Ingeniería y Competitividad
Vol 27 (3) 2025 doi: 10.25100/iyc.v27i3.14913

Vol 27 (3)

ISSN
0123-3033
e- 2027-8284

Original Article

Effect of pH and Ca and P ion concentration on the production of monetite from phosphate rock

Efecto del pH y la concentración de iones Ca y P en la obtención de monetita a partir de roca fosfórica

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Abstract

Introduction: monetite is a significant calcium phosphate phase known for its ability to be absorbed by bone tissues and to create a favorable environment for bone regeneration, positioning it as a biomaterial with high application potential.
Objectives: this study aims to obtain monetite directly from phosphate rock extracted in the Boyacá region of Colombia.
Methodology: leaching experiments were carried out using phosphoric rock and nitric acid at three different concentrations: 2, 4, and 5 M. The leach liquor was subsequently neutralized with sodium hydroxide (NaOH) at three different pH ranges: 3–4, 4–5, and 6–7. The obtained products were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to verify the presence of the monetite phase and its morphology.
Results:: the results showed that the monetite phase exhibits higher stability within a pH range of 3 to 4. It was also determined that pure monetite (100%) can be obtained using NaOH concentrations of 2 M and 5 M. At neutral pH values, the precipitation and stability of other phases such as hydroxyapatite were observed.
Conclusions: the direct production of monetite from phosphate rock from Boyacá is feasible under controlled pH and concentration conditions, with the acidic range being the most favorable for monetite stability.

Keywords: Monetite; calcium phosphates; biomaterial; hydrometallurgical route; phosphate rock leaching; neutralization with NaOH; characterization by XRF, XRD and SEM.

Resumen

Introducción: la monetita es una fase significativa de fosfatos de calcio destacada por su capacidad de ser absorbida por los tejidos óseos y de crear un ambiente propicio para la regeneración del hueso, lo que la posiciona como un biomaterial con alto potencial de aplicación.
Objetivos: el objetivo de esta investigación es obtener monetita directamente a partir de roca fosfórica explotada en el departamento de Boyacá, Colombia.
Metodología: se realizaron lixiviaciones de roca fosfórica utilizando ácido nítrico a tres concentraciones diferentes: 2, 4 y 5 M. Posteriormente, el licor de lixiviación se neutralizó con hidróxido de sodio (NaOH) en tres rangos de pH: 3–4, 4–5 y 6–7. Los productos obtenidos fueron caracterizados mediante fluorescencia de rayos X (FRX), difracción de rayos X (DRX) y microscopía electrónica de barrido (SEM) con el fin de verificar la presencia de la fase monetita y su morfología.
Resultados: los resultados mostraron que la fase monetita presenta mayor estabilidad en un rango de pH entre 3 y 4. Asimismo, se determinó que puede obtenerse monetita con una pureza del 100% utilizando concentraciones de NaOH de 2 M y 5 M. En condiciones de pH neutro se evidenció la precipitación y estabilidad de otras fases, como la hidroxiapatita.
Conclusiones: la obtención directa de monetita a partir de roca fosfórica de Boyacá es viable bajo condiciones controladas de pH y concentración, destacándose el rango ácido como el más favorable para su estabilidad.

Palabras clave: Monetita; fosfatos de calcio; biomaterial, ruta hidrometalúrgica, lixiviación de roca fosfórica; neutralización con NaOH, caracterización por FRX, DRX y SEM.

How to cite?

Soto-Calle G, Rojas-Reyes N, Gómez-Zapata A, Díaz-Bello S. Effect of pH and Ca and P ion concentration on the production of monetite from phosphate rock Ingeniería y Competitividad, 2025, 27(3)e-20414913

