

## **RAMAN SPECTROSCOPY OF IRON OXIDE OF NANOPARTICLES (Fe<sub>3</sub>O<sub>4</sub>)**

Panta P.C.<sup>1,2</sup>, Bergmann C.P.<sup>1</sup>

<sup>1</sup>*Ceramic Materials Laboratory, Federal University of Rio Grande do Sul,  
Av. Osvaldo Aranha 99, sl. 705C, CEP 90035-190, Porto Alegre, RS, Brazil*

<sup>2</sup>*Department of Chemistry and Physics, University of Santa Cruz do Sul, Santa Cruz do  
Sul, Brazil, Av. Independência 2293, CEP 96815-900, Santa Cruz do Sul, Brazil*

### **Abstract**

Nanoparticles of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) were obtained by coprecipitation with synthesis time of 30, 60 and 90 min. The morphology of the samples was investigated by scanning electron microscopy (SEM) and structural characteristics were obtained by X-ray diffraction (XRD). The crystallite size was calculated from the spectrum X-ray diffraction with the application of the Scherrer equation and Winfit. The crystallite size varied from 4.6 to 14.4 nm when calculated by Scherrer equation and when calculated by the single line ranged from 7.5 to 22.3 nm Winfit. The degree of graphitization was studied by Raman spectroscopy where spectrums were analyzed with different lasers: 514 nm (0.75 mW power used) and 785 nm (1.2 mW power used). The dominant structures of the spectra are in 215, 276, 398, 487, 654 and 1300 cm<sup>-1</sup> when using the laser 514 nm. The spectrum produced with laser 514 nm is characteristic peak of magnetite in 654 cm<sup>-1</sup>. The spectrum produced by laser 785 nm has a peak at 670 cm<sup>-1</sup>, shifted relative to the laser 514 nm. The spectrum generated by laser 785 nm peaks characteristic of maghemite encountered due to possible oxidation of the sample caused by the high power laser. The experimental results were satisfactory and are according to the survey.

**Keywords:** nanoparticles; coprecipitation; Raman spectroscopy; magnetite.

### **1. Introduction**

The nanoparticles of iron oxide are a major focus of research in physics, chemistry, engineering and materials science, among others. Research is because their main magnetic properties such as superparamagnetism, high coercivity, low Curie temperature, high magnetic susceptibility, among others, which occur due to the nanometric size. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles can have various applications in nanotechnology, such as pigment, drug delivery, targeting, magnetic resonance imaging for clinical diagnosis, recording material, hyperthermia, catalyst, etc. [1, 2] These nanoparticles have an ability to interact in different ways with different biological molecules due to their properties such as high specific area and wide variety of surface functionalization.

Many methods have been developed for preparing magnetic nanoparticles, such as polyols, microemulsions, laser pyrolysis, sonochemistry, coprecipitation, hydrothermal, etc. [3]. In a convenient and cost-effective production method is coprecipitation that has the potential to satisfy the increasing demand for direct preparation of  $Fe_3O_4$  nanoparticles (water-based). Techniques for the synthesis of nanoparticles determine their size and can be well controlled by the surfactant. Furthermore, if process conditions such as the pH of the solution, the reaction temperature, stirring speed, solute concentration and surfactant are carefully controlled in order to obtain nanoparticles of iron oxide with size and desired shape [1- 3].

This work has focused on the preliminary results of the synthesis process of the nanoparticles of iron oxide by the coprecipitation method in which the particles can be well controlled. Subsequently characterizations were conducted by XRD, TEM and Raman spectroscopy.

## 2. Experimental

### 2.1 Materials

Ferrous chloride tetrahydrate ( $FeCl_2 \cdot 4H_2O$ , 99%), ferric chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ , 99%), were obtained from Sigma Aldrich (EUA), tetramethylammonium hydroxide (25 – 28%, w/w) was obtained from Vetec (Brazil). Distilled water was used for preparation of the solutions after deoxygenation with dry argon for 10 min. The divalent ( $FeCl_2 \cdot 4H_2O$ ), trivalent ( $FeCl_3 \cdot 6H_2O$ ) iron salts and aqueous ammonium hydroxide (25–28%, w/w) were also deoxygenated with dry argon before use. All the other chemicals used in this work were analytical reagent grade from commercial market without further purification.

### 2.2 Preparation of Iron Oxide Magnetic Nanoparticles

Method previously published by Kim et al. was chosen for the iron oxide magnetic nanoparticles preparation. Nanoparticles were prepared by coprecipitation of  $Fe^{2+}$  and  $Fe^{3+}$  salts solution and  $NH_4OH$  solution using peristaltic pump. Our reaction apparatus can be seen in Figure 1.

