

Tunneling the size of iron oxide NPs using different alcohols and proportions water-alcohol

F.L. Rivera, J. Sanchez-Marcos, N. Menendez, P. Herrasti* and E. Mazarío**

Universidad Autónoma de Madrid, Facultad de Ciencias, Departamento de Química Física Aplicada, 28049 Madrid, Spain

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Abstract. In this work the properties of iron oxide magnetic nanoparticles (MNPs) synthesized by electrochemical method using different water-alcohol proportions and alcohols have been investigated. The syntheses were carried out using 99% iron foils acting electrodes in a 0.04 M NaCl solutions at room temperature applying 22 mAcm^{-2} on the working electrode, mostly obtaining magnetite nanoparticles. The impact of the electrolyte in the size of the synthesized MNPs has been evaluated by transmission electron microscopy (TEM), X-ray diffraction (XRD), chronopotentiometric studies, and magnetic characterization. The results have shown that nanoparticles can be obtained in the range of 6 to 26 nm depending on the type of alcohol and the proportions in the mixture of water-alcohol. The same trend has been observed for all alcohols. As the proportion of these in the medium increases, the nanoparticles obtained are smaller in size. This trend is maintained until a certain proportion of alcohol: 50% for methanol, and 60% for the rest of alcohols, proportions where obtaining a single phase of magnetite is not favored.

Keywords: electrochemical synthesis; magnetic nanoparticle; conductivity; alcohol mixture; electrolyte

1. Introduction

Magnetic nanoparticles (MNPs) have attracted special attention in the scientific field in recent years due their specific properties, Hughes (2000). They show remarkable superparamagnetism, high field irreversibility, high saturation field, extra anisotropy contributions or shifted loops after field cooling, Tartaj *et al.* (2003). Magnetite nanoparticles (Fe_3O_4) is being widely used for several applications, such as biomedical Gao *et al.* (2009), water decontamination, Mazarío *et al.* (2019) and catalysis Gawande *et al.* (2013), among others. An important challenge for the synthesis and application of these materials is to control the nanoparticle size, aggregation state, and the morphology of the particles in order to preserve their functionality. In most of the cases, the synthesis method used is the responsible of the clearance of the material properties. Even though, the synthesis methods have been improved in the last years, ensuring particle size and its distribution are still problems that need to be solved. The most widely used aqueous synthetic routes are the production of iron oxide via Fe^{2+} and Fe^{3+} co-precipitation. It has being settle down, the role of the initial parameters in the final shape and size of the nanoparticles by this synthesis route. Where, the size and morphology of the MNPs is controlled by adjusting the pH, reaction temperature and the ionic species concentration ratio, Butt

and Jafri (2015). Despite this control, this method gives a wide distribution of sizes (Fang *et al.* 2012). Thermal decomposition and hydrothermal method are also used to produce MNPs with controlled size and morphology. Although these methods are commonly used to synthesized Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite), they require complicated processes and high temperatures, Han *et al.* (2016).

The oxidation of iron foils immersed in an electrolytic medium via electrochemical method is another way to obtain precursor ions for the formation of iron oxides. The first mention of the electrochemical synthesis was suggested by Pascal *et al.* (1999), describing the synthesis of maghemite nanoparticles in organic media with a range of 3-8 nm, controlled by the current density applied through the electrodes. The reaction was processed in solutions of tetraoctylammonium bromide in N,N-dimethylformamide (DMF) and 5% of distilled water. This method describes the generation of metal cations in organic medium from a sacrificial anode and the anodic oxidation of water. Later on, Cabrera *et al.* (2008) published and upgrade version of the method and describes the synthesis of magnetite nanoparticles by the anodic dissolution of iron foils immersed in an aqueous ionic salt. Few years later, the mechanism that involves the electrochemical synthesis was described, (Lozano *et al.* 2017). The advantages of aqueous electrochemical synthesis compared with the co-precipitation method are that the nanoparticle size can be controlled by changing the applied current, the distance between electrodes, temperature and the aqueous medium. It is also possible to control the production by increasing the electrodes area, varying the applied current or a combination of both, Cabrera *et al.* (2008). Recently, a 3D-printed prototype of an electrochemical flow cell for the

*Corresponding author, Professor,
E-mail: pilar.herrasti@uam.es

**Co-corresponding author, Ph.D.,
E-mail: eva.mazario@uam.es

synthesis of superparamagnetic magnetite nanoparticles of medium size between 15 and 30 nm was constructed by (Lozano *et al.* 2018) and improved the production rate by a factor of six compared with the standard synthesis.