https://doi.org/10.25100/iyc.v27i3.14913

Received: 27/05/25
Reviewed: 21/07/25
Accepted: 23/10/25
Online: 12/11/25

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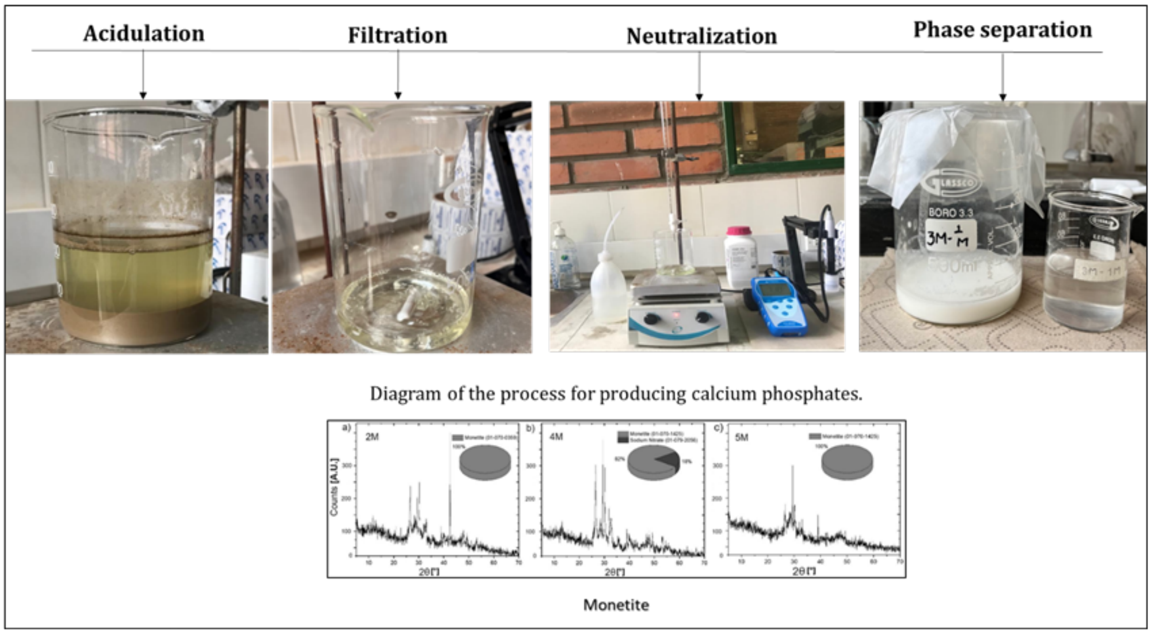
Why was this study conducted?
This study was carried out because the monetita found is an option in the generation of biomaterials from natural resources that the department of Boyaca has. Phosofrica rock has great potential to be treated by means of hydrometallurgical processes

What were the most relevant findings?
The most relevant findings were the conditions under which this species can be obtained, because if concentrations and pH are changed, the predominant species is hydroxyapatite.

What do these findings contribute?
The results obtained contribute to the biomaterials industry, taking into account that the monetite has so far begun to be studied and offers good properties when used as a biomaterial for prostheses and eye replacements



Introduction

In recent years, bone regeneration materials have gained significant importance in dental and orthopedic surgeries. Among the available options for bone substitutes, calcium phosphate-based materials have emerged as the most reliable due to their similarity to the mineral component of bone (1). Calcium phosphates can create a biocompatible environment that promotes the formation of new bone tissue (2).

A specific phase of calcium phosphates that has gained prominence in the field of biomaterials is monetite ($CaHPO_4$), also known as anhydrous calcium phosphate (3), (4), (5), (6), (7), (8). This phase is notable for its resorbable properties, facilitating the controlled decomposition of the material. This characteristic allows monetite to be replaced by newly formed bone tissue, often eliminating the need for a second intervention to remove the material, thereby ensuring the integration of the bone fragment without residues by the end of the recovery process (4), (7).

The application of calcium phosphates depends on their specific morphology and chemical composition. The choice of calcium phosphate is based on the biological need to be met. In some cases, the material must exhibit toughness and impact resistance, while in others, good solubility is required (9), (10), (11).

Studies have been conducted to explore the potential of monetite in water purification. Although hydroxyapatite is the most studied material among calcium phosphates, it is believed that monetite possesses greater solubility due to being an acidic calcium phosphate (12).

The formation of calcium phosphates requires solutions with calcium ions (Ca^{2+}) and phosphate ions (PO_4^{-3}) (13). The type of material synthesized largely depends on the pH. According to Suchanek (14), at pH levels below 4, the most stable calcium phosphate is monetite, while at pH levels above 4, hydroxyapatite becomes the predominant thermodynamic phase. This factor is crucial for controlling the manufacturing process of calcium phosphates. Besides pH, the Ca/P molar ratio influences the formation environment. However, there is evidence that during precipitation, various species can form, presenting variations in the obtained molar ratios (15), (1), (16). It is an area of research that continues to evolve to optimize process conditions and improve efficiency.

