

STRUCTURAL AND VIBRATIONAL STUDIES OF FATTY ACIDS-FUNCTIONALIZED IRON OXIDE NANOPARTICLES VIA ALKALINE CO-PRECIPITATION ROUTE

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Abstract

The preparation and functionalization of iron oxide magnetic nanoparticles (MNPs) are of great importance in a diverse range of applications. However, their structural and magnetic properties can be influenced by the process of coating making these MNPs undesirable for certain applications. For that reason, this work is focused in the understanding of iron oxide nanoparticles functionalized with fatty functional lauric acid (LA) and oleic acid (OA) organic molecules. The synthesis was carried out using the aqueous alkaline co-precipitation route of Fe⁺² and Fe³⁺ salts. The characterization was done by several spectroscopy techniques. X-Ray Diffraction (XRD) measurements reveal uncoated iron oxide nanoparticles with mean diameter of 11.8 ± 2 nm obtained from Debye-Sherrer formula. The spinel crystal structure and lattice parameter was found to be 8.38 ± 0.01 Å which means that the stoichiometric structure is not affected by the functionalization process. This size decreased at around 9.7 ± 2 and 8.6 ± 2 nm for coated with OA and LA which are in agreement with Transmission Electron Microscopy (TEM) measurements. X-ray Photoelectron Spectroscopy (XPS) measurements determined that iron atoms have valences of +3 and +2, with a total ratio of iron atoms Fe⁺³: Fe⁺² of 2:1 which confirmed the stoichiometric relation used for magnetite (Fe₃O₄). Fourier Transform Infrared Spectroscopy (FTIR) measurements show that LA and OA-molecules are chemisorbed onto MNPs surface ascribed to bridging bidentate interaction. The thermal stability of the functional groups anchored to magnetite surface was studied by thermogravimetric analysis (TGA) at certain range of temperatures. From TGA measurements we calculate the number of functionalized molecules anchored to the surface of Fe₃O₄ nanoparticles. Micro-Raman spectroscopy was introduced to study the stabilization of organic molecules on MNPs surface.

Keywords: Iron oxide nanoparticles, magnetite, fatty acids, co-precipitation route

1. INTRODUCTION

The nanotechnology has developed to such an extent that it has become possible to fabricate, characterize and tailor the functional properties of magnetic nanoparticles including superparamagnetic iron oxide nanoparticles (SPIONS), in particular for high density magnetic recording media, non-enzymatic sensors for certain analytic reduction and clinical uses in diagnostics and in biomedical applications such as drug delivery, hyperthermia, magnetic resonance imaging (MRI), magnetofection, etc. [1-5]. The application of ultrafine iron oxide particles for in vitro diagnostics has been practiced for nearly 40 years [6] and in the last decade, increased investigations with several new forms of iron oxides have been carried out in the field of nanosized magnetic particles (mostly maghemite, γ -Fe₂O₃, or magnetite, Fe₃O₄, single domains of about 5-20 nm in diameter) [7].

On the other hand, quantum size effects and the large surface area of magnetic nanoparticles dramatically change some of the magnetic properties and exhibit superparamagnetic behaviour and a quantum tunnelling of magnetization, because each particle can be considered as a single magnetic domain [8]. Moreover, based on their unique mesoscopic chemical, physical, thermal, and mechanical properties, superparamagnetic



nanoparticles offer a high potential for several biomedical applications, as mentioned above. These particles combine properties of high magnetic saturation, biocompatibility and interactive functions at the surface. Besides, the surfaces of these particles could be modified through the creation of new atomic layers of organic polymer, surfactants or acid organic suitable for further functionalization by the attachment of various bioactive molecules [9]. Then, the superparamagnetic particles accumulate, e.g., in tumor tissue, they can play an important role in detection through Magnetic Resonance Imaging (MRI) or electron microscopic imaging to locate and measure binding or as drug carrier for certain anti-cancer drugs, they can also carry other activity compounds. It is remarkable that the most suitable form of magnetic nanoparticles for biomedical applications is ferrofluid and it should be biocompatible with certain dose limit. Ferrofluids are stable colloidal suspensions of magnetic nanoparticles in carrier liquid. For suspension stability, MNPs are usually made charged or coated with substances like surfactants or long chain polymers. The biocompatibility of surfactant/polymer coated magnetic fluids is determined by both the core magnetic materials and the coatings [10-11]. The ferrofluids own limited applications in biological field, i.e. in physiological buffer (pH > 7). The coating of long chain polymer molecules and/or other surfactants on SPIONS serves as protective layer on the nanoparticles and minimizes the direct exposure of the iron oxide surface to the biological environment. Several surfactant, polymer and organic molecules (citrate, polyaspertic acid, dextran, chitosan, carboxylates, siloxanes, sulfates, phosphonates and phosphates) coated iron oxide magnetic fluids have been tested for biocompatibility [12-14]. There is a variety of carboxylic acid coatings; they have been produced including oleic acid, folic acid and lauric acid [14]. For instance, Jadhav et al. implemented oleic acid coating Fe₃O₄ nanoparticles in tumor cells in order to study their interaction for hyperthermia applications [15]. Pradhan et al. studied the cellular interactions of lauric acid and dextran-coated magnetite nanoparticles [16].

