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Use of calcium phosphates to remove nickel, copper and cobalt ions from aqueous solutions

B. Lizoul[1], F. Kzaiber[1], A. Chemaa[2], E. Benharef[2], J. El Hajri[2] and E. Zahidi[2]*

[1]University Sultan MoulaySlimane, High School of Technology, Laboratory of Applied Engineering and Technologies. Beni-Mellal, Morocco.
[2]University Chouaïb Doukkali, Faculty of Sciences, Department of Chemistry, El Jadida, Morocco.

Abstract : This work concerns the use of amorphous tricalcium phosphate and apatitictricalcium phosphate to remove nickel, copper and cobalt ions from aqueous solutions. The amorphous or apatitic calcium phosphates were first exposed to separate solutions of Ni(II), Cu(II) or Co(II) salts for 48 hours at room temperature, then residual solids and solutions were separated and analysed. X-ray photoelectron spectroscopy, X-ray diffraction and infrared spectroscopy were applied to observe chemical and structure modifications in the solid phosphates whereas inductively coupled plasmaatomic emission spectrometry measurements were performed to evaluate the metal ions content changes in both solids and solutions. These analyses and measurements demonstrate the ability of amorphous and apatitic phosphates to remove metal ions from aqueous solutions. They assist in identifying the mechanisms involved in the metal ions transfer from solutions to solid phosphates and clarifying differences with respect to the widely studied hydroxyapatite system. Finally, they reveal, for copper and cobalt ions, the conversion of these phosphates to $Cu_2(PO_4)(OH)$ and $Co_3(PO_4)_2.8H_2O$.

Keywords : Amorphous calcium phosphate; apatitic calcium phosphate; hydrolysis; exchange; dissolution-precipitation.

1 Introduction

The pollution of water by organic and inorganic discharges remains one of the major problems to be solved in zones with heavy industrial activities. Unlike organic waste, which can often be easily metabolized or destroyed, inorganic pollutants, usually concentrated with metal ions, can only be transformed from labile toxic forms to more insoluble or less available forms to minimize their harmful effects on organisms. Methods investigated for such transformations are based on chemical precipitation phenomena, ion exchange or adsorption processes (1-3).

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Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ is considered as a special inorganic compound with reference to its high removal capacity for divalent heavy metals from aqueous solutions (4-8). The first results on the use of hydroxyapatite for metal ion capture were reported byin 1981 (9). The mechanisms evoked in the immobilization processes of metal ions by HA correspond to i) the complexing of the metal ions on the surface of solid phosphate; ii) an ion-exchange between calcium ions of the solid phosphate and the metal ions of the solutions occurring without any changes of the HA structure; iii) a dissolution-precipitation process where calcium and orthophosphate groups are dissolved together and the metal ions precipitate by homogeneous or heterogeneous (involving the remaining HA solid) nucleation; iv) substitution of calcium in HA by divalent metal ions during coprecipitation(10, 11).

Specific properties of HA arise from its very low water solubility and its high stability in a wide pH range. This is not the case of its known derivatives, in particular, the amorphous calcium phosphate (ACP) $Ca_9(PO_4)_6$ and the apatitictricalcium phosphate (TCP) $Ca_9(PO_4)_5(HPO_4)OH$. These phosphates, when placed in a humid space or introduced in aqueous solutions, undergo substantial changes and spontaneously transform into hydroxyapatite. It is therefore judicious to discover how these differences may or may not benefit ACP and TCP when used to remove metal ions from solutions.

The aim of this work is to evaluate the ability of ACP and TCP to remove metal ions from aqueous solutions. The experimental method used submitstricalcium phosphates to Ni(II), Cu(II) or Co(II) solutions and then observes the changes occurring on the phosphates and the solutions after 48 hours of exposure. Taking advantage of the power of X-ray photoelectron spectroscopy in the unambiguous identification of solid constituents, this technique has been applied to detect subtle changes that occur in the chemical composition of solid phosphates after being exposed to metal ion solutions.