The making of calcium phosphates, and more precisely of monetite, is not an entirely new work, as it has been the subject of several studies (17), (18), (19), (20), (21), (22), (23), (24), (25). But obtaining monetite from phosphate rock is not a job easily found in the literature. For this reason, this work proposes the extraction of monetite from solutions with Ca and P, obtained directly from the leaching of phosphate rock (PR) from the municipality of Pesca, Boyacá, Colombia. When PR is dissolved in acidic solutions, various elements can be obtained in ionic form due to the nature of this rock (26), (27), (28). The study investigates the influence of the high concentration of the acidic solution, the pH range in the precipitation of monetite, and the morphology of the obtained products.

doi: 10.25100/iyc.v27i3.14913

Materials and Methods

A metallurgical process was developed to manufacture monetite using phosphate rock from the municipality of Pesca, Boyacá, Colombia, as raw material. It was found that these rocks can yield solutions enriched with P and Ca ions. The reactions to obtain precipitates from a leached PR solution were carried out with pH control in different ranges.

Preparation of the leaching solution

The mineral was crushed and ground, and then the sample was sieved to obtain a material with particle sizes smaller than 106 µm.

Batches of 75 g of the sample were leached in 225 mL of nitric acid (HNO_3) to 65%, mark MERCK. For the leaching tests, 500 mL reactors with agitation were used, maintaining constant agitation for 24 hours. Laboratory tests were conducted at three different acid concentrations: 2, 4, and 5 M, to determine their influence on the formation of the precipitates. Following agitation, the solutions with P and Ca ions were separated by filtration and used as the raw materials for this study. 10 mL of each of the three solutions obtained from the acid leaching were added to a beaker with constant magnetic agitation, where they were reacted with a 0.5 M NaOH mark MERCK solution to reach the three pH ranges established for analysis, which were between 3 and 4; between 4 and 5; and between 6 and 7. From each range, 3 solid precipitates were obtained, obtaining 9 powder samples for subsequent analysis. The pH meter used was Apera Instruments Premium Series PH8500-SA. Once the solution was adjusted to the desired pH, the agitation was stopped. The samples were washed to remove soluble materials from the precipitates and dried on heating plates at 70 °C.

Compositional and mineralogical analysis

The constituent species of the precipitate were analyzed using X-ray diffraction. A Panalytical X'Pert Pro MPD device was used, operating under conditions set for a 2θ axis scan from 5° to 70°, with steps of 0.02° and a time of 0.5 s/step. Cu radiation with a wavelength (λ) of 1.5406 Å was used. Phase identification and analysis were performed using the X'Pert High Score Plus software.

Compositional analysis was carried out using a Panalytical Epsilon 13V 1.5 X-ray fluorescence apparatus, suitably configured and calibrated for reading powder samples. The respective standards delivered with the equipment by the supplier were used.

Morphological characterization

The different morphologies of the obtained materials were observed using a JEOL JSM-7000F scanning electron microscope (SEM), equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS) probe connected to INCA software for compositional characterization. Images were acquired at various magnifications and from different areas of the samples.

Results and Discussion

Mineralogical and elemental composition of PR.

From the X-ray diffraction spectrum analysis of the PR sample used as the initial raw material, it was found that the predominant species were fluorapatite, quartz, and calcite, with concentrations of 59%, 34%, and 7%, respectively (see Figure 1).

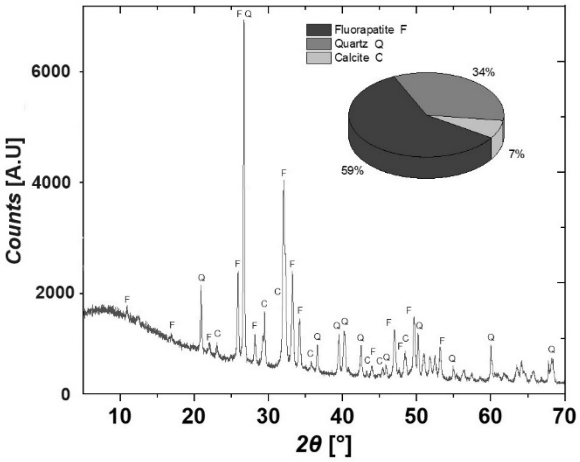


Figure 1. X-ray diffraction spectrum and pie chart showing the percentage distribution of the main mineralogical phases detected in the PR sample.

