Synthetic alkaline-earth hydroxyapatites: Influence of their structural, textural, and morphological properties over Co^{2+} ion adsorption capacity

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This work addresses the synthesis of nanocrystalline barium, strontium, and calcium hydroxyapatites (Ca-HAPs) via the chemical precipitation method, followed by calcination. To give a coherent picture of the most important structural, textural, and morphological properties of these materials and to investigate the influence of these characteristics over Co^{2+} ion adsorption capacity from aqueous solutions, the powders prepared were systematically characterized by X-ray diffraction, N_2 -physisorption measurements, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry, and Fourier Transformed Infrared spectroscopy (FTIR). The results clearly showed that the Ca-HAP obtained exhibits better nanocrystallinity, greater structural stability, high surface area, high total pore volume, and mesoporosity, compared with the other synthesized hydroxyapatites, and that these physicochemical properties share a direct correlation with favorable Co^{2+} ion adsorption capacity at room temperature and pressure. The results proved that the physicochemical features of resulting alkaline-earth hydroxyapatites, prepared via the chemical precipitation method, played a fundamental role during the adsorption of heavy metal (with high toxicity) from aqueous solutions.

Keywords: *barium hydroxyapatite, strontium hydroxyapatite, calcium hydroxyapatite, chemical precipitation synthesis, Co^{2+} ion adsorption*

1. Introduction

Currently, calcined alkaline-earth phosphates, such as hydroxyapatites, are identified as promising adsorbent materials that can play an important role in environmental remediation due to their interesting chemical composition and surface, which can offer effective solutions for low-cost decontamination of many aquatic systems [1]. In particular, hydroxyapatites are crystalline compounds that belong to the apatite family, with the general chemical formula $\text{M}_{10}(\text{PO}_4)_6(\text{OH})_2$, which consists of a cationic metal (M) such as calcium, barium, or strontium, among others, and phosphate and hydroxyl ions. These compounds exhibit very low water solubility under alkaline conditions and are characterized by having a $K_{sp} < 10^{-40}$; additionally, they are materials that possess high chemical and thermal stability [2]. To the best of our knowl-

edge, the calcium hydroxyapatite (Ca-HAP) is the most typical hydroxyapatite compound, which has been thoroughly synthesized by using different advanced methods such as mechano-chemical treatment [3], hydrothermal synthesis [4], aqueous solution combustion technique [5], and the sol-gel combustion process [6], among others. However, Ca-HAP is most often synthesized by the typical chemical precipitation method under alkaline conditions from aqueous solutions containing calcium divalent cations, phosphate ions, and hydroxyl groups, followed by calcination at high temperature [7]. It is well-known that the synthetic Ca-HAP is considered an efficient water remediation material due to its important physical and chemical features; it has been demonstrated that when the primary powders of insoluble hydroxyapatite, formed by the chemical precipitation synthesis method, are treated at high temperatures, this generates a group of crystals named apatites, with interesting ion-exchange properties [8]. As a consequence, their metallic di-

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valent cation adsorption behavior in aqueous solutions is well understood [9–13]. In this context, several researchers have reported the high removal capacity of Ca-HAp for divalent cations such as Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , and Sr^{2+} from aqueous solutions. Ma *et al.* [14] reported the efficient removal of Co^{2+} and Sr^{2+} ions from aqueous solution as a function of different adsorption parameters by synthetic Ca-HAp nanoparticles prepared by precipitation method. Another study reported the influence of different sorption parameters in the removal of Co^{2+} from aqueous solutions by Ca-HAp and found significant decontamination results [15]. Janusz and Skwarek [16] studied the kinetics and statics of cobalt adsorption at the hydroxyapatite/electrolyte interface using radioactive isotope ^{60}Co and found that the cobalt ions adsorption results in the increase of the electrokinetic potential. Vahdat *et al.* [17] used the hydroxyapatite and magnetic nanocomposite of hydroxyapatite to recover and remove lead ions from an aqueous solution and found that these adsorbents have a satisfactory potential to adsorb lead ions. Also, was reported the reaction of lead ions with hydroxyapatite granules and the results show that porous hardened hydroxyapatite granules can be used as an efficient phosphate source for the immobilization of lead ions from aqueous media, organic ligands tend to interfere with the water purification procedure [18]. As we can see, the Ca-HAp has contributed extensively to this field. However, the contribution that other alkaline-earth hydroxyapatites, such as barium and strontium hydroxyapatites (Sr-HAp), can offer to the field of environmental restoration has not been widely studied. Additionally, to our knowledge, little literature about the synthesis and physicochemical properties of hydroxyapatites other than Ca^{2+} compositions of hydroxyapatites, such as alkaline-earth metal cations of Ba^{2+} and Sr^{2+} , are available. Thus, the environmental use of different hydroxyapatites compounds remains a concern that merits further attention. In this line of research, further studies are necessary to obtain novel results of other attractive adsorbent materials in light of the interest in the adsorption properties of other alkaline-earth hydroxyapatites.