2 Materials and methods

Tricalcium phosphate was prepared by the double decomposition method previously developed (12) where where a calcium nitrate solution is rapidly introduced into a di-ammonium phosphate solution adjusted to pH= 9 with ammonia (d=0,92). As soon as it is formed, the solid is separated from the solution by filtration, washed by an alkaline solution of ammonia (pH=10) and then separated into two parts. The first part is immediately introduced into aqueous solutions of metal ions and the other part is dried at 80°C for 48 hours before being exposed to the metal ion solutions. According to the results reported previously (12), the fresh calcium phosphate prepared in these conditions and the one dried at 80°C correspond respectively to amorphous tricalcium phosphate $Ca_9(PO_4)_6$ and apatitictricalcium phosphate $Ca_9(PO_4)_5(HPO_4)(OH)$.

Experiments testing the ability of phosphates to remove metal ions from the solutions were performed by adding 3,2g of amorphous phosphate or 0,32g of apatitic phosphate in 150 ml of 0.02M solutions of Ni(II), Cu(II) or Co(II) prepared from ($Ni(NO_3)_2,6H_2O$), ($CuSO_4,5H_2O$) or ($Co(NO_3)_2,6H_2O$) salts dissolved in distilled and degassed water. The prepared mixture is then stirred at room temperature and its pH measured. After 48 hours of exposure, the residual solids are separated from the solutions by filtration, washed with 250 ml of distilled and degassed water, dried at 80 °C for 14 hours and then analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XPS spectra were performed with a Kratos spectrometer using monochromatic aluminium Kα with photoionization power of 150W. The XPS survey-scan spectra are recorded with an analyser pass energy of 160eV and a resolution of 1eV. During the photoemission process, a low energy electron beam is switched on to reduce the effect of positive charge accumulated on the sample surface. The energy of the XPS peaks are corrected using the C(1s) peak at 284,6eV. The XRD analyses were performed with an advancedBrucker D8 diffractometer using a copper anticathode ($\lambda_{CuK\alpha}$ = 1.5405Å) subjected to an accelerating voltage of 50keV and an emission current of 40mA. XRD patterns are recorded in 2θ ranges of 10-80 degrees with a scan step of 0.02 and an acquisition time of 14s per step. The infrared spectra were obtained with a Brucker Vertex 70FTIR spectrometer. Each infrared spectrum is the ratio of 20 scans performed at a resolution of 4 cm^{-1} with the solid sample at 1% of KBr and a reference spectrum recorded with pure KBr. Chemical analysis focused on the determination of calcium, phosphorus, nickel, copper and cobalt content and was performed using inductively coupled plasma atomic emission spectrometry.

3 Results

3.1 Characterization of the synthesized calcium phosphate

To avoid the effect of water on the freshly prepared phosphate, all the analyses were performed using phosphate dried at 80° for 14 hours. The chemical analyses of calcium and phosphorus give an atomic ratio of Ca/P= (1.50 ± 0.01), which is characteristic of tricalcium phosphate. To verify the validity of this value, a small part of the phosphate was calcined at 900°C and then analyzed by XRD. The absence of calcium pyrophosphatelines or hydroxyapatite lineson its XRD pattern (the decomposition products that would form if the Ca/P ratio is less than 1.5 for the pyrophosphate or greater than 1.5 for the hydroxyapatite) proves that the ratio of the prepared phosphate is in fact 1.5 (13). The XPS spectrum of the phosphate dried at 80°C (Fig.1a) shows all the peaks attributed to the calcium phosphate compounds except a signal observed at 284.6eV, which is assigned to C(1s) of carbon. This peak, whose intensity varies by replacing the sample holder, is due to the contribution of the adhesive tape used to fix the sample rather than the presence of impurities in the phosphate. The XRD pattern of the phosphate dried at 80°C (Fig.1b) shows diffraction lines identical to those reported for synthetic TCP (12).

