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Polyacrylic acid-coated iron oxide magnetic nanoparticles: The polymer molecular weight influence

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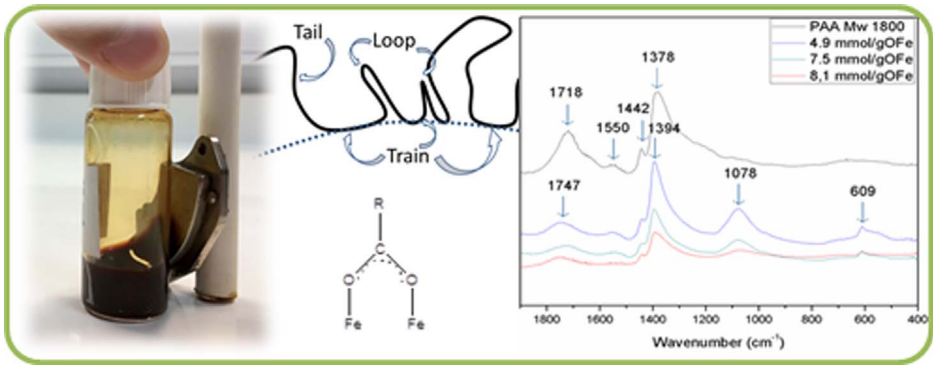
GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic nanoparticles (MNPs), in particular, magnetic iron oxide-based nanoparticles were found to be useful as catalysts and as devices for data storage, environmental remediation and several biomedical applications, due to their excellent properties, such as biocompatibility and high magnetic moment. Polyacrylic acid (PAA) is a weak polyelectrolyte that can be used to stabilize the MNPs. To the best of our knowledge, the influence of PAA molecular weight and PAA concentration over the magnetic and structural properties of iron oxide nanoparticles has not been previously reported. The aim of this paper is to describe the differences evidenced in the properties of different magnetic materials by using PAA for iron oxides stabilization by one-pot coprecipitation synthesis. Iron oxide-based magnetic nanoparticles stabilized by polyacrylic acid (PAA) polymers were efficiently prepared and exhaustively characterized. The influence on the employment of two different low PAA molecular weights, Mw 1800 g/mol and 5000 g/mol, in three different iron salts: PAA ratios was analyzed. In summary, the main results showed that: for a certain PAA reactor feed higher oligomer quantities are present in MNPs as higher is the involved molecular weight of the polymeric chain; when molecular weight raises the contribution of loops and tails also does it, allowing having higher polymer contents. For both PAA's Mw employed as the adsorbed PAA increases particles hydrodynamic diameters decreases, and their distribution becomes narrower; the PAA adsorbs onto iron oxides by chemisorption (the most probable interaction is the bidentate bridging). For the studied cases z potential values depend much more on the PAA's quantity adsorbed onto the iron oxides than on the PAA's Mw. MNPs are superparamagnetic and choosing the right shape of particle distribution is not central

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for getting estimates of the magnetization saturation, the average particle diameter and its standard deviation, while better fits are found with Normal and Log-Normal particle size distributions.

1. Introduction

From some decades up to now, nanomaterials are being widely prepared and employed for a variety of applications. Magnetic nanoparticles (MNPs) were found to be useful as catalysts and as devices for both data storage and environmental remediation, among many other possibilities [1]. They are also employed for several biomedical applications, such as drug delivery systems [2] and contrast agents for MRI [3]. In particular, the preparation and application of magnetic iron oxide-based nanoparticles as biocatalysts [4], hyperthermia devices [5], therapeutic agents for cancer treatments and magnetic media have been reported [6] due to excellent properties, such as biocompatibility and high magnetic moment [7].

As a result of their small size, MNPs agglomeration is a well-known fact. Thus, many efforts have been conducted to achieve the necessary and desired nanoparticles stability on the corresponding ferrofluids suspensions. One of the most widely employed strategy consists on preparing the MNPs through coprecipitation from iron salts, in presence of a stabilizing agent. The aqueous coprecipitation method of MNPs synthesis produces biocompatible iron oxide NPs of non-toxical reagents at lower temperatures than other methods, such as thermal decomposition preparation process. However, a broad NPs size distribution and poor repeatability was reported for this method [8].