Cobalt is used in the manufacture of superal-

loys for use at high temperatures, such as ceramics and paint dryers, as well as a catalyst, among other uses [19]. It is widely known as heavy metal with a high degree of toxicity that negatively impacts fauna, flora, and human health, via contaminated water, when it is accumulated in the tissues of living organisms. It is also recognized that the major factors of toxicity for cobalt are its carcinogenic and teratogenic characteristics [20]. Therefore, the removal of cobalt from hazardous wastewater is a primary concern around the world.

The aim of this research was dedicated to the preparation, and structural and textural characterization of barium, strontium, and Ca-HAp compounds. Efforts were made to conclude the physicochemical characterization of well-defined synthesized hydroxyapatites powders, obtained by the chemical precipitation method followed by calcination, for their posterior application to the removal of highly toxic contaminants from aqueous solutions such as cobalt divalent ions and to evaluate the influence of structural, textural, and morphological properties of materials in the adsorption system proposed.

2. Experimental

2.1. Materials and methods

Barium nitrate tetrahydrate [$\text{Ba}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99–100 wt.% purity)], strontium nitrate tetrahydrate, [$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99–100 wt.% purity)], calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99–100 wt.% purity)], and diammonium hydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$ (99–100 wt.% purity)] were purchased from Sigma-Aldrich and used as analytical-grade starting chemical precursors without further purification.

2.2. Synthesis and characterization of alkaline-aerth hydroxyapatites

Barium hydroxyapatite (Ba-HAp), Sr-HAp, and Ca-HAp were synthesized through the chemical precipitation method, followed by calcination, according to the procedure reported by Kanna *et al.* [21]. Separately, the chemical precursors containing the respective alkaline metals, phosphate, and

hydroxyl ions, were mixed under constant stirring; the precipitates were filtered, washed with sufficient distilled water, and dried at 120°C for 2 h in an electrical oven. The powders obtained were calcined at $1,100^{\circ}\text{C}$ for 2.5 h in a muffle furnace to attain its crystallization. Finally, the resulting dried solids were ground to obtain fine powders in an agate mortar. Afterward, they were physicochemically characterized and directly used as solid adsorbents. To determine the purity and crystalline structure of the synthesized alkaline-earth hydroxyapatites, a DISCOVER D-8 powder diffractometer connected to a copper anode X-ray tube was used with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation, operating at 40 kV. The diffraction patterns were scanned with a sweeping of 15° – 80° in 2θ and a scan step of $0.03^{\circ} \cdot 6 \text{ s}^{-1}$. The spectra of the powders obtained were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) files, and their crystallites size was determined by the line broadening at half the maximum intensity of the peaks (FWHM) using the Debye and Scherrer equation [22]. N_2 -physisorption measurements at -196°C were made to determine the Brunauer–Emmett–Teller (BET) surface area, mean pore diameter (d_p), total pore volume, and N_2 adsorption-desorption isotherms of the prepared materials by using the BEL Japan INC model Belsorp Max physisorption equipment. The powder samples were previously accurately weighed and heated with N_2 at 200°C for 2 h in a vacuum before measurements. Scanning electron microscopy (SEM) studies were made to determine the morphology of the synthesized powders, using a JEOL-JSM-6701F emission scanning electron microscope operating at 5.0 kV and $19.5 \mu\text{A}$. For this purpose, the samples were first sprinkled on metallic supports and covered with gold for 120 s, using the cation-sputtering AJA ATC 1500 model and a Denton Vacuum Desk II platter; the analysis of the samples was performed with a $5,000\times$ magnification. The semi-quantitative elemental chemical composition of alkaline-earth hydroxyapatite powders was determined by using energy-dispersive X-ray spectroscopy (EDS) technique with a JEOL-JSM-5900LV system equipped with an EDS Oxford microprobe; previously, also the samples were