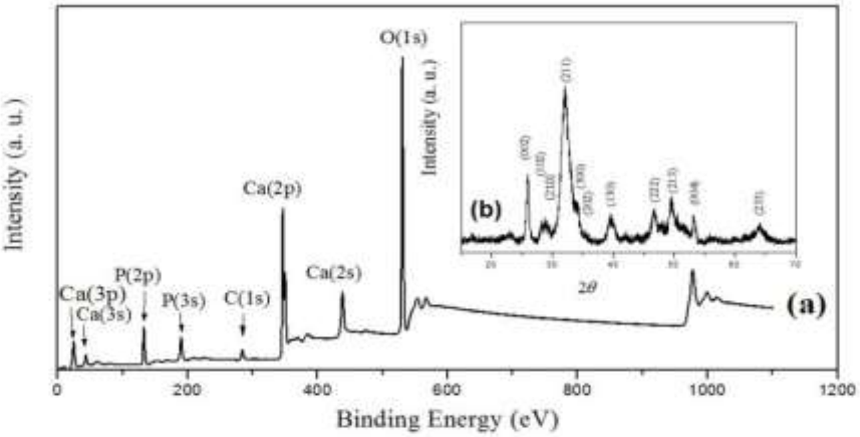

Figure 1. XPS spectrum (a) and XRD pattern (b) of the apatitictricalcium phosphate.

3.2 Use ofthe ACP to remove metal ions from aqueous solutions

3.2.1 Solution of Ni(II)

When ACP is added to the nickel solution with an initial pH of 4.54, the pH of the mixture undergoes large fluctuations making it difficult to read a pH value during the solid-liquid stabilization phase. After 10 minutes of exposure, the pH reaches a value of 7.04. After 100 minutes, the pH decreases to 6.63, increases to 6.75 and remains stable at this value for the remainder of the experiment. After 48 hours of exposure, the residual solid is separated from the solution, dried and then analyzed by XPS, XRD and FTIR. The XPS spectrum of the residual solid (Fig. 2b) shows, in addition to Ca, O and P signals, new XPS and Auger peaks, which can be easily attributed to Ni(II) (14-15). Compared to the XPS spectrum of the tricalcium phosphate (Fig.2a), it appears that unlike the oxygen and phosphorus peaks, whose intensities are only slightly affected, the calcium signals undergo significant decreases suggesting that upon contact with the solution, the phosphate undergoes a decrease in its calcium content.A process that seems to occur in parallel with a transfer of the nickel from the solution to the phosphate. This observation is strongly supported by the chemical analysis of the residual solution, which shows that 48% of the nickel ions are removed from the solution after being exposed to amorphous phosphate (Fig.3).

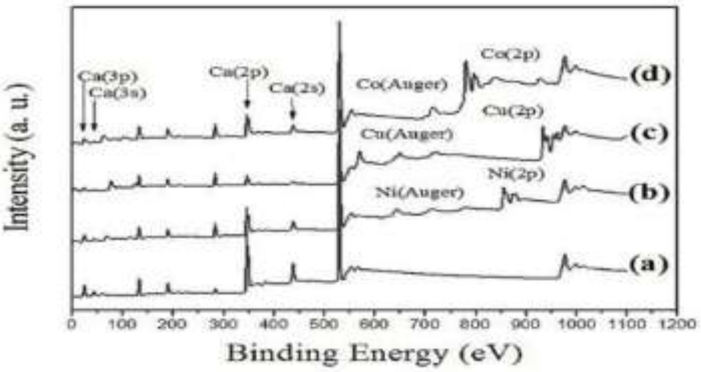

Figure 2.XPS spectra of ACP after exposure to solutions of nickel (b), copper (c) or cobalt (d) (the XPS spectrum (a) of the TCP is given for comparison).

