Contribution of adsorption of metals using calcium phosphates in the presence of support polyethylene glycol

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Abstract

The extraction of metals from supports based on calcium phosphate was investigated; we conducted experiments with metal solutions at various concentrations, and using two carriers' calcium phosphate hydroxyapatite and hydroxyapatite in the presence of polyethylene glycol polymer. The results show a metal retention of selectivity with excellent yields. The kinetic study shows that the extraction equilibrium is fast for both matrices used. The present work relates to the adsorption of metal ions of cadmium, cobalt and copper. The adsorptive capacity of calcium phosphates been interpreted in terms of adsorption isotherms by exploiting both the Langmuir and Freundlich model. The highest adsorption quantities are improved out in the presence of PEG and reached 0.7 mmol / g, 0.66 mmol / g and 0.62 mmol / g respectively for the cadmium, copper and cobalt.

Keywords: calcium phosphate, polyethylene glycol, adsorption, metals, isotherms.

Introduction

Pollution by harmful metals is a major environmental problem, and the search for matrices having a large storage capacity of these metals is necessary. Several compounds have been used for the extraction of metals [1]. Calcium phosphate has a crystalline structure that offers interesting adsorption properties, and many studies have been conducted on the determination of heavy metals in aqueous solution [2- 5]. Apatites were also used for the removal of dyes [6] bisphenol pollutants [7] and pesticides [8, 9] which constitute a danger to the environment. Carpeau and Lacout [11] have shown that the hydroxyapatite can be used as storage of radioactive waste material. This is due to the existence of the reaction sites negative charge carriers at the surface that allows broad environmental applications [12]. Many authors have exploited the chemical stability of calcium phosphates, and their ability to hold a large number of chemical elements [13-16]. To explain the adsorption, mechanisms have been proposed for Pb^{2+} ions Zn^{2+} and Co^{2+} [10]. In this study, we carried out a comparative study of metal absorption by hydroxyapatite only and in the presence of polyethylene glycol polymer noted PEG.

2. Materials and methods

2.1. Materials used

Solutions of different concentrations of metal salt were prepared, using cobalt chloride, cadmium chloride and copper chloride. Hydroxyapatite primarily used is synthesized in the laboratory by double decomposition method [17]. HAp-PEG composite was synthesized by method of double decomposition in the presence of polyethylene glycol [18].

2.2. Extraction method

The process of adsorption of ions on the hydroxyapatite is performed by contacting 0.2 g in 50 ml of metal solution at room temperature and stirring the mixture. The metal loaded carrier is separated from the supernatant solution by filtration. The residual content of the metal ion is measured by spectroscopy flame atomic absorption.

The amount adsorbed Qa is determined by the following expression:

$$Qa = \frac{C_0 - Ce}{m} \cdot V$$

With m: 0.2 g mass of the adsorbent
Q_a: adsorbed amount (mg / g)
C_0: initial concentration (g / L)
C_e: equilibrium concentration (g / L)
V: volume of the solution (L)

And we will follow the adsorption kinetics at different concentrations of metal ion. The purpose of the study of the variation Qa function of time is to determine the time of balance, which is related to the number of active sites present in our phosphate and the metal ion saturation. Qa = f (time).
The experimental procedure and kinetic study are applied in the same way for both matrices of the study.

2.3. Apparatus

The SAA analysis was performed with atomic absorption spectrometer (oven method) Shimadzu - AA 6300 and ASC - 6100 Autosampler

