

Production of hydroxyapatite from phosphoric rock

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Abstract

The article focuses on processes used to obtain hydroxyapatite from phosphate rock in the municipality of Pesca (Department of Boyacá, Colombia) by leaching with nitric acid. An analysis was carried out to evaluate the influence of different concentrations of leaching acid and treatment time on the recovery of phosphorus and calcium ions. The results indicated that maximum recovery of phosphorus and calcium ions was achieved by increasing concentration to 5M. The influence of the concentration of the precipitating agent was also analyzed and it was found that, although increased concentrations improve the pH adjustment rate, the purity of the HAp obtained decreases at higher concentrations, possibly due to the formation of other species associated with sodium hydroxide. Following washing with deionized water, pure HAp was obtained as a final product, which was characterized using XPR, XRD, SEM/EDS and FTIR.

Keywords: phosphate rock; acid leaching; hydroxyapatite.

Obtención de hidroxiapatita a partir de roca fosfórica

Resumen

El presente trabajo se centra en la obtención de hidroxiapatita (HAp) a partir de roca fosfórica proveniente del municipio de Pesca del departamento de Boyacá, por medio de la lixiviación con ácido nítrico. Se llevo a cabo un análisis para evaluar la influencia de la concentración del ácido lixivante y el tiempo del tratamiento en la recuperación de iones de fósforo y calcio. Los resultados indicaron que al incrementar la concentración ácida hasta 5M se logró la máxima recuperación de dichos iones. También se analizó la influencia de la concentración del agente precipitador y se encontró que, si bien, el aumento en la concentración mejora la velocidad de ajuste del pH, se observa una disminución en la pureza de la HAp obtenida, esto posiblemente debido a la formación de otras especies asociadas al hidróxido de sodio. Después de un lavado con agua desionizada se obtuvo como producto final, HAp pura, la cual fue caracterizada por FRX, DRX, SEM/EDS y FTIR.

Palabras clave: roca fosfórica; lixiviación ácida; hidroxiapatita.

1 Introduction

Hydroxyapatite (HAp) is a calcium phosphate that, due to its composition and mechanical properties, is considered one of the most versatile and effective biomaterials with application, in particular, in bone tissue regeneration, in particular in dental coating and orthopedic devices [1,2]. However, its uses are not limited to these specific areas. Research has shown HAp to have potential applications in the fields of aesthetic medicine, water

treatment filters and the manufacture of carbon dioxide sensors [3].

The most commonly used method in the manufacture of HAp is hydrothermal synthesis, which relies on using chemical precursors under basic pH conditions to precipitate HAp and its associated compounds from aqueous solutions enriched in phosphate (PO_4^{-3}) and calcium (Ca^{+2}) ions [3-5]. In the present work hydrometallurgical processes were used only.

Phosphorus pentoxide (P_2O_5) can be obtained from

phosphate rock (PR), which is considered to be the raw material for the production of elemental phosphorus (P) and other elements including calcium (Ca), sodium (Na) and magnesium (Mg) [6,7]. PR is generally found in the form of natural fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$) in apatite deposits [8].

Generally, phosphoric acid is obtained by leaching PR to obtain P-enriched solutions [9,10]. Other elements, such as Ca, are also leached during this process, because of the nature of PR [11]. Leaching is a chemical process used to recover soluble substances; it frequently involves the use of acids to dissolve the components of interest [12]. Although PR deposits are the principal natural source used to extract elemental P, information on its processing as a raw material to obtain HAp remains scarce.

Some deposits with the capacity to support the exploitation of PR are found in Colombia. In 2022, the Colombian Geological Service (SGC) identified three areas of interest in the department of Boyacá [13].

The objective of this study is to establish a laboratory-based hydrometallurgical processing route by examining different leaching conditions for obtaining HAp from PR. These conditions include acid concentration levels and treatment time. In addition, an analysis was also carried out of the impacts of sodium hydroxide (NaOH) concentrations when used as agents for precipitating the species found.