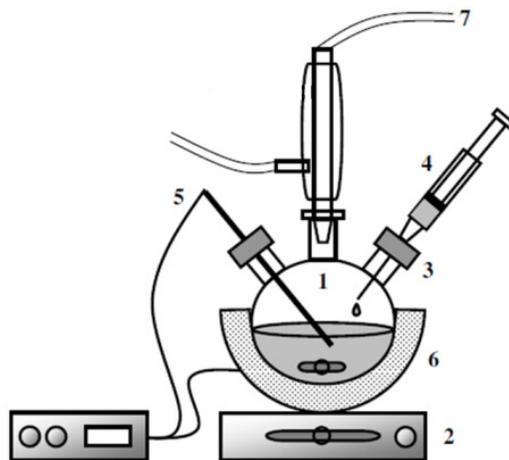
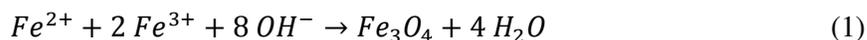


Figure 1. Reaction apparatus used for the iron oxide nanoparticles preparation. 1 - Flat bottom flask with three outlets, 2 – Stirrer, 3 - Sealing Stoppers, 4 - syringe for addition of reagents, 5 - thermocouple connected to temperature controller, 6 - Warm Blanket and 7 - Line Vacuum / Argon.

The principle of reaction is given by:



according to the results of thermodynamic model of this system, a complete precipitation of  $Fe_3O_4$  is expected while maintaining a molar ratio of 1:2 to a non-oxidizing environment [4].

Salts ferric chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ , > 99%) and ferrous chloride tetrahydrate ( $FeCl_2 \cdot 4H_2O$ , > 99%) obtained from Aldrich were dissolved in water deionized water (40 ml) previously degassed. During the reaction the pH must be controlled initial and final reaction. Besides these, the temperature and agitation rate should also be controlled in reaction [5-6]. The following is performed to pass the inert gas (argon) in the system under stirring and heating  $75 \text{ }^{\circ}\text{C} \pm 15 \text{ }^{\circ}\text{C}$ . Starts dripping of 100 ml of ammonium hydroxide ( $NH_4OH$ , 25%) obtained by Vetec. Just after mixing the solutions, the color of the solution changed from light brown to black, indicating the forming of  $Fe_3O_4$  nanoparticles, which was allowed to crystallize completely for another 30, 60 and 90 min under rapid stirring. After this time period, the magnetic nanoparticles were washed three times with pure water with the help of a magnet [1].

### 2.3 Characterization of Prepared Magnetic Nanoparticles

For the characterization of the material were used the technique of X-ray diffraction using a Philips X 'equipment Pert MPD, 40 kV and 40 mA. The angular range was 5 to  $75^{\circ}$  and  $0.05^{\circ}$  and step of counting time 3 seconds for each step. The analysis of scanning electron microscopy (SEM) were performed on a JEOL microscope, model JSM 6060 with maximum operating voltage of 30 kV and nominal resolution of 3.5 nm. The voltage was 20 kV (see bar scale). Scanning Electron Microscopy (SEM) was used to determine an approximate particle size of prepared nanoparticles. The Raman spectra were recorded at room temperature by a Raman spectrometer (Renishaw brand - inVia Raman, with an Excitation laser line of 632.8 nm from a He-Ne laser. The integration time is collecting the Raman signal was 60 seconds.

### 3. Results and Discussion

The characterization of the resulting powders after heat treatment was performed by means of X-ray diffraction (XRD) to verify the presence of crystalline phases. For this purpose the X-ray diffractometer Philips X'Pert MPD was used, equipped with graphite monochromator and fixed anode operated at 40 kV and 40 mA, which uses a radiation wavelength ( $\lambda = 0.154056 \text{ nm}$ ) of  $Cu-K\alpha$ . The angular range was 5 to  $75^{\circ}$  and  $0.05^{\circ}$  and step of counting time 3 seconds for each step.