Another important parameter, but less explored is the effect of the presence of alcohol in the electrolytic media. It has already described that the electrochemically synthesized magnetite in aqueous solutions gives larger nanoparticles with a lesser narrow size distribution in comparison with a mixture water-ethanol media, Starowicz *et al.* (2011), (Karimzadeh *et al.* 2016a). Therefore, solvent content is described as an important parameter that influences in the nucleation and growth of the MNPs. The solubility of oxygen and ions could be affected by changing the solvent. A mixture of ethanol and water can reduce the solubility of the Fe^{3+} and Fe^{2+} and oxygen influencing in the growth and aggregation of magnetite nanoparticles. Dang *et al.* (2009) produced magnetite nanoparticles with a narrow size distribution sonochemically synthesized in a water-ethanol mixture. Marín *et al.* (2014), obtained magnetite nanoparticles with a size between 8-10 nanometers by electro-oxidation of a steel bar using $(\text{CH}_3)_4\text{NCl}$ and NaCl both in a water/alcohol mixture. They found that ethanol induces low particle size and reduction currents. They also observed that the presence of ethanol in the electrolyte avoids agglomeration of the nanoparticles. Recently, Starowicz *et al.* (2011), described the electrochemical synthesis of magnetic nanoparticles in LiCl solution in the presence of ethanol and water. The average size of the rounded shape nanoparticles (5-40 nm) were adjusted through water ethanol ratio.

The aim of this work is to amplify the study of the effect of the alcohol content in the size distribution of the magnetite nanoparticles synthesized via electrochemical method using not only ethanol mixture but also different long chain alcohols and proportions. This article describes the effect of the organic solvents used, triggered in the size and crystallinity of the magnetic nanoparticles obtained. This new process is carried out in 0.04 M NaCl solution in a mixture of water-alcohol, where the content of alcohol was varied in the range 0-70%. Four different alcohols (Methanol, Ethanol, 1-Propanol and 2-Propanol) have been used.

2. Materials and methods

2.1 Electrochemical synthesis

The reagents used in the experiments were NaCl , Methanol, Ethanol, 1-Propanol, and 2-Propanol, all 99.5%, Panreac and distilled water. Iron foil was purchased in Goodfellow (99.999%). The synthesis process was carried out in a solution of 0.04 M of NaCl in a mixture of water alcohol ($\text{H}_2\text{O} = 100\% - X$), ($\text{Alcohol} = X$), where X is equal to ($X = 10, 20, 30, 40, 50, 60$ and 70%) in a final volume of 100 mL. The electrochemical process was conducted in an open glass cell. The counter electrode was an iron foil and a working electrode was a 2.25 cm^2 iron foil. The current applied to the working electrode was 22 mAcm^{-2} . The syntheses were performed at 25°C during a

period of 60 minutes under constant stirring. The samples were collected and washed several times with distilled water and centrifuged at 8000 rpm for 15 min. The washed sample was dried overnight at 60°C in a vacuum oven, for further characterization.

2.2 Electrochemical characterization

Chronopotentiometric studies were performed simultaneously to the nanoparticle synthesis, applying the same current density, (22 mAcm^{-2}) in a period of 60 minutes for the different water-alcohol proportions. In these cases, a reference electrode of Ag/ClAg was used in order to record the potential as a function of synthesis time. A potentiostat/galvanostat Autolab (model PGSTAT302N) has been used.

2.3 Sample characterization

In order to corroborate the MNPs structure X-ray diffraction experiments were recorded between 15° and $80^\circ 2\theta$, at a 0.04 scan step using an X-pert PRO Theta/2Theta diffractometer, equipped with a secondary monochromator, and a $\text{CuK}\alpha$ radiation source. The data were refined by means of the Fullprof suite based on the Rietveld method. The refined parameters included scale factors, background coefficients, peak width and profile parameters (Thompson-Cox-Hastings) and cell dimensions, among others.