2 Materials and methods

2.1 Materials

A sample of PR from the municipality of Pesca was prepared. The sample was crushed and ground to a particle size of less than 103 μm and then sieved to ensure that 80% of the total complied with the standardized granulometry. This sample was characterized chemically and mineralogically using Epsilon 13V 1.5 Malvern Panalytical X-ray fluorescence and Empyrean Panalytical XRD equipment respectively. The operating conditions for the latter were set for a sweep in the 2θ axis from 5° to 70° with steps of 0.02° and a time of 0.5 s/step. In addition, Cu radiation with wavelength λ of 1.5406 \AA was employed, along with X'pert High Score Plus software for data processing.

2.2 Leaching tests

The PR sample was subjected to leaching processes at laboratory scale, in solutions of nitric acid (HNO_3) between 2 and 7 M and leaching times of 24 h, in order to analyze the dissolution behavior of P and Ca ions as a function of the acid concentration. The leaching process was carried out in beakers with mechanical agitation at fixed speed and maintaining a constant 1/3 sample(solid)/solution(liquid) ratio. The P and Ca present in the acid leaching solution was analyzed using the semi-quantitative XRF characterization technique.

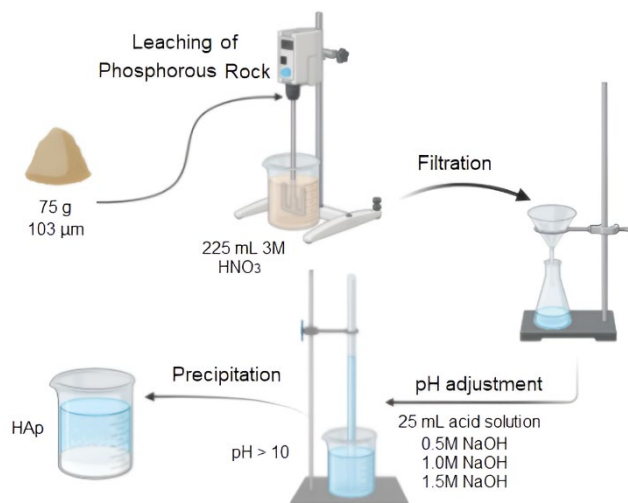


Figure 1: Schematic diagram of the process used to obtain hydroxyapatite from phosphate rock.
Source: the authors

2.3 Precipitation of HAp

NaOH solutions at concentrations of 0.5, 1 and 1.5 M were added as precipitating agents to 25 mL of the 3M HNO_3 solution obtained from the acid leaching of the PR, until a pH greater than 10 was reached (see Fig. 1). During the reaction, a precipitate forms as the alkalinity of the solution increases. Once the pH reached a desired value, the agitation was suspended. The product obtained, composed of a colorless liquid phase and a white solid phase, was left to stand for 24 h, after which the two phases were separated by filtration.

The solid phases were dried using a heating plate at a temperature of 70°C for 30 min. The samples obtained were labeled H05, H10 and H15 and prepared for XRF and XRD analysis. In this study, the reference samples obtained during the process were washed with deionized water in order to eliminate water-soluble species.

2.4 Characterization of the HAp

A compositional characterization of the samples obtained was carried out using XRF and an Oxford Instruments energy dispersive X-ray spectroscopy probe (EDS) coupled to a JEOL JSM-5910LV SEM. Structural characterization was carried out using XRD.

3 Results and Discussion

The different characterization techniques performed on the PR sample showed that the predominant species were fluorapatite (FA), which accounted for 59% of the total, quartz (Qz) with 34% and calcite (CaC) with 7%. The principal amplification peaks for each of these minerals are presented on the right side of Fig. 2. XRD analysis is semi-quantitative and assumes an error of approximately $\pm 5\%$ by

