

Use of dicalcium phosphate dihydrate to remove nickel ions from aqueous solutions

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Abstract

The removal of nickel ions from aqueous solutions by dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was investigated by X-ray photoelectron spectroscopy, X-ray diffraction, infrared spectroscopy, thermal analysis and inductively coupled plasma - atomic emission spectrometry. The results of this investigation demonstrate the ability of dicalcium phosphate to remove nickel ions and help identify the mechanism responsible for the transfer of these metal ions from solution to solid phosphate. The results show that, on the one hand, when the phosphate was exposed to the nickel solution for less than 1200 minutes, the nickel retention mechanism was dominated by a substitution process, as evidenced by the equimolar exchanges between the nickel extracted from the solution and the calcium released by phosphate, as well as the preservation of the initial phosphate structure. On the other hand, for exposure times greater than 1200 minutes, the transfer of nickel occurs by the dissolution of the dicalcium phosphate and the precipitation of a new phase of isomorphic structure with $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

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1. Introduction

Heavy metals are the main inorganic pollutants of wastewater produced in areas where industrial activities are intense. Due to their harmful effects, these pollutants are subject to strict regulations regarding their tolerated content in the environment [1-4]. Consequently, there is an increasing demand for materials and technologies that can transform these toxic pollutants from labile forms to more insoluble or less available forms and consequently limit their effects [5-8]. The selection criteria for these materials and techniques combine the costs of implementation and operation but also the efficiency of the processes selected [9-13]. Calcium phosphates as available materials which are inexpensive and easy to prepare are known as excellent candidates for use in heavy metal removal processes [14-16]. The mechanisms evoked for the elimination of metal ions by phosphate compounds combine: i) the ion-exchange between the calcium ions of the solid phosphate and the metal ions of the solutions; ii) the complexing of the metal ions on the surface of solid phosphate iii) the dissolution and precipitation process where calcium and orthophosphate groups of the solid phosphate are dissolved together and the metal ions precipitate by homogeneous or heterogeneous (involving the remaining solid phosphate) nucleation iv) the substitution of the calcium ions by divalent metal ions during coprecipitation. These mechanisms are controlled by several parameters such as the nature of the metal ions, their concentrations, the contact time between the phosphate and solutions, the temperature and the pH of the metal ion solutions [17-20]. Stoichiometric hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was the first calcium phosphate material tested in the process of retaining heavy metal ions in aqueous solutions [17, 21-27]. This was the case due to distinctive properties HA compared to all other calcium phosphates. Its very low solubility value ($K_s = 10^{-116,8}$) [28] which testifies to its great stability in water, imposed few restrictions on the solutions of metal ions into which it could be introduced. The cationic and anionic substitution features allowed by the HA crystal lattice classify it among the best materials to be applied in the metal ion retention processes controlled by ion exchange [21, 22, 27]. Compared to HA, the DCPD crystal lattice also offers several possibilities for cationic substitution, but this phosphate remains very soluble ($K_s = 10^{-6,59}$) and is therefore less stable [28]. Introduced into aqueous solutions or placed in a humid space, DCPD undergoes substantial changes and spontaneously transforms into hydroxyapatite [28-33]. The difference of reactivity between HA and DCPD leads to discover how the low stability of the latter and the modifications caused by its contact with aqueous solutions could give an advantage or on the contrary a disadvantage to this phosphate when used to remove metal ions from solutions. An earlier study by El Hamidi et al. [34] has shown that DCPD exposed to copper solutions incorporate a quantity of copper which does not exceed 25% with respect to the calcium ion content of the phosphate. This incorporation, which occurs without modification of the structure of the DCPD, involves a simple exchange between the calcium and copper ions. A recent work devoted to the study of the retention of copper and nickel by tricalcium phosphate revealed a completely different behavior of these two metals [35]. While in the case of nickel, the retention involves a simple exchange with calcium ions, for copper, the retention occurs through the dissolution of the tricalcium phosphate and the precipitation of a new metal phosphate [35]. All these similarities and differences motivate the present work devoted to the study of the retention of nickel by the DCPD.

