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Simultaneous Synthesis and Characterization of Quinolinates to Obtain Cobalt Ferrite

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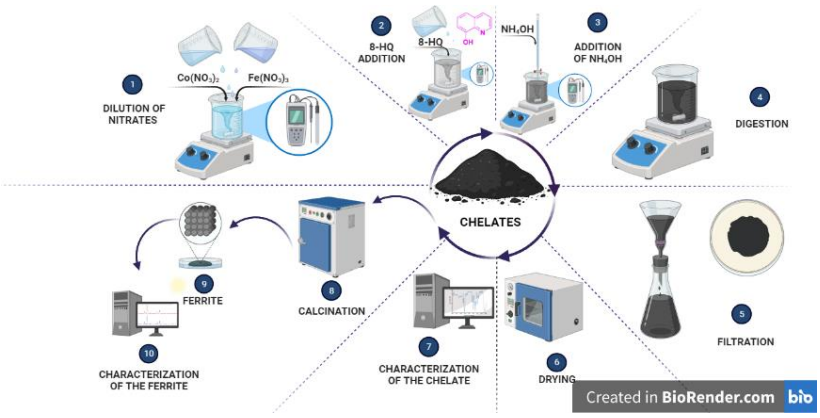
8-Hydroxyquinoline and its derivatives are compounds with a variety of applications in various fields of knowledge such as medicine, biological sciences, and chemistry. Many of these applications are possible because 8-hydroxyquinoline forms stable and insoluble metal chelates with a range of metals such as copper, cobalt, calcium, iron, and nickel. One of the possible applications of 8-HQ chelates is the production of metal oxides by thermal decomposition, however, there are few studies in the literature using quinolinates for this purpose. If the chelates are synthesized simultaneously, it is possible to obtain double oxides such as cobalt ferrite, which has numerous applications due to its magnetic properties. In this way, the present work aims to the simultaneous synthesis of cobalt II and iron III quinolinates at different pH values, as well as their characterization by XDR, SEM, TEM, FTIR and Raman analysis. Finally, the quinollinate synthetized were applied as precursors to obtain cobalt ferrite by thermal decomposition.

Graphical abstract



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1. Introduction

The compound 8-hydroxyquinoline (8-HQ), also known as 8-quinolinol or oxine [1] has the molecular formula C_9H_7NO and the structural formula shown in Figure 1. It is an organic compound made up of two rings, one phenolic fused to a pyridine ring [2].

8-HQ and its derivatives have a wide range of applications in various fields, such as biology [3], pharmacology [4], antimicrobial treatments [5], medicine [6], and chemistry, including diodes [7], dyes [8] and the production of metal oxides [9] and other functionalities. Thus, its versatility and usefulness make it a valuable asset in multiple industries. 8-HQ forms stable and insoluble chelates with several metals [1] due to the proximity of the hydroxyl group to the pyridine ring nitrogen [2]. This ability is a result of its versatile ligand

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properties [10].

The literature presents studies that use metal chelates with 8-HQ in combination with materials such as Ga [11], Fe [12], Co [13], Ca [14], Al [15], Ni, Cu [16], with the most different uses. However, few studies report the use of metal quinolinates to obtain oxides.

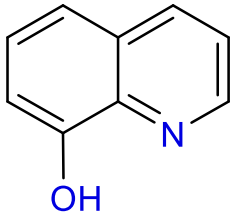

Fig.1. Structural formula of 8-hydroxyquinoline.

8-HQ's ability to form stable chelates makes it an ideal candidate for synthesizing mixed oxides through synthetic methodologies. By adding a solution containing two metal ions to a single recipient, the metal ions react with the chelating agent and produce two chelates in the same suspension. This approach allows for the thermal decomposition of a mixture of oxides, resulting in the formation of perovskites such as strontium titanate ($SrTiO_3$) [17] and lead titanate ($PbTiO_3$) [9].

Ferrites, with the general formula MFe_2O_4, are another class of mixed oxides that can be formed via the thermal decomposition of simultaneously synthesized quinolinates. Their magnetic properties have attracted the interest of many researchers, providing numerous applications in water treatment, biomedicine, and catalysts, for example [18].