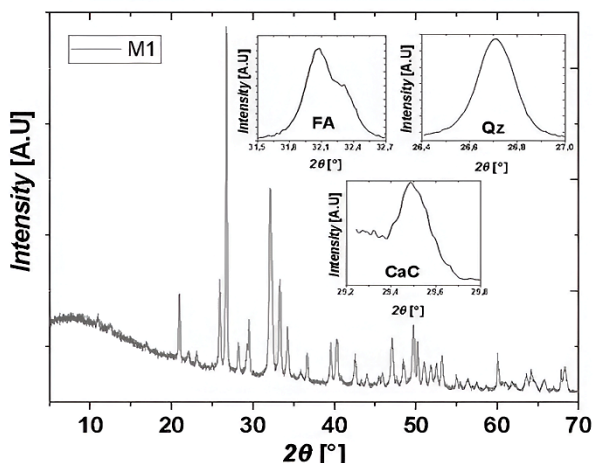


Figure 2. X-ray diffraction spectra for the PR sample. FA is fluorapatite, Qz is quartz and CaC is calcite.
Source: the authors

Table 1.
Elemental and oxide composition of the PR sample

Element	[%]	Oxide	[%]
P	13.44	P ₂ O ₅	26.81
Ca	36.76	CaO	37.00
Si	12.48	SiO ₂	25.67
Mg	3.54	MgO	6.89
Al	1.29	Al ₂ O ₃	2.45
K	0.23	K ₂ O	0.21
Ti	0.09	TiO ₂	0.09
Mn	0.02	MnO	0.02
Fe	1.06	Fe ₂ O ₃	0.92

Source: the authors

weight. The elemental chemical analysis of the PR sample rendered the following percentages for P and Ca: 13.44% and 36.76%, respectively, with a P₂O₅ content of 26.81% and CaO content of 37%, as shown in Table 1. It should be noted that the error reported by the XRF equipment is less than 0.05%. The deposit may therefore be classified as a good source for the obtention of by-products with higher added value such as HAp. It is, in other words, a high-grade deposit [14].

3.1 Effects of acid concentrations

Fig. 3 presents the leaching behavior of P and Ca. The enriched solutions were analyzed using XRF. The PR sample showed an increase in the release of ions of interest when dissolved using concentrations of 2 to 5M HNO₃, with the highest extraction levels occurring at 5M. As the acid concentration of the solution increased above this value, recovery rates decreased, a finding that may be associated with the degree of solubility of the RP. Furthermore, increased concentrations did not result in higher levels of dissolution of P and Ca, possibly due to the formation of insoluble compounds that reduce the efficiency of the process. [15].

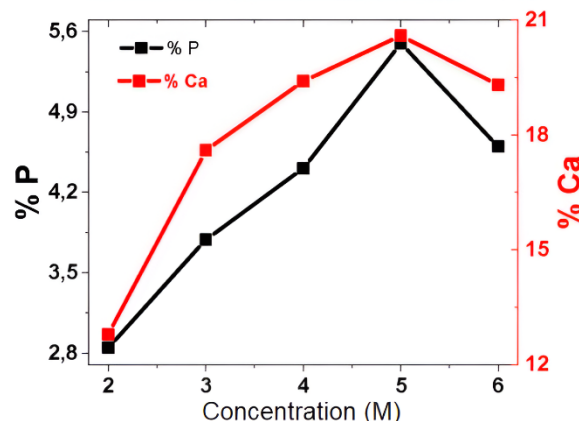


Figure 3. Extraction of P and Ca ions over 24 h at different acid concentrations.
Source: the authors

3.2 The effects of time

Fig. 4 shows that for periods exceeding 18 h, time has no significant effect on the leaching of P and Ca. It was determined that 18 h after the leaching process began, a leached fraction of 0.281 P was obtained in the solution, while at 48 h only a further 0.008 was obtained ($X = M$ dissolved/M total, where M is P or Ca).

The behavior of Ca during extraction was similar to that of P, maximum recovery having occurred by 24 h ($X = 0.466$) and extraction remained stable after this time. It is probable that the reaction might reactivate the extraction of P and Ca. However, to validate this hypothesis the duration of the protocol would have to be extended, which might lead to the formation of insoluble compounds and further decrease the efficiency of the process. [15].