mounted on an aluminum holder with carbon conductive tape and later covered with a gold layer of approximately $150 \text{ \AA}$ in thickness for better conductivity, and the analysis was performed in three different zones of the respective samples. To complement the characterizations, Fourier transformed infrared spectroscopy (FTIR) analyses were performed to determine the chemical characteristics and purity of the powders studied, for which a spectrophotometer Nicolet Magna 550 was used, and the samples were mixed with KBr in a conventional manner.

2.3. Co^{2+} ions adsorption

Test of Co^{2+} ion adsorption in aqueous solutions with the synthesized Ba-HAp, Sr-HAp, and Ca-HAp powders was conducted by typical batch experiments at room temperature and pressure. Separately, in closed glass vials, 0.1 g of each alkaline-earth hydroxyapatite powder was mixed with 10 mL of a cobalt ion solution (50 mg L^{-1}) at $\text{pH} = 6.8$. The pH values of the liquids, measured at the end of the experiments, were assumed to be equilibrium pH and were 6.5 ± 0.01 for the Ba-HAp system, 7.4 ± 0.02 for the Sr-HAp system, and 6.2 ± 0.01 for the Ca-HAp system, measured using a digital pH meter (Cole-Parmer model 05669-20) with a glass electrode. The samples were stirred at room temperature ($20 \pm 1^{\circ}\text{C}$) using a mechanical shaker and water bath with controlled temperature for 24 h; once the 24 h had concluded, the solids were completely separated from the liquid phases by centrifugation at 3,000 rpm for 5 min, and 1 mL of the liquid phases was taken for cobalt measurements. The cobalt concentrations in the clear aqueous phases were determined by ultraviolet (UV)-visible spectrophotometry, using a Lambda 10 Perkin-Elmer Spectrometer at $\lambda = 260 \text{ nm}$, previously calibrated with a blank and six standard cobalt solutions, with concentrations ranging from 10 mg L^{-1} to 100 mg L^{-1} , prepared from a stock solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100.7 wt.%, Baker), with a correlation factor (R^2) of 0.9972. The UV spectrophotometric determination of cobalt was carried out by the hydrogen peroxide and sodium bicarbonate method, with a

cobalt concentration detection limit of 4 mg L⁻¹ [23]. All the experimental data were obtained in triplicate. The percentage of cobalt ions adsorbed from the solutions in the adsorbents was determined using Eq. (1):

$$Ads(\%) = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_f are the cobalt concentrations in solution before and after adsorption in (mg/L).

3. Results and discussion

3.1. Synthesis

The Ba-HAp, Sr-HAp, and Ca-HAp obtained in this study were successfully prepared. The overall base reaction for the formation of these alkaline-earth hydroxyapatites via nitrate metallic salts and diammonium hydrogen phosphate ions, respectively, under basic conditions (NH₄OH) can be summarized by Eq. (2), where M is the metal (Ba, Sr, or Ca):

Then, the presence of alkaline-earth metal divalent ions and phosphate ions in the chemical precipitation reaction produce powders of barium, strontium, or Ca-HAps, such as in the present case.

3.2. Characterization and Co²⁺ Ions Adsorption

All the alkaline-earth hydroxyapatites synthesized in this study were subjected to a systematic physicochemical characterization according to the different analytical techniques described above, and the results are explained and discussed in terms of the effects exerted by their main structural, textural, and morphological properties over Co²⁺ ion adsorption. Table 1 summarizes the obtained main textural characteristics and Co²⁺ ion adsorption capacities of the synthesized alkaline-earth hydroxyapatites in percentage. As can be seen, the Ca-HAp sample showed the highest cobalt adsorption capacity under experimental conditions, with a

