PREPARATION OF A MAGNETITE FERROFLUID STABILIZED WITH A NATURAL POLYMER

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Abstract:

In this work, the synthesis of magnetic fluid is presented, consisting of nanometric magnetic particles (Fe_3O_4), stabilized in an aqueous medium with a natural protein. The final products were characterized by Mössbauer Spectrocopy, Fourier Transform Infrared spectroscopy, X-ray diffraction, Laser light scattering, termogravimetry, transmission electron microscopy and Scanning electron microscopy. The results show that products present adecuate morphological and magnetic characteristics to produce ferrofluids with potential applications in medicine and biology

1 INTRODUCTION

Development of new technological areas has encouraged the study of iron oxides either in avant-garde technology applications as in the biological camp. Among these applications there is their use in preparation of magnetic fluids to be employed as magnetic inks, magnetic seals in engines, optical memory instruments, gyroscopes, magnetic refrigeration units, cellular mark and separation, contrast media in clinical imagenology and hyperthermia and medicines transport and liberation media with magnetic fluids. [1,2]. The last applications are involved in Magnetic carrying technology, MCT, used at the beginning for treatment of wastewater, and now consisting in ferrofluids or magnetic fluids use as a contrast medium in clinical imagenology and for carrying of interest compounds to specific places, among other applications [3].

Ferrofluids are made up of magnetic nanoparticles dispersed in a liquid carrying medium (aqueous or organic) and must have even magnetic as fluid properties.

Magnetic particles by themselves are not adequate to transport medicines, having limits for controlling the amount of drug carried and release rate. To overcome these impasses, magnetic particles can be covered with a biodegradable polymer serving as support for pharmaceutical drugs or for biologically-active compounds. Ferrofluid is directed by means of an external magnetic field toward interest tissues, where the supported or adsorbed substances are released in a controlled rate along polymer degradation [1, 3, 4].

To have a ferrofluid, which consists in a magnetic nuclei with a polymeric shell, which can be employed in transportation of compounds to target places for biological applications, this must have some determinate properties such as very small sized superparamagnetic particles (smaller than 1.4 µm, with magnetic nuclei smaller than 20 nm) in suspension, to allow an uniform capillar distribution to the target place; an appropriated magnetic response to external fields and gradients at flux rates as found in biological systems. Materials employed in covering and stabilization of magnetic particles must also have some important properties such as capacity to carry chemical-therapeutic substances in appropriated doses, biodegradability, a controllable or predictable drug-release rate in the desired place, superficial properties allowing maximum biocompatibility and minimum antigenicity, high compatibility with employed medicines and minimum toxicity for their decomposition products [3,5]. Particles must also be disperse in a liquid carrying medium, appropriated for biological systems, and this monodispersions must be very stable to avoid particle aggregation [2,6].

Among substances employed as magnetic nuclei magnetite is. This has been known for several centuries, having its magnetic and conductor properties been used widely. Moreover, it is a substance appropriate to be implemented as magnetic particles, due to its low toxicity (LD50 in rats: 400mg/Kg) and that is tolerated by the human body [3]. In addition to magnetite there are reports of ferrofluids that employ nanoparticles of maghemite and hematite [7] and different ferrites [8.9].

An important aspect in preparation of ferrofluids is the search for a medium which provides an adequate stability to the colloidal particle suspension. This stability may be achieved by two mechanisms: one, modifying surface with a surfactant adsorbed in the composed particle surface (nuclei, shell) generating an entropic repulsion able to surpass the Van der Vals attraction and the dipolar magnetic attraction between particles [1,2], and two, forming a superficial net charge and a double electrical layer with appropriated thickness which avoids aggregation of particles by creating electrostatic repulsion between them. Besides providing stability to the sol polymeric cover, it may also provide chemical stability to the magnetite nuclei, avoiding its accelerated oxidation and the adsorption of therapeutical substances.

There is a broad variety of substances employed for magnetic covering for its application in TTM. Among the ones reported in literature there are biodegradable polymers such as dextran, albumin and starch [10]. There also are polymers of the polyalchilcianoacrylates, as polyethyl-2-cianoacrylate, with very reactive monomers which polymerize easily in different media, including aqueous, poly(lactic acid)(poly(DL-Lactide) and poly(DL Lactide-co-glycolide) [3,11,12].

Besides utilization of biodegradable polymers, preparation of ferrofluids consisting in magnetic nuclei covered with an amorphous silica shell has been reported in literature. Due to the reactivity of superficial sylanol groups, this kind of particles may link compounds with biological activity or with functional groups with different properties, as for example, fluorescent substances [13,14].

Magnetic nanoparticles may be obtained through different synthetic methods. One of the most common is obtaining magnetite by chemical coprecipitation method, starting from a mixture of iron salts 2^{+} and 3^{+} in a highly alkaline medium [1,5]. There are also reports of particles obtained through synthesis in organic phase; thermal decomposition of al alkaline solution of Fe (III) quelate; sonochemical decomposition of an iron (II) salt followed by thermal treatment, starting from Fe (III) acetylacetonate at high temperatures in presence of phenyl ether, alcohol, oleic acid and oleynamine [5] and through Sol-Gel, in which particles crystallize from an iron (III) hydroxide gel [3].