3. Results

We conducted a comparative study about the adsorption on the two matrices

3.1 Comparing of adsorption of cadmium on the only Hydroapatite matrix and HAp- PEG composite

The surface of hydroxyapatite was modified by grafting organic molecules end to improve the adsorption capacity; the matrix is a composite of polyethylene glycol and hydroxyapatite noted HAp-PEG "1000"[18].
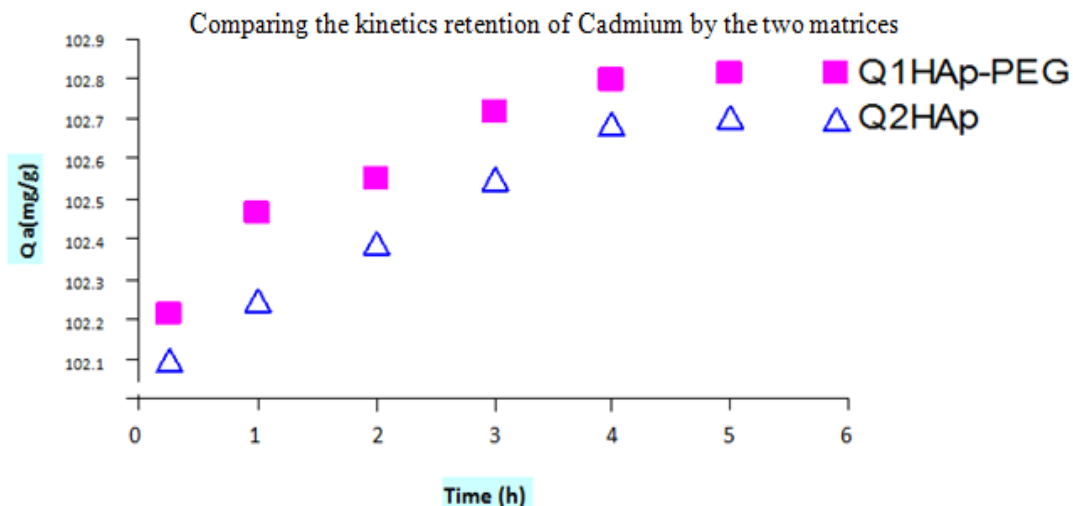

Figure 1: Comparison of the adsorption kinetics

The presence of grafted polyethylene glycol improved adsorption of cadmium ions. In the remainder of the study we will work only by the composite: HAp-PEG.

3.2 Adsorption of chemical elements in the matrix hydroxyapatite / polyethylene glycol

Figure 2 shows the evolution of the three elements of adsorption on a matrix hydroxyapatite- polyethylene glycol. The adsorption affinity for calcium phosphates studied evolves in the following order: Co> Cd> Cu; This shows that the ion exchange between the metal and the Ca^{2+} ion, probably depending on the size of the metal.
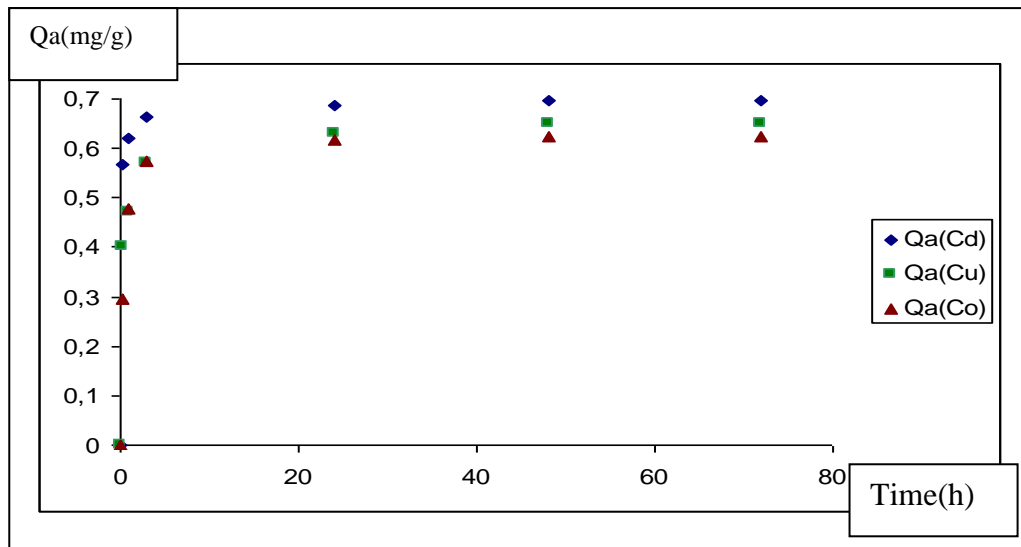
Figure 2: Kinetics of adsorption on the matrix hydroxyapatite-polyethylene glycol
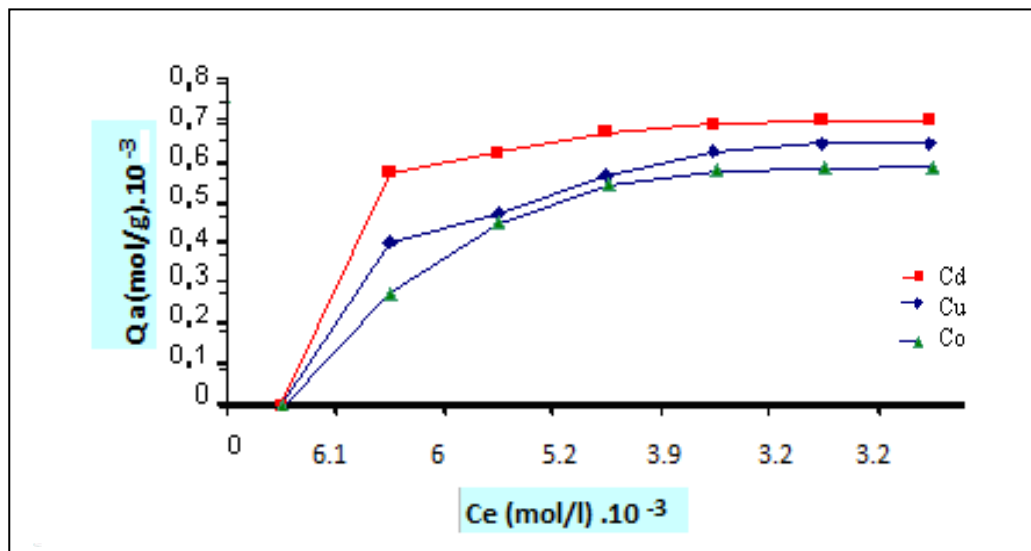