2. Materials and methods

DCPD was prepared using a double decomposition method where a solution of 0,1M of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), was gradually added to 0,1M solution of diammonium phosphate solution prepared from $((\text{NH}_4)_2\text{HPO}_4)$, at room temperature. The solid formed in these conditions was separated from the solution by filtration, dried at 80°C for one night and then analyzed. The XPS analysis was performed with a Kratos spectrometer using monochromatic aluminum K_α with photoionization power of 150W. The XPS survey scans spectra were recorded with an analyzer pass energy of 160 eV and a resolution of 1 eV. A low energy electron beam was systematically used to

reduce the effect of positive charges accumulated during photoemission process. The XPS peaks energies were corrected using the C(1s) carbon signal as a reference. The XRD analysis were performed with a Brucker D8 Advanced diffractometer using a copper anticathode ($\lambda_{\text{CuK}\alpha} = 1.5405 \text{ \AA}$) submitted to an accelerating voltage of 50 keV and an emission current $I_{\text{emission}} = 40 \text{ mA}$. XRD patterns were recorded in 2θ ranges of 10-80 degrees with a step scanned of 0.02 and an acquisition time of 14s per step. The infrared spectra were collected with a Nicolet iS10 thermo scientific spectrometer ATR-FTIR. Each spectrum corresponds to the ratio of 32 scans recorded at a resolution of 4 cm^{-1} with solid sample and the background spectrum recorded in the same conditions without any sample. Thermogravimetric analysis (TGA) were performed by Shimadzu DTG model-60h in air with at a heat rate of 5°C/min . The SEM/EDS analyses were performed using a microanalyzer Bruker XFLASH 6/10 Scanning Electron Microscope coupled with X-ray energy dispersive spectroscopy to produce photographic images and the elemental chemical analysis. The observations were made on a microscope Hitachi S570. Samples with a mass of 10 mg are coated with a carbon deposit to avoid the effects of surface charge. The settings used were, accelerating voltage (20 kV), working distance (35 mm), beam current ($0.4 \cdot 10^{-10} \text{ A}$), tilt angle of the specimen (0°) and analysis time at each point (0.6 s). Calcium and nickel contents in solids and solutions were obtained through the inductively coupled plasma atomic emission spectrometer measurements whereas the phosphorus amounts were determined by spectrophotometry method described by Gee and Dietz [36, 37]. The experiments testing the capability of the phosphate to remove nickel from solution were carried out by introducing 0,3 g of DCPD powders into 150 mL of a 10^{-2}M aqueous solution of nickel prepared by dissolving $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ in distilled and deionized water. After different periods of contact between the phosphate and the nickel solution, the residual solids formed were separated from the solution by filtration, washed with deionized water, dried at 80°C for 14 hours and then analyzed.

3. Results and Discussions

3.1. Characterization of the synthesized dicalcium phosphate dihydrate

The chemical analysis of the synthesized calcium phosphate gives an atomic ratio ($\text{Ca/P} = 1 \pm 0.01$) characteristic of DCPD. Its XPS spectrum (**Fig.1a**) shows all the peaks characteristics of a calcium phosphate except a signal observed at 284.6 eV which is assigned to C(1s) of carbon [38]. This carbon cannot be attributed to the phosphate due to the change of its intensity by replacing the sample holder. It represents the contribution of the adhesive film used to fix the DCPD powders to the holder. The purity of the phosphate is also verified by XRD and IR. Its XRD pattern (**Fig.1b**) matched perfectly to the standard data of DCPD given in JCPDS n°# 0072-0713# while its IR spectrum (**Fig.1c**) identical to those presented by Berry et al. [39] and Sekar et al. [40] shows only the characteristic bands of DCPD.

