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Effects of surfactants on the magnetic properties of iron oxide colloids

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ABSTRACT

Iron oxide nanoparticles are having been extensively investigated for several biomedical applications such as hyperthermia and magnetic resonance imaging. However, one of the biggest problems of these nanoparticles is their aggregation.

Taking this into account, in this study the influence of three different surfactants (oleic acid, sodium citrate and Triton X-100) each one with various concentrations in the colloidal solutions stability was analyzed by using a rapid and facile method, the variation in the optical absorbance along time.

The synthesized nanoparticles through chemical precipitation showed an average size of 9 nm and a narrow size distribution. X-ray diffraction pattern and Fourier Transform Infrared analysis confirmed the presence of pure magnetite. SQUID measurements showed superparamagnetic properties with a blocking temperature around 155 K. In addition it was observed that neither sodium citrate nor Triton X-100 influences the magnetic properties of the nanoparticles. On the other hand, oleic acid in a concentration of 64 mM decreases the saturation magnetization from 67 to 45 emu/g. Oleic acid exhibits a good performance as stabilizer of the iron oxide nanoparticles in an aqueous solution for 24 h, for concentrations that lead to the formation of the double layer.

1. Introduction

In the last decades, iron oxide nanoparticles have been extensively investigated for biomedical applications. There are several types of iron oxide nanoparticles, but the most commonly used are magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) [1,2]. Among these two, magnetite is the most used in biomedical applications due to its proven biocompatibility [3–5]. These nanoparticles possess an important characteristic, superparamagnetic property: below a certain particle size (in the order of tens on nanometers) the magnetic moments of adjacent atoms remain aligned acting as one large magnetic moment for the whole particle. Therefore, when a magnetic field is applied the whole nanoparticle aligns with that field; when the magnetic field is removed the nanoparticle returns to its original randomly orientated state. The lack of remnant magnetization after the removal of external fields enables the particle to maintain their colloidal stability and avoids aggregation, making it feasible for biomedical applications [6,7].

Iron oxide nanoparticles are positively charged but without surfactants tend to be instable in solution and to aggregate rapidly. Moreover, for biomedical applications, coated iron oxide nanoparticles enhance their biocompatibility and decrease their cytotoxicity [8,9]. Therefore, several surfactants have been tested in order to achieve the most stable colloid as possible. There are several classes of surfactants that can be used to form a monolayer on the iron oxide nanoparticles surface. Some examples are carboxylates such as sodium citrate [10] and oleic acid [11–13], synthetic polymers such as Triton X-100 [14] and PVA [15] (Polyvinyl alcohol) or inorganic materials such as silica and gold [16]. In this work we studied the influence of concentration of three different surfactants (oleic acid, sodium citrate and Triton X-100) on the stability of colloidal solutions containing Fe_3O_4 nanoparticles (NPs). The stability along time was evaluated through optical absorbance and dynamic light scattering measurements. The main objective was to understand how the surfactants influence the stability of the iron oxide colloidal solution and its magnetic properties.

2. Materials and methods

2.1. Iron oxide nanoparticles synthesis

All the chemical reagents used in this research work were of analytical grade and used without further purification.

Iron oxide nanoparticles were synthesized using an adapted method of Gnanaprakash and coworkers [17] based on chemical

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co-precipitation. Briefly, ferrous and ferric chlorides were dissolved in deionized water to achieve a concentration of 1 M. An appropriate amount of the above mentioned solutions was mixed in order to obtain a molar ratio of 1:2 (Fe^{2+}:Fe^{3+}) and dilute to 100 ml of deionized water with deaeration of O_2 with bubbling N_2. Further, 10 ml of NH_4OH 25% was rapidly added under vigorous stirring and kept for 5 min. Deionized water was added to stop the reaction, the precipitate was left to settle, and the top water layer was discarded. The magnetic nanoparticles were washed three times with deionized water, and pH of the final suspension was adjusted to 7 with diluted HCl. A part of the suspension was lyophilized (Vaco 2, Zirbus) in order to obtain dry nanoparticles for further characterization.

For the stabilization of the iron oxide nanoparticles, an appropriate amount of sodium citrate, oleic acid and triton X-100 was added to a known volume of the magnetite suspension. The mixture was allowed to react for 1 h under stirring. Finally, the samples were sonicated for 5 min.

2.2. Characteristics of the surfactants

2.2.1. Oleic acid

Oleic acid is a commonly used surfactant to prevent the agglomeration of the iron oxide nanoparticles due to its higher affinity to magnetite.

This compound is a monounsaturated fatty acid that can be found naturally in many plant or animal products. The chemical structure of oleic acid makes it a very good surfactant for magnetite nanoparticles since the oleic acid chain possesses a terminal carboxylic acid with negative charge that has high affinity to magnetite nanoparticles surface due to their positive charge [13].