Transmission electron microscope (TEM) studies were conducted with a JEOL JEM 1010 operating at acceleration voltage of 100 kV. The size and size distributions (through the distribution width parameter σ) were obtained using with the open source ImageJ software, using TEM images and counting at least 300 nanoparticles ISO13322-1.

Magnetic characterization was performed on dried powder using a vibrating sample magnetometer (VSM; MLVSM9 MagLab 9T, Oxford Instruments). Magnetization curves with a maximum applied field of 3 T have been measured at 290 K. The saturation magnetization (M_s) was achieved by fitting the values of magnetization to the inverse of the magnetic field.

3. Results and discussion

The electrochemical formation mechanism of magnetite nanoparticles in aqueous solution has been previously reported by different authors, for example (Lozano *et al.* 2017), described a correlation between the species present in the reaction and the pH of the solution that was monitored along the synthesis time in the proximities of the surface electrodes. The pH in the bulk solution at time 0 is around 7, as soon as a current density is applied, the pH value close to the anode dropped to 4 due to the generation of H^+ and the pH value in the proximities to cathode raised to 9.5 due to OH^- generation during H_2 evolution from water reduction. Six minutes later a sudden increase in pH was recorded near both electrodes, around this period the precipitation of magnetite takes place. Afterwards, the pH reached a plateau and then decrease with the time. These facts, were explained by the following reaction mechanism: an oxidation in the anode ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$) followed by

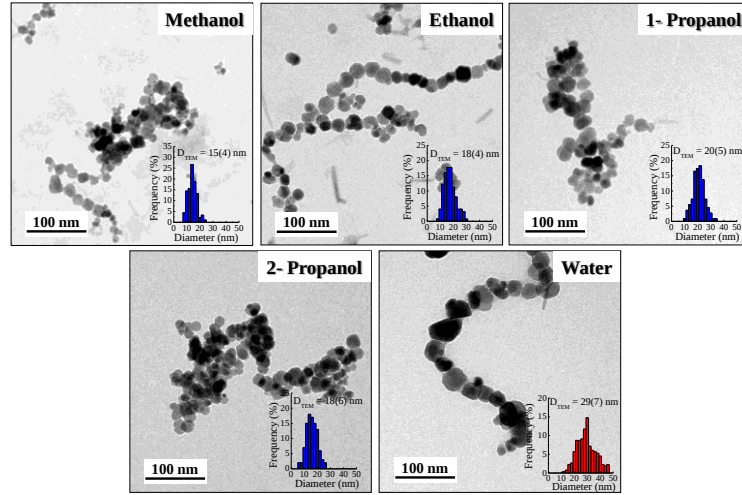
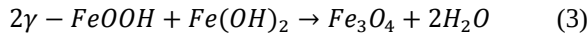
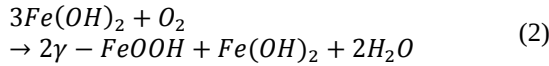
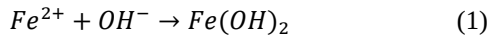


Fig. 1 TEM images and nanoparticle size distribution obtained for a 20% alcohol proportion

the water reduction in the cathode, ($2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$), while the recombination of these products takes place in solution, Eqs. (1)-(3).



Other very recent studies, Montoya *et al.* (2017) have shown through Raman spectroscopy that the mechanism of magnetite formation is the one described, although the authors identify an intermediate product in the oxidation of $Fe(OH)_2$, the green rust ($GR(Cl^-)$) that is later transformed into lepidocrocite (γ - $FeOOH$). The redox reaction between $Fe(OH)_2$ and (γ - $FeOOH$) results in the formation of (γ - $FeOOH$) $_2$ $FeOH^+$ and finally the precipitation of Fe_3O_4 .

Some authors, who have studied the electrosynthesis of magnetite in mixtures of water and ethanol, Dang *et al.* (2009), Marín *et al.* (2014), (Karimzadeh *et al.* 2016b) have concluded that the presence of ethanol in the electrolyte does not modify the mechanism of magnetite formation, but the presence of alcohol may acts as an impurity affecting the solute/solvent interaction and therefore, surface characteristics of samples prepared in water and those prepared in the presence of alcohol are expected to be different. Therefore, the purpose of this work is not to discuss the mechanism of magnetite formation in water-alcohol mixtures, but to analyze the structural, morphological and magnetic changes of the nanoparticles obtained in these media, both varying the type of alcohol and its composition in the mixture.