The purpose of this study is to present a synthetic route and characterization of chelates to obtain cobalt ferrite via simultaneous thermal decomposition of iron III and cobalt II quinolinates.

2. Material and Methods

To carry out the simultaneous synthesis of the chelates, iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) and cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) were added to a 250 mL beaker in a 2/1 molar ratio. The salts were then diluted with water and transferred to a 1000 mL beaker under constant mechanical agitation. In another 250 mL beaker, 8-HQ was diluted in acetic acid (CH_3COOH) 50% (v/v) and after dilution, the 8-HQ solution was mixed with the metal nitrate solution in the 1000 mL beaker. Concentrated nitric acid (HNO_3) was added to lower the pH of the system to 1.

A 10% (v/v) solution of ammonium hydroxide (NH_4OH) was then added until the pH of the system reached 6. The system was then stirred continuously for 2 h and then left to stand for 3 h to allow digestion to occur. After this period, the filtration process was carried out and the precipitate obtained was dried in an oven at a temperature of 55 °C for 24 hours.

After drying, the precipitate was collected from the filter paper and transferred to an agate mortar, and the precipitate was crushed, then the solid obtained was stored and identified as pH06-Chelate. This study was conducted at two pH levels: 6 and 9. The procedure described was for the chelate synthesized at pH 6, but the same procedure was applied to the chelate synthesized at pH 9, except that NH_4OH was added until the pH reached 9, thus obtaining the pH09 chelate sample. The pH06-Chelate and pH09-Chelate samples were characterized by XRD, SEM, TEM, FTIR and Raman.

To obtain the cobalt ferrite, the pH06-Chelate and pH09-Chelate samples were calcined separately in a furnace to a temperature of 500 °C in an air atmosphere and a gas flow of 5 L/min, resulting in the pH06-Ferrite and pH09-Ferrite samples corresponding to the calcination of the pH06-Chelate and pH09-Chelate samples, respectively. After calcination, the samples were crushed in an agate mortar and characterized by XRD, SEM, and TEM.

3. Results and Discussion

Figure 2 shows the reaction mechanism for synthesizing metal chelates with 8-HQ. Firstly, 8-HQ is mixed with acetic acid [14] to form an 8-HQ solution. As 8-HQ is an amphoteric compound and forms an ionic equilibrium between the 8-hydroxyquinolinium ($HOx.H^+$) and oxynate (Ox^-) ions, it is possible to shift this equilibrium by adding a basic or acidic solution to the reaction medium. In general, at acidic pHs there is protonation of the nitrogen leading to the formation of the $HOx.H^+$ ion, generating small amounts of the metal complex. On the other hand, in a basic environment the formation of the Ox^- ion predominates, which leads to greater precipitation of the chelates.

There is a change in color when the metal nitrate solution, $Co(NO_3)_2$ or $Fe(NO_3)_2$, is mixed with the 8-HQ solution due to the precipitation of quinolinates, as well as a decrease in pH (pH = 2) after the metal nitrate solution is mixed with the 8-HQ solution, as eq. 1 and eq. 2 indicate. In the reaction medium, HNO_3 is formed, decreasing the pH. Although the formation of chelates can be observed (change in color and pH) when metal nitrates are added to 8-HQ, the yield of this reaction is low, as the reaction medium is highly acidic and the formation of the $HOx.H^+$ ion dominates.

Concentrated HNO_3 is added to the medium in order to break up the precipitate formed. In the next step, NH_4OH (eq. 3) is slowly infused into the solution in order to shift the balance in favor of the formation of Ox^- ions and, subsequently, leading to the formation of the $Co(C_9H_6NOH)_2.2H_2O$ and $Fe(C_9H_6NOH)_3$ chelates. Before the pH reaches 6, the medium becomes stable when the pH approaches 4. This stability is attributed to the formation of a buffer solution between $CH_3COOH_{(aq)}$, and $CH_3COONH_{4(aq)}$ as shown in eq. 4, 5 and 6.

