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DEVELOPMENT OF THE NANOPARTICLE SYNTHESIS PROCESS

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1. Introduction

Nanotechnology has, in recent years, stood out as a rapidly growing area of research, with numerous applications also in the biomedical area, including drug delivery [1], image diagnosis [2], cancer treatment [3] and other biomedical applications [4]. In the area of applications, nanoparticles (NPs) have stood out: hyperthermia and radiosensitization. Hyperthermia consists of exposing a certain tumor tissue to high temperatures (between 40 °C and 44 °C), using radiofrequency on magnetic nanoparticles (NPM) making them vibrate and release energy [5], causing heating of the cells and, consequently, their death or weakening, leaving them more sensitive to the effects of radiation or chemotherapy drugs [6]. Radiosensitization aims to apply, to tumors, materials with a high atomic number, in order to increase the probability of ionization occurring within them, leading to an increase in the energy deposited and destroying them [7]. Elements indicated as good candidates for this type of procedure must, in addition to presenting chemical and physical stability, have a high atomic number and low toxicity to the organism. Studies carried out with erbium oxide NPs (Er2O3-NP) show a dose increase factor (DEF) of up to 1.09 when irradiated in 6 MV clinical systems [8].

In this work, with the objective of obtaining NPs with the presented properties, synthesis and characterization were proposed using the elements Cobalt (Co) and Nickel (Ni). To achieve this, the preparation methodology must follow a protocol in which the size, morphology and crystalline structure provide adequate responses, in this case $CoFe_2O_4$ and $NiFe_2O_4$ NPs. The use of coprecipitation for the production of the NPs in question was proposed. This method is generally used to obtain oxides and consists of the homogeneous or heterogeneous coprecipitation of aqueous solutions of metal salts by the addition of a base in the presence of an inert atmosphere. The composition, shape and size of the particles are dependent on the nature of the reactants, reaction temperature and ionic strength of the medium. The particles obtained are not covered by any organic groups, which allows easy modification of the surface with organic molecules of interest.

2. Methodology

$CoFe_2O_4$ samples were produced using the coprecipitation method [11]. Firstly, stoichiometry calculations were carried out in order to determine the proportions of the reagents that would be used in the production of the samples, these being Cobalt (II) Chloride hexahydrate ($CoCl_2$ * $6H_2O$) and anhydrous Iron (III) Chloride ($FeCl_3$). While the reagents were weighed, 200 ml of deionized water was placed in an inert nitrogen atmosphere (N2) in a Becker. After these procedures, the experimental scheme was assembled by coupling the N2 flow and the mixer in the volumetric flask. Then, 0.5067 g of $CoCl_2$ * $6H_2O$ and 0.6909g of Fe Cl3 were dissolved in 100 ml of deionized water under mechanical stirring, and 4 ml of ammonium hydroxide, which is the precipitating agent for the reaction, was added to the solution after the dissolution of the reagents. Then, pH tests were used to ensure that it was at the desired level, between 9 and 11. With the reaction already in effect, the rest of the deionized water was added and the solution remained under mechanical stirring for 40 minutes. After this time interval, the mixer was turned off and the N2 atmosphere was maintained, the solution was placed at rest with a magnet positioned underneath the volumetric flask, in order to help with the precipitation process.

Then, excess water was removed from the solution and the precipitate was separated into falcon tubes and centrifuged for 10 min at 10,000 rpm, the process was repeated two more times adding deionized water to the solution and a final time with acetone, in order to remove as many impurities as possible. After cleaning, the precipitate was placed in a vacuum to dry. After drying, the precipitate became a powder that was separated and sealed in four quartz tubes for heat treatment. The heat treatment was carried out on two $CoFe_2O_4$ samples, one at 50°C for 10 hours and the other at 70°C for 10 hours. Then, both were removed from their respective quartz tubes to be prepared for analysis using the x-ray diffraction method. The preparation process boils down to grinding the sample in a mortar, which is then spread over the sample holder that is fitted to the DRX machine. Therefore, XRD measurements were taken for the two samples in question and a brief analysis of the results obtained revealed that the structure of both was amorphous, indicating that the temperatures used were not enough to reinforce the crystalline structure of the samples. Therefore, one of the next steps will be to heat treat the $CoFe_2O_4$ samples at higher temperatures and analyze them using XRD. In addition to the $CoFe_2O_4$ samples mentioned above, two others of the same material were also produced with the inclusion of 111In to be analyzed using the perturbed angular correlation technique. However, in both cases, the resulting samples were not active enough for the analysis in question, so such measurements could not be made, and the plan to use this technique to analyze the samples was abandoned.

3. Results and Discussion

To use the technique, the samples must be in powder format, and after obtaining the diffractogram, it was converted to an XY extension and using the origin software to plot the graphs showing the characteristic peaks of the material's crystalline structure. The graph presented refers to the post-synthesis $CoFe_2O_4$ sample, as shown it is not possible to observe characteristic peaks, that is, the sample has no defined shape or is amorphous as it is called. Figure 2 shows the diaphragtogram of the previous sample after heat treatment at 70°C for 10 hours in vacuum.