56.84 ± 1.08%, in comparison to the Ba-HAp and Sr-HAp samples, with cobalt adsorption capacities of 6.03 ± 0.39% and 17.46 ± 0.79%, respectively. It can clearly be observed that the Ca-HAp sample showed a better Co²⁺ ion adsorption capacity by 9.75 orders of magnitude compared to the Ba-HAp sample and in 3.36 orders of magnitude when compared to the Sr-HAp sample. Also, it was observed that the synthesized Ca-HAp exhibits better textural properties compared to the other synthesized hydroxyapatite materials, which is highly relevant for adsorption purposes, and also specifically showed a high surface area, low mesoporosity, and high total pore volume. On the other hand, changes in pH values of the solutions after the absorption of Co²⁺ ions were observed. A possible explanation for this drop in equilibrium pH can be attributed to a mechanism of the exchange of H⁺ ions from the surface groups of hydroxyapatite presented by Eqs 3 and 4. According to this, the H⁺ ions are released from the solid surface into the aqueous media, which changes the final pH of the solutions. However, in this study, it was observed that this drop in pH value was very small.

To confirm the effective presence of Co²⁺ ions in the aqueous solutions used in the adsorption experiments for Ba-HAp, Sr-HAp, and Ca-HAp adsorbents, the chemical distribution of cobalt species in aqueous media, as a function of pH at 25°C, was determined by the Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA) computer software [24]; this software was employed for a cobalt concentration of 50 mg L⁻¹ (Figure 1). According to this speciation diagram, the predominant cobalt species in aqueous solution, up to pH 8, is the divalent cationic form Co²⁺; at a pH > 8, the neutral condensate Co(OH)₂ and a negatively charged chemical species Co(OH)₃⁻ are predominant, up to pH 10.

Based on the literature data, the divalent metal cations adsorption on alkaline earth-hydroxyapatites can occur by following mechanisms: A mechanism of the exchange of H⁺ ions from the surface groups of hydroxyapatite [14, 15] or by an ion-exchange mechanism between the divalent cations contained in the solution and the divalent cations of hydroxyapatite [10, 18, 25].

Table 1. Textural characteristics of synthesized alkaline-earth hydroxyapatite materials and Co^{2+} ion adsorption capacities in percentage.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	V_t ($\text{cm}^3 \text{g}^{-1}$) ^b	d_p (nm) ^c	Co^{2+} ion adsorption capacity (%)
Ba-HAp	0.5216	0.0011	8.9231	6.03 ± 0.39
Sr-HAp	1.3874	0.0057	16.5310	17.46 ± 0.79
Ca-HAp	59.7000	0.1120	7.5046	56.84 ± 1.08

^aBET surface area.^bTotal pore volume by N_2 adsorption at $p/p_o = 0.99$.^cMean d_p .

Ba-HAp, barium hydroxyapatite; BET, Brunauer–Emmett–Teller;

Ca-HAp, calcium hydroxyapatite; d_p , pore diameter; Sr-HAp, strontium hydroxyapatite.

Fig. 1. Chemical distribution of cobalt ionic species in aqueous media as a function of pH.

According to Smiciklas et al. [15], the mechanism of the exchange of H^+ ions from the surface groups of hydroxyapatite with divalent metal cations (M) can be seen through Eqs (3) and (4).

In this mechanism, an exchange between the Co^{2+} ion from the aqueous solution and the H^+ ion

present on the surface of the hydroxyapatite is carried out, and as a result, the Co^{2+} ion is uptake and the H^+ ion is released to the aqueous phase.

On the other hand, the ion-exchange mechanism of the Co^{2+} ion with Ba, Sr, and Ca, as divalent metal cations (M) of the hydroxyapatite, can be seen in Eq. (5):

This mechanism suggests that the metal ion adsorp-

tion on alkaline earth-hydroxyapatites can be considered as an ion-exchange mechanism between the cobalt divalent cations contained in the contaminated solution and the divalent cations of Ba^{2+} , Sr^{2+} , or Ca^{2+} present in the hydroxyapatite crystal lattice.