Figure 3: Isotherm of Langmuir adsorption on matrix hydroxyapatite-polyethylene glycol

4. Discussion

The hyperbolic shape of the curves of the Langmuir isotherm asymptotically approaches a constant limit. This curve appears to be a type I isotherm according to the classification Langmuir. We can therefore conclude that the selected materials adsorb a single layer of adsorbate. Indeed beyond the first layer the solute-solvent interactions outweigh the interactions solute-surface.

The Langmuir and Freundlich isotherms adsorption of selected metals on composite hydroxyapatite-polyethylene glycol are combined in the following figures:

The results of studies of the kinetics adsorption on matrix hydroxyapatite-polyethylene glycol show that the adsorption of three chemical elements is marked by two principal characteristics a rapid adsorption in the first moments, and a maximum adsorbable quantity at equilibrium.

During the period of rapid adsorption, chemical elements are retained on the surface by electrostatic bonds managed by intermolecular forces of attraction. The equilibrium is then reached when the forces of solvation and those intermolecular attractions are of the same magnitude. It is found that the maximum quantities adsorbed are slightly higher for the matrix hydroxyapatite-polyethylene glycol compared to those of the single HAp matrix.
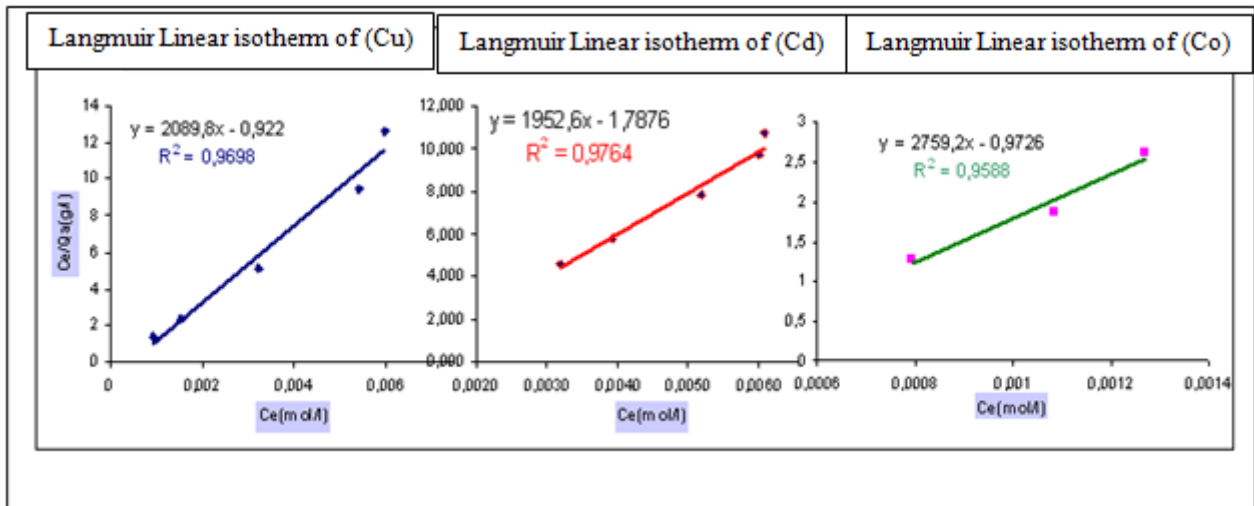
Lamhamdi et al

