

Magnetic Nanoparticles Obtained by Homogeneous Coprecipitation Sonochemically Assisted

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The present work demonstrates preparation of magnetic nanoparticles by a novel method. Magnetic nanoparticles with potential for biomedical and environmental applications were obtained by homogeneous coprecipitation method sonochemically assisted. The effect of ultrasonic cavitation on changing the reaction environment was studied. The chemical reaction media used here was very similar to those used for Sono-Fenton process. The ultrasonic energy has driven the growth of particles; smaller diameter nanoparticles were obtained by applying a higher power. For the first time, it was demonstrated the iron oxide nanoparticles synthesis at pH lower than 6.

Keywords: *magnetic nanoparticles, homogeneous coprecipitation, sonochemistry*

1. Introduction

Nowadays nanotechnology is very important for the advancement of science, since it makes use of the manipulation of matter on a scale in which materials show different characteristics than those displayed in the micro and macro scale¹. These properties changes are attributed to the large increase in surface area in relation to the volume². In this context, magnetic nanomaterials, such as iron oxide, particularly magnetite (Fe₃O₄) have been applied in various fields such as drug carriers and contrast agents in magnetic resonance imaging³.

For this application, certain parameters must be controlled during the synthesis, such as the size and shape of the nanoparticles⁴. The control of the size, as well as size distribution, is necessary because allows the control of the material's properties, such as superparamagnetism and hyperthermia⁵.

Depending on its size, iron oxides particles present different behaviors when an external magnetic field is applied. It is known that abrupt changes in magnetic properties occur when the particle size is reduced of micrometer scale to nanometer. In nanoscale phenomena of finite size and surface effects start to dominate the magnetic behavior of individual nanoparticles⁶. Frenkel & Dorfman³ were the first to suggest that particles of ferromagnetic material below a critical particle size (less than 15 nm for common materials) would consist of magnetic monodomains, presenting a uniform magnetization state at any field.

The magnetic behavior of these particles above a certain temperature, the blocking temperature (T_B), is the same of the paramagnetic particles, except that a large magnetic moment and, consequently, susceptibility are presents. For biomedical applications, nanoparticles that exhibit superparamagnetic behavior at body temperature (T_B under the human's body temperature) are the most studied because of the absence of magnetic remanence and present a fast change in the magnetic state in the presence of an external magnetic field⁷.

Concerning the particles shape, ellipsoid-shaped nanoparticles (elongated) are more cytotoxic than those with spherical shape. The production of several inflammatory cytokines by human monocytes can be induced when ellipsoid-like nanoparticles are present inside the body. Moreover, the spherical nanoparticles are also more appropriate for drug transport and delivery into specific targets than other forms, such as hexagonal and cubic^{7,8}.

There are different methods for iron oxide nanoparticle syntheses described in the literature such as microemulsion; sol gel process and co-precipitation. Darbandi et al.⁹ described a method to synthesize iron oxide nanoparticles from a water/oil microemulsion, at room temperature. In this synthesis, the surfactant stabilizes the system and form a layer around the final nanoparticles. Roth et al.¹⁰ have studied the synthesis of nanoparticles by precipitation of iron salt precursors in alkaline medium, without using any surfactant agent as stabilizer. However, these methods do not allow a strict control of particle size. In this context, synthesis have been sonochemically assisted, since using ultrasound it is

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possible to change the reaction medium, allowing to achieve higher energy and pressure values in a lower time interval (acoustic cavitation)^{11,12}. Another wet chemical route is the homogenous coprecipitation by using urea decomposition, at 80°C, which results in a gradual rise in pH, keeping the alkaline medium and thus allowing co-precipitation at higher temperatures¹³.

The aims of this works were to prepare magnetic iron oxide nanoparticles by homogeneous coprecipitation method sonochemically assisted and to evaluate the influence of ultrasound power during synthesis. The main scientific contribution of this work was to obtain iron oxide nanoparticles at pH around 6.

2. Material and Methods

The synthesis by homogeneous coprecipitation was performed by mixing a 0.01 mol.L⁻¹ ferrous chloride precursor solution with 2,0 mol.L⁻¹ urea, using different ultrasound amplitudes in which sample. Three samples were made: C_50, with 50% of amplitude; C_60, with 60% of amplitude; and C_70, with 70% of amplitude.