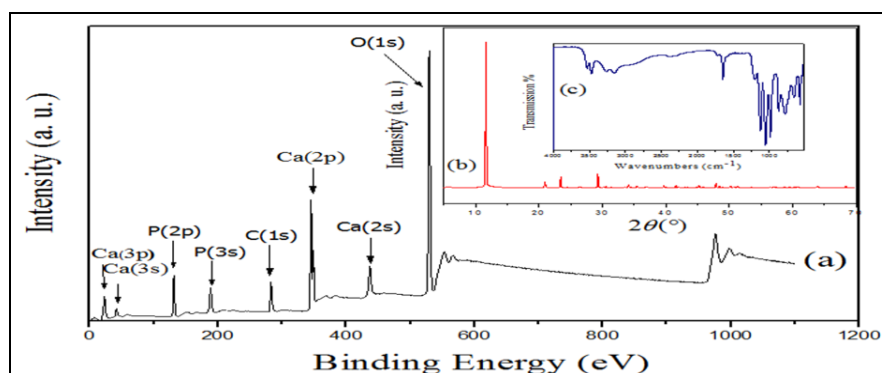


Figure 1. XPS spectrum (a), XRD pattern (b) and IR spectrum (c) of DCPD

3.2. Evidences of nickel ions removal by DCPD

Chemical analyses of the nickel solution exposed to DCPD reveal that after 45 minutes of exposure, the amount of nickel is reduced by 20% with respect to the initial concentration (**Fig.2a**). This amount expressed as nickel removal yield remains substantially the same even after 1200 minutes of contact with the solid phosphate. Once this time is exceeded, the amount of nickel lost by the solution begins to increase significantly and reaches 100% after 8740 minutes of exposure. The results presented in (**Fig.2b**) show that the loss of nickel is not the only effect caused by the contact between the solution and the phosphate. The changes in the amounts of calcium observed in the solution are certainly the consequence of a transfer of calcium ions from the solid phosphate to the solution. As shown in the (**Fig.2**), up to 1200 minutes of exposure, the amount of calcium released by the phosphate remains of the same order of magnitude as the amount of nickel removed from the solution. By delaying the contact between the solid and the solution beyond 1200 minutes, the amount of calcium begins to increase significantly. After 8740 minutes of treatment, this amount reaches the maximum that can be produced assuming the complete dissolution of the initial mass of DCPD.

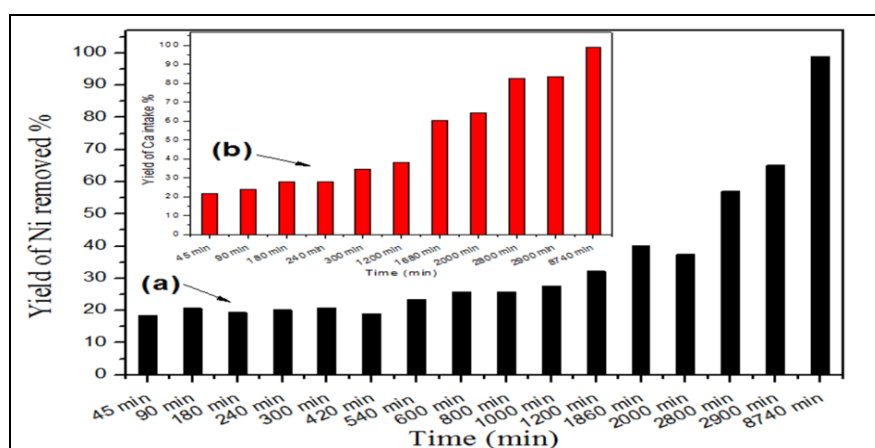


Figure 2. Yield of nickel removed from the solution (a) and yield of calcium transferred to the solution (b).

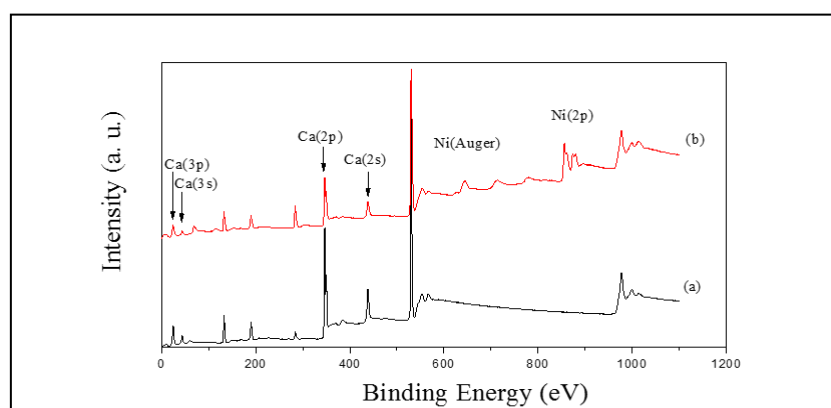


Figure 3. XPS spectra of DCPD before (a) and after exposure to nickel ion solution (b)