This paper describes the preparation of water base ferrofluid of compositions coated with lauric acid (LA), oleic acid (OA) and without capping for comparison. The lauric acid (dodecanoic acid) and oleic acid ((9Z)-octadec-9-enoic acid) have been chosen for the stabilization of magnetic particles in aqueous-based magnetic fluids. The aim of this work is to synthesize, functionalize and characterize the structural and vibrational properties of MNPs after acid-coating. The analysis of the nanoparticles properties was done by XRD, TEM, FT-IR, XPS, TGA and micro-Raman spectroscopy.

2. MATERIALS AND METHODS

All the reagents were of analytical grade and used as received. The salts used for magnetic fluid synthesis were iron (II) chloride (FeCl₂.9H₂O), iron (III) chloride (FeCl₃. 9H₂O), lauric acid C₁₂H₂₄O₂), oleic acid (C₁₈H₃₄O₂) and NH₄OH. The chemicals were purchased from VETEC (iron (III) chloride and, oleic acid (OA), lauric acid (LA), ammonium hydroxide and ethanol) and Merck (iron (II) chloride). These were analytical grades (99.9 %) purity and used without further purification. Ultrapure water (Megapurity System®, resistivity of 18.3 M Ω cm) was used in all experiments.

Synthesis of uncoated and coated Fe₃O₄ nanoparticles with LA and OA (labelled as Fe₃O₄@OA and Fe₃O₄@LA) were prepared by co-precipitation in N₂ atmosphere to avoid quick oxidation of magnetite phase into maghemite [17-18]. For that, iron salts (FeCl₃. 9H₂O, FeCl₂.9H₂O - under Ar atmosphere 99 % purity) and NH₄OH (24 mL) were injected trough the solution turning it into a dark brown-black colour, typical of the magnetite phase formation.

The solution was washed and decanted using a magnet several times up to keep the pH \sim 7. Afterwards, solutions containing LA or OA in the 1:2:2 stoichiometric relations were added into a round-bottom flask containing 80 mL of distilled deoxygenated water and magnetic nanoparticles. After that the solutions were kept under stirring with N₂ for at least 30 min and heated to 80 °C.

XRD data were collected using a Bruker D8 equipment with Cu-K_{α} radiation (λ =1.54056 Å) in the range from 8 to 80 degrees, with a step of 0.05 degrees at room temperature (RT). We have used Crystallographic software to study the main diffraction peaks. Besides, the Materials Analysis Using Diffraction (MAUD, version 2.33) program was included to analyse the crystallographic parameters. For TEM measurements we employed



the Titan (200 kV) microscope equipped with a special high-brightness Schottky-field emission electron source. Infrared spectra of diluted samples were taken in a range of 4000 to 400 cm⁻¹ in a Shimadzu IRP restige-21 model. XPS measurements were performed by using SPECS equipment. For XPS fitting the CASA-XPS (2.316 DEV52 version) program was used. TGA measurements were carried out in a stationary air atmosphere (no purge) from room temperature up to 800 °C using a Linseis thermal analyser (Linseis, Germany). The heating rate was 5 °C/min. The powder samples were placed in cups of aluminium oxide. Raman spectra were taken by using HR800 Horiba Raman spectrometer. A grating with 600 grooves per mm⁻¹, a CCD detector cooling by air, and an Olympus BX-41 metallographic microscope attached to the spectrometer were employed. Raman spectra were collected in backscattering configuration, using a silicon wafer for the calibration. The fit of the micro-Raman spectra was done with Origin 8.0 software and the χ^2 was used as the numerical factor for a good fitting.