Figure 4: Linear Transform of the Langmuir isotherm on the matrix hydroxyapatite-polyethylene glycol
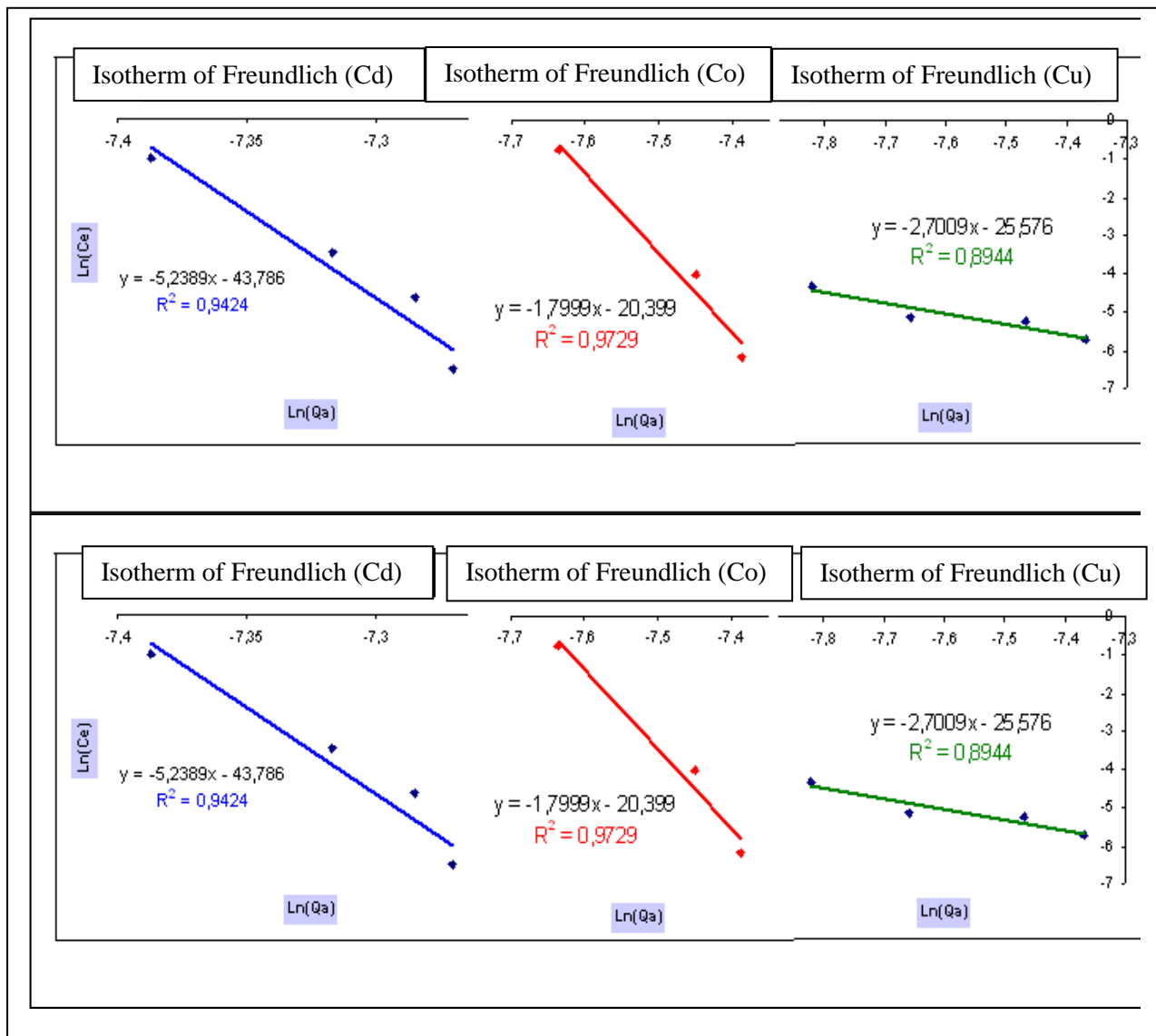