Based on opposite variations in the amount of nickel and calcium in the solution, it is easy to deduce that the transfer process involves not only the solution but also the solid phosphate. To confirm this observation, a solid phosphate exposed first to the nickel solution for 1200 minutes was isolated, washed, dried and analyzed using XPS. Its spectrum (**Fig.3b**) shows in addition to calcium, oxygen and phosphorus signals, new XPS and Auger peaks that are attributed to nickel [41, 42]. Compared to the XPS spectrum of the DCPD (**Fig.3a**), it appears that, unlike the peaks of oxygen

and phosphorus whose intensities are only slightly affected by the establishment of nickel peaks, the calcium signals are strongly reduced. This implies that when exposed to the solution, the phosphate loses its calcium ions and incorporates nickel ions. In order to observe other changes induced by the phosphate-solution contact, the residual solids produced after different exposure times were analyzed by X-ray diffraction and IR spectroscopy. Their XRD patterns and IR spectra show that (**Fig.4** and **Fig.5**), for exposures of less than 1200 minutes, the structure of the solids is maintained as confirmed by the non-alteration of the intensities of the XRD lines and the IR bands. However, a careful analysis of the XRD patterns shows that the increase in contact time induces small and continuous displacements of the diffraction lines to high angles (**Fig.6A**). Such displacements can certainly be correlated with changes in the calcium and nickel content previously observed by XPS.

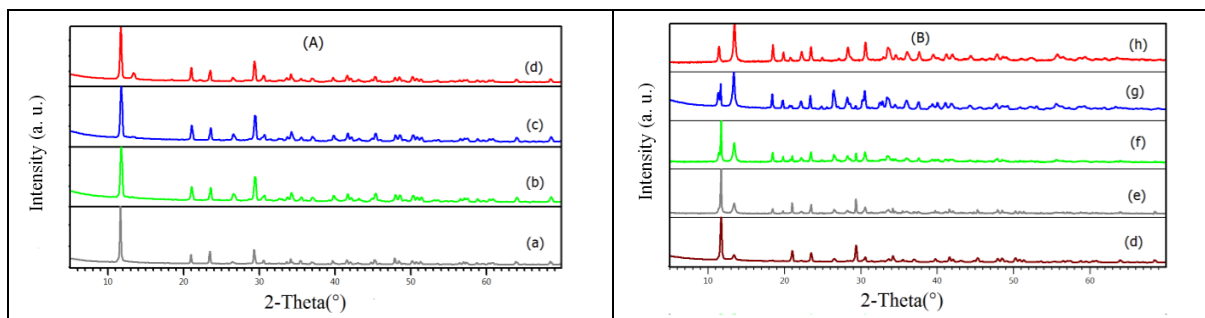


Figure 4. XRD patterns of DCPD before (a) and after exposure to nickel ion solution for 90 min (b) 420 min (c) 1200 min (d) 1680 min (e) 2900 min (f) 6000 min (g) and 8740min (h).

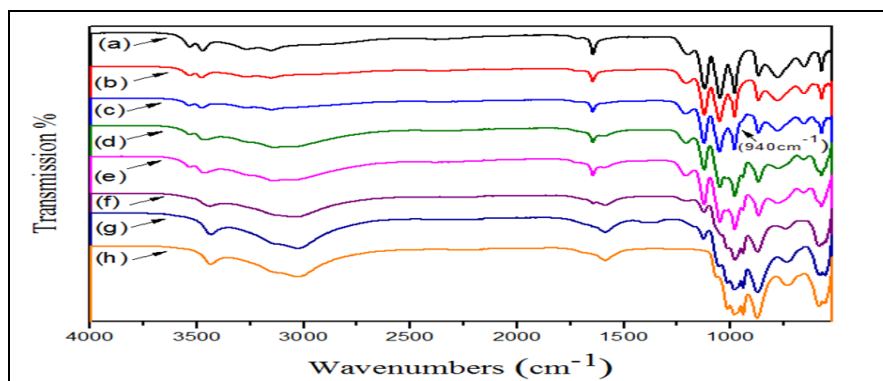


Figure 5. IR spectra of DCPD before (a) and after exposure to nickel ion solution for 90 min (b) 420 min (c) 1200 min (d) 1680 min (e) 2900 min (f) 6000 min (g) and 8740min (h).