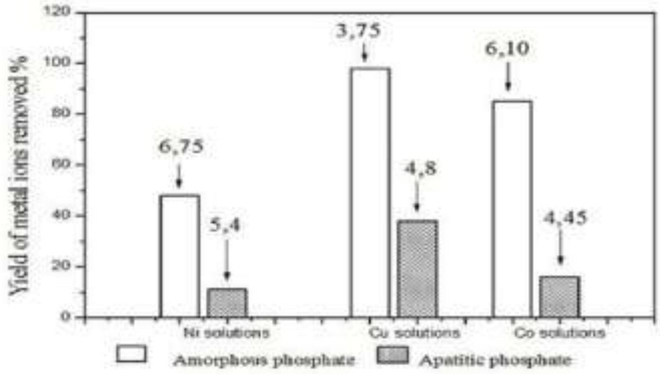

Figure 3.Metal ion yields eliminated by ACPand TCP (the indicated valuesrepresent the pH reached at the end of each experiment).

The XRD diagram of the residual solid shows only two broad lines similar to those observed in the case of amorphous phosphates (Fig.4a) (12).Its IR spectrum (Fig.4b) reveals two unresolved bands centred at 1050 and 620 $cm^{-1}$and areperfectly comparable to those found in spectra of amorphous phosphates. A small shoulder observed at 875 cm^{-1} and attributed to HPO_4 groups indicates that upon contact with the nickel solution, the solid phosphate undergoes a partial hydrolysis of its PO_4^{3-} ions according to the following reaction (1):

$$(PO_4^{3-})_{solid} + H_2O \rightarrow (HPO_4^{2-})_{solid} + (OH^-)_{solid} \qquad (1)$$

This reaction produces hydroxyl groups, which are difficult to detect on this IR spectrum, because of the wide band of water, which masks the characteristic hydroxyl band of the phosphates at 3560 cm^{-1}.

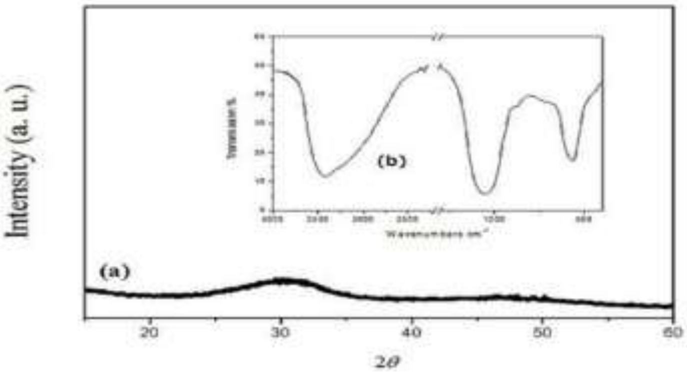

Figure 4.XRD pattern (a) and IR spectrum(b) of the ACP after exposure to the nickel solution.

3.2.2 Solution of Cu(II)

When ACP is introduced into the copper solution with an initial pH = 2.82, significant variations of pH are observed at the beginning. After 10 minutes of exposure, the mixture acquires a pH = 4. This value decreases and then stabilizes at 3.75for the remainder of the experiment. The XPS spectrum of the residual solid (Fig. 2c) shows in addition to Ca, O and P signals, XPS and Auger peaks attributed to Cu(II) (16). Focusing on the intensity differences between the XPS spectrum of the initial phosphate (Fig. 2a) and that of the residual solid, it is easy to see that the appearance of XPS and Auger peaks of Cu is accompanied by a significant reduction of calcium signals. These changes, more pronounced than those observed for nickel, suggest that the process of copper transfer from solution to the solid phosphate is more intense. This suggestion is supported by the results of the residual solution analysis, which indicates that 96% of copper ions are removed after contact with ACP (Fig.3).