3. RESULTS AND DISCUSSIONS

TEM images (**Fig. 1a, b and c**) further confirm the quasi-spherical shape and uniformity of these particles coating with OA and LA which act as surfactant giving stability in aqueous medium. Our Fe₃O₄ nanoparticles tend to agglomerate in the presence of oleic acid coating. Nevertheless, agglomeration is often avoided by increasing the shell coating [19-20]. The highlighted different diameters for Fe₃O₄ coated with OA and LA are: 6.2 nm, 7.8, 9.3 and 8.4 nm. The mean grain size is 7.9 nm and 8.7 nm for Fe₃O₄@LA and OA, respectively. These values are closer to the obtained by the XRD measurements above (9.7 ± 2 and 8.6 ± 2 nm).In **Fig. 1d, e and f** we summarizes all the powder diffraction patterns. The diffractograms reveal only one phase associated to spinel cubic structure of Fe₃O₄. Also, Miller planes have been indexed using JCPDS file 19-0629. The broadened peaks observed are associated to nanoscopic size of the MNPs. XRD powder diffractogram of Fe₃O₄ nanoparticles in **Fig. 1d** exhibited broad peaks at $2\theta = 30.5$; 35.7; 43.4; 53.8; 57.6; 62.7; 71.2 and 74.6° .

The mean diameter $\langle D \rangle$ was calculated using Debye-Sherrer formula: $\langle D \rangle = \frac{k\lambda}{\beta \cos \theta}$, where λ is the wavelength

 $(\lambda = 1.54056 \text{ Å})$ and θ is the Bragg angle. Assuming a spherical shape the particle diameter is obtained by setting K = 0.916 when β is the full width at half maximum line breadth [17]. The mean diameter of the nanocrystallites of pure magnetite was 11.8 ± 2 nm. In addition, the average crystallite diameter for Fe₃O₄@OA and Fe₃O₄@LA were found to be very close at around 9.7 ± 2 and 8.6 ± 2 nm (see **Fig. 1e and f**). This means that the oleic and lauric acid surfactant agents act as dispersant and controlled the mean diameter of the crystallites during the nucleation process. The lattice parameter of Fe₃O₄, Fe₃O₄@OA and Fe₃O₄@LA nanoparticles was 8.38 ± 0.01 Å. Furthermore, not ferrihydrite, wüstite and hematite phases was regarded in the XRD patterns. Nevertheless, it is not possible to affirm the non-existence of γ -Fe₂O₃ phase because of their similar stoichiometric structure. This will be discussed later using XPS.It is also noteworthy that, the process of functionalization did not affect the structural identity of magnetite phase. This is an important factor because they need to be magnetic to be used in process such as drug-delivery or clinical trials using magnetic hyperthermia [2].

The adhesion of the organic functional groups to the surface of Fe₃O₄ was studied by FTIR spectroscopy, which is a crucial and mandatory technique to study MNPs functionalized with organic compounds. The bands observed in **Fig. 1g** at around 1092 cm⁻¹ is consistent with ethanol which remains as part of the surface due to the presence of the hydroxyl groups associated to v CH₂ vibration mode at around 2900 cm⁻¹. These peaks are observed even in pure magnetite sample obtained by co-precipitation route. In **Fig. 1g** the corresponding stretching modes to H-C-H for LA can be seen without difficulty. More exactly, the antisymmetric mode v_{as} CH₂ with 2918 cm⁻¹ and symmetric (v_s CH₂) with 2848 cm⁻¹ are regarded. Additionally, we can observe the region of the spectrum corresponding to v_{as} CH₃ and v_s CH₃ at 2955 and 2870 cm⁻¹, respectively. On the other hand, for oleic acid coating the MNPs in **Fig. 1h** we can see and additional peak shift to the red region in relation to CH₂ and CH₃ at 2955 and 2879 cm⁻¹. This could be related to v CH (H-C=C-H) or simply v CH(C=C) [21]. Worthy mentioning that the oleic and lauric acids present similar IR spectra, with the only difference in the double bound C=C presented in the ninth and tenth carbon of the chain H-C=C-H with four additional CH₂



terminations. The vibrations associated to v {as: s} CH₂ are also observed clearly for Fe₃O₄@LA and OA, but in less proportion respecting to pure magnetite. In addition, the vibration modes corresponding to v-CH₂ of LA and OA samples were not altered in relation to their corresponding organic pure compounds. For Fe₃O₄@OA and Fe₃O₄@LA, the vibrational mode corresponding to carbonyl C=O chains disappeared completely. Instead of that, two new vibrations appeared, with high broad line centred at 1633 and 1439 cm⁻¹, that corresponded to carboxylate symmetric (v_s COO⁻) and antisymmetric (v_{as} COO⁻) modes of vibration, respectively. The wavenumber separation, Δ , between the v_{as}(COO⁻) and v_s(COO⁻) IR bands can be employed to determine the kind of interaction between the carboxylate head and the metal atom. The largest Δ (200~320 cm⁻¹) is corresponding to the monodentate interaction and the smallest Δ (<110 cm⁻¹) is for the chelating bidentate.



