Liquid-Solid Extraction of Heavy Metals from Aqueous Solutions Diluted by Amorphous Tricalcium phosphate

H. Elaidi, I. Ismi, L. Chafki, E. H. Rifi, A. Lebkiri, Z. Hatim

Abstract— The effect of physical and chemical parameters on the retention of copper from dilute aqueous solutions by Amorphous Tricalcium Phosphate $Ca_3(PO_4)_2,nH_2O$ (TCPam) was studied. The kinetics shows that the extraction equilibrium is fast, equilibrium is reached in about 70 minutes of agitation of the system. The adsorbed amount of metal per unit mass of support q increases with increasing pH of the metal solution. The saturation of 15 mg of the support is carried out by his contact with 100 ml of solution of cooper to $12.60 \cdot 10^{-4}$ M where q_{max} is equal to 118.51 mg/g. The total purification of a copper solution to 6.35 ppm is realized with a weight of 70 mg of TCPam. Moreover, the treatment of a mixture of divalents metals shows that the selectivity follows the following order: Cd > Zn > Cu > Co.

Index Terms— Liquid-solid extraction, Copper, Calcium phosphate

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1 INTRODUCTION

The discharge of waste containing heavy metals, including aquatic (sea, river ...) leads to the accumulation of metal ions in various organisms (plant, fish ...) and their transfer to humans through the food chain. This accumulation of heavy metals in water, air and soil is a serious environmental problem that affects every country in the world and for the following two main reasons:

- The wide variety of metals and the large number of chemical combinations to which they can participate.

-Toxic effects they may cause.

Although they are trace elements through their important role in various biological systems, metal ions such as Mn^{2+}, Zn^{2+}, Cu^{2+} and Fe^{2+} can cause toxic effects when present in large quantities. Other heavy metals such as Cd, Hg, Cr and Pb are, however, highly toxic even at trace levels. It is therefore essential to completely eliminate these ions present in wastewater (industrial effluents, domestic ...) or reduce their amount below permissible limits set by the discharge standards.

The application by industrial restrictions setting maximum limits for heavy metals in liquid effluents, has encouraged the development of various techniques and methods, more and more specific and effective to meet those limits. Most commonly used are the adsorption [1-2], electrolysis, solubilization, flotation, precipitation [3-4], ion exchange, liquid-liquid extraction [5-8] liquid-gel extraction [9-12], liquid-solid extraction [13-18].

Among the different methods for separation and preconcentration of metal ions, the solid phase extraction is still one of the most used methods seen the various advantages it offers as the reusability of the solid phase, non-use toxic solvents, and the fact that it generates little waste. As the solid phase, a wide variety of natural or synthetic materials are used as heavy metal adsorbents (silicates, ion exchange resins, chelating resins, zeolites, apatites, calcium phosphates ...). [19-21].

The importance of calcium phosphate used for the decontamination of waste water, is their ability to bind a wide range of metal species in dilute aqueous solution with high efficiency, and they exhibit a chemical stability over a wide range pH. Many studies have been conducted to assess the potential retention of calcium phosphate synthetic vis-à-vis heavy metals in soil and water [22-23]. The properties of retention of these calcium phosphates depend on their physicochemical characteristics, especially the molar Ca/P ratio, the crystallographic structure and the specific surface.

It's in this context that is entitled our work which aims the treatment of the metallic aqueous solutions by the use of the amorphous tricalcium phosphate as matrix extractante.

2. MATERIALS AND METHODS

2.1. Materials used

In our work the agent extractant used is the amorphous tricalcium phosphate (TCPam), of chemical formula $Ca_3(PO_4)_2$ nH_2O (n = 3.1), it is in the form of fine white powder. This phosphate medium was drawn up by the laboratory of Electrochemistry and Surface Treatment of the Faculty of Sciences of El Jadida, Morocco

2.2. Extraction technique

A known mass of the phosphate medium is brought into contact with 100 ml of a solution of copper of concentration, and of pH known. The extractions are realized in beakers under stirring at fixed temperature. The quantity of the matrix adsorbante was beforehand introduced into a bag obtained from the filter paper, closed by a wire allowing its suspension in the solution. This procedure facilitates the samles in the metallic solution without risk of training of the grains of the support (medium) in samples to be measured. The adsorption of the metal is translated by simultaneous variations of its concentration in solution, and that to the surface of the solid. The quantity of copper adsorbed by unit mass of adsorbing solid q, is given by the following relation:

$$q = \frac{(C_i - C_f)}{m} \times V$$

With C_i (mg/l) and C_f (mg/l) are respectively the initial concentration and the concentration at time t of Cu^{2+} ions in the metal solution, and m (g) the mass of solid adsorbent.