The elemental chemical analysis of the PR reports P and Ca percentages of 13.44% and 36.76%, respectively (see Table 1). The presence of these two chemical elements, as the main or most abundant components in phosphate rocks, not only allows these minerals to be classified as ideal for sustainable agriculture but also highlights their importance as a strategic and industrial mineral (28). Table 2 reports only the chemical elements found in concentrations above 1%, which together make up approximately 68.5% of the sample.

Both the mineralogical analysis and the elemental composition of this raw material allow it to be classified as a sedimentary phosphate rock (29).

Table 1. Elemental composition of the PR mineral sample.

Element	Composition [%]
Ca	36.76
P	13.44
Si	12.48
Al	1.29
Mg	3.54
Fe	1.06

Elemental analysis and phase analysis of precipitates obtained at different HNO3 concentrations and different pH ranges.

Figure 2 shows the XRF results for the quantity of Ca and P in each of the 9 solid precipitates obtained from RP leaching, filtration and neutralization with NaOH. It can be deduced that the condition to obtain the highest amount of Ca (>43%) is at a nitric acid concentration of 2 M and a neutralization at a pH between 6 and 7. To obtain the highest amount of P (>17%) is at a nitric acid concentration of 4 M and a neutralization at a pH between 4 and 5. The presence of minor elements such as Fe, Mg, and Al, as well as some trace elements, was observed, but these are not reported for the practical purposes of this work.

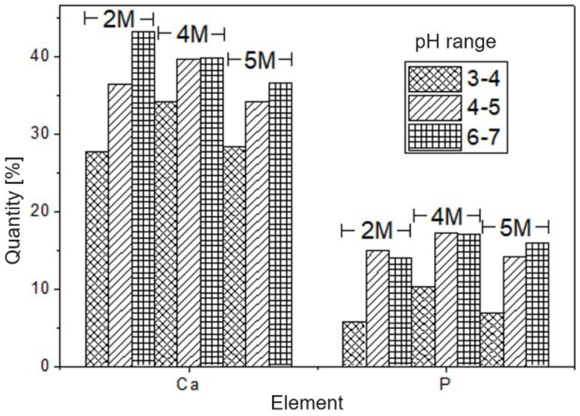


Figure 2. Quantity of Ca and P in the precipitates obtained at 2, 4, and 5 M HNO_3 and the three precipitation pH ranges.

The number of phases determined based on the semi-quantitative analysis of the XRD spectra for the 9 solid precipitates is presented in Table 2. It is observed that the calcium phosphate phase for the pH condition in the range of 3-4 is monetite or anhydrous calcium phosphate ($CaHPO_4$). These results were obtained after washing the samples with deionized water to remove the soluble compounds that appeared during the precipitation process, such as sodium nitrate ($NaNO_3$). These results demonstrate that it is possible to precipitate monetite from phosphate rock leachate by controlling the pH during the neutralization process.

Table 2. Phases present in the 9 solid precipitates. $CaHPO_4$ is monetite, $Ca_5(PO_4)_3OH$ is hydroxyapatite, and $NaNO_3$ is sodium nitrate.

	pH		**Phase [%]**	
[HNO_3]	**range**	**$CaHPO_4$**	**$Ca_5(PO_4)_3OH$**	**$NaNO_3$**
2 M	3-4	100	-	-
	4-5	58	42	-
	6-7	-	100	-
4 M	3-4	82	-	18
	4-5	73	27	-
	6-7	-	94	6
5 M	3-4	100	-	-
	4-5	53	47	-
	6-7	57	43	-

The XRD spectra of the constituent phases for the powders synthesized in the pH range of 3-4 are shown in Figure 3, where the majority species is monetite ($CaHPO_4$).

By increasing the presence of OH^- ions and adjusting the conditions to a pH range of 4-5, another calcium phosphate species known as hydroxyapatite ($Ca_5(PO_4)_3OH$) was observed. However, monetite remains the majority phase under the established conditions (see Figure 4).

When the conditions approached the neutral pH of the solution, the precipitate formed at 2M and 4M concentrations showed hydroxyapatite as the majority species (see Figure 5). However, at a concentration of 5M, the compound monetite-hydroxyapatite still appeared. According to Suchanek (14), for pH > 4, the thermodynamically most stable calcium phosphate is hydroxyapatite.