Fig. 1 TEM pictures obtained for uncoated Fe₃O₄ (a) and coated with OA (b) and LA (c) with their respective electron diffraction pattern. Bar length of 50 nm and 100 nm, (d) schematic representation of the interaction of Fe₃O₄ with carboxylate chains of fatty acids. XRD powder patterns obtained for uncoated Fe₃O₄ (d) and coated with OA (e) and (f) LA. The crystallographic planes (hkl) are also indicated. FTIR spectrum for Fe₃O₄, pure LA and LA coating Fe₃O₄. (g) FTIR spectrum for pure OA and OA coating Fe₃O₄ (h)

The medium range Δ (140~190 cm⁻¹) is for bridging bidentate. In our study, Δ (1633-1439 = 194 cm⁻¹; 1624-1431 = 193 cm⁻¹) for OA and LA coating MNPs, respectively. This is ascribed to bridging bidentate coordination (**Fig. 1d**). So we assumed that in both cases carboxylate groups are chemisorbed onto the Fe₃O₄ nanoparticles (see **Fig. 1d**) and the oxygen atoms in the carboxylate are coordinated in a symmetric form in the nanoparticles surface forming a covalent bonding. This interaction was also observed in the case of Cobalt nanoparticles by Wu *et al* [21, 22]. From the low wavenumber region (1000 to 400 cm⁻¹) of the FTIR spectra, pure Fe₃O₄ depicts



peaks of vibrations at 620, 588 and 442 cm⁻¹ corresponding to Fe-O and confirming the presence of only Fe₃O₄. Besides, FTIR spectroscopy is a useful tool at the time to determine the presence or coexistence between γ -Fe₂O₃ and Fe₃O₄ inverse spinel phases, especially the vacancy order in crystals based on the presence of Fe³⁺-oxygen stretching for tetrahedral coordination at 750 to 550 cm⁻¹ [23-26]. However, by analysing this region not γ -Fe₂O₃ phase was formed in the sample confirming the presence of single Fe₃O₄ phase.



Fig. 2 Fitted high resolution X-ray photoelectron spectra of Fe₃O₄ nanoparticles coated with LA (a) Fe₂p region and OA (b) Fe₂p region and (c) Fe₋3p region. Fe₂p (green colour lines) and Fe₃p (blue colour lines). Fitted high resolution X-ray photoelectron spectra of Fe₃O₄ nanoparticles coated with LA (d) O-1s region, (e) C-1s region and coated with OA (f) O-1s region and (g) C-1s region. (h) TGA curves for: pure Fe₃O₄ (black) and coated with de lauric acid (blue) and oleic acid (green)

XPS measurements were applied to Fe₃O₄@LA and OA samples in the region from 695 and 730 eV, they are shown in **Fig. 2a) and b**). From the fit we determined the corresponding components to the sites Fe (2p_{3/2}) and Fe (2p_{1/2}) with 19.66 and 39.34 % for Fe₃O₄@LA sample, respectively. From which we observed that Fe²⁺/Fe³⁺ is around 49.97 %. This result agrees with the stoichiometric relation Fe²⁺/Fe³⁺ = 50 %. From the same manner for Fe₃O₄@OA we obtained for the sites Fe (2p_{3/2}) and Fe (2p_{1/2}) that the relation between the Fe²⁺ and Fe³⁺ is around 50 %. On the other hand, the width line of the Fe⁺³ (2p_{3/2}) is ~ 200 higher than the corresponding site Fe²⁺ (2p_{3/2}), this indicates that the corresponding peak could be fit by using two other peaks: Fe³⁺ (+A) and Fe³⁺ (B). Information that confirmed the presence of the tetrahedral (A) and octahedral sites (B). In **Fig. 2c)** the fit in the region between 50.27 and 61.9 eV for the Fe (3p) site is shown, in which we confirm again the relation Fe²⁺ (3p)/Fe³⁺ (3p) is 50 %. Besides, the obtained information from the fit of the C (1s) XPS region in **Fig. 2f) and g**) provided evidence about the nature of the surface presented in samples M₃ and M₄, due to the XPS spectra could be deconvolutioned by using the corresponding peaks to C-H: 284.51 (82.5 %), 284.55 (84.2 %) eV and O=C-O: 288.44 eV (10.1 %), 288.12 eV (3.26 %) carboxylic groups, respectively. Furthermore, the O (1s) XPS region for Fe₃O₄@LA and OA samples are shown in **Fig. 2d) and f**) which reveal the presence of the peaks corresponding to [Fe-O]_A: 530.95 and 529.9 eV, with 55.12 % and 52.92 %, respectively. In