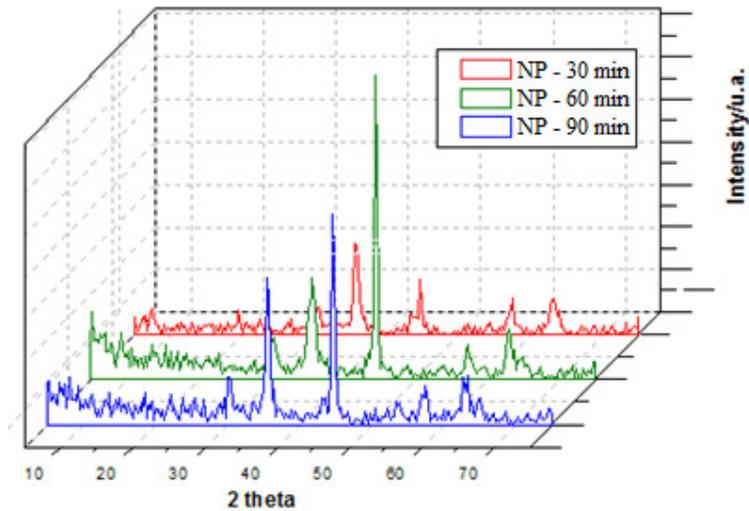


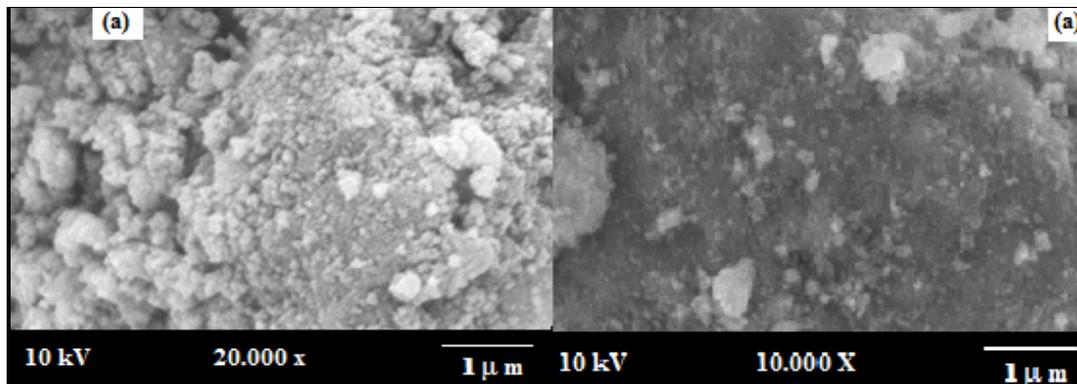
Figure 2. Analysis of X-ray diffraction.

The XRD peaks (Figure 2) showed the formation of a spinel type crystal structure of the inverse characteristic of magnetite. We also observed a mixture of  $\alpha$  and  $\gamma$  phases of  $Fe_2O_3$  (hematite and maghemite), and magnetite ( $Fe_3O_4$ ). The mean particle diameters were also calculated from the XRD pattern according to the linewidth of the (3 1 1) plane reflection peak using Scherrer equation (2)

$$D = \frac{K \cdot \lambda}{b \cdot \cos \theta} \quad (2)$$

The equation uses the reference peak width at angle  $\theta$ , where  $\lambda$  is the X-ray wavelength (1.5418 Å),  $b$  is the width of the XRD peak at half height and  $K$  is a shape factor, about 0.9 for magnetite and maghemite [2]. The results were 9.5 nm for magnetite nanoparticles. The crystallite size was calculated from the X-ray diffraction spectrum by applying the Scherrer equation ranging from 4.6 to 14.4 nm as calculated by the calculated by the single line Winfit ranged from 7.5 to 22.3 nm.

The analysis of scanning electron microscopy (SEM) were performed on a JEOL microscope, model JSM 6060 with maximum operating voltage of 30 kV and nominal resolution of 3.5 nm. The voltage was 20 kV (see bar scale).



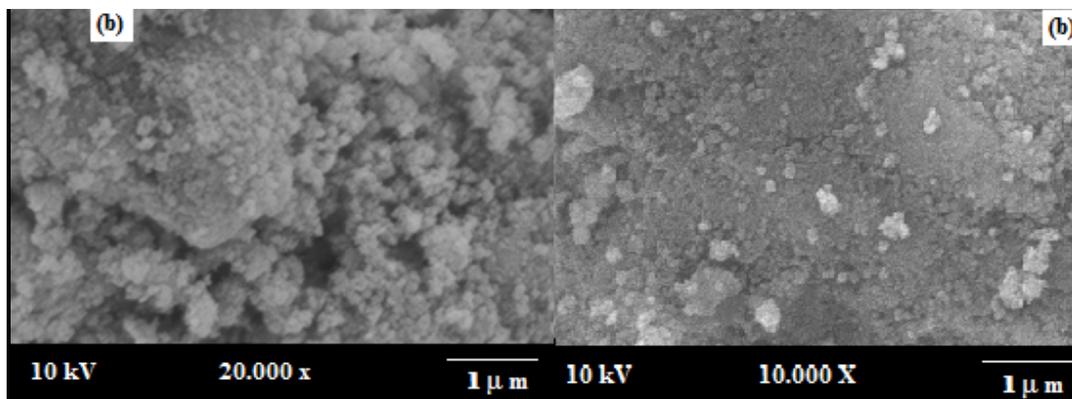


Figure 3. SEM micrographs showing the morphology of iron oxide, (a) 30 min and (b) 90 min.