Figure 5: Linear Transform of the Freundlich isotherm of the matrix hydroxyapatite-polyethylene glycol

2587

4. 1. Adsorption Mechanism
Many studies on adsorption metals in aqueous solutions of ions on calcium-phosphate based matrices indicates that these ions are exchanged with Ca^{2+} of the solid [19] and that for large concentrations of ions, the elimination follows a different mechanism other than diffusion, namely the dissolution-precipitation, this study in showing that hydroxyapatite is used as materials for the decontamination of polluted solutions by cadmium [20]. Other authors [21] have concluded that the sorption of Cd^{2+} on hydroxyapatite is limited to a superficial phenomenon.

Our study shows that the presence of PEG has an important role in improving the adsorption capacity of metals and consequently the increase of the specific surface of HAp.

The adsorption of ions on the mechanism HAp- PEG could be a combination of three mechanisms [22]

- Ion exchange between metal ions contained in the contaminated solution and the Ca2 + ions present in the solid. This ion exchange is done through dissolution of apatite followed by precipitation according to following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + x\ M^{2+} \longrightarrow Ca_{10-x}M_x(PO_4)_6(OH)_2 + x\ Ca^{2+}$$
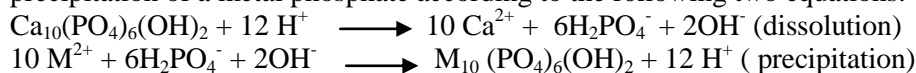
This makes it possible that these metal ions are not only exchanged with Ca^{2+} of apatite, but also adsorbed on the surface or attached in preexisting cationic gaps.

- Complexing of the metal ions on the surface of solid apatitic.

- A dissolution-precipitation

The latter metal ion removal process takes place in two processes: the dissolution of hydroxyapatite followed by precipitation of a metal phosphate according to the following two equations:

$$Ca_{10}(PO_4)_6(OH)_2 + 12\ H^+ \longrightarrow 10\ Ca^{2+} + 6H_2PO_4^- + 2OH^- \text{ (dissolution)}$$
$$10\ M^{2+} + 6H_2PO_4^- + 2OH^- \longrightarrow M_{10}(PO_4)_6(OH)_2 + 12\ H^+ \text{ (precipitation)}$$

The hyperbolic shape of the curve (Figure 3) of the Langmuir isotherm tends asymptotically to a constant limit value. This curve appears to be a type I isotherm according to the classification Langmuir. We can therefore conclude that the matrices adsorb a single layer of adsorbate. Indeed beyond the first layer the solute-solvent interactions outweigh the solute-surface interactions.

Conclusion

The comparative study between adsorption HAp alone and that of matrix hydroxyapatite-polyethylene glycol shows that the majority of the adsorbed amount of the three elements occurred in the first moments for both matrices. We are thus witnessing a physisorption. The study showed that the matrix hydroxyapatite-polyethylene glycol adsorbs slightly better than the single HAp. The adsorption kinetics of the three elements follows the model of Langmuir and Freundlich for both matrices. These results show the importance of the application of phosphate apatite in the environmental field.

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