3.1 Effect of chain longitude of the alcohol in the synthetic process

In the electrochemical synthesis process, it is expected that the conductivity and the dielectric constant of the medium, among other factors, will affect the electrochemical process. For this reason, it would be expected that

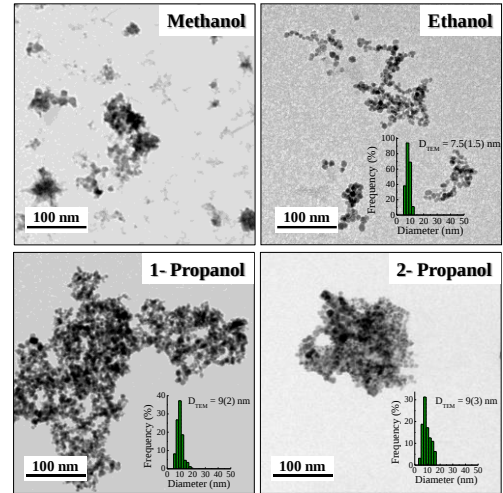


Fig. 2 TEM images and nanoparticle size distribution obtained for a 50% alcohol proportion

at least when the alcohol content is low, the characteristics of the electrosynthesized Fe_3O_4 nanoparticles were similar to those obtained in aqueous solution, as the alcohol physicochemical properties also do. However, as shown in the TEM images of Fig. 1, when nanoparticles are electrosynthesized in a 20% alcohol proportion of methanol, ethanol, 1-propanol or 2-propanol respectively, the particle sizes distribution obtained in all cases are very similar, (15(4), 18(4), 20(5), 18(6) nm, although smaller than those obtained under the same conditions only in water (29(7)nm).

When the percentage of alcohols increases in the medium up to values of 50%, the response is similar (Fig. 2), showing a more noticeable decrease in size. Some characteristics parameters of the samples synthesized in 50% media are summarized in Table 1.

The decrease in particle size compared to those obtained in water solution is significant with any of the alcohols used in the electrolyte solution probably due to the extent the lifetime of some precursors during the electrosynthesis that promotes the formation of low size magnetite nanoparticles,

Table 1 Some characteristic properties extracted from TEM, XRD and VSM analyses when the synthesis is carried out in 50% of alcohol

Samples 50% Alcohol	TEM _{diameter} (nm)	Crystal size (nm)	Lattice Parameter (Å)	M _s (emu g ⁻¹)
Methanol	< 7.5	10(1)	8.383(1)	16
Ethanol	7.5	7.4(1)	8.386(2)	61
1-Propanol	9	8.7(1)	8.376(1)	70
2-Propanol	9	7.7(1)	8.373(2)	65
Water	29(7)	30(1)	8.394(1)	80

Table 2 Physical properties of the different solvents used

	Water	Methanol	Ethanol	1-propanol	2-propanol
Density (gmL ⁻¹)	1	0.789	0.792	0.803	0.786
Viscosity (mPa.s)	0.89	0.54	1.20	1.96	1.96
Dipole moment (D)	1.85	1.69	1.69	1.68	1.66
Dielectric constant	80.3	33	24.5	20.2	18
Conductivity (50:50) (mScm ⁻¹)	4.42	2.45	1.57	1.51	1.34

Table 1.

The presence of alcohol in the media decreases the solvent dielectric constant leading to a reduction of the critical radius of the particles during nucleation, Chen and Chang (2004). It affects the crystal growth rate by influencing the surface entropy factor increasing it. Therefore, the final size of the nanoparticles formed is dependent on the nature and composition of the solvent, implying nucleation and growth of particles are strongly dependent on the solvent ratio. This effect is observed for all alcohols employed but is greater in the case of methanol. With this alcohol, it is necessary to take into account the effect of the viscosity of the medium, a factor that also affects the interaction between solute and solvent, Table 2.

Due to the low viscosity of this medium compared to the other alcohols studied, the interaction between methanol and the magnetite nanoparticles will be greater. In addition, the mechanisms mentioned previously for the formation of magnetite nanoparticles, demonstrate the existence of intermediate species in the formation of this compound, whose interaction with solvent molecules will decisively affect the nucleation and growth processes that occur during the generation of nanoparticles. It would be clear that in the case of methanol exists a greater interaction with the nucleus formed and their growth is more retarded. This fact is shown in the X-Ray diffractograms, where only the methanol one, in the 50% proportion, shows impurities that it is not the case of the rest of alcohols where a unique phase with a space group Fd-3m is detected, Fig. 3.

