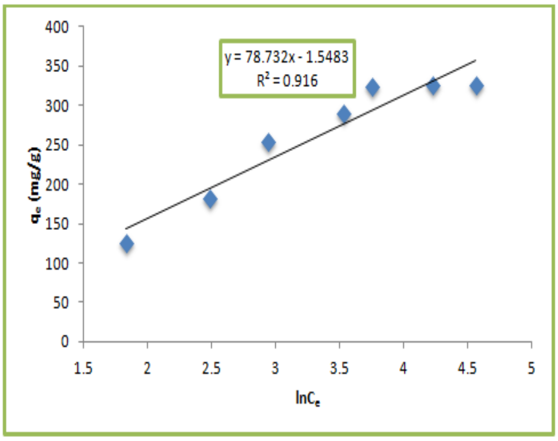

Figure 11. Temkin isotherm model

Table 4. Parameters of the isotherms Freundlich, Langmuir and Temkin.

<table>
<tr><th colspan="6"><i>Freundlich</i></th></tr>
<tr><td colspan="2"><i>1/n</i></td><td colspan="3">K_F</td><td>R^2</td></tr>
<tr><td colspan="2"><i>0.3558</i></td><td colspan="3"><i>75.72</i></td><td><i>0.8772</i></td></tr>
<tr><th colspan="6"><i>Langmuir</i></th></tr>
<tr><td>q_m $(mg.g^{-1})$</td><td><i>Relative difference (%)</i></td><td>K_L</td><td>ΔG^0_{ads}</td><td>R_L</td><td>R^2</td></tr>
<tr><td><i>370.37</i></td><td><i>12.19</i></td><td><i>0.0997</i></td><td><i>-4.249</i></td><td>$0.065<R_L<0.49$</td><td><i>0.9937</i></td></tr>
<tr><th colspan="6"><i>Temkin</i></th></tr>
<tr><td colspan="2">$A\ (L.mg^{-1})$</td><td colspan="2">$\Delta Q\ (Kj.mol^{-1})$</td><td>B_1</td><td>R^2</td></tr>
<tr><td colspan="2"><i>0.98</i></td><td colspan="2"><i>132.7</i></td><td><i>78.732</i></td><td><i>0.916</i></td></tr>
</table>

4. Conclusion

The present work has shown that the tricalcium phosphate can be used effectively for the removal of cadmium from the aqueous solution over a wide concentration range.

Kinetic data follows pseudo second-order kinetic model, indicating that chemisorption mechanism may play an important role for the adsorption of cadmium on TCP. The adsorption process is controlled by the intraparticular diffusion.

The Freundlich equation is not appropriate for the experimental results. Adsorption behavior is described by a monolayer Langmuir type isotherm, the value of the maximum adsorption capacity is q_m=370.37 mg/g. The Gibbs free energy of adsorption (ΔG◦) of Cd(II) on TCP, as calculated from the Langmuir constant was found to be -4.249 kJ/mol. The negative value of ΔG◦ confirmed the feasibility of the process and the spontaneous nature of sorption of Cd(II) on TCP.

The equation of Temkin leads to the determination of the variation of adsorption energy. The adsorption reaction of the Cd(II) onto TCP is exothermic.

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