The extraction yield of the metal is given by the following relation:

$$R = \frac{(C_i - C_f)}{C_i} \times 100$$

2.3. Method of analysis

Copper solutions were prepared by dissolving salt of $Cu(NO_3)_2$ in distilled water. The pH of the solution is adjusted with concentrated nitric acid. Copper in solution was determined by atomic absorption with flame (air/acetylene) at 324.8 nm on a spectrometer type Unicam 929 AA spectrometer. Calibration of the spectrometer was carried out using standard solutions of metal. The calibration range is between 0.5 ppm and 2 ppm. The correlation coefficient is 0.999.

3. RESULTS AND DISCUSSIONS

3.1. Extraction kinetics

The study of the equilibrium adsorption of copper on the amorphous tricalcium phosphate was made by the the follow-up of the simultaneous variations of copper concentration and the pH of the aqueous solution in function of time. The operating conditions are: 15 mg of the phosphocalcic support was contacted with 100 ml of a copper solution at an initial concentration of 10^{-4} mol/l and pH equal to 5.5. The mixture is stirred and samples were carried out carefully and determined by atomic absorption with flame. The results obtained are the subject of the figure (1). According to the kinetic curves, we notice, during the first minutes of the contact (t<70 min), the speed setting Cu^{2+} ions to the phosphocalcium medium is rapid leading to a significant fall in the concentration of metal ions Cu^{2+} to the supernatant solution accompanied by an increase of the pH which increased from 5.5 to 5.88. The equilibrium time is estimated at 70 minutes of contact with the adsorbent matrix. The progressive increase of pH is certainly due to the presence of basic species in particular ions phosphates on the surface of the material. The calculation shows that under these experimental conditions the extraction yield is about 68%.
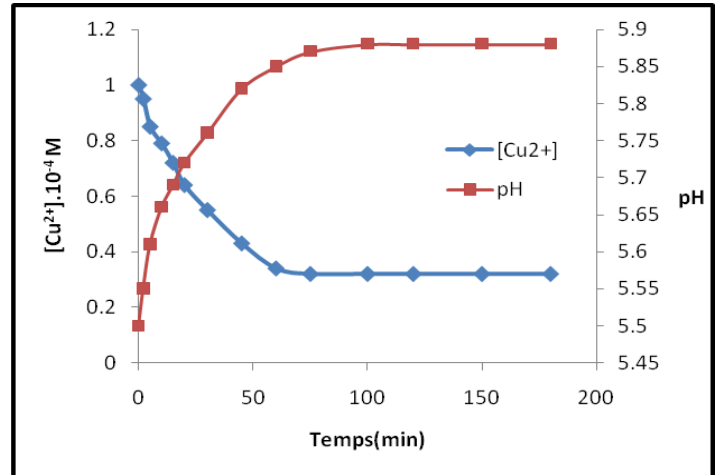

Fig 1 Simultaneous variations in the concentration of copper and the pH of the aqueous solution in function of time

To put in evidence the mechanism of adsorption of metal ions Cu^{2+} on calcium phosphate studied, we studied the instant change in the concentration of Ca^{2+} ions released from the solid in the solution during the adsorption process and the concentration residual Cu^{2+} ions as a function of time. The curves are shown in Figure (2).
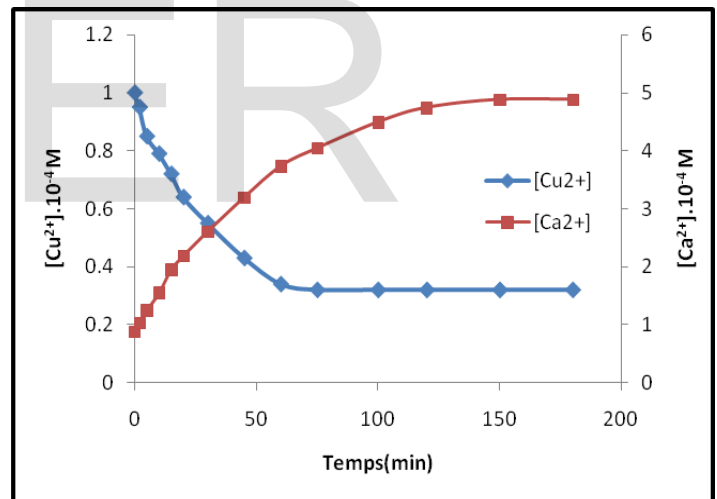

Fig 2 Variations simultaneous of the concentration of copper and calcium versus time