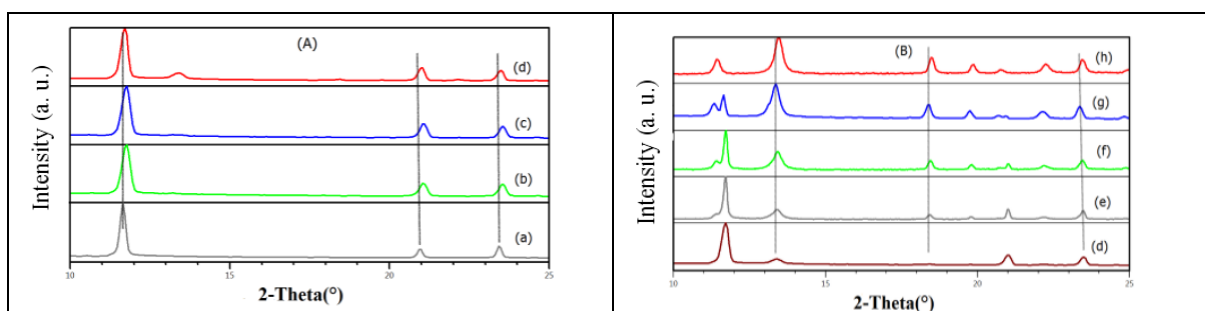


Figure 6. XRD patterns of DCPD (a) and the isolated phosphates after 90 min (b) 420 (c) 1200 min (d) 1680 min (e) 2900 min (f) 6000 min (g) 8740 min (h) of treatment (the vertical segments are drawn to highlight the displacement of diffraction lines)

When the contact time is extended to 1200 minutes, the XRD pattern of the residual solid reveals two additional new lines, while its infrared spectrum displays a small shoulder at 940 cm^{-1} (**Fig.4** and **Fig.5**). By maintaining the contact for more than 1200 minutes, the intensity of these new lines gradually increases and their positions shift towards high diffraction angles, while the characteristic lines of the DCPD undergo a significant decrease then disappear completely after 8740 minutes. For this exposure time, the chemical analysis of the residual solid gives an atomic ratio of ($\text{Ni/P}=1.51\pm0.01$) while its XRD diagram exhibits diffraction lines identified unambiguously to the $\text{Ni}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$ structure (standard PDF data N° #00-046-1388# (**Fig.7**) [43]. This identification is also confirmed by IR analysis which gives an infrared spectrum where only the characteristic bands of $\text{Ni}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$ reported in the literature are present (**Fig.8**) (**Table.1**) [43]. It is also corroborated by thermogravimetric analysis which shows the complete disappearance of the mass loss at 450°C due to the transformation of the orthophosphate groups (HPO_4^{2-}) into pyrophosphate groups ($\text{P}_2\text{O}_7^{4-}$) and in fact proves the quantitative conversion of DCPD (**Fig.9**) [43]. Finally, this identification is confirmed by XEDS mapping (**Fig.10**), which indicates that the residual solid is composed mainly of nickel and phosphorus with a nickel / phosphorus atomic ratio of 1,54 not much different from the value of 1,5 obtained by the chemical analysis

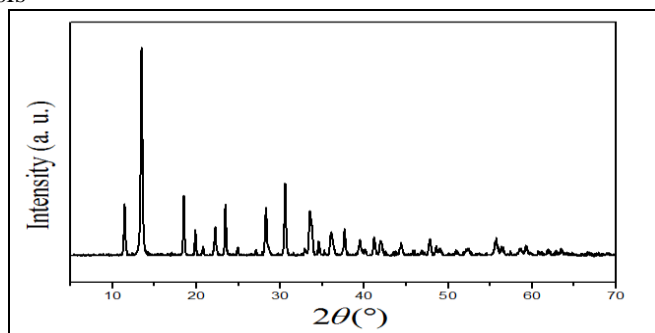


Figure 7. XRD pattern of the solid phosphate isolated after 8740 min of exposure.