According to Monteil and Fedoroff [26], physisorption through an ion-exchange mechanism for Co^{2+} ion adsorption by Ca-HAp occurs, suggesting that the Co^{2+} ion can be exchanged for the Ca^{2+} ion in the Ca-HAp crystal lattice, due to the fact that the cobalt crystal radius is less than the calcium crystal radius. Sugiyama *et al.* [27] carried out an extended X-ray absorption fine structure (EXAFS) analysis of Pb^{2+} ion adsorption behavior on Sr-HAp, which revealed that the divalent metal ion-exchange characteristics are strongly influenced by the nearest-neighbor distances of the Sr-O bond of Sr-HAp, respectively. Therefore, the Co^{2+} ion, with a minor crystal radius of 0.72 Å, can, in ascending order, exchange the divalent cations in the hydroxyapatite crystal lattice of Ca^{2+} , Sr^{2+} , and Ba^{2+} ions with crystal radii of 1.14 Å, 1.18 Å, and 1.35 Å, respectively [28]. Therefore, it is important to highlight that based on the literature data, both above-described mechanisms work. Consequently, it was deduced that the Co^{2+} ions adsorption on the alkaline earth-hydroxyapatites can be a result of both mechanisms. In fact, in this study, Sr-HAp, Ba-HAp, and Ca-HAp were effectively used as materials for the decontamination of solutions contaminated by cobalt.

On the other hand, the structural characteristics of Ba-HAp, Sr-HAp, and Ca-HAp powders, prepared via the chemical precipitation method followed by calcination treatment at 1,100°C by 2.5 h, were determined by X-ray diffraction, and their patterns are shown in Figure 2. As can be seen, the results show that the prepared hydroxyapatite powders contain crystalline phases with several intense fine peaks. Figure 2A shows a principal crystalline phase with intense peaks appearing in the range of 20–35, 2θ , when compared and identified with the JCPDS file No. 83-0990; other peaks of lower intensity and quantity were detected in this diffractogram, attributed to the presence of crystalline tribarium bisphosphate (V) phase, according

to JCPDS file No. 80-1615; These identified phosphate phases exhibited the presence of a Ba-HAp structure. The obtained structural results are in accordance with those described in the literature [29]. The presence of this phase can be attributed to the effect of calcination temperature treatment adopted for this sample after the precipitation synthesis, which can affect the non-formation of pure phase Ba-HAp [30]. Crystallite size for the principal peak of the Ba-HAp crystalline phase was estimated to be between 75 nm and 84 nm, according to the Debye-Scherrer equation [22]; these results indicate that this material is nanocrystalline. Therefore, it was concluded that the Ba-HAp is highly crystalline constituted mainly of barium diphosphate phase and a lesser amount of tribarium bisphosphate (V) phase.

Figure 2B shows the XRD pattern for Sr-HAp. A main higher intensity crystalline phase of strontium phosphate was found, according to JCPDS file No. 85-0502, this obtained result is in concordance with the reported by Sugiyama *et al.* [31]. The identification of this calcined alkaline-earth hydroxyapatite phase was also reported by Mousa *et al.* [29]. Additionally, only traces of strontium phosphate were detected as belovite phase according to JCPDS file No. 70-1511. The obtained crystallite size for this material was between 50 nm and 84 nm from the main diffraction lines of higher intensity in their crystalline phase and the results also show that this material is nanocrystalline.

For the structural analyses of the obtained calcined Ca-HAp (Figure 2C), it was observed that this material shows intense peaks considerably sharp and that exhibiting only a single phase, attributable to a pure crystalline structure, with diffraction lines characteristic of a typical Ca-HAp compound [30, 32], which is confirmed with the JCPDS 09-0432 file. Derived from the Debye-Scherrer equation, this sample reveals a crystallite size of 38–70 nm, confirming nanocrystallinity.

In general, the XRD results of the synthesized alkaline-earth hydroxyapatite powders (Figure 2) show main phases of well-crystallized compounds, exhibiting intense peaks that correspond to Ba-HAp, Sr-HAp, and Ca-HAp phases, according to the main standard XRD patterns (JCPDS cards No.

Fig. 2. XRD patterns of synthesized alkaline-earth hydroxyapatite powders prepared via chemical precipitation method followed by calcination at $1,100^{\circ}\text{C}$: **(A)** Ba-HAp, **(B)** Sr-HAp, and **(C)** Ca-HAp. Ba-HAp, barium hydroxyapatite; Ca-HAp, calcium hydroxyapatite; Sr-HAp, strontium hydroxyapatite.

83-0990, 85-0502 and 09-0432), respectively, confirming that the obtained products were nanocrystalline hydroxyapatite samples.