Both complexes become more stable with octahedral geometry. In the case of cobalt with a +2 charge, the chelating agent coordinates with the metal, forming a transplanar structure at the equatorial positions together with two water molecules at the axial positions. This configuration indicates that the cobalt chelant is a hydrated compound. [19, 20], as well as having a trans-octahedral structure [21].

Once the chelates were obtained, they were characterized by XDR, SEM, FTIR and Raman. Figure 3 shows the diffractogram of 8-HQ and samples pH06-Chelate and pH09-Chelate from 5 to 35 degrees of 2 theta. The diffractogram of 8-HQ (a) was indexed to crystallographic chart 00-039-1857 from the JCPDS database, which has an orthorhombic crystal system and space group Fdd2-43. The 8-HQ analyzed has the most intense peaks located in the region between 5 and 35° (2θ), with the peaks at 9.32, 12.21, 14.09, 15.11, 18.74, 19.76, 23.20, 25.53, 27.96 e 28.51 ° (2θ) which is consistent with what has been reported in the literature [22]. The diffractograms of the metal quinolinates can be compared

with the diffractogram of 8-HQ to check whether chelation has taken place. In general, when such a comparison is made, it is possible to notice the appearance and disappearance of peaks, which is an indication that the chelation reaction has taken place. This has been observed in other studies with different metals, such as nickel [16] and aluminum [23].

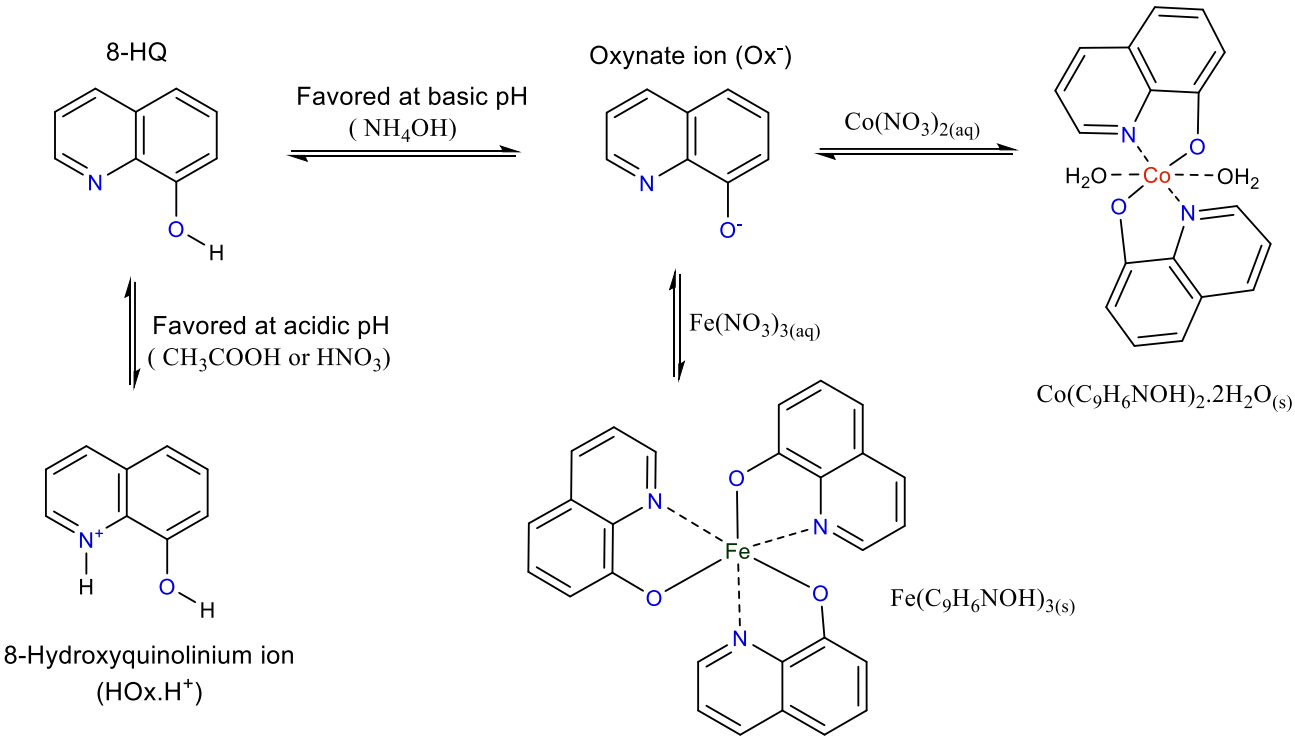

Fig. 2. Mechanism of metal chelate formation.