During the synthesis, the reaction medium was heated and stirred at 80°C, which correspond to the urea decomposition temperature. When temperature reached 80°C, the ultrasonic power was instantly turned on and the nucleation process has started, as observed by the changes in the color of the solution (Figure 1). After one hour, the ultrasound was turn off and the precipitated was washed several times with distilled water. All samples were dried in ovens and analyzed by X-ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM) in order to evaluate its crystalline phases and morphology, respectively.

3. Results and Discussions

Figure 2 present the graph of pH changes in functions of the temperature for samples C_70, C_60 and C_50. As it can be observed, as temperatures increase the pH decrease until a inflection point at 67°C, 72°C and 75°C, for samples C_70, C_60 and C_50, respectively; after that the pH sharply increased up to 6.2. When water is irradiated with ionizing radiation, the initial radical species generated are hydrated electrons, hydrogen atoms and hydroxyl radicals, and the initial molecular species formed are hydrogen and hydrogen peroxide¹³. The H₂O₂ formed will cause the decrease in pH and its concentration will depends on the ultrasound power. As observed in figure 1, the higher the amplitude, shorter the

pH before curve inflection. It can also be observed that for short amplitude the pH start increasing near 80°C, where the urea decompositions take place. As it will be discussed latter, the short ultrasound amplitude allows the syntheses of pure magnetite. The pH curve presents an abrupt decrease from 80°C to 82°C, corresponding to the Magnetite precipitation.

Figure 3 presents the X-ray powder diffraction for samples. As observed from de Bragg Peak Position of the standard PDF file, pure magnetite phase was formed when using ferrous chloride in the urea homogenous precipitation assisted with lower energy ultrasound, suggesting different reaction mechanisms with the counterions and free radicals in solution produced by the cavitation effect. Using XRD data and Scherrer's equation the crystallite sizes was calculated for samples obtained from ferrous chloride precipitation (Table 1).

The difference in the crystallite size may be occurring due to a possible growth of goethite at surface of oxidized magnetite or as isolated goethite particles, as it will be seen later in the scanning electron microscopy figures.

Fe²⁺ + The chemical reaction media used here to synthesizes iron oxide magnetic nanoparticles, has propitiated an environment very similar to those used for Sono-Fenton process¹⁴. Fenton process, consist of a mixture of ferrous ion and hydrogen peroxide generating hydroxyl radicals (OH•) at room temperature as described by Walling et al.¹⁵. When Fenton reagents, Fe²⁺/H₂O₂, are coupled with ultrasound, active hydroxyl radicals will be generated¹⁶ followings the sonochemistry reactions described below, which will to produce the intermediate complex (Fe-O₂H²⁺):

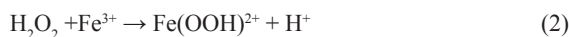


Table 1. Results of the Scherrer's Equation.

Samples	B (°)	2θ _B (°)	D (nm)
C_50	0.27	35.59	36.171
C_60	0.26	35.29	37.422
C_70	0.28	35.62	34.89

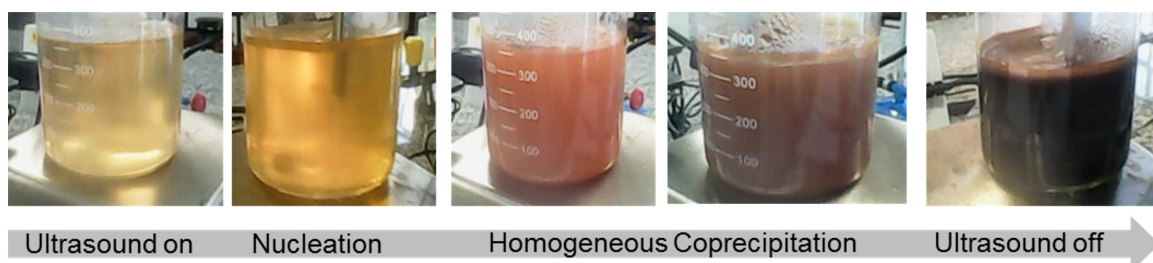


Figure 1. Changes in the solution color during ultrasonic cavitation: nucleation and homogeneous coprecipitation.