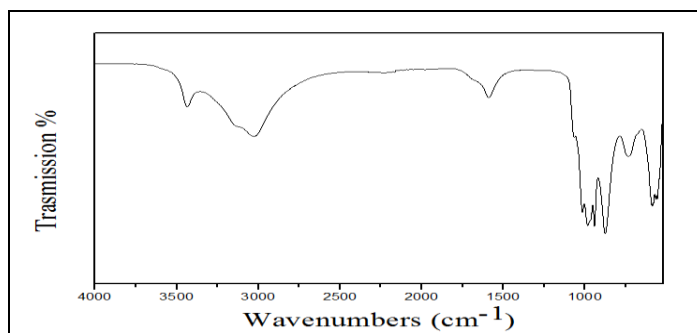


Figure 8. IR spectrum of the solid phosphate isolated after 8740 min of exposure.

Regardless of the contact time between the solid phosphate and the solution, the results obtained clearly demonstrate the ability of the DCPD to remove nickel ions from the solution. Although complex, the mechanism controlling the elimination of nickel ions by DCPD seems to involve two different processes. The first operates as soon as the contact between the phosphate and the solution is made and extends up to 1200 minutes, while the second operates for contact times greater than 1200 minutes. The following section highlights the main characteristics of these two processes.

3.3 Mechanisms involved in the retention of nickel ions by DCPD

Chemical analysis of the nickel solution following its exposure to DCPD shows that its amount of nickel decreases while that relating to calcium increases. The XPS analysis performed on the residual solid proves that the phosphate loses its calcium ions and retains nickel ions when submitted to the solution. Up to 1200 minutes of contact between

DCPD and the nickel solution, nickel retention and calcium loss occur without any modification of the structure of DCPD, as revealed by XRD and IR analyzes. This implies that the mechanism of nickel ion retention by DCPD for exposure times less than 1200 minutes is dominated by a simple exchange between nickel and calcium. The displacements of the diffraction lines towards the high angles observed with the increase in the exposure time are then explained by the replacement of calcium by nickel ions of small ionic radius (0.069 nm against 0.1 nm for calcium ions) [44]. It is therefore easy to understand that the exchange mechanism leads to the formation of solid solutions of nickel and calcium phosphate isomorphic to DCPD and described by the formula $\text{Ca}_{1-x}\text{Ni}_x(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$. The emergence of the diffraction lines associated with the $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ phase in addition to the decrease in the intensities of the DCPD diffraction lines observed subsequently and which occurs without any displacement of their positions; indicate that the limit of these solid solutions is given by the composition of the residual phosphate produced after 1200 min of exposure. This composition is characterized by an overall amount of nickel of 32% relative to the calcium. However, considering the results of the thermal analysis which give both the quantity of the HPO_4 groups and the relative proportions of the DCPD with respect to the $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ phase, the composition of the limit of these solid solutions can be described by $\text{Ca}_{0.75}\text{Ni}_{0.25}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$. The discrepancy in the nickel amounts being attributed to the presence of the $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ phase which in turn corresponds to the composition: $\text{Ca}_{2.47}\text{Ni}_{0.53}(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$. By focusing on the nickel limit content in solid solutions of DCPD type, it is surprising to note that this limit is exactly the same as that observed by El Hamidi et al. in experiments where DCPD was exposed to copper solutions of different concentrations [34]. In this case, the composition described by $\text{Cu}_{0.25}\text{Ca}_{0.75}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ is obtained even when the ratio between the copper content in solution and the calcium content of the solid phosphate reaches a value of 40%, an exactly identical amount to that of nickel used in this work. This implies that the limits of these solid solutions are mainly set by the phosphate rather than by the nature of the metal ions exchanged with calcium.

Table 1. The observed IR bands and their assignments of the solid phosphate produced after 8740 min of exposure.