$$2Fe(NO_3)_3.9H_2O_{(aq)}+3C_9H_6NOH_{(ác)} \leftrightarrows 2Fe(C_9H_6NOH)_{3(s)}+6HNO_{3(aq)} \quad \textbf{(Eq. 01)}$$

$$Co(NO_3)_2.6H_2O_{(aq)}+2C_9H_6NOH_{(ác)} \leftrightarrows Co(C_9H_6NOH)_{2(s)}+2HNO_{3(aq)} \quad \textbf{(Eq. 02)}$$

$$HNO_{3(aq)}+CH_3COOH_{(aq)}+2NH_4OH_{(aq)} \rightarrow NH_4NO_{3(aq)}+CH_3COONH_{4(aq)}+2H_2O_{(l)} \quad \textbf{(Eq. 03)}$$

$$NH_4OH_{(aq)} \leftrightarrows NH^+_{4(aq)} + OH^-_{(aq)} \quad \textbf{(Eq. 04)}$$

$$CH_3COONH_{4(aq)} \rightarrow NH^+_{4(aq)} + CH_3COO^-_{(aq)} \quad \textbf{(Eq. 05)}$$

$$CH_3COOH_{(aq)} \leftrightarrows H^+_{(aq)} + CH_3COO^-_{(aq)} \quad \textbf{(Eq. 06)}$$

Regarding to the different reaction media (pH 6 and pH 9), when comparing the two diffractograms in Figure 3, it is not possible to identify any significant differences; however, the pH06-Chelate sample showed more defined peaks than the pH09-Chelate sample. This suggests that at pH 6 it was possible to obtain a compound with a more crystalline structure than at pH 9.

Figures 4 and 5 show the FITR spectra in the 1700 to 400 cm^{-1} range and the RAMAN spectra in the 1800-400 cm^{-1} range for the pH09-Chelate (a) pH06-Chelate (b) 8-HQ and (c) samples.

When comparing the spectra of 8-HQ with the spectra of the metal chelates, there are significant differences between the spectra [24, 25]. This finding is attributed to the formation of stable compounds through the interaction of deprotonated oxygen and nitrogen from 8-HQ. Changes in the reaction medium cause changes in the FTIR spectra, which is why it is common to compare the spectra of the complexes with that of 8-HQ. These comparisons can be used to determine whether or not chelation has occurred. The observation of the spectrum of 8-HQ with the synthesized chelates shows the appearance and disappearance of some bands, which is a strong indication that the proposed products were formed.

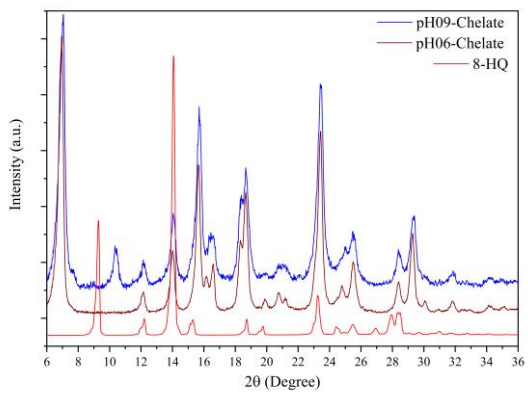

Fig. 3. Diffractograms of pH06-Chelate, pH09-Chelate and 8-HQ samples.