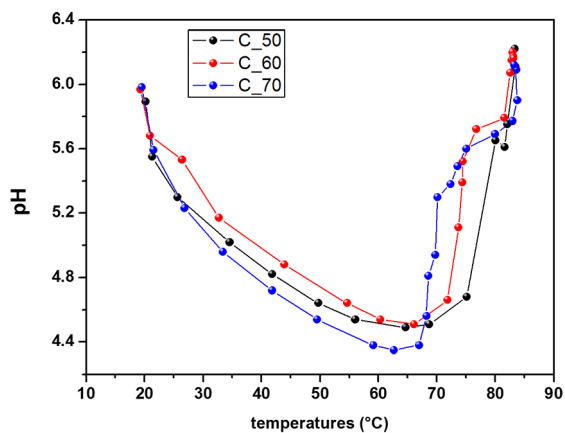
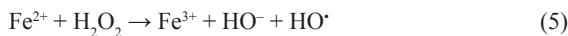
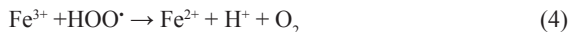


Figure 2. pH variation as a functions of the temperature for samples C_50, C_60 and C_70.

In Fenton process, the rate of reaction between H_2O_2 and Fe^{2+} increases with an increase in temperature leading to formation of more number of hydroxyl radicals, which in turn results in enhanced degradation efficiency¹⁷. However, for higher amplitude ultrasound at $\text{pH} > 4$, the formation of Fe (II) complexes reduces the generation of free radicals and also regeneration of ferrous ion will gets inhibited by the precipitation of ferric oxyhydroxides¹⁸. Since iron ions can oxidize in the presence of oxygen, it may have formed goethite around the magnetite (creating a nucleus of magnetite involved in a goethite layer), which helps the generation of larger nanoparticles than it was expected. It can be considered that the reaction medium became more oxidant in the presence of the species produced in sonolysis, causing the formation of goethite.

Figure 4 presents the SEM morphology images analysis of the samples C_50 (a, d); C_60 (b, e) and C_70 (c, f). As it can be observed, sample C_50 (Figure 4d) present rounded-like shaped particles with lower aggregation than those particles obtained using higher ultrasound amplitude (Figure 4e, f). Samples obtained using higher amplitudes, as observed in XRD, present goethite and magnetite phases. The elongated particles observed in samples C_60 and C_70 are characteristic of goethite.

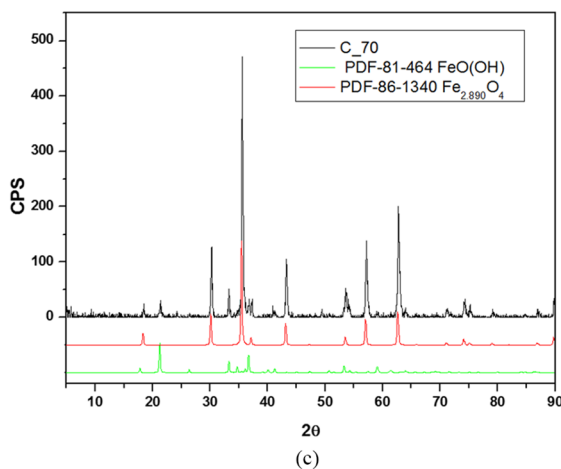
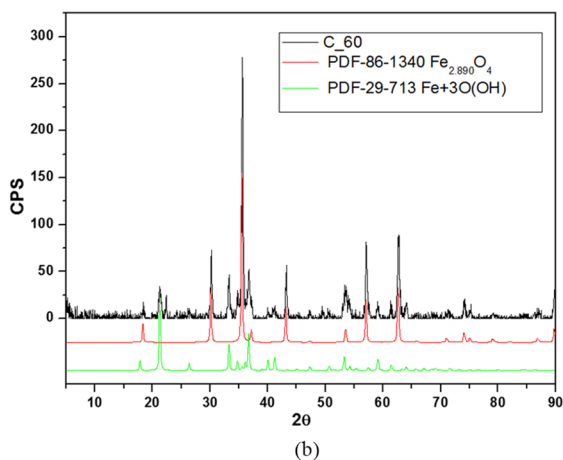
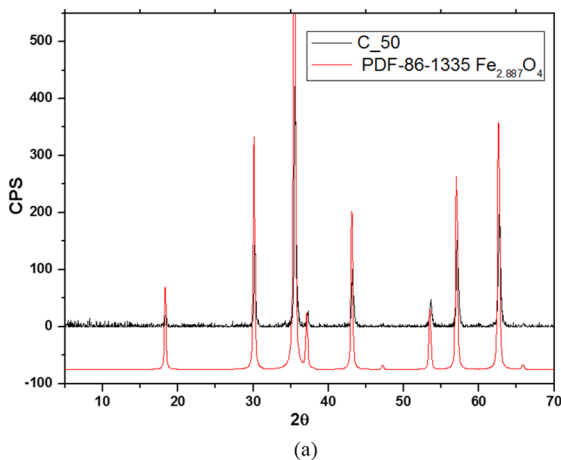