An upward tendency in the percentage of P and Ca ions, similar to that presented in Figs 3 and 4, was also reported by Tekin et al. (2001) [16] and Taha et al., (2013) [17], who studied the effects of ultrasound on the kinetics of the dissolution of PR in HNO₃ at molar concentrations between 0.01 and 0.1 M for durations of up to 5 min, and of PR from the western Abu Tartur Desert in the same acid at different agitation conditions.

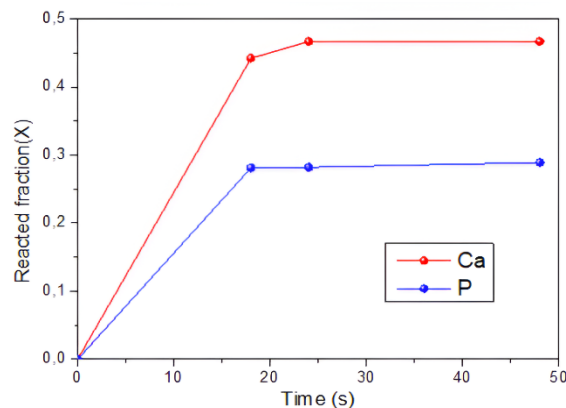


Figure 4. Dissolution of P and Ca ions in a 3 M HNO₃ solution.
Source: the authors

3.3 The effect of NaOH concentration on HAp precipitation

NaOH is a common and effective agent used to modify pH levels during the precipitation of HAp [9]. After varying the concentrations in order to adjust pH, XRD and XRF showed that increased concentrations favor the formation of sodium nitrate (NaNO_3), decreasing the percentage of P present in the precipitate. Table 2 presents the values, in % wt, of the results of the compositional analysis of the samples obtained from HAp, for NaOH concentrations of 0.5; 1 and 1.5 M, respectively.

The Ca/P molar ratio is close to 1.6 for the pure HAp species, a finding that makes it possible to establish potential uses it might be put to or the biological needs it could meet [18]. However, when the molar ratios for the samples obtained in the laboratory were calculated, the Ca/P ratio of 1.6 was not found, probably because of an excess of Ca, most likely associated with the presence of mineralogical species associated with this element. Thus, in order to enhance the use of these materials in biological applications, the Ca/P molar relation must be adjusted using additional processes.

The analysis of the crystalline phase of the HAp samples was performed using XRD assays. The diffraction spectra (diffractograms) for the powders, synthesized with different concentrations of NaOH, are presented in Fig. 5.

Fig. 5 shows the characteristic triple peak of monoclinic HAp, which is presented in the range of 31° to 33° in the 2θ axis with the main Miller indices (h k l) (221), (-222) and (-360), for the peaks, with intensities of 100, 52.6, and 61.4 %, respectively. Some studies have reported that in the monoclinic phase, HAp displays piezoelectric properties [20], which has led this species to be considered suitable for bone tissue regeneration, since it can remain electrically active and stimulate the tissues at a controllable rate [21,22].

Table 2.
Elemental analysis of HAp samples.

Element	Composition [%]		
	H05	H10	H15
P	13.01	10.21	12.71
Ca	37.68	34.62	37.88
Mg	6.83	6.22	7.00
Si	0.53	0.50	0.37
Al	0.54	0.41	0.47
Cl	0.22	0.22	0.21
Ti	0.01	0.01	0.01
Mn	0.02	0.01	0.01
Fe	0.34	0.262	0.28

Source: the authors

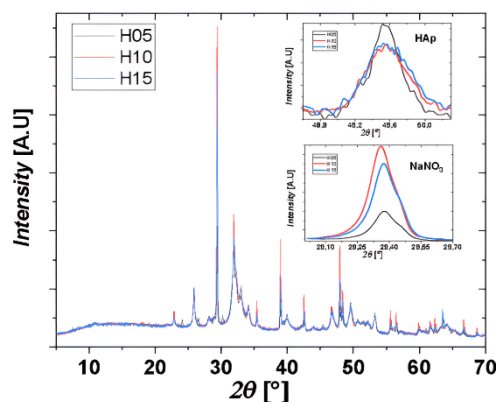


Figure 5. XRD spectra for the different HAp samples
Source: the authors

Table 3.
Mineralogical phases present in the synthesized samples (in percentages).