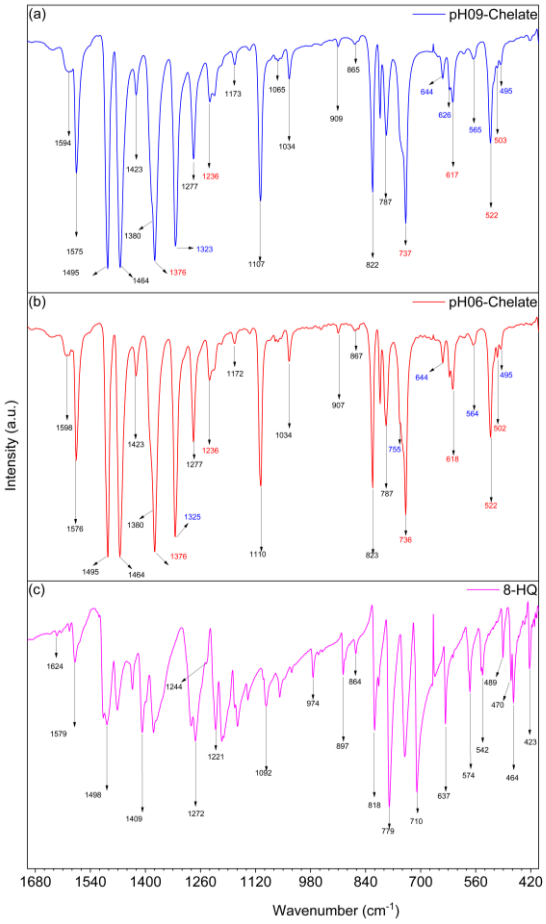

Fig. 4. FTIR spectra for sample pH09-Chelate (a), pH06-Chelate (b) and 8-HQ (c).

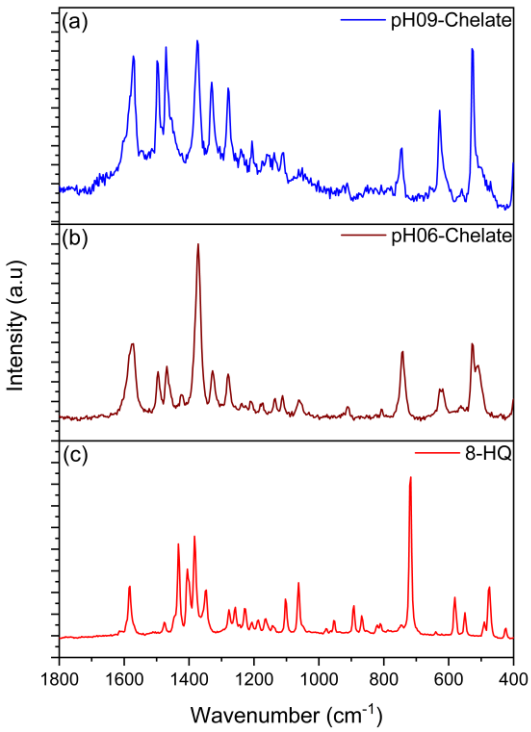

Fig. 5. Raman spectra for sample pH09-Chelate (a), pH06-Chelate (b) and 8-HQ (c).

The main vibration bands of 8-QH are located at [24]: 1635, 1588, 1508, 1473, 1439, 1416, 1385, 1286, 1273, 1215, 1204, 167, 1140, 1094, 1060, 975, 894, 866, 818, 808, 781, 741, 711 cm^{-1} and the main bands for the cobalt chelate are at [26]: 1625, 1582, 1493, 1470, 1425, 1380, 1330, 1268, 122, 1207, 1178, 1142, 1107, 1068, 1023, 895, 829, 810, 787, 755, 727, 668, 628, 545, 488 cm^{-1} and for the iron chelate in [26]: 1610, 1580, 195, 1462, 1426, 1384, 1375, 1268, 1242, 1184, 1140, 1112, 1060, 1035, 918, 835, 810, 783, 733, 745, 613, 533, 509, 415 cm^{-1}. Nearly all reported bands were identified with minor variations. The band near 3443 cm^{-1} (IR) is characteristic of 8-HQ and refers to the stretching of the O-H bond of the phenolic group [25]. However, it is not observed in anhydrous metal chelates [27]. At 3047 cm^{-1} (IR) it corresponds to the C-H deformation of the aromatic ring. The vibration of the C=N bond is observed at 1625 cm-1 (IR) [25]. The band in the 1600 cm^{-1} region (IR) refers to the C=C stretching vibration [14]. One of the characteristic bands of aromatic compounds was observed at 780 cm^{-1} (IR) and is attributed to the out-of-plane C-H vibration [26]. The band at 1093 cm^{-1} (IR) in the spectrum of 8-HQ refers to the vibration of the O-H bond [28, 29]. When chelation reaction occurs, this band disappears and the C-O band located at 1100 ± 15 cm^{-1} increases in intensity, indicating the formation of the complex. By comparing the vibration of the C-O bond between the metal chelates, it can be seen that it is characteristic of the 8-HQ.