Analyzing the structural characteristics of the synthesized alkaline-earth hydroxyapatites by XRD (Figure 2), to examine their structural influence over Co^{2+} ion adsorption capacity, the following observations were made. It is important to emphasize that all the synthesized hydroxyapatite samples exhibited the typical crystalline structure, showing well-defined peak characteristics with high intensity, which correspond to alkaline-earth hydroxyapatite structures as was described above; according to these results, it is suggested that there is not a notable structural difference between the Ba-HAp, Sr-HAp, and Ca-HAp samples;

however, comparing their nanocrystallinity, it is observed that Ca-HAp is more nanocrystalline than the Ba-HAp and Sr-HAp samples, since the main Ca-HAp peaks are wider and their determined crystallite sizes are smaller. These features can improve the immobilization of Co^{2+} ions in their structure, for it is widely known that the physicochemical properties of nanocrystalline materials significantly influence ion-exchange capacity [33]. It is well-known that the sintering temperature needed to obtain materials could change the crystallinity or purity of materials; indeed, the crystalline phases can increase or decrease as a function of temperature [34]. However, in our investigation, the calcination treatment at $1,100^{\circ}\text{C}$ for 2.5 h was necessary for reaching a complete crystallization and struc-

Fig. 3. N_2 adsorption-desorption isotherms of (A) Ba-HAp, (B) Sr-HAp, and (C) Ca-HAp powders. Ba-HAp, barium hydroxyapatite, Ca-HAp, calcium hydroxyapatite; Sr-HAp, strontium hydroxyapatite.

tural stability; however, these conditions also allowed the complete decomposition and volatilization of ammonium or nitrate traces in the synthetic process. The previous results suggest that the stability of crystalline phases in the materials studied are greatly dependent on the differences of ionic radii values of the alkaline-earth metals present in the hydroxyapatites (metallic ionic radius $Ca < Sr < Ba$) [28], which allow a better atomic rearrangement in the crystal structure of the materials, stabilizing its crystallinity [4]. Thus, it can be suggested that the difference in nanocrystallinity and structural stability directly influence Co^{2+} adsorption behavior in the following order: Ca-HAp > Sr-HAp > Ba-HAp.

Figure 3 shows the nitrogen adsorption-desorption isotherms of the prepared calcined Ba-

HAp, Sr-HAp, and Ca-HAp samples. In this regard, the results show differences for three hydroxyapatites. The N_2 adsorption-desorption hysteresis loop features characteristics of porous materials. As can be seen in Figure 3A, according to the International Union of Pure and Applied Chemistry (IUPAC), Ba-HAp presented a type II isotherm with hysteresis, which corresponds to non-porous materials or macroporous adsorbents. On the other hand, the surface area, measured by the N_2 BET method for this material, was $0.52 \text{ m}^2 \text{ g}^{-1}$, as well as a total pore volume is $0.001 \text{ cm}^3 \text{ g}^{-1}$ and a mean d_p is 8.92 nm ; this value is usually associated with mesoporous materials ($2 \text{ nm} < \text{size} < 50 \text{ nm}$).

Figure 3B corresponds to the nitrogen adsorption-desorption isotherm of Sr-HAp prepared via the chemical precipitation method.

For this material, it is observed that, according to IUPAC, the N_2 adsorption-desorption isotherm is type II (without hysteresis), which is characteristic of non-porous or macroporous material. This result is in agreement with the smooth morphology of this material, obtained by SEM studies. The sample possesses no apparent porosity, however; the N_2 adsorption-desorption behavior can be due to its clustered space, with a large mean d_p of 16.53 nm for mesoporous material and BET surface area of $1.38 \text{ m}^2 \text{ g}^{-1}$, as well as a total pore volume of $0.005 \text{ cm}^3 \text{ g}^{-1}$. Figure 3C shows the N_2 adsorption-desorption isotherm of Ca-HAp with a type IV N_2 adsorption-desorption isotherm that, according to IUPAC, corresponds to mesoporous materials. According to Table 1, the Ca-HAp sample showed the highest BET surface area ($59.70 \text{ m}^2 \text{ g}^{-1}$) and the smallest mean d_p (7.50 nm), compared to the Ba-HAp and Sr-HAp materials. An adsorbent material with a high BET surface area means that there is a greater number of active surface sites on the adsorbent material for the removal of a greater quantity of contaminant species. Therefore, as was observed in this study, calcined Ca-HAp showed better textural properties, suggesting a direct correlation with Co^{2+} ion adsorption capacity. Other textural properties such as total pore volume (V_T) has an effect over the Co^{2+} ion adsorption behavior due to a greater total pore volume, with which a higher amount of cobalt chemical species can be in contact with more specific active sites, as was confirmed for the Ca-HAp sample, which has the highest total pore volume ($0.1120 \text{ cm}^3 \text{ g}^{-1}$) when compared to the other synthesized hydroxyapatites. On the other hand, the Ca-HAp material presented the lowest value of mean d_p , as is observed in Table 1.