Figure 3. XRD pattern of the samples: (a) C_50; (b) C_60 and (c) C_70.

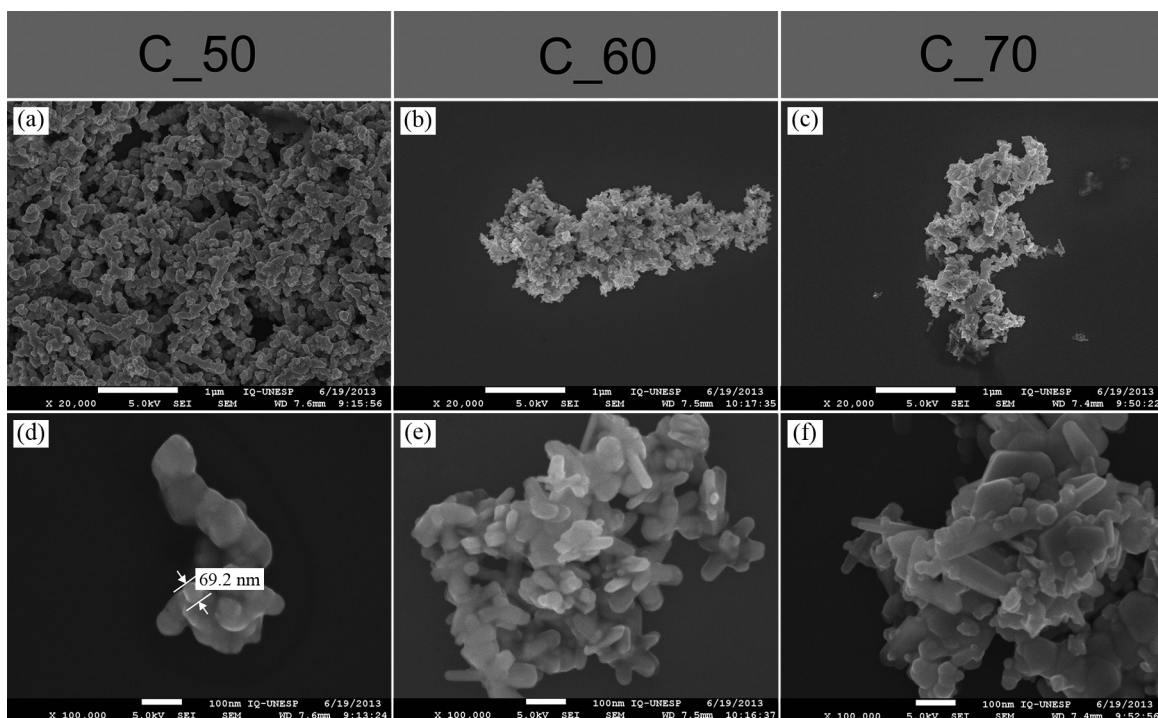


Figure 4. SEM images of the samples: C_50 (a, d); C_60 (b, e) and C_70 (c, f). Scale Bars: (a), (b) and (c) is 1 μm ; (d), (e) and (f) is 100 nm.

4. Conclusions

Iron oxide nanoparticles were obtained by sonochemically assisted homogeneous coprecipitation. Samples obtained from iron chloride(II) solutions showed a magnetite phase with crystallite size inversely proportional to the percentage of amplitude applied. The higher the energy dissipated in the reaction medium higher is the number of nuclei formed, leading to formation of precipitates with a smaller particle size. This behavior suggests that the ultrasonic energy accelerates the reactions. It is expected that this acceleration can interrupt the growth of particles, thus creating smaller diameter nanoparticles by applying a higher

power. Sono-Fenton process can be addressed to explain the pH variation during the reaction, creating a chemical environment for nanoparticle synthesis. Nevertheless, the sharply rise in pH due to homogenous coprecipitation through urea decomposition at $\sim 80^\circ\text{C}$, allow its magnetite synthesis at pH ~ 6.2 . Usually, magnetic iron oxides are formed at pH higher than 9.