Furthermore, the XRD analysis shows that, unlike the previous case of nickel, the residual solid is not amorphous (Fig.5a). Its structure, which fits no known apatitic phosphate, is identified as the structure of $Cu_2(PO_4)(OH)$according to the standard PDF data #00-033-0481#(17). This identification is confirmed by FTIR analysis through the IR spectrum, which reveals all the characteristic bands reported in the literature(18,19).

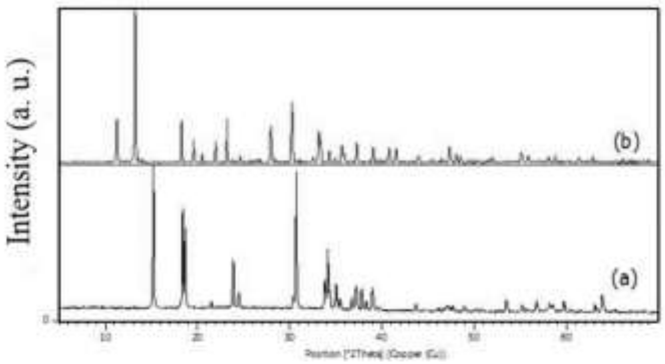

Figure 5. XRD patterns of the ACP afterexposure to solutions of copper (a) or cobalt (b).

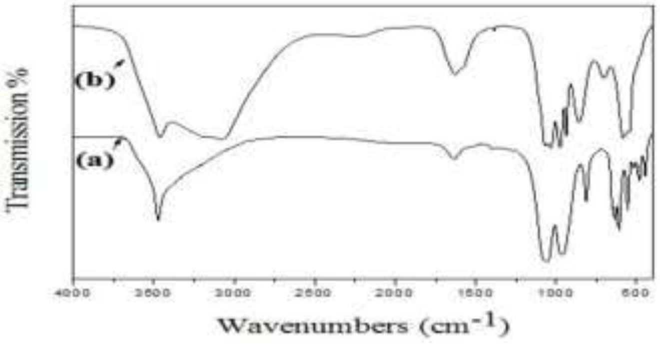

Figure 6.FTIR spectra of the ACP after exposure to solutions of copper (a) or cobalt (b).

3.2.3 Solution of Co(II)

During the first step of adding ACPto the cobalt solution with an initial pH = 3,55, the pH of the mixture undergoes significant variations and reaches a value of 6,8. This value decreases slightly and stabilizes at 6,10 for the rest of the experiment. The XPS spectrum of the solid removed from the solution after 48hours of contact (Fig.2d) shows, in addition to Ca, O and P signals, XPS and Auger peaks assigned to Co(II) (20). As observed previously with nickel and copper, the establishment of Co peaks occurs with a significant decrease inCa signals (Fig. 2a). The chemical analysis of the residual solution shows that 85% of the cobalt ions are removed after being exposed to ACP (Fig.3). The XRD analysis indicates that the residual phosphate (Fig.5b) is not amorphous and cannot be compared to any apatitic phosphate. Its XRD pattern is completely indexed in the $Co_3(PO_4)_2.8H_2O$ system according to the standard PDF data # 33-0432 # (21).A result strongly supported by the

FTIR analysis, which gives an IR spectrum with all the characteristic bands reported in the literature (22) (Fig.6b, Table 2).

3.3 Use of the TCP to remove metal ions from aqueous solutions

When TCP is added separately to the Ni (II), Co (II) or Cu (II) solutions, the pH of each mixture undergoes large fluctuations during the solid-liquid stabilization period.For the nickel solution, the pH value measured after this period is 5.77. This value decreased slightly and remained at 5,4 for the rest of the experiment. The same behaviour is observed for the copper solution with initial and final pH values of 5.36 and 4.80. For the cobalt solution, the pH value measured after 10 minutes is 4.10. This value increased to 4.66, then decreased and stabilized at 4.45 until the end of the experiment. The XPS spectra of the residual solids show, in addition to the Ca, O and P signals, XPS and Auger peaks of Ni (II) (Fig.7b), Cu(II) (Fig.7c) and Co(II) (Fig.7d). As observed in the case of amorphous phosphate, the appearance of nickel, cobalt or copper peaks occurs with a significant decrease in calcium signals (Fig.7a).