2.2.2. Sodium citrate

Sodium citrate is a common surfactant used in the synthesis of silver, gold and alumina nanoparticles due to its high solubility in several solvents and because it has a high degree of stabilization of the nanoparticles. Its chemical structure, like oleic acid, has a negative charge which will facilitate the attachment to negative nanoparticles such as Fe_3O_4, enhancing the particles dispersion and stabilization in suspensions.

2.2.3. Triton X-100

Triton X-100 is a non-ionic surfactant from the class of the alkyl phenyl polyethoxylate (PEO) surfactants, composed of a PEO hydrophilic chain and a hydrophobic aromatic group. It is compatible with other surfactants non-ionic, anionic and cationic. This surfactant is utilized in the production of detergents, emulsifiers, wetting agents, solubilizers and dispersants [18].

These different surfactants were used in the iron colloidal solutions with the concentrations indicated in Table 1.

Table 1
Tested concentrations of the three surfactants used (oleic acid, sodium citrate and triton X-100) and their respective dilution for suspension analyzed by UV–VIS measurements.

	Pristine NPs	Oleic acid	Sodium citrate	Triton X-100
Concentrations (mM)	–	8	1.25	17
		16	2.5	26
		32	5	34
		64	10	43
		128	20	52
		196	30	61
Dilution	1:100	1:100	1:100	1:200

2.3. Characterization

UV–VIS spectrophotometer (*PG Instruments model T90+*) was used to perform the absorbance spectra of colloidal solutions containing iron oxide nanoparticles coated with different surfactants: oleic acid, sodium citrate and triton X-100. The measurements were acquired using a quartz cuvette with high purity water and the same concentration of surfactant used in the samples preparation placed in the reference beam to avoid the absorbance of surfactant. The colloidal solutions prepared are the ones shown in Table 1, where the concentration of surfactant was changed keeping the dilution constant to ensure that the absorbance spectra do not saturate.

Hydrodynamic diameter of the nanoparticles was measured by means of dynamic light scattering (DLS) equipment (Avid Nano) using the *blade cell*® at 20 °C. X'Pert PRO *PANAlytical* X-ray diffractometer was used to obtain X-ray diffraction patterns of the pristine iron oxide nanoparticles previously lyophilized. The 2θ values were taken from 15° to 80° using a Cu Kα radiation (λ = 1.54060 Å) with a step size of 0.033°. Transmission electron microscopy (TEM) images were obtained using a *Hitachi H-8100 II* with thermo ionic emission LaB6. TEM analysis was performed in a little quantity of nanoparticles suspended in pure water that were placed in a Kevlar 25 mesh grid. FTIR spectra of the samples were obtained using a Nicolet 6700 – Thermo Electron Corporation Attenuated Total Reflectance-Fourier Transform Infrared spectrometer (ATR-FTIR). The concentration of iron in the samples was measured using the 1,10-phenanthroline colorimetric method [19]. The DC magnetic properties were performed using a 7T SQUID magnetometer (S700X; Cryogenic Ltd.). The zero-field-cooled (ZFC) and field-cooled (FC) measurements were performed by cooling the sample to 5 K at zero fields or in the presence of an external field of 100 Oe, respectively. All the magnetic measurements were carried out in increasing temperature range 5–320 K. Isothermal magnetization curves were obtained for fields up to 5 T for temperatures of 10 and 320 K.

3. Results and discussion

3.1. Iron oxide NPs

The structure, size and morphology of the synthesized Fe_3O_4 nanoparticles were evaluated prior to functionalization with surfactants. The structure was analyzed through XRD spectra of the powder while the size and the morphology evaluated from TEM analysis.

Fig. 1 shows the XRD patterns obtained for pristine and coated Fe_3O_4 nanoparticles. Comparing XRD pattern of m-NPs with standard diffraction spectrum for magnetite and maghemite powders (JCPDS 00-019-0629 for magnetite and JCPDS 00-039-1346 for maghemite) for the synthesized product we clearly identify the diffraction peaks of crystalline cubic magnetite structure. The average particle size was calculated to be 9.75 nm using the Scherrer's equation $\tau = K\lambda/\beta\cos\theta$, where τ is equivalent of particles average core diameter; K is the grain shape factor (K = 0.94); λ is the incident X-ray wavelength; β denotes the full width at half-maximum (in radians) of the highest intensity, and θ is the corresponding diffraction angle (2θ = 35.6141). Pristine and coated nanoparticles XRD patterns are similar, denoting that the surfactant does not change the Fe_3O_4 nanoparticles crystalline structure.

TEM image of pristine Fe_3O_4 nanoparticles showed that the mean particle size is roundly 9–10 nm and agrees with the value calculated from XRD data. Moreover the size distribution is quite narrow, 6–16 nm. This is very interesting considering that for biomedical applications the nanoparticles must have a size below