The sharpness and intensity of the reflexions is an indication of the high crystallinity of the MNPs. The particles obtained in the different mixtures water-alcohol show an almost spherical shape, except in the case of methanol where also some impurities can be observed, Fig. 2. These impurities are due to the formation of γ -FeOOH, this compound is the precursor of the magnetite in the mechanism proposed by (Lozano *et al.* 2017) and one of the intermedium proposed by Montoya *et al.* (2017). As we

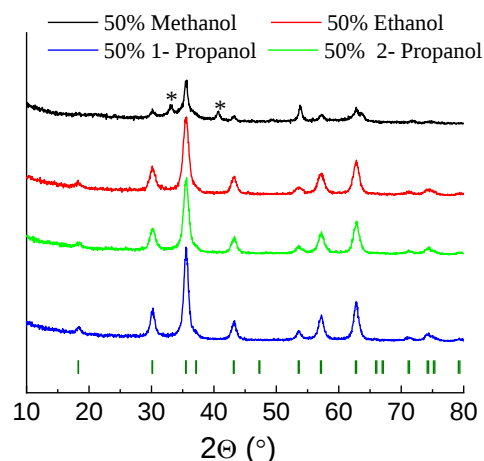


Fig. 3 XRD diffractograms of samples synthesized in an electrolytic medium with 50% of alcohol proportion. Vertical marks (|) Bragg positions of space group Fd-3m. (*) indicted the FeOOH peaks

have previously indicated the lower viscosity value of the water-methanol mixture produces a quickly generation of lepidocrocite and this excess cannot react with enough $\text{Fe}(\text{OH})_2$ to form magnetite. The rest of the water-alcohol 50% mixtures studied present in all cases, a unique phase of magnetite, (Fig. 3) and nanoparticles with rounded shape, (Fig. 2). From these results it could be conclude that the length of the alcohol chain used affects both the conductivity of the solution and the size of the nanoparticles obtained, so the use of different alcohol can tunnel that size varying between 20 to 7 nm depending of the type and proportion of alcohol. The unusual behavior of the methanol medium is also reflected in the magnetic properties. Fig. 4 shows the magnetic behavior of the magnetite obtained in the different 50% water-alcohol media. It can be observed how the presence of FeOOH obtained in the methanol mixture causes a decrease in

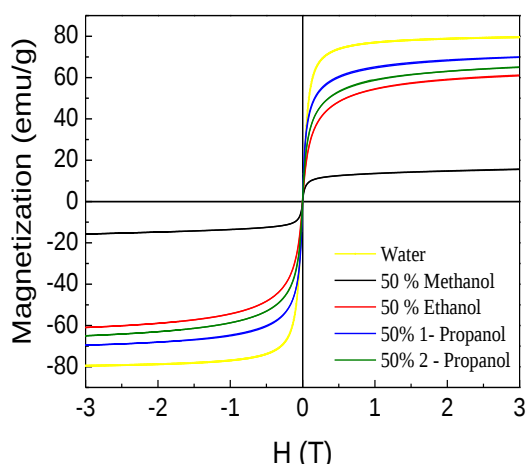


Fig. 4 Room temperature magnetization curves of iron oxide nanoparticles generated electrochemically in water and in several mixtures 50-50 water-alcohol

magnetization due to the non-magnetic character of this compound. The other materials show a behavior according to the size of the synthesized nanoparticles, the saturation magnetization values are summarized in Table 1.

3.2 Effect of the alcohol percentage content in the synthesis mixture: 1- propanol

To compare the results obtained for an alcohol at different percentages in water, 1-propanol has been chosen. Fig. 5, depicts TEM microscopy images of samples synthesized in an electrolytic solution of 1-propanol in a range from 10 to 70%. For comparison, image of nanoparticles synthesized in water solution was also

included. Quasispherical rounded shape nanoparticles were produced in all cases, Fig. 5.