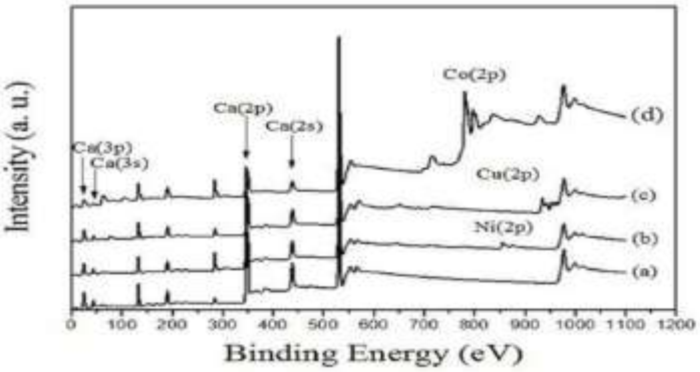

Figure 7.XPS spectra of the TCP before (a) and after exposure to solutions of nickel (b), copper (c) or cobalt (d).

These results suggest that upon contact with the solution, tricalcium phosphate loses its calcium and incorporates metal ions.The process of ion transfer between the solid and the solution is confirmed by the chemical analysis of the residual solutions, which show that in the presence of TCP, the metal ion contents decrease by 11% for nickel, 38% for copper and 16% for cobalt (Fig.3). It is important to note that this decrease, despite being significant, is lower than that obtained using amorphous phosphate. The XRD patterns of the solids separated from the solutions are displayed in (Fig.8). They show that the phosphate isolated from the nickel solution retains the apatitic structure (Fig. 8b), whereas the other two solids correspond to a mixture of an apatitic system and a crystalline phase with a structure of $Cu_2(PO_4)(OH)$ (Fig.8c) in the case of copper and a structure of $Co_3(PO_4).8H_2O$ (Fig. 8d) for cobalt.

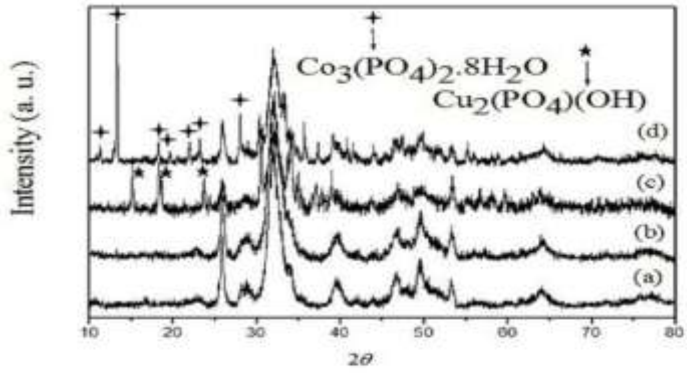

Figure 8.XRD patterns of the TCP before (a) and after exposure to solutions of nickel (b), copper (c) or cobalt (d).

4 Discussion

X-ray photoelectron spectroscopy measurements prove the capture of nickel, copper and cobalt ions by ACP and TCP when exposed to solutions of these ions. The chemical analyses carried out on residual solutions show that their metal contents are significantly reduced. These results demonstrate the ability of tricalcium phosphates to remove metal ions from aqueous solutions. However, the distinct behaviours of ACP and TCP towards metal ion solutions indicate that the mechanisms involved in the transfer of metal ions between the solutions and these phosphates are complicated. In the case of nickel, the ACP and TCP lose calcium and incorporate nickel without significant change in the initial structures of the phosphates. For copper or cobalt, the amorphous phosphates retain metal ions and transform into new phases described by structures of $Cu_2(PO_4)(OH)$ or $Co_3(PO_4)_2.8H_2O$.For the same contact time with solutions, the apatitic phosphates change only partially into these phases.