Among a number of possible stabilizing agents, some carboxylated compounds, such as citric, polyacrylic, poly (acrylic-co-maleic), humic and gallic acids have been employed [9,10]. It is important to remark that polyelectrolytes not only stabilize the particles, but also they can flocculate them. According to several reports, flocculation takes place when polymers of high molecular weight are used because two or more colloidal particles could be bound to each other. This process is commonly named 'bonding' [11,12]. The agglomeration and particle size of composite nanoparticles are influenced by the type of the surfactant employed and its concentration [13].Among these surface modification substances, polyacrylic acid (PAA) has been used to stabilize MNPs by providing electrostatic and steric repulsion against particle aggregation [14]. The synthesis of PAA-Coated Magnetite Nanoparticles has been reported following thermal decomposition route [15] or initiated atom transfer radical polymerization [14].

PAA is a weak polyelectrolyte with a variable degree of dissociation, which depends on the solution pH and ionic strength. Moreover, PAA is a water-soluble polymer with a high binding capacity. It also has a high density of reactive functional groups, which provides a strong linkage between the iron oxide and biomolecules, making it very attractive for biomedical applications [16].

The final product dependance on pH, reagent, surfactant and iron salt ratio has already been studied. Also, the mechanisms of nanoparticles formation over the magneto-structural properties has been reported [17]. To the best of our knowledge, the influence of PAA molecular weight and PAA concentration over the magnetic and structural properties of iron oxide nanoparticles has not been previously reported. The aim of this paper is to describe the differences evidenced in the properties of different magnetic materials by using PAA for iron oxides stabilization by one-pot synthesis. To this purpose, the influence on the employment of two different low PAA molecular weights, Mw 1800 g/mol and 5000 g/mol, under three different iron salts/ PAA ratios was exhaustively analyzed. Studies of the final products were conducted *via* Fourier Transformed Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), Dynamic light scattering (DLS), z-potential, Thermogravimetric analysis (TGA) transmission electron microscopy (TEM) and magnetic measurements. The influence of PAA molecular weights on the final oligomer quantities present on MNPs for a certain reactor feed, on the MNPs hydrodynamic diameter and their sizes distribution and on z-potential was determined and explained.

From FTIR studies, the possible interactions between the polymeric chains and the iron oxides, both present in the MNPs were elucidated and described. From magnetic measurements results, superparamagnetic response was characterized. It was shown that most relevant parameters are roughly independent on proposed particle size distributions. The results obtained by XRD and TEM were compared and related with those estimated from magnetization measurements.

2. Materials and methods

2.1. Materials

For iron oxide MNPs preparation, two different iron salts were used as starting materials: $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ (both from Cicarelli Laboratory, Argentina). Furthermore, two PAA were employed: Mw 1800 g/mol and 5000 g/mol both purchased from Polysciences. Other reactants were also incorporated: NH_4OH (Biopack, Argentina), HCl (Biopack, Argentina), and bidistilled water.

2.2. Methods

PAA-coated MNPs were prepared through coprecipitation method, according to Lin and collaborators [18]. Briefly, 4.75 g of $FeCl_3.6H_2O$ and 2.45 g of $FeSO_4.7H_2O$ were dissolved in 80 mL of milli-Q water at 60 °C, under N_2 atmosphere. Then, PAA was added to the system (0.32, 0.49 and 0.63 g) and vigorous stirring was maintained for 30 min. After this, 10 mL of NH_4OH were quickly added, resulting in a color change from orange to black.

By following the above-mentioned procedure six different ferrofluids were thus obtained: three different PAA concentrations for each Mw employed. Each of them was purified by dialysis (until pH and

Fig. 1. MNPs response under the presence of a permanent magnet.