Structurally, monetite is a material that crystallizes in a triclinic lattice belonging to the space group P-1 (#2). Its six most intense diffraction peaks are located on the 2θ axis between 26° and 33°, corresponding to the planes (0 0 2); (2 0 0); (-1 2 0); (-1 -2 1); (2 0 1); and (-2 0 2) with intensities of 92.2; 92.1; 100; 45.5; 34.2; and 43.6%, respectively. The monetite patterns identified in the samples are indexed in the ICSD crystallographic database with the codes No. 01-070-0359; 01-070-1425; and 01-070-1520. The lattice parameters are a = 6.9100 Å; b = 6.6270 Å; c = 6.9980 Å; y V = 309.28 Å3

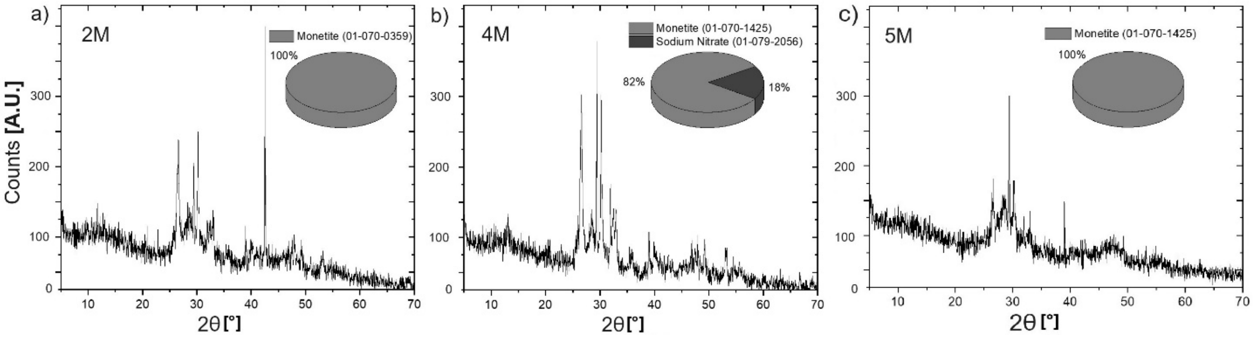


Figure 3. X-ray diffraction spectra and pie charts showing the percentage distribution of the main mineralogical phases detected in the powdered materials synthesized in the pH range of 3-4.

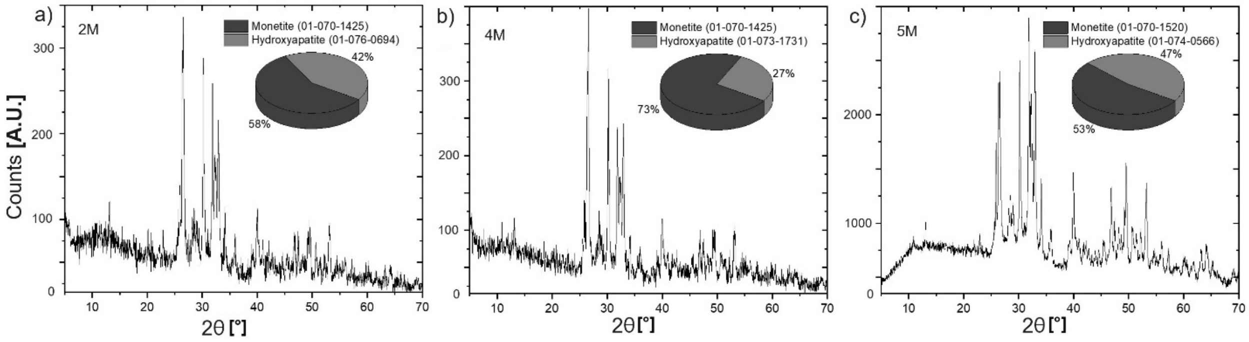


Figure 4. X-ray diffraction spectra and pie charts showing the percentage distribution of the main mineralogical phases detected in the powdered materials synthesized in the pH range of 4-5.