addition, fit of the corresponding region to O=C-O are 531.33 (12.87 %) and 531.19 (13.19 %) eV. Thus, the presence of carboxylic groups is confirmed by this analysis and is complemented by FTIR.

TGA was employed to determine the thermal stability of MNPs coated with the organic molecules and the number of molecules adhered to Fe_3O_4 surface. In **Fig. 2h** the TGA analysis for samples Fe_3O_4 @LA and OA are shown. We can observe principally for Fe_3O_4 @LA and OA, a complete decomposition of the organic part at around 450 °C. In the samples: Fe_3O_4 @CA and Fe_3O_4 @LA there were a total weight loss of 5.2, 21 and 22 %, respectively.

In the case of Fe_3O_4 nanoparticles, the significant weight loss (5.2 %) can be explained due to adsorption of water and ethanol on MNPs surface as it was shown by FTIR analysis. On the other hand, assuming that the total weight loss corresponds to the organic molecules, we can calculate the number of molecules (ligands) adhered to MNPs surface. The calculation of the ligands number (n) on the MNPs surface will take previous consideration of the next steps: m_2 as the total mass of the organic molecules bound to one nanoparticle (NP), which were lost during the carbonization process; m_1 is the sample mass and p the percentage of weight loss, m_2 . For our samples the next equation must be considered:

$$p = \frac{m_2}{m_1 + m_2} x \ 100\% \tag{1}$$

For m₁ we will use the relation m₁= $\rho_1 xV_1$; where V₁= $\pi < D > 3/6$ and <D > is the MNP diameter. For m₂ the relation m₂ = n $\overline{M}_2 x$ 6.023 x 10⁻²³ g, where \overline{M}_2 is the molecular mass de m₂ expressed in grams. Furthermore, for the calculation of m₁ we will take the density expressed in g/cm³. Therefore, the number of ligands will be:

n =
$$\frac{6.022 \times 10^{23} \times \pi \rho_1 < D >^3 p}{6 \overline{M}_2 (100 - p)}$$
 (2)

where $\overline{M}_2 = 200.3178$ and 282.4614 g/mol are the molecular weights for lauric and oleic acids and $\rho_1 = 5.17$ g/cm³ is the magnetite density (1nm³=10⁻²¹ cm³), respectively. Using a mean diameter for coated MNPs with OA and LA (*<D>* = 9.7 ± 2 nm, 8.6 ± 2 nm) obtained from Sherrer's equation. Calculations to obtain the value of n was done for magnetite coated with LA and OA, using Eq. [2], these values are summarizing in **Table 1**. The superficial area or active surface of the MNPs is expressed in squared meters per gram (m²/g). To obtain these values for both samples we used the relations: m₂= $\rho \times V_1 y S_{NP}=\pi \times D^2$. We obtained for oleic acid m₂ = 2.47 x 10⁻¹⁸ g and S_{NP} = 2.95 x 10⁻¹⁶ m², while for lauric acid m₂ =1.72 x 10⁻¹⁸ g and S_{NP} = 2.32 x 10⁻¹⁶ m², while for lauric acid m₂ =1.72 x 10⁻¹⁸ g and S_{NP} = 2.32 x 10⁻¹⁶ m², while for lauric acid molecules. Warner *et al.* suggested that surface area is a crucial factor for adsorption process of metal pollutants [27]. In this report they used Brennaur-Emmet-Teller (BET) analysis and fcc hard sphere model to estimate surface area with values > 100 m²g⁻¹. Thus, the surface areas obtained from our data are in the acceptable range.