Phase	Percentage		
	H05	H10	H15
HAp	73	51	54
NaNO_3	27	49	46

Source: the authors

Table 4.
Network parameters for the patterns of the mineralogical phases found in the synthesized of hydroxyapatite samples.

Phase	Sample	Network parameters			
		\bar{A}	\bar{b}	\bar{c}	\bar{V}
HAp	H05				
	H10	9.421	18.843	6.881	1057.96
	H15				
NaNO_3	H05 (A)	5.070	5.070	16.820	374.43
	H10 (B)	5.070	5.070	16.829	374.63
	H15 (C)	5.072	5.072	16.835	375.08

Source: the authors

Table 3 reports the values, in percentages, for the two main mineralogical phases detected in the samples at the different molar concentrations at which they were treated. These phases correspond to HAp, which belongs to the monoclinic crystalline system (code 01-076-0694) in the database consulted [19] and NaNO_3 , which belongs to the rhombohedral crystalline system (codes 01-076-2243 (A), 01-072-1213 (B) and 01-079-2056 (C)). Table 4 reports the values for the lattice parameters and unit cell volumes for each of the phases.

The data recorded in Table 4 indicate a slight variation in the lattice parameters for the NaNO_3 phase that leads in addition to a variation in the volume of the unit cell. This may be associated with the forces or intensity of the chemical interactions that occur during the reactions as the molarity of the solution increases.

The concentration of NaOH is an important variable, considering that there is a significant increase in the formation of NaNO_3 species and a decrease in the volume of the solution and the time required for pH conditions to adjust. This finding is evident in both the XRD and XRF results as the purity of the HAp obtained decreases.

3.4 Obtaining pure HAp

The solid phase product obtained was washed using deionized water in order to increase the purity of the HAp and increase the Ca/P ratio to bring it closer to a value of 1.6 for biological applications [23]. This is a figure informed by the percentages that favor the formation HAp and the fact that NaNO_3 is highly soluble in water. In the morphological analysis, polyhedral agglomerates of variable size and homogeneous diameter were observed. Fig. 6 shows an SEM image of the product obtained after the washing process.

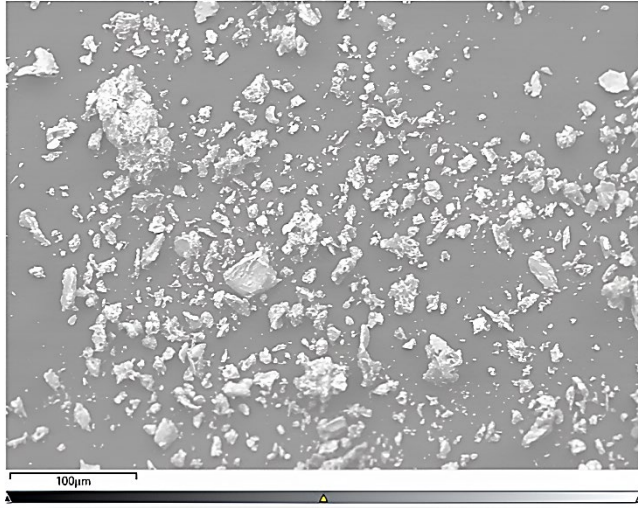


Figure 6. Powdered material obtained following washing with deionized water.

Source: the authors

Table 5.
Ca/P ratio for HAp sample.

Element	HAp sample	
	% weight	g/mol
Ca	54.39	40.08
P	24.75	30.97
Ca/P	1.7	

Source: the authors

The analysis of elemental composition showed P, Ca and Mg percentages of 16.140 %, 44.85 % and 7.40 %, respectively.