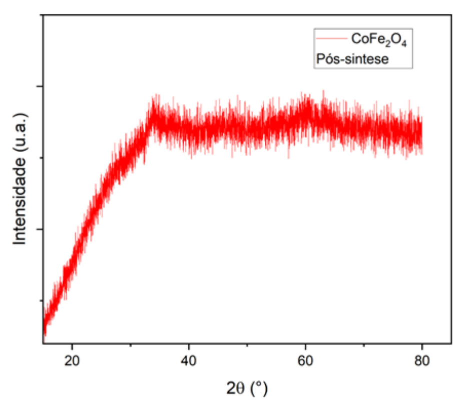

Figure 1: X-ray diffraction spectrum of the post-synthesis $CoFe_2O_4$ sample. Source: Authors.

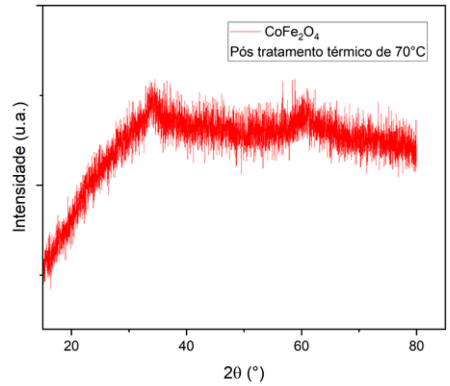

Figure 2: X-ray diffraction spectrum of the $CoFe_2O_4$ sample after heat treatment at 70 °C for 10 hours. Source: Authors.

When analyzing the $CoFe_2O_4$ spectra, it was possible to conclude that the samples in question are amorphous, so that their spectra do not present the intensity peaks characteristic of this material. It is possible that heat treatment at higher temperatures is necessary for the formation of the crystalline structure in $CoFe_2O_4$ NPs, more tests will be carried out in order to investigate this hypothesis. Figure 6 refers to $NiFe_2O_4$ treated at a temperature of 70°C for 10 hours, and figure 7 shows the structure resulting from a heat treatment at 150°C for 10 hours. Heat treatment was carried out in a vacuum to prevent oxidation. The two diffractograms presented more defined peaks, that is, the results are closer to what was expected.

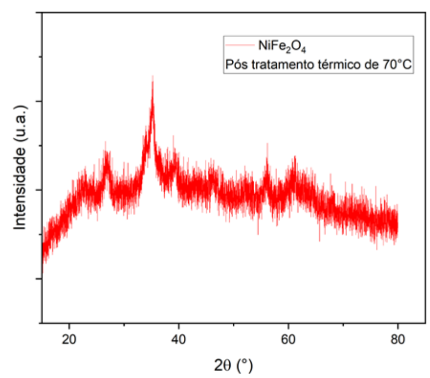

Figure 3: X-ray diffraction spectrum of the NiFe2O4 sample after heat treatment at 70 °C for 10 hours. Source: Authors.

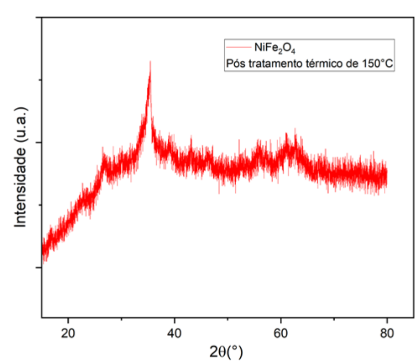

Figure 4: X-ray diffraction spectrum of the NiFe2O4 sample after heat treatment at 150 °C for 10 hours.

Source: Authors.

The results for these samples show interspersed intensity peaks, thus revealing that the samples are not amorphous. It is possible to compare the highest intensity peak in the spectrum of our $NiFe_2O_4$ samples with another present in specific literature. Therefore, we can confirm that the structure of our $NiFe_2O_4$ samples is close to what was expected, and consequently, that the method used in the synthesis of the samples and the heat treatment was effective.

4. Conclusions

The coprecipitation technique carried out at room temperature and with the proportions of reagents used, does not provide enough energy for the system to result in the formation of the crystalline structure. Thus, by providing more energy with heat treatments, it was possible to observe the formation of small peaks related to the magnetite structure. This result is visible for the $NiFe_2O_4$ sample. However, this was not observed for the $CoFe_2O_4$ sample, so new tests must be carried out in the synthesis process. The stoichiometry appears to be adequate, as there is no formation of phases other than that relating to the inverted spinelium structure of magnetite. The use of origin software was essential for identifying the characteristic peaks. The next steps will be to reproduce the samples to refine the diffractogram using the GSAS software, which uses the Riteveld method, making it possible to obtain crystalline parameters of the unit cell. In addition to XRD, transmission and scanning electron microscopy characterizations will also be carried out to confirm the average size of the nanoparticles, their shape and their distribution of the elements.

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