From the analysis of the size obtained by TEM micrographs, it is easy to observe a decrease in the mean value and standard deviation among the MNPs synthesized with an increase in the alcohol percentage. The size of the smallest particles obtained at $X = 70\%$ could not be determined, where the presence of an acicular product is perfectly evident in the TEM micrograph. This product, as in the case of working with 50% of methanol is assigned to the intermediate lepidocrocite. Therefore, it is settled down that we are able to control the polydispersity and mean diameter of MNPs by controlling the 1-propanol percentage, from 10% till 60%. The same tendency was obtained in the case of methanol, ethanol and 2- propanol, but in these cases the impurities appeared at 50%, 60% and 60% percentage of alcohol, respectively.

The XRD patterns of samples synthesized in an electrolytic mixture of H_2O - 1-propanol in different proportions are visualized in Fig. 6(a). For comparison XRD diffractogram of sample synthesized in aqueous conditions is also depicted. The most important feature shows in the diffractograms are the reflexions attributed to a spinel cubic structure with space group (Fd-3m). There is not any contribution of foreign reflexions that could be assigned to the presence of impurities, except for the 70% of 1-propanol. There is an increase of the width of the reflexions with the increase of alcohol percentage in the electrolyte solution that are related with the crystalline size of the samples, Fig. 6(b). To confirm this fact, the Rietveld analysis was performed and the crystallite size and lattice parameter of the different samples were summarized in Table 3. The size variation in the magnetite crystals synthesized in different solvent proportions suggests

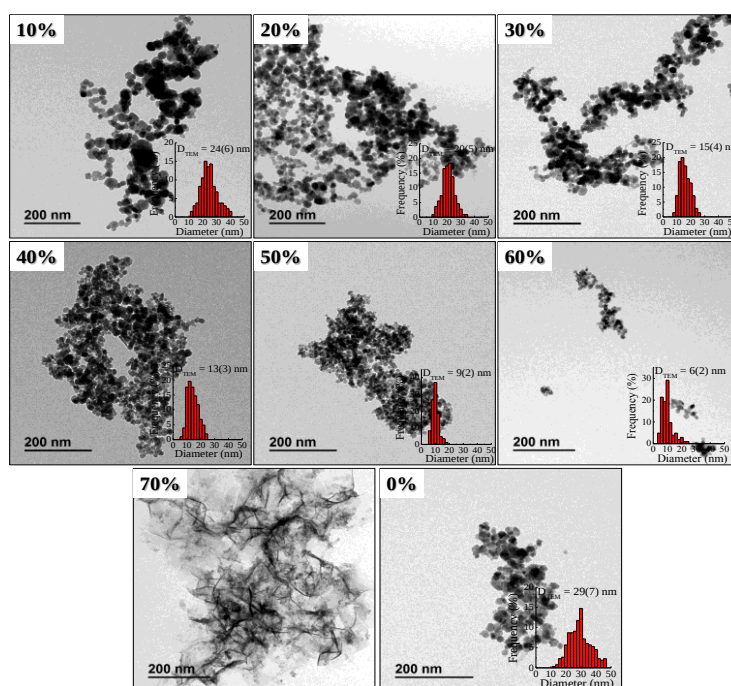
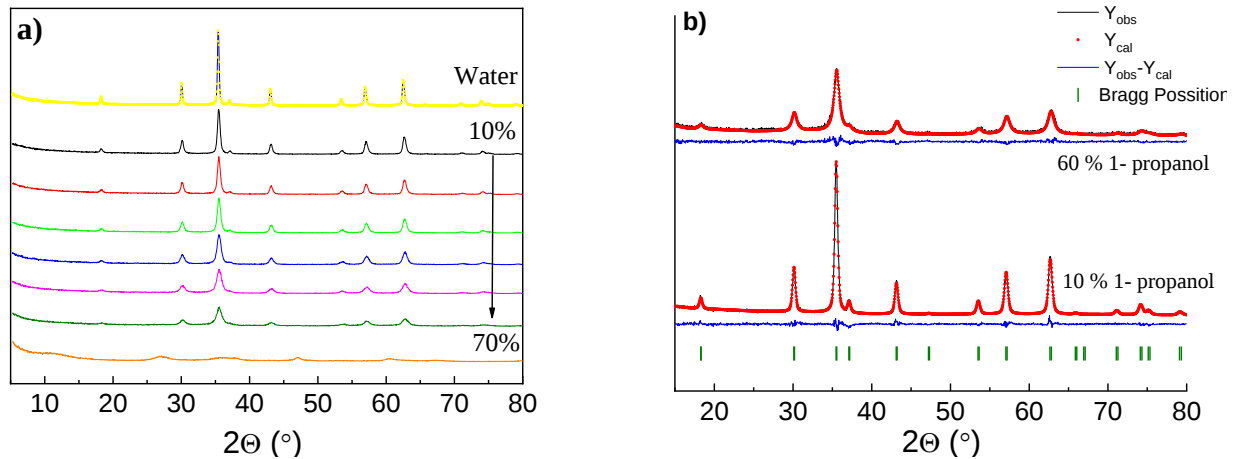