IR bands (cm^{-1})	IR bands observed by Kullyakool et al. [43]	Assignment
3435	3437.68	$\nu_3\text{H}_2\text{O}$ antisymmetric stretching
3143	3146.89	$\nu_1(\text{H}_2\text{O})$ symmetric stretching
3030	3037.29	
1596	1595.59	$\nu_2\text{H}_2\text{O}$ symmetric bending
1071	1075.96	$\nu_3(\text{PO}_4^{3-})$ antisymmetric stretching
1018	1018.81	
989	990.04	$\nu_3(\text{PO}_4^{3-})$ antisymmetric stretching
942	943.58	$\nu_1(\text{PO}_4^{3-})$ symmetric stretching
876	884.47	
742	745.57	vibrational mode of water
589	595.67	$\nu_4(\text{PO}_4^{3-})$ out of plane bending vibration

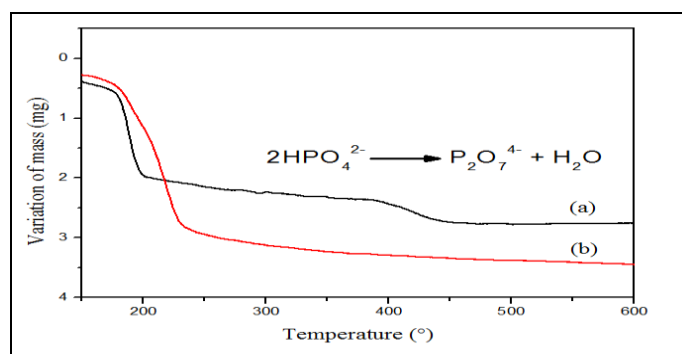


Figure 9. ATG curves of DCPD (a) and of the solid phosphate isolated after 8740 min of exposure to the nickel solution (b)

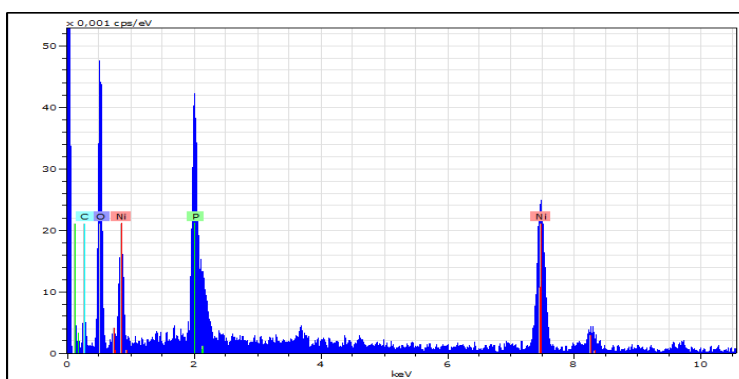


Figure 10. XEDS mapping of the solid phosphate isolated after 8740 min of exposure to the nickel solution.

When the exposure time exceeds 1200 minutes, the transfer of calcium and nickel ions between the solution and the solid becomes intense as indicated by the large variations in their quantities. This intensification is accompanied by a gradual conversion of $\text{Ca}_{0.75}\text{Ni}_{0.25}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ into $\text{Ni}_3(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$ phase as evidenced by the opposite changes of the intensity of their diffraction lines. Such a transformation is therefore the consequence of the progressive dissolution of the mixed phosphate $\text{Ca}_{0.75}\text{Ni}_{0.25}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ followed by the precipitation of the $\text{Ni}_3(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$ phase and involves the intervention of a dissolution-precipitation mechanism as a process of retention of nickel ions under these conditions. However, the fact that the progressive intensification of the diffraction lines associated with the $\text{Ni}_3(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}$ phase is accompanied by their displacement towards high angles indicates that the retention of nickel ions by this phosphate is also done by an exchange process with calcium. This process continues in parallel with the dissolution of the mixed phosphate and then gives rise, after 6000 minutes of exposure, to a solid with a composition described by $\text{Ca}_{1.18}\text{Ni}_{1.82}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. For a contact time of 8740 min, the transformation of this solid is completed by the formation of the pure nickel phosphate $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. The results presented in this work demonstrate the ability of DCPD to remove nickel ions from aqueous solutions. The transfer of nickel to solid phosphate involves a simple exchange with calcium at the beginning and then a dissolution-precipitation and an ionic exchange processes when the exposure time exceeds 1200 minutes. This behavior appears to be different from that observed with stoichiometric hydroxyapatite [45]. In this case, the retention of nickel is dominated by the ionic exchange. The same mechanism intervenes when the nickel solution is exposed to apatitic or amorphous tricalcium phosphates [35]. However, it is surprising to note that in the case of HA or tricalcium phosphates, the amounts of nickel retained from solution remain relatively small compared to that of other metal ions such as Co, Cu and Zn [35, 46]. The particularity of nickel seems to be attributed to its small size and its high hydration energy which gives it a fairly wide sphere of hydration and therefore limits its exchange process with calcium [44]. Another characteristic related to the presence of nickel is its