The Raman spectra were recorded at room temperature by a Renishaw Raman spectrometer mark - Raman inVia with a linear laser excitation of 514 nm and 785 nm (He-Ne). For each sample, exposed 10 sec, three distinct points were measured and displacement occurred between 100 and 1400  $\text{cm}^{-1}$  (Figure 4).

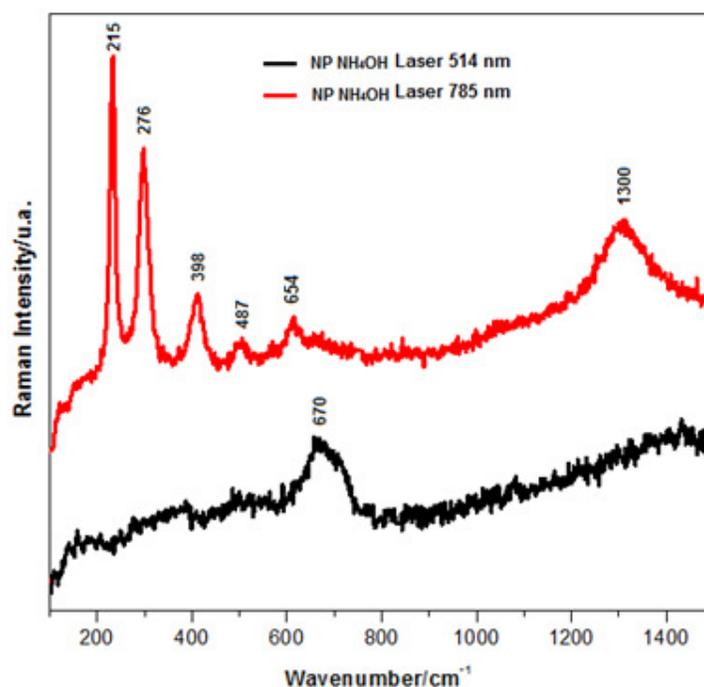


Figura 4. Espectros Raman das NP óxido de ferro obtida em Diferentes lasers : 514 nm e 785 nm.

Raman spectroscopy was employed to determine the nature of the iron oxide core (magnetite), where the Raman effect is caused by the molecular effects produced from certain energy irradiated on the sample. However, it is known that magnetite has a weak Raman scattering, especially for lower laser powers that are low so that there are no phase transformations induced by the laser. According to Li Y.S, *et al.* (2012), the Raman spectrum peaks of magnetite were investigated, where from certain vibrational modes, peak 670  $\text{cm}^{-1}$  was identified as a band characteristic.

Shebanova, O. N. *et al.* (2003) conducted some experiments using various powers of the laser Raman spectrum for magnetite. And they concluded that above some critical value of the laser power, the Raman spectra passed to indicate the characteristics of maghemite bands due to the effects of oxidation of the material. Thus, in this work we used two different types of lasers 514 nm (power 0.75 mW) and 785 nm (power 1.2 mW) with different powers, which produced different Raman spectra from the same sample. The dominant structures of the spectra are in 215, 276, 398, 487, 654 and 1300  $\text{cm}^{-1}$  when the laser used is 514 nm.

According to Figure 4, is observed in the spectrum produced by the laser 514 nm, the characteristic peak of magnetite, 670  $\text{cm}^{-1}$ , and the laser 785 nm has a peak at 654  $\text{cm}^{-1}$  shifted from the peak 670  $\text{cm}^{-1}$ . In addition to this, are also found characteristic of maghemite peaks that occur because of high power laser probably oxidized the sample.

To purchase these spectra we used the 785 nm laser with a power of 1.2 mW, which produced very similar spectra for all measured samples. The results confirm the formation of  $\text{Fe}_3\text{O}_4$  since obtained Raman spectrum has identical features to the cited work by Si H. *et al.* (2008) and Slavov L. *et al.* (2010). The spectra show peaks magnetite and maghemite because there is a partial oxidation by the incidence of high-power laser. All samples were also measured using the laser 514 nm (power 0.75 mW), but due to low power impressive results were not obtained due to poor spreading of magnetite.

#### 4. Conclusions

Magnetic nanoparticles of iron oxide were prepared by two-step process. In the first step, magnetite nanoparticles were produced by coprecipitation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts solution with  $\text{NH}_4\text{OH}$  solution formed magnetite nanoparticles. Resulting samples of nanoparticles were analyzed utilizing XDR, Raman and SEM. It was found that prepared nanoparticles revealed the magnetic properties in water suspension when external magnetic field was applied, that particles were generally spherical in shape and have particle size below 9.5 nm and that they tend to form agglomerates. When using Raman spectroscopy, the obtained one sample peaks vary with the potency and the laser 514 nm and 785 nm.

#### Acknowledgements

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