Table 1 Values of weight loss p (obtained by TG measurements), mean diameter of the MNPs (D, nm),surface (m²/g) and number of ligands for the MNPs (n)

Sample	<i>D</i> (nm)	% lost mass (p)	Surface (m ² /g)	ligands (n)
OA	9.7	21	119	1400
LA	8.6	22	135	1460

The micro-Raman spectra were fitted using Lorentzian-like functions (**Fig. 3a and b**). [28]. The bands at 293, 353, 405, 634, 685 and 726 cm⁻¹ confirm the formation of maghemite phase [28-30]. Meanwhile, the broad band at 246 cm⁻¹ can be assigned to hematite Raman mode [28]. Besides, one band at 497 cm⁻¹ is clear seen in the spectrum, Slavov *et al.* associated this band to hematite [31]. Recalling that maghemite is a metastable iron oxide phase which tends to change to hematite after laser exposition [28]. Soler *et al.* observed the



formation of weak bands of hematite after changing power intensity (2.4 mW) that conducted to sample heating [29]. It means that during laser exposition an oxidation process can be expected due to increase of temperature. This fact has been proven in several literatures where laser power can be the main factor of phase transformation and loss of chemical stability [28-32]. On the other hand magnetite is susceptible to transformation depending on the used laser power. Hanesch mentioned that the most prominent band associated with magnetite under 0.7 mW laser power should have its exact position in the range from 661 to 676 cm⁻¹ [28]. In our case that band is not seen assuming that magnetite has been partially oxidized to maghemite because of 0.5 mW laser power used in our experiment. Nevertheless, one weak band at 548 cm⁻¹ associated to magnetite is shown [33]. Interestingly one weak band at ~ 900 cm⁻¹ can be assumed to ethanol organic layer formed after washing the nanoparticles solution [34]. This could confirm our assumption made by FTIR and TGA analysis. This band was not seen for magnetite coated with LA. Nevertheless, additional bands at 1040 and 1126 cm⁻¹ better describe carbon residues from ethanol [34]. Two additional bands at 1341 and 1588 cm⁻¹ are regarded. de Faria *et al.* also observed these feature bands at 1320 and 1560 cm⁻¹, but they were not assigned to maghemite formation [32]. However, Hanesch emphasized the presence of this band to hematite under 1mW laser power (time of exposition: 2 min) [32].

After being coating with oleic and lauric acids (**Fig. 3c**) two intense bands at ~220-290 cm⁻¹ are appreciated suggesting clear formation of hematite. Raman bands attributed to iron oxide phases (300-800 cm⁻¹) are still present but with medium intensity. The bands at ~ 968 (C=C-H out of plane), 1155, 1298 (CH₂ twisting modes of vibration), 1461 cm⁻¹ (shoulder, CH₂ scissoring) are related to the presence of organic chains of acid/oleate confirming the presence of organic molecules on nanoparticles surface [29, 35]. Comparing with uncoated samples two bands at 1559 and 1607 cm⁻¹ indicate organic ligands or carbon residues chemisorbed on magnetic surface.



Fig. 3 Micro-Raman spectrum for uncoated magnetite (a) low and high region (b) under 0.5 mW laser power. (c) Micro-Raman spectrum for magnetite coated with OA and LA



4. CONCLUSION

The synthesis and functionalization of Fe₃O₄ nanoparticles with fatty acids were achieved with help of the alkaline co-precipitation chemical route. This method is not difficult with a low-cost and high reproducibility. The characterization of the MNPs by XRD technique shows crystallites with very small diameter of 11.8 \pm 2 nm. Meanwhile, the average crystallite diameter for Fe₃O₄@OA and Fe₃O₄@LA were found to be very close at around 9.7 \pm 2 and 8.6 \pm 2 nm. By TEM analysis we deduced quasi spherical shape, monodispersity and high crystallization. Thus, the oleic and lauric acid surfactant agents act as a dispersant and shape-controlled factor of the crystallites during the nucleation process. FTIR, XPS, TGA and micro-Raman analysis confirmed the adhesion of the carboxylic groups on MNPs surface. Besides, TGA measurements help to determine the weight loos of the organic material of the samples associated to the stability of functional groups on the Fe₃O₄ nanoparticles surface at certain range of temperatures. In addition, the number of ligands anchored to the MNPs surface is possible to be estimated. Mostly important they revealed high superficial area (119.4 m²/g) that is for example a crucial value for adsorption process of trace metals from contaminant waters.

ACKNOWLEDGEMENTS

This work was supported by a grant (No. 013-2013) from the National Council of Science, Technology and Technological Innovation (CONCYTEC/FONDECYT-Peru). Ramos Guivar Juan A. is also grateful to FONDECYT (Grant No. 0218-2014).

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