Synthesis and characterization of magnetic nanoparticles coated with silica through a sol-gel approach

(Síntese e caracterização de nanopartículas magnéticas revestidas com sílica através de um processo sol-gel)

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Abstract

This paper investigates the influence of reaction medium pH on silica-coating of magnetite nanoparticles. Magnetite nanoparticles were prepared by means of a reduction-precipitation method using ferric chloride as a starting material, which was partially reduced to ferrous salts by Na$_2$SO$_3$, before alkalining with ammonia. The particles were coated by sol-gel method with either ammonia or HCl aqueous solutions for either base- or acid-catalyzed hydrolysis, respectively. Powder X-ray diffraction, Fourier-transform infrared, and Zeta Potential were used for the characterization of oxides and of the coated magnetic nanoparticles. The observed difference of pH$_{IEP}$ in KCl solution for pure silica (2.0), magnetite (5.0), and silica-coated magnetite (2.3) samples confirms that the coating process was effective since the charge surface properties of coated magnetic nanoparticles are close to that of pure silica, even though the Fourier-transform infrared spectra did not evidence the formation of Fe-O-Si bonds.

Keywords: magnetite, coating, nanoparticles.

INTRODUCTION

Chemically synthesized magnetic nanoparticles have drawn much attention [1-3] due to the unique magnetic properties associated to their size magnitude and distribution uniformity. Among these particles, magnetite nanoparticles have been widely studied with biomedical applications in view, such as magnetic resonance imaging for clinical diagnosis, magnetic drug targeting, hyperthermia anti-cancer strategy, and enzyme immobilization [4-11].

Magnetite ($\text{Fe}_3\text{O}_4$), a common magnetic iron oxide, has a cubic inverse spinel structure with oxygen forming a FCC closed packing and Fe cations occupying the interstitial tetrahedral and octahedral sites [12]. The electrons can hop between Fe$^{2+}$ and Fe$^{3+}$ ions in octahedral sites even at room temperature, rendering magnetite an important half-metallic material [13]. Due to the anisotropic dipolar attraction, unmodified magnetic nanoparticles of iron oxides tend to aggregate into large clusters and thus lose the specific properties associated with single-domain. In addition, the reactivity of iron oxide particles has been shown to increase greatly as their dimensions are reduced and they may undergo rapid biodegradation when exposed directly to biological systems [14, 15]. Suitable coating is essential to prevent such limitation [16]. Silica coating of magnetic nanoparticles has become a promising and important approach in the development of magnetic nanoparticles for both fundamental study and technological research. The formation of a silica coating on the surface of iron oxide nanoparticles could help prevent their aggregation in liquid and improve their chemical stability. Another advantage of silica-coating iron oxide nanoparticles is that the silanol-terminated surface groups may be modified with various coupling agents to covalently bind to specific ligands.
[17-19]. Finally, the most important is that the silica layer provides magnetic nanoparticles with a surface chemically friendly to biological systems.

Among various chemical synthesis coating methods, the sol-gel process offers several advantages, including good homogeneity, low cost, and high purity.

The electrical nature of the sample-water interface is the result of the hydrolysis of the surface species followed by pH-dependent dissociation of surface hydroxyls. A characteristic property of the sample surface is the condition of surface zero charge, known as zero point of charge (zpc), which is usually determined by some form of acid–base titration technique. Surface characteristics may also be investigated by electrokinetic phenomena, which involve the inter-relation between mechanical and electrical effects at a moving interface. Electrokinetic results are generally expressed in terms of zeta potential, which may be calculated from the electrophoretic mobility of particles through a field with known strength. The term, isoelectric point (iep) refers to conditions under which the zeta potential is zero. The surface potential need not be zero when the zeta potential is zero, particularly in the case of specifically adsorbed ions, hence the zpc and iep need not be the same [20].

In this work, zeta-potential measurements are used to monitor coating efficiency besides its characterization by X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy.

**EXPERIMENTAL**

**Materials**

Reagent grade FeCl\textsubscript{3}·6H\textsubscript{2}O and Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O, ammonium hydroxide, ethyl alcohol, acetone, chloridric acid (Synth), and tetraethyl orthosilicate (TEOS - Aldrich 98%) were used as purchased.

**Iron oxide nanoparticle synthesis**

The method proposed in [21] was used in the preparation of nanoparticulate magnetite. Magnetic particles were synthesized using 15 mL FeCl\textsubscript{3}·6H\textsubscript{2}O (2 mol.L\textsuperscript{-1}) dissolved in 0.25 mol.L\textsuperscript{-1} HCl, 10 mL of Na\textsubscript{2}SO\textsubscript{4} stock solution (1 mol.L\textsuperscript{-1}), and 25.4 mL of ammonium hydroxide solution diluted to a total volume of 400 mL. The reaction was carried out in 1000-mL 3-necked round bottom flask by bubbling a protective gas (nitrogen) for ensure an inert atmosphere. Just after mixing Fe\textsuperscript{3+} and SO\textsubscript{4}\textsuperscript{2−}, the color of the solution changed from light yellow to red and afterwards back to yellow. At that moment, the diluted ammonia solution was poured into the solution quickly under vigorous stirring and a black precipitate was formed. The reaction was continued by stirring for an additional 30 min. The supernatant was discarded and the black precipitate was centrifuged with distilled water. This procedure was repeated five times and then, the precipitate obtained was centrifuged with acetone and subsequently placed in a desiccator and dried at room temperature. Then, the sample was reduced in a Pyrex tube under H\textsubscript{2} flowing at 50 mL.min\textsuperscript{-1} for 2 h at increasing temperature from 20 to 250 °C at a rate of 10 °C.min\textsuperscript{-1} which was held for a total heating period of 2 h. This sample was labeled Mt.