inhibitory effect on the transformations occurring on calcium phosphates in aqueous solution. Such an effect is clearly demonstrated by comparing the behavior of DCPD in a nickel solution and in pure water. As has been successfully established, the DCPD placed into contact with water transforms into octacalcium phosphate $\text{Ca}_8(\text{PO}_4)_4(\text{HPO}_4) \cdot 5\text{H}_2\text{O}$ (OCP) which in turn gradually converts to HA [28-33]. Paradoxically, neither OCP nor HA are observed when the DCPD is exposed to the nickel solution. Based on experiments with DCPD prepared in the laboratory, these intermediate phosphates are only detected when the DCPD is exposed to pure water for more than 1200 minutes (**Fig. 11**). Surprisingly, in the presence of nickel ions, this exposure time coincides with the period necessary for the appearance of the $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ phase. This suggests that when the DCPD dissolution-precipitation process begins to occur, the presence of nickel ions would favor the precipitation of the mixed nickel and calcium phosphate rather than that of the less insoluble octacalcium phosphate. A systematic study of the effect of nickel should be carried out to elucidate its role on the inhibition of the formation of octacalcium phosphate and hydroxyapatite and paradoxically on the stabilization of metallic phosphate.

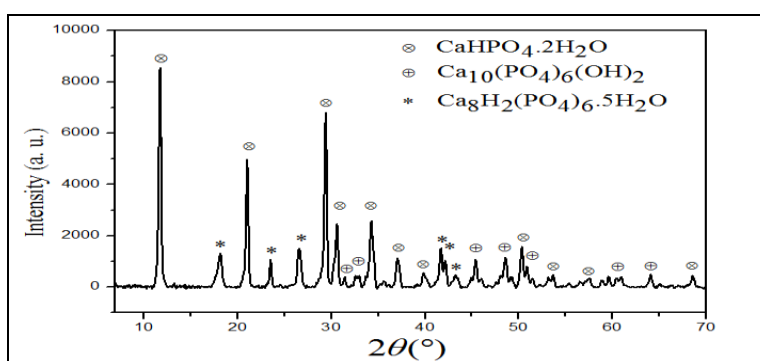


Figure 11. XRD pattern of DCPD after its exposure to pure water for 8740 min (diffraction lines of octacalcium phosphate and hydroxyapatite are identified according to PDF data N° #01-074-1301# and N° #00-054-0022#).

4. Conclusion

This study demonstrates the ability of the dicalcium phosphate dihydrate to remove nickel ions from aqueous solutions. It shows that when this phosphate is exposed to a solution of nickel ions for an exposure time of up to 1200 minutes, the transfer of nickel to the solid phosphate is dominated by a simple exchange with calcium ions. This exchange leads to the formation of mixed nickel and calcium phosphates with a structure identical to DCPD and the limit of which is described by the formula $\text{Ca}_{0.75}\text{Ni}_{0.25}\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. When the exposure time is extended above 1200 min, a new nickel and calcium phosphate phase isomorphous with the structure of $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is formed. In this case, the retention of nickel takes place by a process of dissolution of the phosphate with DCPD structure and also by a process of exchange intervening in the new phase. Up to 8740 minutes of exposure, the initial amount of nickel is completely removed from the solution and the DCPD is completely transformed into $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. This transformation different from what is observed when DCPD is submitted to pure water, suggests an important effect of nickel ions, in particular by inhibiting the formation of octacalcium phosphate and hydroxyapatite as intermediates observed during the conversion of the dicalcium phosphate dihydrate in water.

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