To clarify these differences, a freshly prepared amorphous calcium phosphate is immersed in pure water for 48 hours and then separated by filtration, washed, dried and analysed by XPS and XRD. Its XPS spectrum (Fig. 9a) shows a slight increase in calcium peaks while the XRDpattern (Fig.9b) reveals the crystallization of amorphous phosphate in an apatitic system.

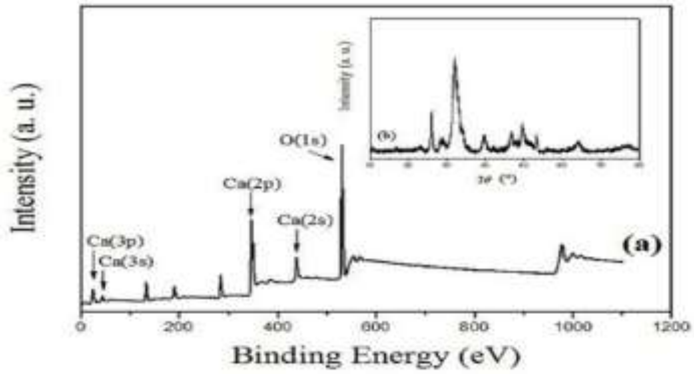

Figure 9: XPS spectra (a) and XRD pattern (b) of ACP after immersion in pure water.

Two mechanisms can be evoked for the transformation of amorphous tricalcium phosphate to apatitic phosphate. The first one occurs only in solution and corresponds to the precipitation-dissolution process. During this process, the dissolution of the relatively soluble amorphous tricalcium phosphate leads to the precipitation of an insoluble crystallized phosphate with a stoichiometry corresponding to an atomic ratio of Ca/P >1,5. This mechanism is influenced by several parameters and becomes important at a low pH (23). The second mechanism corresponds to the internal hydrolysis of PO_4^{3-} groupsaccording to the reaction (1).

As established elsewhere, the hydrolysis reaction occurs when amorphous phosphate is dried between 20 and 120°C and leaves the Ca/P atomic ratio unchanged(12,23). Focusing on the results obtained with amorphous and apatitic phosphates when they are exposed to nickel solutions, these mechanisms cannot explain the conservation of the structure of the phosphates after their treatment in solutions and their subsequent drying. A process involving a simple exchange between calcium and nickel may be considered the dominant mechanism in this case. The preservation of the phosphate structure even after its drying at 80°C indicates that the presence of nickel ions inhibits the hydrolysis of PO_4^{3-}groups and delays its crystallization. A similar effect has been demonstrated by Guerra-Lopez et al.(24) in the study of the effects of nickel on the formation of calcium phosphate. This study shows that the presence of Ni(II) during the precipitation of the phosphate inhibits the establishment of the apatitic phase.

For copper and cobalt solutions, the structural changes that occur in solid phosphates cannot be attributed to a simple exchange between calcium and metal ions. In these cases, pH measurements indicate that copper or cobalt solutions remain acidic (pH <7) throughout the experiment (Fig.4);these conditions stimulate the dissolution of the phosphates. According to these observations, the mechanism responsible for the transfer of metal ions is the dissolution of calcium phosphate and the precipitation of new phases of copper phosphate or cobalt phosphate. If it occurs, this mechanism would be strongly influenced by the solubility of the solid phosphates. High solubility should intensify the mechanism and contribute to the enhancement of the ion elimination process. Given that for similar conditions of pH, temperature and ionic strength, the solubility constants for amorphous and apatitic phosphates are respectively (Kps = 10^{-32}) and (Kps = 10^{-85}) (25).It is possible to assign the high ion removal efficiencies observed with amorphous phosphate to its very high solubility.