While analyzing the surface morphology of the synthesized materials by SEM (Figure 4), it was discovered that the synthesized Ba-HAp powder in this work was composed of small particles with irregular form, homogeneously distributed, smooth, elongated, and with an average diameter between 3 μm and 9 μm , as shown in Figure 4A. Figure 4A also shows the EDXS analysis of the synthesized Ba-HAp, revealing only the presence of barium, oxygen, and phosphorous in the prepared

material; other elements were not detected. The experimental element distribution map for Ba-HAp shows that the element distribution was homogeneous. According to EDXS results, the Ba/P molar ratio of the prepared Ba-HAp was determined to be 1.87, which is in agreement with the stoichiometric value.

From the SEM image (Figure 4B), it can be observed that the Sr-HAp presents particles in the form of flakes, which are homogeneously distributed and non-porous. These particles appear smooth, irregularly elongated, with cluster formation and low porosity. Thus, this indicates that single particles are not isolated and that the grain agglomerates are relatively interconnected (Figure 4B). The EDXS spectrum (Figure 4B) shows the presence of Sr, O, and P elements in the synthesized material, which conforms to the chemical composition of Sr = 64.82 wt.%, O = 23.28 wt.%, and P = 11.89 wt.%, as can be seen in Figure 4B, which corresponds to the Sr-HAp, according to the XRD pattern obtained, as is shown in Figure 2B. The experimental chemical composition values of the principal Sr-HAp ceramic are in agreement with the theoretical chemical composition results obtained for this material (Figure 4B). The experimental element distribution map from the EDXS spectra for Sr-HAp also shows a homogeneous composition. On the other hand, according to EDXS results, the Sr/P molar ratio of the prepared Sr-HAp was determined to be 1.92; this Sr/P mole ratio is typical of stoichiometric hydroxyapatites. Figure 4C shows that the Ca-HAp powder was made up of flat and elongated particles of irregular shape, with greater porosity compared to the other samples studied, with particle sizes ranging from 1 μm to 10 μm and its Ca/P ratio of 1.78, which is in agreement with the stoichiometric value reported. The SEM results of these prepared materials, via chemical precipitation, clearly indicate the surface morphology differences between the three powders. In this context, surface characteristics such as grain sizes, morphology, porosity, and surface area make the materials highly reactive with specific ions present in an aqueous solution [35]. All the prepared hydroxyapatite materials showed the typical morphology

Fig. 4. SEM micrographs at 5,000 $\times$ and EDXS analysis of (A) Ba-HAp, (B) Sr-HAp, and (C) Ca-HAp powders. Ba-HAp, barium hydroxyapatite; Ca-HAp, calcium hydroxyapatite; Sr-HAp, strontium hydroxyapatite.

of alkaline-earth hydroxyapatite and there were apparently not significant morphological differences between alkaline-earth materials, which meant that morphology is not a decisive factor in Co^{2+} ion adsorption capacity; however, the Ca-HAp possesses better porosity, a characteristic that improved its adsorption capacity, as was observed in this study.