doi: 10.25100/iyc.v27i3.14913

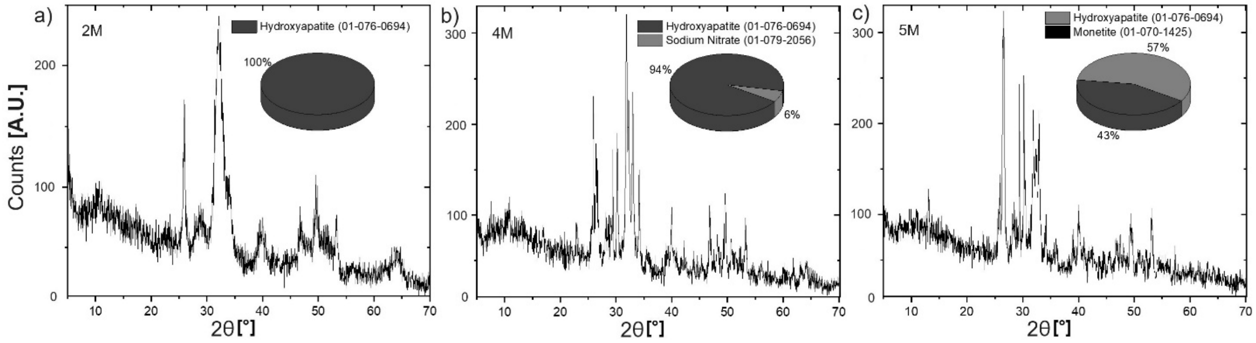


Figure 5. X-ray diffraction spectra and pie charts showing the percentage distribution of the main mineralogical phases detected in the powdered materials synthesized in the pH range of 6-7.

Figure 6 shows the enlargement of the peak corresponding to an intensity of 100% for the plane (-1 2 0), detected at a position on the 2θ axis near 30.2° for the spectra of the samples obtained at an HNO_3 concentration of 4 and 5 M, and pH values between 3 and 5. Based on the analysis of the results reported in Table 3, these conditions are the most favorable for the formation of the monetite phase.

Precipitates morphology

The morphology of the precipitated particles was also analyzed by SEM, for different acid concentrations and as a function of the neutralization pH.

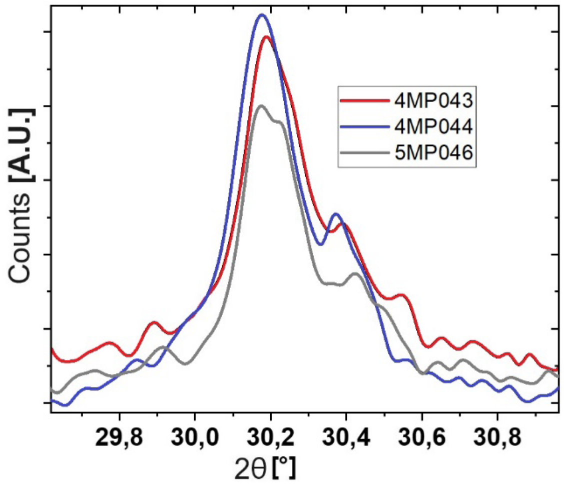


Figure 6. Enlargement of the peak with the highest intensity for the monetite phase obtained in the samples treated at 4 and 5 M with pH ranges between 3 and 5.