Fig. 5 TEM images of iron oxide nanoparticles generated electrochemically in water-1-Propanol under different volumetric proportions (v/v), where H_2O (100-X): 1-Propanol (X)



(a) XRD of iron oxide nanoparticles generated in Water-1-Propanol in alcohol volumetric proportions 10 to 70%

(b) Rietveld analysis of samples synthesized with 10 and 60% of 1-propanol

Fig. 6 X-ray diffractograms of iron oxide nanoparticles generated electrochemically in Water-1-Propanol under different volumetric proportions (v/v), where H₂O (100-X): 1-Propanol (X). b)

Table 3 Resume of some of the values obtained in Rietveld analysis, TEM microscopy and magnetic characterization

Sample 1-Propanol	TEM _{diameter} (nm)	Crystal size (nm)	Lattice parameter (Å)	M _s (emu g ⁻¹)	σ (mS/cm)
0%	29(7)	30(1)	8.394(1)	80	4.22
10%	24 (6)	22(1)	8.378(1)	79	3.54
20%	20 (5)	18(1)	8.376(1)	75	2.76
30%	15 (4)	15(1)	8.374(1)	73	2.27
40%	13 (3)	11(1)	8.370(2)	72	1.90
50%	9 (2)	8.8(1.5)	8.368(2)	70	1.51
60%	6(2)	7.9(1.5)	8.367(2)	62	1.21

a strong dependence of the crystal growth with the conductivity of the medium (Table 3).

Fig. 7, shows the hysteresis loops, measured at room temperature (290K), of samples synthesized from 0% till 70% showing a S-type loops and zero coercivity field values characteristic of superparamagnetic behaviour. A comparison of the saturation magnetization of the different samples is reported in Table 3. The M_s values obtained are slightly lower than the reported value for bulk magnetite (80 emu g⁻¹), and decrease with the increase of the percentage of 1-propanol in the media. This decrease could be related with the appearance of spin canting, surface death layer or spin frustration as a result of the decrease in the particle size (Negi *et al.* 2017). This effect would become dominant with decreasing particle size (Mørup *et al.* 2013). In sample 70% of 1-propanol the value of M_s is about 2 emu g⁻¹, indicating that the powder obtained under this conditions has apparently not magnetic behaviour. TEM also confirms the main presence of acicular shaped compounds, such as FeOOH that are not magnetic iron oxide compounds (Hirt *et al.* 2002).

In order to understand and differentiate the role of the water-alcohol mixture in the formation of MNPs, the evolution of the potential vs time was recorded during

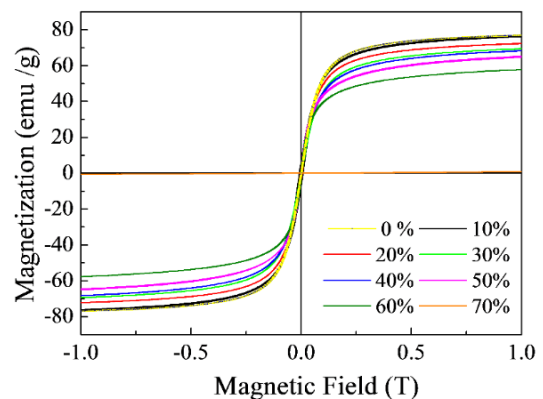


Fig. 7 Room temperature magnetization studies of iron oxide nanoparticles generated electrochemically in Water-1-Propanol under different volumetric proportions (v/v), where H₂O (100-X): 1-Propanol (X), X = 10, 20, 30, 40, 50, 60% and 70%.