Fourier transformed infrared analyses obtained at the KBr baseline in the 4,000–500 cm^{-1} region confirmed the formation of Ba-HAp, Sr-HAp, and Ca-HAp powders, as can be seen in Figure 5A–C. Concerning the FTIR spectrum, similar absorption bands were found for Ba-HAp, Sr-HAp, and Ca-HAp samples. FTIR spectrum of calcined Ba-HAp in Figure 5A showed broadband centered at 3,439 cm^{-1} , which is attributed to the presence of hydroxyl groups on the material surface due

to surface-adsorbed water. In addition, other very small bands were observed at 1,630 cm^{-1} and 1,440 cm^{-1} , attributable to the vibration of OH^- groups. This additional band indicates the presence of more hydroxyl groups bonding within the material structure. The vibrational band observed at 2,362 cm^{-1} corresponds to KBr vibrations used as analysis support. Other vibrational bands at 1,116–509 cm^{-1} were identified by FTIR analysis, and these were identified as phosphate groups $(\text{PO}_4)^{3-}$, which correspond to the Ba-HAp crystalline phase; other functional groups were not observed in the spectrum. Figure 5B shows the FTIR spectrum of the calcined Sr-HAp sample, in which a clearly noticeable broad vibrational band at 3,446 cm^{-1} that corresponds to the hydroxyl group OH^- is attributable to the presence of humidity in the

Fig. 5. FTIR spectrum of (A) Ba-HAp, (B) Sr-HAp, and (C) Ca-HAp powders. Ba-HAp, barium hydroxyapatite; Ca-HAp, calcium hydroxyapatite; Sr-HAp, strontium hydroxyapatite.

sample [2]. Vibrational bands at $2,857\text{ cm}^{-1}$, attributable to KBr, can also be observed, as well as at $1,633\text{ cm}^{-1}$, due to the presence of OH^- groups. The moderate-intensity peak at $2,857\text{ cm}^{-1}$ is assigned to KBr vibrations used as analysis support. An FTIR deconvolution shows vibrational bands at $1,438\text{--}538\text{ cm}^{-1}$, attributable to the phosphate groups $(\text{PO}_4)^{3-}$ vibration that corresponds to the structure of Sr-HAp, according to Zhanglei et al. [36]. Figure 5C shows the FTIR spectrum of the calcined Ca-HAp sample; a characteristic noticeable broad vibrational band at $3,439\text{ cm}^{-1}$ was observed, which was assigned to the hydroxyl group OH^- , attributable to the presence of humidity adsorbed in the sample. Other vibration bands at $1,640\text{ cm}^{-1}$ and $1,459\text{ cm}^{-1}$ were also observed and suggest the presence of OH^- groups, attributed

to stretching vibration of surface-adsorbed H_2O molecules [37]. A notorious absence of peaks located between $3,250\text{ cm}^{-1}$ and $1,750\text{ cm}^{-1}$ was seen, as well. An FTIR deconvolution shows characteristic vibrational bands at $1,459\text{--}511\text{ cm}^{-1}$, attributed to the vibration bands of a phosphate group $(\text{PO}_4)^{3-}$ that corresponds to Ca-HAp [38]. No others peaks were visible in the spectrum. In regard to FTIR results, were showed the characteristic bands of the successful synthesis of alkaline-earth hydroxyapatites prepared by the chemical precipitation method followed by calcination.

In general, it can be clearly observed that the processes for the removal of many hazardous contaminants of nuclear and environmental interest, from aqueous solutions by solid adsorbents, are of particular interest around the world, to guarantee

the availability of clean drinking water. In this context, the adsorption capacity of solid adsorbents to be used as water decontaminants mainly depends on the crystalline structure, structural stability, surface area, and porosity as was shown in this study. Thus, it can be established that the structural, textural, and morphological characteristics of alkaline-earth hydroxyapatites make it possible to interpret the connection that exists between these physicochemical properties and the adsorption process of an important contaminant, of both environmental and nuclear interest, present in aqueous solutions. Indeed, the characterization and evaluation have a significant impact on the development of novel materials for heterogeneous catalytic processes or adsorption purposes.

4. Conclusions

In summary, barium, strontium, and Ca-HAP powders were successfully synthesized via the chemical precipitation method, followed by calcination, and used as adsorbent materials for the removal of Co^{2+} ions present in aqueous solutions. The results show that the as-prepared Ca-HAP exhibited better microstructural, textural, and morphological properties for adsorbent purposes when compared with as-prepared Ba-HAP and Sr-HAP and that these properties may play an important role in their adsorption applications, as was demonstrated in this work. The results presented in this study have established valuable information on the removal character of different synthetic calcined alkaline-earth hydroxyapatites and represent the initial phase in the research of interesting materials. Future research should aim to investigate the entire wastewater adsorption process of these inorganic materials to study the influence of the aforementioned physicochemical parameters.

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