doi: 10.25100/iyc.v27i3.14913

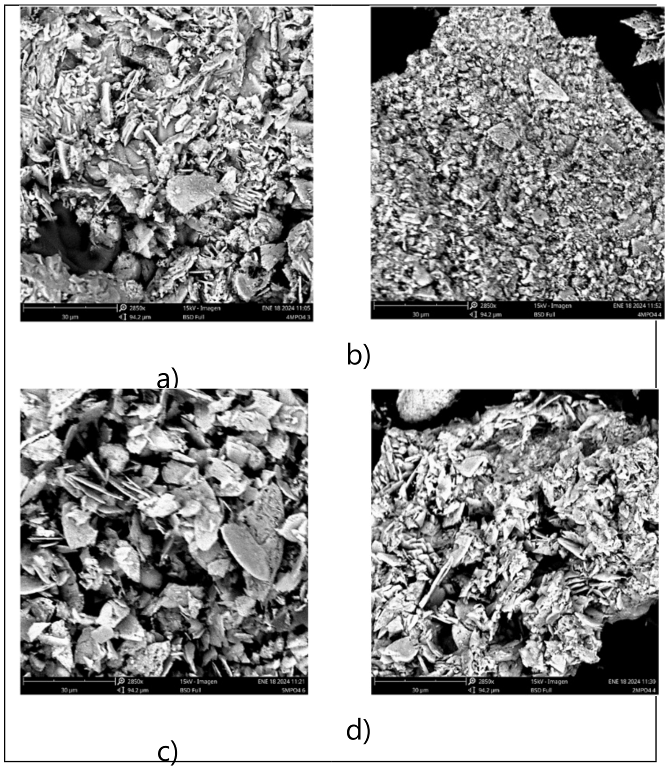


Figure 7. Microstructures of precipitates at 4M for a pH range of 3–5. a) concentration 4M with pH=3, b) 4M with pH=4 , c) 5M with pH=5 y d) 2 M with pH=4.

Figure 7 shows images of the powdered materials obtained at molar concentrations of 4 M and pH values between 3 and 5. In general, the formation of micrometer-sized structures (< 30 μm) in the form of plates or sheets with flat surfaces can be observed. This structure evidences that the hydrometallurgical processes with concentrations of 4M and pH values between 3 -5 presents established of species as monetite and hydroxyapatite. With the established manufacturing parameters, the result shows the growth of grains with a polymodal size distribution. It is important to mention that the samples were dried at a temperature of 70°C, so it is possible that an increase in this variable could modify the structure of the monetite[8]. It can be observed in the figure 7 a) a sheets littler than figure 7 c) with a pH=3. It means that mayor pH mayor obtention of the specie monetite. However, the objective of this study is to obtain monetite through hydrometallurgical treatments, that is, from an acid-base reaction starting from liquor rich in Ca and P obtained from the leaching of a natural source of these ions, such as phosphate rock (PR).

To determine the use or application of these obtained materials, it is necessary to develop further specific characterization tests to assess their potential as biomaterials.

Conclusions

It can be concluded that the leaching of phosphate rock (PR) is an efficient treatment. By obtaining a solution enriched in Ca and P and varying the pH, different stable species, such as hydroxyapatite and monetite, can be generated under various conditions. This study focused on these species.

The diffraction patterns indicated that monetite can be obtained as the predominant mineralogical phase in the pH range of 3 to 6; however, under stricter conditions, monetite is the most stable calcium phosphate at a pH of 3 to 4. As the solution’s pH approaches neutrality, the environment favors the formation of another species known as hydroxyapatite.

At a pH between 5 and 6, a compound of monetite-hydroxyapatite can be formed. It is necessary to study the properties resulting from the combination of these mineralogical phases, as there is the possibility that they complement each other and can be used in various applications, such as in the medical field. During the precipitation process, a third species known as $NaNO_3$ was also identified, which has solubility properties that facilitate the separation of calcium phosphates through rinsing with deionized water. However, it is necessary to ensure enough washes for the purification of the species of interest.

Acknowledgments

This work was funded by Universidad Nacional de Colombia, Medellín and the project MinCiencias SGR - CTI call 006-2019, BPIN 2020000100507 and Universidad Santo Tomas by your direction. We also thank the CECOLTEC S.A.A. companies for the support received.

CrediT authorship contribution statement

Conceptualization - Ideas: Gloria Soto-Calle , Néstor Rojas-Reyes , Adrián Gómez-Zapata , Sandra Díaz-Bello. Formal analysis: Adrián Gómez-Zapata. Data curation: Néstor Rojas-Reyes. Investigation: Gloria Soto-Calle. Methodology: Gloria Soto-Calle , Néstor Rojas-Reyes. Project Management: Sandra Díaz-Bello. Supervision: Sandra Díaz-Bello. Validation: Gloria Soto-Calle , Néstor Rojas-Reyes , Adrián Gómez-Zapata , Sandra Díaz-Bello. Resources: Gloria Soto-Calle. Software: Adrián Gómez-Zapata. Writing - original draft - Preparation: Gloria Soto-Calle , Néstor Rojas-Reyes , Adrián Gómez-Zapata , Sandra Díaz-Bello. Writing - revision and editing -Preparation: Gloria Soto-Calle , Néstor Rojas-Reyes , Adrián Gómez-Zapata , Sandra Díaz-Bello.

Financing: Sistema general de regalías-SGR. Conflict of interest: does not declare. Ethical aspect: does not declare.

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