**Silica-coating of iron oxide nanoparticle**

Silica coating was carried out using modified reported methods [22, 23]. Deng e cols. prepared silica-coated magnetite nanoparticles using different types of alcohols, and various volume ratios of ethanol to water (\(V_{EW}\)). The feeding amount of catalyst and TEOS were also varied and the synthesis products were carefully characterized. In our study we used the optimized experimental conditions obtained in those studies. The formulations of each reaction were the same except for the type of catalyst. Typically 0.04 g of magnetic powder was diluted with 160 mL ethyl alcohol. This dispersion was homogenized by ultrasonic vibration in water bath for 10 min. Finally, 40 mL water, 1 mL TEOS, and either 5 mL ammonia aqueous (pH 10) or 5 mL of acidified (HCl - pH 1.7) aqueous solution were slowly added to this dispersion and stirred for 24 h. At this point, magnetic separation was made with the help of a permanent magnet and the magnetic powder collected alone was thoroughly washed with distilled water six times. These samples were named MtSi-a and MtSi-b, where a and b denote the acid (pH equal 4.1) and basic media (pH equal 11.4), respectively. The samples were placed under humidified atmosphere overnight and next treated in dry room atmosphere for 96 h.

**Glass synthesis**

A silica glass control sample was prepared for zeta potential study. In this case TEOS was added to an acidified (HCl - pH 1.7) aqueous solution, and next added to ethanol in a molar proportion of H\textsubscript{2}O:TEOS:CH\textsubscript{3}CH\textsubscript{2}OH of 4:1:4. The solution was magnetically stirred until gelation. The material was placed under humidified atmosphere overnight and next treated in dry atmosphere for 24 h.

**Characterization methods**

Sample structure, homogeneity, and the formation of silica-coated magnete nanoparticles were evaluated by comparison of FTIR spectra of coated and non-coated samples. For these analyses, samples were compacted with KBr (approximately 1%) and analyzed in transmission mode in a Perkin Elmer Spectrum GX spectrophotometer. X-ray diffraction measurements were performed in a Rigaku model Geigerflex apparatus using Cukα radiation from 20 to 80° (2θ) at a scan rate of 4°.min\textsuperscript{-1} and silicon as an external standard.

Zeta Potential (\(\bar{\zeta}\)) and particle size were determined in a Nano Size ZS apparatus. For zeta potential measurements the ground material was suspended in water and homogenized
with ultrasound for 15 min. After this time, another suspension was made by adding drops of the previous suspension to an aqueous solution of KCL 10⁻³ mol.L⁻¹. The pH of this solution was measured and adjusted with either aqueous NaOH 10⁻³ mol.L⁻¹ or HNO₃ 10⁻³ mol.L⁻¹. ξ was measured as a pH function. For particle size measurements, an aqueous suspension of magnetic powders were ultrasonic for 10 min and next they are left to rest during 30 min.

RESULTS

Magnetite nanoparticles

XRD results (Fig. 1a) showed the presence of two phases corresponding to magnetite and elementary iron in sample Mt. The line broadening observed is essentially due to the nanoparticle size effect. The average particle size of this magnetite sample estimated from breadths of reflection 311 in Scherrer equation was 10 nm.

Fig. 2b shows the FTIR spectra of sample Mt. Since magnetite has an inverse spinel-type structure, it shows bands indicating the vibrations M₄-O-M₆ (ν₁ ≈ 600–550 cm⁻¹), M₆-O (ν₂ ≈ 470 cm⁻¹), and M₄-M₆ (ν₃ ≈ 350–400 cm⁻¹), where M₄ and M₆ correspond to the metal occupying tetrahedral and octahedral positions, respectively [24-26]. Due to instrument limitations, we were unable to observe vibrations type ‘ν₃’, although ‘ν₁’- and ‘ν₂’-type bands were well defined. Table I shows the reported absorbance values of various iron oxides [27, 28].

Table I - IR bands of various iron oxides.

<table>
<thead>
<tr>
<th>Iron oxide</th>
<th>IR bands (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Magnetite</td>
<td>590</td>
</tr>
<tr>
<td>Maghemite</td>
<td>630, 590, 570, 450</td>
</tr>
<tr>
<td>Hematite</td>
<td>540, 470</td>
</tr>
<tr>
<td>Feroxyhyte</td>
<td>1110, 920, 790, 670</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>1026, 1161, 753</td>
</tr>
<tr>
<td>Goethite</td>
<td>890, 797</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>840, 640</td>
</tr>
</tbody>
</table>

Fig. 3 shows the variation of the zeta potential as a function of pH solution for sample Mt. The pH corresponding to the isoelectric point (pH_{IEP}) of this sample is about 5.0.

Figure 1: X-ray diffraction patterns of samples: (a) Mt, (b) MtSi-b, and (c) MtSi-a.

Figure 2: FTIR spectra of (a) glass, (b) Mt, (c) MtSi-b, and (d) MtSi-a.

Figure 3: Variation of the Zeta Potential as a Function of pH Solution for Sample Mt.
observed similar IEP of magnetite nanoparticles is about 5.0, while all nanoparticles remained magnetic after coating and their particle size decreased about 30% after coating, probably due to the expected effect of the silica coating preventing particle agglomeration. In both cases, coated magnetite presented almost the same zeta potential as that of the pure glass sample. Moreover, the nanoparticles remained magnetic after coating and their particle size decreased about 30% after coating, probably due to the expected effect of the silica coating preventing nanoparticle agglomeration.

**ACKNOWLEDGMENTS**

The authors acknowledge financial support provided by FAPEMIG.
REFERENCES