There is also evidence that, when changing the metal, the position of this band changes slightly, such as for copper, zinc, manganese, magnesium, and calcium, which have been identified at 1113, 1112, 1108, 1112 and 1106 cm^{-1} (IR), respectively [26] and for gallium at 1112 cm^{-1} (IR) [27].

This change in vibration frequency can be explained by the change in the electronic distribution of the C-O environment when the metal complex is formed and is influenced by the physical properties of the cation, such as the number of electrons, ionic radius, atomic weight and electronegativity [26]. These changes indicate that the electronic distribution in the molecule, especially in the vicinity of the C-O bond, is greatly affected by chelation [29]. The C-O band was observed in the literature for the iron chelate at 1112 cm^{-1} (IR), while for the cobalt complex at 1107 cm^{-1} (IR) [26].

Similarly, in the synthesized samples, bands were observed at 1106 and 1107 cm^{-1} (IR) for the cobalt and iron chelates and at 1107 cm^{-1} for the pH06-Chelate and pH09-Chelate samples. Raman spectroscopy showed these bands at 1107, 1111, 1112 and 1111 cm^{-1}, respectively.

In general, the spectra of metal chelates are similar to each other, with some significant differences that characterize the metal ligand [26] and even the presence of water in the compound, as is the case with cobalt, where the bands found at 643, 605 and 587 cm^{-1} (IR) suggest that it is a hydrated compound with an octahedral structure similar to that proposed in the mechanism in Figure 1 and in the literature [8]. Therefore, it can be concluded that the metal chelates of interest are the result of the simultaneous synthesis method.

Figure 6 shows the SEM images for sample pH06-Chelate at magnifications of 12 kx (a) and 30 kx (b) and for sample pH09-Chelate at magnifications of 12 kx (c) and 30 kx (d).

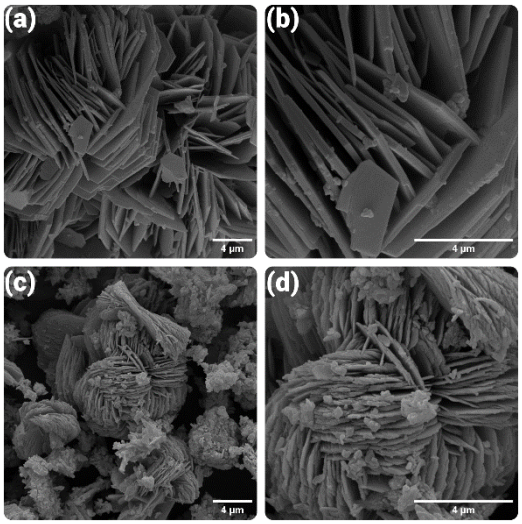

Fig. 6. SEM images for sample pH06-Chelate (a and b) and sample pH09-Chelate (c and d).