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References

- Santos FF. A encruzilhada da nanotecnologia: inovacao, tecnologia e riscos. *Revista de Administração Contemporânea*. 2010; 14(5):983-985.
- Figuerola A, Di Corato R, Manna L and Pellegrino T. From iron oxide nanoparticles towards advanced iron-based inorganic materials designed for biomedical applications. *Pharmacological Research*. 2010; 62(2):126-143.
- Frenkel J and Dorfman J. Spontaneous and Induced magnetisation in ferromagnetic bodies. *Nature*. 1930; 126(3173):274-275. <http://dx.doi.org/10.1038/126274a0>.
- Hannickel A. *Estudo de nanoparticulas de magnetita obtidas pelos métodos de coprecipitação, biossíntese e moagem*. [Dissertation]. Rio de Janeiro: Instituto Militar de Engenharia; 2011.
- Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, et al. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chemical Reviews*. 2008; 108(6):2064-2110.
- Barros VB and Villaescusa VG. Puntos cuanticos: nueva aportacion de la nanotecnologia en investigacion y medicina. *Revista Complutense de Ciencias Veterinarias*. 2011; 5(1):69-102.
- Ribeiro GAP. As propriedades magnéticas da matéria: um primeiro contato. *Revista Brasileira de Ensino de Física*. 2000; 22(3):299-305.
- Salata OV. Applications of nanoparticles in biology and medicine. *Journal of Nanobiotechnology*. 2004; 2(1):3. <http://dx.doi.org/10.1186/1477-3155-2-3>. PMID:15119954.
- Darbandi M, Stromberg F, Landers J, Reckers N, Sanyal B, Keune W, et al. Nanoscale size effect on surface spin canting in iron oxide nanoparticles synthesized by the microemulsion method. *Journal of Physics D: Applied Physics*. 2012; 45(19):1-11.
- Roth H-C, Schwaminger SP, Schindler M, Wagner FE and Berensmeier S. Influencing factors in the CO-precipitation

- process of superparamagnetic iron oxide nano particles: a model based study. *Journal of Magnetism and Magnetic Materials*. 2014; 377:81-89.
11. Reyman D, Serrano R and Garcia-Leis A. Sonochemical synthesis of iron oxide nanoparticles loaded with folate and cisplatin: effect of ultrasonic frequency. *Ultrasonics Sonochemistry*. 2015; 23:391-398.
 12. Kolytyn Y, Cao X, Prozorov R, Balogh J, Kaptas D and Gedanken A. Sonochemical synthesis of iron nitride nanoparticles. *Journal of Materials Chemistry*. 1997; 7(12):2453-2456.
 13. Riesz P, Berdahl D and Christman CL. Free radical generation by ultrasound in aqueous and nonaqueous solutions. *Environmental Health Perspectives*. 1985; 64:233-252.
 14. Wang N, Zhu L, Wang D, Wang M, Lin Z and Tang H. Sono-assisted preparation of highly-efficient peroxidase-like Fe₃O₄ magnetic nanoparticles for catalytic removal of organic pollutants with H₂O₂. *Ultrasonics Sonochemistry*. 2010; 17(3):526-533. <http://dx.doi.org/10.1016/j.ultsonch.2009.11.001>. PMID:19945901.
 15. Walling C. Fenton's reagent revisited. *Accounts of Chemical Research*. 1975; 8(4):125-131. <http://dx.doi.org/10.1021/ar50088a003>.
 16. Pang YL, Abdullah AZ and Bhatia S. Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. *Desalination*. 2011; 277(1-3):1-14. <http://dx.doi.org/10.1016/j.desal.2011.04.049>.
 17. Chakinala AG, Gogate PR, Burgess AE and Bremner DH. Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing. *Chemical Engineering Journal*. 2009; 152(2-3):498-502. <http://dx.doi.org/10.1016/j.cej.2009.05.018>.
 18. Bagal MV, Gogate PR. Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. *Ultrasonics Sonochemistry*. 2014; 21(1):1-14. <http://dx.doi.org/10.1016/j.ultsonch.2013.07.009>. PMID:23968578.