V_{aq} = 100 ml, $[Cu^{2+}]$ = 10^{-4} mol/l, pH_i = 5.5, m_{TCPam} = 15 mg

The results obtained show that the liberation of Ca^{2+} ions of the solid increases as the concentration of Cu^{2+} metal ions retained increases. This may be linked to cation exchange processes between the ions Cu^{2+} of the solution and Ca^{2+} ions from the adsorbent matrix modeled by the following equilibrium:

$$Cu^{2+} (solution) + Ca^{2+} (solid) \rightleftharpoons Cu^{2+} (solid) + Ca^{2+} (solution)$$
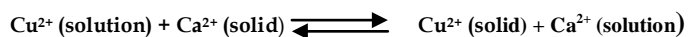
3.2. Effect of pH on the extraction of copper by TCP_{am}

The removal of metal ions from aqueous solutions by adsorption depends on the pH imposed on solution, since it affects the surface charge, the degree of ionization, and the nature of

the ionic species adsorbates. To examine the effect of pH on the retention of copper by the phosphocalcic support, we followed the evolution of the adsorption capacity of metal by TCPam (q = mass of metal adsorbed / unit mass of support) as a function of time at different pH values (3.5 to 6) for a metal concentration equal to 10^{-4} M. The results obtained are shown in Figure (3). Examination of these results shows that the change in pH of the metal solution greatly affects the properties of the adsorption material. Indeed, the extraction equilibrium is more rapid as the pH imposed on the metal solution is small, further raising the pH of the solutions adsorbate is accompanied by an increase in the amount of metal adsorbed at equilibrium extraction. The values of q measured at equilibrium are summarized in Table (1) where q_m increases from 11.87 to 30.94 mg/g when pH increases from 3.5 to 6. These results show that the extraction of the ions Cu^{2+} by TCPam is favored at slightly acid mediums.
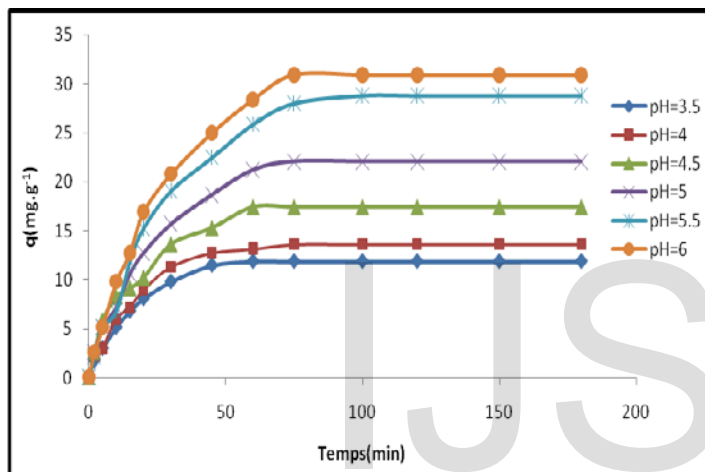

Fig 3 Variations of the adsorption capacity of phosphocalcic medium in copper at differents pH as a function of time
V_{aq} = 100 ml, $[Cu^{2+}]_i$ = 10^{-4} M, m_{TCPam} = 15 mg

TABLE 1

EFFECT OF PH ON THE RETENTION CAPACITY OF TCPAM OF COPPER
V_{aq} = 100 ml, pH_i = 5.5, $[Cu^{2+}]$ = 10^{-4} M

pH	3.5	4	4.5	5	5.5	6
q_m	11.87	13.6	17.4	22.07	28.8	30.94
R%	28	32	41	52	68	73

3.3. Effect of copper concentration on the fixing capacity of TCPam

The influence of the initial concentration of Cu^{2+} ions on the fixing capacity of TCPam was examined to determine the maximum load of copper support. To do this, we studied the saturation of the support by measuring the fixing ability of copper as a function on the initial concentration of copper in the aqueous solution at pH = 5.5.

The saturation curve q = f ($[Cu^{2+}]_i$) is shown in figure (4). It is found that at low metal concentrations, the adsorption capacity of TCPam in ions Cu^{2+} increases rapidly with the initial concentration of Cu^{2+}. Starting from an initial concentration of Cu^{2+} equal to $12.6.10^{-4}$ M, a bearing is obtained, which corresponds to the saturation of the support phosphocalcic in cop-

per. Under our experimental conditions the maximum load of TCPam in Cu^{2+} is close to 118.51 mg/g.