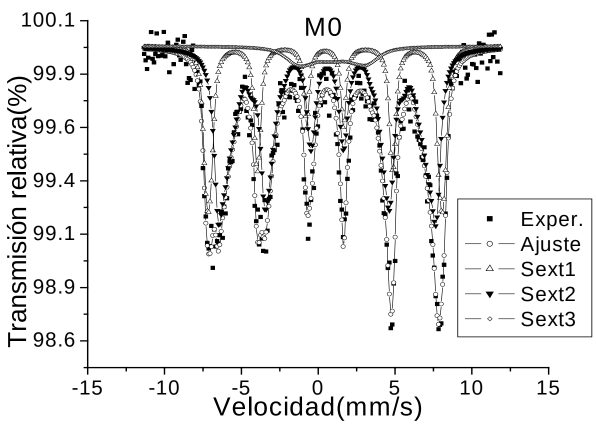
Depending on the synthesis method and reaction conditions, magnetic particles to be employed in ferrofluid preparation can be obtained in sizes from 3 nm diameter to 80 nm, also depending on dispersion medium and surfactant used in magnetic particle stabilization [2,3,11,15].

In literature, magnetic particles, substances covering them and ferrofluids as themselves are structural, magnetically and colloidally characterized by X-ray diffraction, Transmission Electron Microscopy, Zeta potential measurements, magnetization curves, Infrared spectroscopy and Mössbauer spectroscopy, as well as some calorimetry analyses reported and surface adsorption studies [1-15]. These analytical techniques show that particles constituting found ferrofluids have small size in spite of the synthetic route employed. Moreover, colloidal solutions are monodisperse when the polymeric cover has a thickness allowing every particle to be covered but concentration of polymer is not too high, because in this case magnetic particles shall be completely imbibed in a polymeric matrix. In the opposite case, when polymer concentration is too low, magnetic particles tend to aggregate themselves.

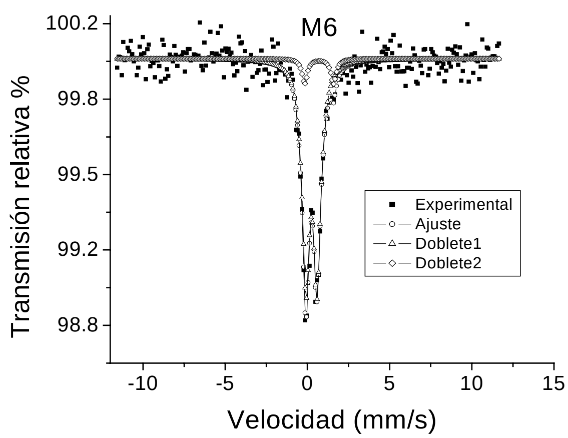
Among those techniques, Mössbauer spectroscopy may give important information about magnetic characteristics of synthesized products. Kuncser et al. [8] studied cobalt ferrite and magnetite ferrofluids with several surfactants through Mössbauer spectroscopy at different temperatures; their results show that it is possible to obtain information about nanoparticles size, dispersion density of these and magnetic anisotropy energy. Surfactants have influence in the magnetic relaxing process and therefore in properties of the ferrofluid at room temperature. Their Mössbauer specters show a strong relaxing effect due to the nanometric size of the particles, especially at high temperatures.

In this work, nanometric magnetite particles were obtained and stabilized with a natural polymer for its potential application in magnetic fluids preparation with possible biological uses. To achieve this purpose, syntheses by coprecipitation, well established in literature, were carried out with modifications developed for the particular studied systems. Pure magnetic particles and particles in the presence of the biodegradable polymer were obtained at different concentrations. For its characterization it were used techniques such as Mössbauer spectroscopy, X-Ray diffraction (DRX), Infrared spectroscopy, Thermogravimetry (TGA), Transmission Electron Microscopy (TEM) and Laser light Static Dispersion.

a



d


M6
Transmisión relativa %
100.2
99.8
99.5
99.2
98.8
-10
-5
0
5
10
15
Velocidad (mm/s)
Experimental
Ajuste
Doblete1
Doblete2

e

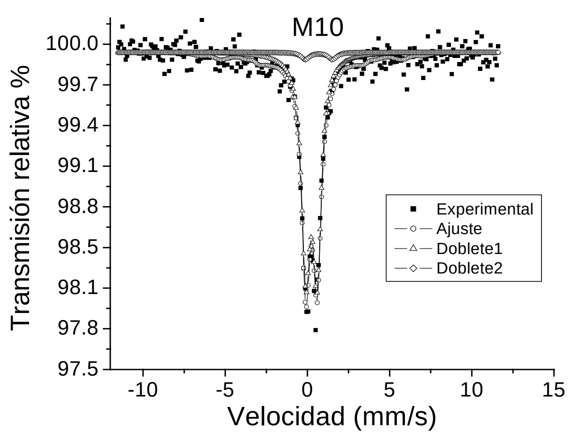

M10
Transmisión relativa %
100.0
99.7
99.4
99.1
98.8
98.5
98.1
97.8
97.5
-10
-5
0
5
10
15
Velocidad (mm/s)
Experimental
Ajuste
Doblete1
Doblete2

Fig1(a-e) Mössbauer espectra of M0, M2.5, M4, M6 y M10