These results have to be compared to the work done on hydroxyapatite when used to remove Ni, Cu, Co, Zn, Cd or Pb ions from solutions (26-33). In these cases, metal ion retention occurs without any change of hydroxyapatite structure, disqualifying the dissolution-precipitation process as the dominant mechanism for this phosphate. Such behaviour is predictable given the low solubility of hydroxyapatite (Kps = 10^{-119}) and its high stability. Based on a kinetic study of the ion removal process, the proposed mechanisms correspond to a rapid complexation of metal ions at specific sites on the surface of hydroxyapatite, followed by ion exchange between calcium phosphate and the metal ions of the solution.

Compared to ACP and TCP, the ion exchange mechanism seems to occur only for nickel. If the solubility differences between tricalcium phosphate and hydroxyapatite are responsible for the divergence of cobalt or copper removal mechanisms, they cannot explain the exception of nickel. The effect of nickel is also observed through the inhibition of amorphous phosphate crystallization. To clarify this distinction, it is important to remember that Ni (II) ions with a small size compared to Cu(II) and Co(II) have a relatively high hydration capacity (34).Placed in solution with amorphous phosphate, nickel ions tend to associate with free water molecules close to the phosphate surface. Such combinations would make the water molecules less mobile and therefore unavailable to participate in the hydrolysis reaction of the PO_4^{3-} groups(reaction (1)), thereby inhibiting the crystallization of the phosphate. Indeed, it is well established that the method of preserving the amorphous structure of freshly prepared tricalcium phosphate consists in its lyophilization carried out immediately after its precipitation. This operation removes water-free molecules from the solid and blocks the hydrolysis reaction. For apatitic calcium phosphate, the small size of Ni (II) versus Ca (II) is expected to improve the exchange process. However, the results obtained show that the amount of nickel eliminated in this case is the lowest compared to all the other tests. This effect could be due to the hydration of nickel, which would increase its ionic radius in solution and thus make it difficult to incorporate into the apatite phosphate network.This could also be the consequence of the formation of complex nickel layers on the phosphate surface, which would constitute a barrier to the exchanges between calcium and nickel.Such an effect has been evoked to explain the non-equimolar exchange between calcium ions and Cu(II) or Zn(II) when solutions of these ions are exposed to a carbonated calcium – deficient hydroxyapatite (10).

This work demonstrates the ability of ACP and TCP to remove nickel, copper and cobalt ions from aqueous solutions. Significant differences are observed between these two phosphates in their activity with respect to the metal ions but also by comparison with hydroxyapatite. In fact, the development of the $Cu_2(PO_4)OH$ or $Co_3(PO_4)_2$, $8H_2O$ phases when ACP and TCP are exposed to copper or cobalt solutions contrasts well with the behaviour of stoichiometric HA. Nevertheless, the unambiguous identification of these phases strongly supports the observations made when non-stoichiometric hydroxyapatite (of biological origin) described by the general formula $Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ (x<1) was used to remove Cu or Co ions from aqueous solutions (35). On the basis of the SEM-EDS examinations of this hydroxyapatite after its use and the values of the metal ion and orthophosphate concentrations in the residual solutions, with reference to the solubility data for copper phosphates and cobalt phosphates, the formation of $Cu_2(PO_4)OH$ or $Co_3(PO_4)_2,8H_2O$ has been suggested as products of the reaction between this non-stoichiometric apatite and the copper or cobalt ions.

5 Conclusion

This work shows that amorphous tricalcium phosphate and apatitictricalcium phosphate introduced into solutions containing nickel, copper or cobalt ions remove different amounts of these metal ions.XPS measurements reveal that after exposure to metal ion solutions, amorphous and apatitic phosphates lose their calcium ions and incorporate the metal ions. The mechanisms involved in the transfer of the metal ions from solutions to the solid phosphates are dominated by an ion exchange in the case of nickel and by the dissolution of the solid phosphate followed by the precipitation of new phases with structures of $Cu_2(PO_4)(OH)$ and $Co_3(PO4)_2.8H_2O$ in the case of copper and cobalt.

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