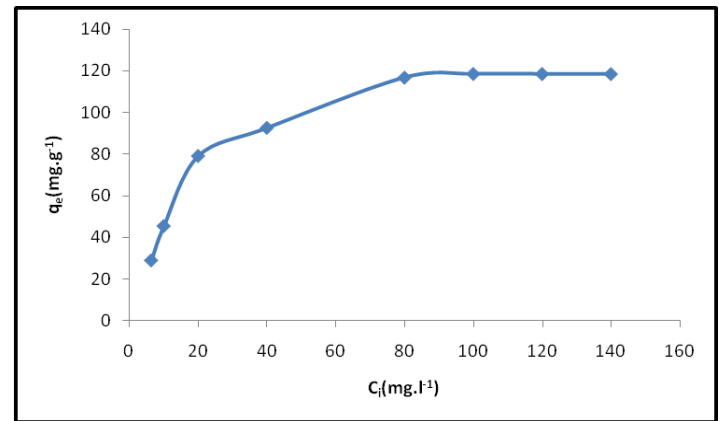Figure (4): Saturation support TCPam by copper
V_{aq} = 100 ml, pH_i = 5.5, m_{TCPam} = 15 mg

3.4. Exhaustion of an aqueous solution of copper

The knowledge of the maximum load support studied copper is essential, because It provides information on the amount of TCPam needed to decontaminate a given volume of the metal solution. This study was performed by placing aqueous solutions of copper having the same characteristics (V_{aq} = 100 ml, pH_i = 5.5, $[Cu^{2+}]$ = 10^{-4} M) amounts of solid (TCP_{am}) of increasing mass. Stirring is maintained for 8 hours, time more than enough to reach the extraction equilibrium. The results are summarized in Table (2). From these results we can see that the copper removal efficiency increases with increasing mass of the phosphocalcic support introduced (R = 99%, m_{TCPam} = 70 mg), which shows a purification almost total of the solution at 6.35 ppm copper. These data experimental are consistent with a potential application of these materials in the wastewater treatment.

TABLE 2

EXHAUSTION OF A SOLUTION OF COPPER BY TCPAM
V_{aq} = 100 ml, pH_i = 5.5, $[Cu^{2+}]$ = 6.35 ppm

m_{TCPam} (mg)	0	15	20	30	45	60	70
pH_f	5.5	6.24	6.83	7.12	7.25	7.25	7.25
$[Cu^{2+}]_f$ (ppm)	6.35	2.03	1.77	1.52	0.82	0.12	0.06
R%	-	68	72	76	87	98	99

3.5. Selectivity of the method

To test the selectivity of the phosphocalcic support investigated vis-a-vis the divalent metals, we have prepared an equimolar mixture of copper nitrate, zinc, cobalt, and cadmium at a concentration of 10^{-4} M. The pH of the solution was set at 5.5. In a volume of 100 ml of this mixture, we have introduced a quantity of TCPam of mass equal to 60 mg .The experimental procedure is the same as that used for a single metal in solution. After extraction equilibrium, the mixture was filtered and

the cations in the mixed filtrate were measured. The extraction of these metals yields are summarized in Table (3).

TABLE 3

TREATMENT OF AN EQUIMOLAR MIXTURE OF DIVALENT IONS BY TCP$_{AM}$

Métal (M^{2+})	Cu	Cd	Zn	Co
[M^{2+}]$_i$ (ppm)	6,30	11,70	6,75	4,45
[M^{2+}]$_f$ (ppm)	3,01	3,08	2,88	2,32
Rayon ionique (pm)	73	95	74	65
R%	52	73	57	45

We note that the selectivity of extraction follows the following order: Cd> Zn> Cu> Co. This is explained by the fact that the metal cations whose ionic radius is large are preferentially fixed on TCPam.

4. CONCLUSION

The aim of our study was to investigate the influence of physicochemical parameters on the adsorption of copper on amorphous tricalcium phosphate. The main results are:

❖ The fixation kinetics of copper on the medium studied is relatively fast, the equilibrium time is estimated at about 70 minutes stirring system.

❖ The increase in pH during the experiment shows that the phosphate medium equilibrates with the metal solution by consuming protons H$^+$.

❖ Simultaneous monitoring of the evolution of the concentration of Ca^{2+} ions released from the solid and the residual concentration of Cu^{2+} ions in the supernatant solution, led us to affirm that the retention of copper by amorphous tricalcium phosphate occurs by several mechanisms competitive. Copper can behave as an exchangeable cation, or adsorb to the surface of the material.

❖ The study devoted to the saturation of TCPam in copper showed that an amount of 15 mg of this substrate is saturated from a solution of copper 12.6.10^{-4} M where q$_{max}$ equals 118.51 mg / g.

❖ The complete purification of a copper solution at 6.35 ppm is performed by a weight of about 70 mg of the phosphocalcic support.

❖ Treatment of a mixture of divalent metal shows that selectivity follows the following order:

Cd > Zn > Cu > Co.
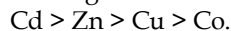
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