galvanostatic synthesis for the different 1-propanol mixtures, for comparison the case of 100% of H₂O was also measured. Fig. 8 shows the variation of potential for different water-1-propanol solvents. The potential that pass

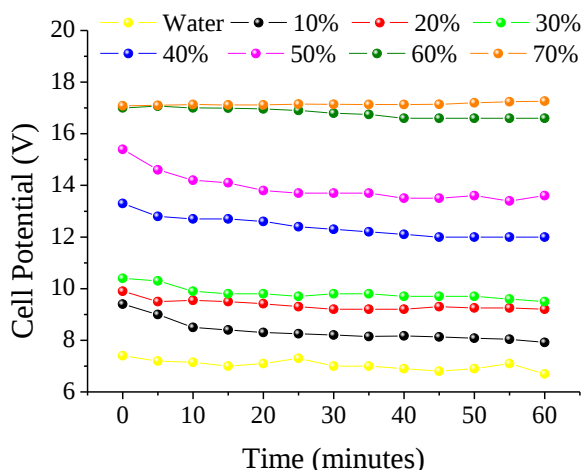


Fig. 8 Static measurement of the cell potential measured between anode and cathode vs time. Cases of electrochemical synthesis in different proportions of 1-propanol and 100% of water content %

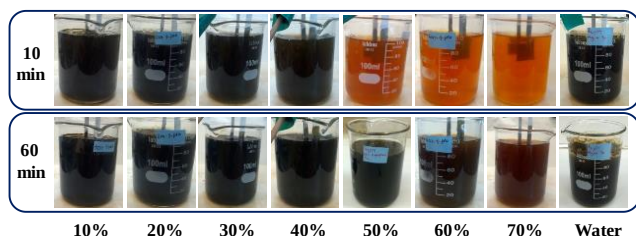


Fig. 9 Color evolution of the synthesis as a function of the % alcohol for a fixed time of 10 minutes and 60 minutes in the case of 1-propanol, water images were added as a control

thought the electrodes during the syntheses in 100% aqueous solution is the lowest because of the high electric conductivity of the solution. As the percentage of 1-propanol increase the potential also does, because of the increase of the resistance of the electrolytic solution, reaching a value of about 17 V in cases 60 and 70% of 1-propanol. As higher is the contribution of alcohol in the media, higher is the electrical resistance suggesting that the alcohol directly affects the system by inducing a slow kinetic and therefore it would be more difficult the recombination of the intermediate products in the medium to form magnetite nanoparticles. In addition, when the alcohol concentration increases the conductivity in the solution decreases, and that is strongly related to the nucleation and growth of the MNPs, Thanh *et al.* (2014).

Fig. 9 shows the colour of the solution at a fixed time of 10 and 60 minutes for all the 1 – propanol percentages under study and also for water. Colour evolution of the synthesis with time supports this theory. It can be seen that the synthesis of MNPs with the highest content of alcohol are more retarded in comparison with the rest of alcoholic solutions and for the alcohol free electrolyte. Typically, synthesis mechanism exhibits several colour changes along the synthesis period, starting from yellow, then going to orange, grey and ending with the magnetite black colour.

The coloration gradient at a fixed time (10 min) is a clear indicator of the influence of the alcohol in the decrease of the synthesis rate and particle size. Fig. 9 describes a proportional increase to darkness colour when the content of alcohol decreases. This phenomenon is also related with a higher consumption of energy during the synthesis and as a consequence an increase in the potentiometric curves.

4. Conclusions

In this work, it could be observed that

- The size distribution of the Fe_3O_4 electrosynthesized nanoparticles can be controlled adjusting the water/alcohol proportion mixtures.
- We can also establish that the nucleation, monodispersibility and crystal growth can be modulated by using different alcohols and percentages of alcohol in a mixture water/alcohol.
- The proportion of any alcohol used can be tuned to obtain a specific size distribution, but only until certain amount of the organic solvent since a small water proportion compared to the alcohol does not give magnetite MNPs and we obtain mainly a product without magnetic properties.
- The length of the chain of the alcohol also plays an important role in the formation and growth of the MNPs due to the different conductivity and viscosity.
- The results of this work are expected to offer a way to synthesize MNPs with a narrow and specific size distribution modulating the type and amount of organic solvent used in the electrolytic media.

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