Fig. 7A) illustrates to the SEM/EDS analysis in in false-color scale for the elements found in higher concentrations in a particular part of the sample. Fig. 7B) gives the Ca distribution and Fig. 7C) gives the P distribution. The EDS data obtained for the Ca/P molar ratio are recorded in Table 5 shows the Ca/P ratio for HAp sample was 1.7, possibly because the HAp was calcium-rich [24]. There is evidence that the Ca/P molar ratio calculated from EDS data may lie in a range between 1.5 and 2.0. [24].

Fig. 8 shows the diffraction pattern of the HAp sample. It may be observed that following washing, the only detected species was HAp, in unaltered monoclinic phase, which displayed the characteristic triad in the peaks 31.77(1)°, 32.19(1)° and 32.90(6)°, corresponding to the Miller indices (h k l) (221), (-222) and (-360), respectively, of which an enlarged view is presented in the upper right section of the figure.

Fig. 9 illustrates the infrared spectrum, showing the fundamental bands of the principal hydroxyl (OH⁻) and phosphate (PO₄⁻³) groups of the HAp. The hydroxyl group is responsible for the bands centered around 630 cm⁻¹ and 3,448 cm⁻¹. For the phosphate group, bands were present at 963 cm⁻¹, corresponding to a stretching vibration (1.046 cm⁻¹ and 1.098 cm⁻¹) associated with asymmetric stretching, and 568 cm⁻¹, associated with bending vibration [26]. A very well-defined fringe was also observed at 1639 cm⁻¹, which is attributed to water absorption.

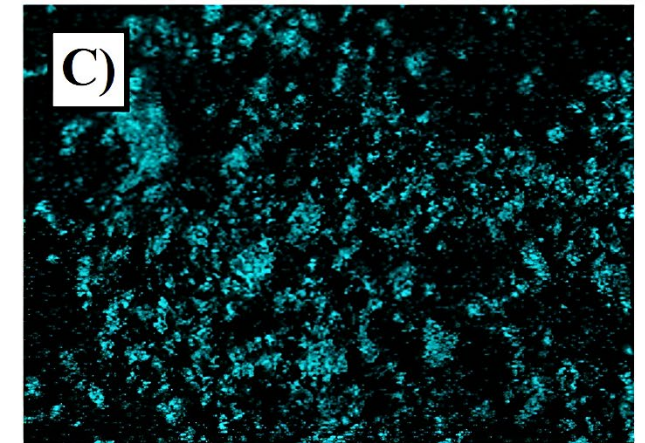
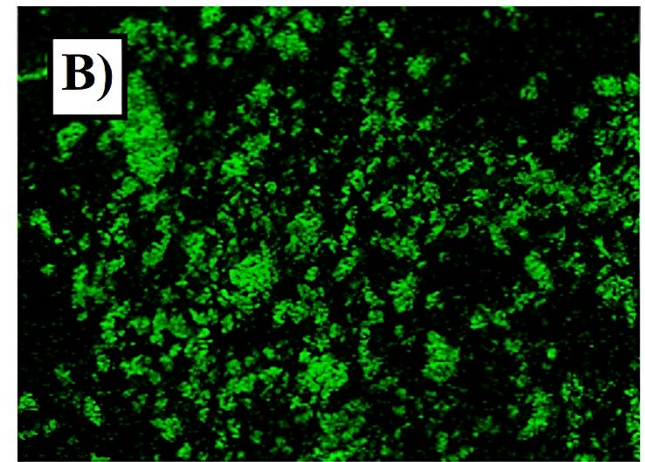
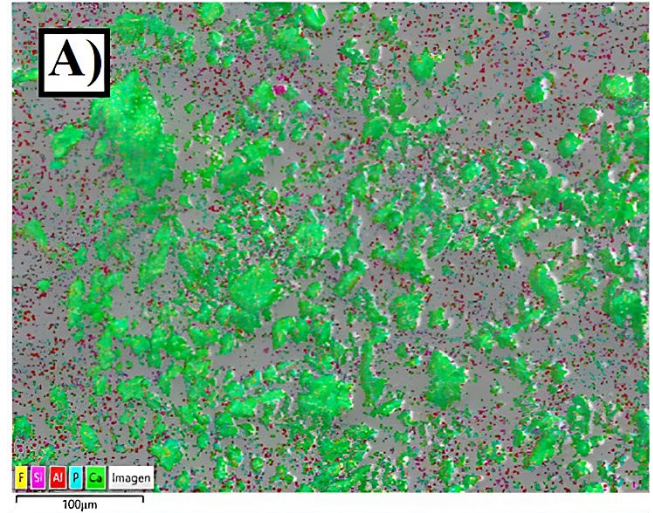