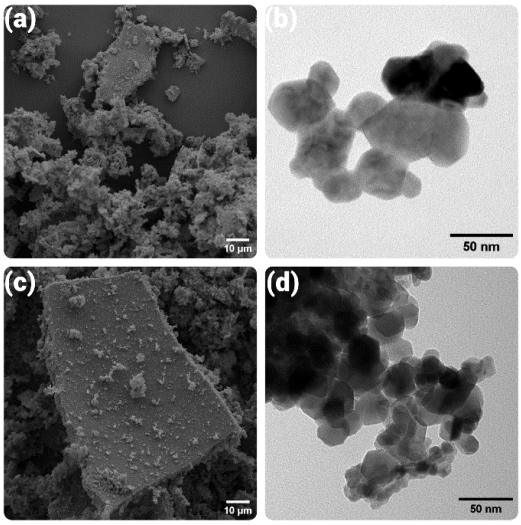

Fig. 8. SEM images for sample pH06-Ferrite (a and b) and sample pH09- Ferrite (c and d).

The analysis of the SEM images of the synthesized precipitates shows that the quinolinates have different morphologies, which was expected since both Co and Fe chelates were identified by XRF, FTIR and Raman.

One of the morphologies is well defined and resembles the appearance of a flower composed of several leaves (nosheets), which was attributed to the cobalt chelate. Figure 6-b shows the nosheets growing in the shape of a flower. This change in structure may be related to the presence of Fe ions in the reaction medium. The second morphology, attributed to the iron chelate, has a slightly less defined shape with the appearance of a cluster of different sizes. Regarding the pH, it can be seen that the compounds synthesized at pH 6 are larger and more crystalline than those produced at pH 9.

After characterization of the chelates, the pH06-Chelate and pH09-Chelate samples were calcined at 500°C in a synthetic air atmosphere to form cobalt ferrite. Figure 7 shows the diffractogram for samples pH06-Ferrite and pH09-Ferrite. At both synthesis pHs, the diffraction peaks characteristic of $CoFe_2O_4$, whose crystalline structure is of the CFC type, were observed.

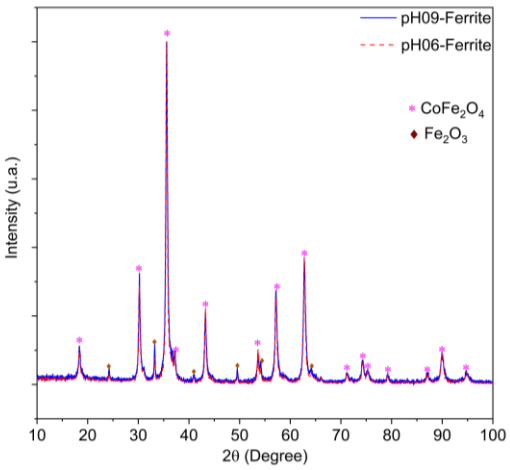

Fig. 7. Diffractogram of pH06-Ferrite and pH09-Ferrite samples.

Figure 8 shows SEM images at 2.5 kx magnification (a) and TEM images (b) for sample pH06-Ferrite and SEM images at 2.5 kx magnification (c) and TEM images (d) for sample pH09-Ferrite. This shows that only one morphology is formed at both pH values and the sintering process occurred in both samples at 500°C.

4. Conclusions

The different characterization techniques were used to verify the formation of cobalt and iron chelates at both pH values. The simultaneous methodology showed that the precipitation of Co and Fe with 8-HQ leads to the formation of chelates with individual morphological and constitutional characteristics. Based on these results, it appears that $CoFe_2O_4$ can be produced by a solid-state reaction using this precipitation method.

Considering the pH interference, it is possible to conclude that chelates are formed at both pHs, with pH 6 producing a precipitate that has a more crystalline structure than pH 9. Finally, the proposed synthesis route for obtaining $CoFe_2O_4$ by thermal decomposition of quinolinates synthesized by the simultaneous method proved to be a relatively simple and fast synthesis process, indicating that it is a very promising option for the preparation of mixed oxides.

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Author Contributions

Alessandro Retizlaf: data curation, methodology, writing – original draft provides. Mariana de Souza Sikora: data curation, formal analysis, visualization. Sirlei Dias Teixeira: data curation, methodology. Henrique Emilio Zorel Junior: conceptualization, resources, investigation, visualization.

Giancarlo V. Botteselle: funding acquisition, supervision, writing – review & editing.

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