Figure 7. SEM/EDS images for HAp sample. A) False-colour map for F (yellow), Si (magenta), Al (red), P (turquoise) and Ca (green). B) False-colour map, green for Ca. C) False-colour map, turquoise for P.

Source: the authors

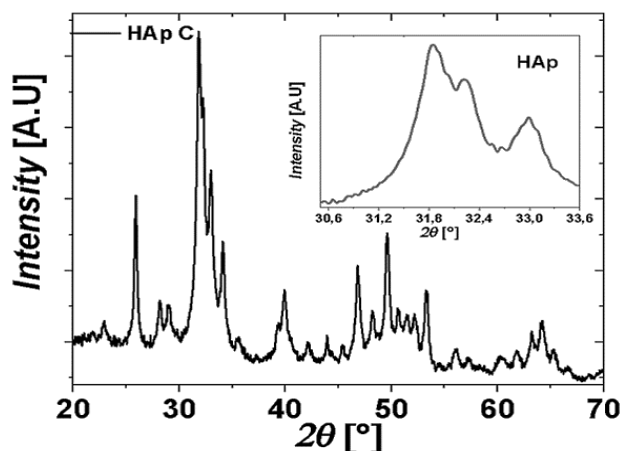


Figure 8. XRD spectra for the HAp sample following washing with deionized water.

Source: the authors

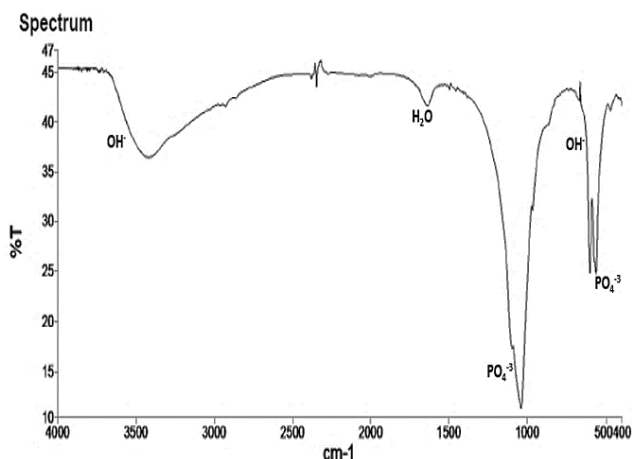


Figure 9. Infrared spectrum for the HAp sample

Source: the authors

4 Conclusion

This article has explored the potential of PR as a raw material for obtaining HAp by acid leaching of P and Ca ions, and their subsequent precipitation with NaOH. The analysis of P and Ca dissolution behavior permitted an evaluation of the availability of these elements in solution. It was observed that agitation time did not significantly affect the recovery of P and Ca. In addition, for acid solution concentrations higher than 5 M, it was not possible to obtain solutions enriched in the ions of interest. The results indicated that it was possible to obtain the species under the established conditions. However, the concentration of the precipitating agent influenced the purity of the HAp obtained.

The addition of NaOH solution above 0.5 M favored the formation of NaNO_3 , a highly water-soluble compound. This property facilitates the cleaning of the species of interest by washing with deionized water. Adjustment of pH to values above 10 indicated that HAp is the most stable calcium phosphate under this condition. Although HAp is considered

to be a high potential biomaterial, complementary studies should be carried out because of the nature of the rock. These should include long-term biocompatibility tests in order to determine the potential biological applications of this material obtained from PR.

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