

Stability of Functionalized Magnetic Particles in a Physiologic Fluid

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ABSTRACT

Magnetite with an average particle size of 20 nm was doped with cobalt ($\text{Fe}_{3-x}\text{Co}_x\text{O}_4$) in order to make small changes in the coercivity ($H_c = 0$ to 0.4 KOe). Cobalt-doped magnetite was covered in a core/shell type; magnetite/silica, magnetite/adipic acid and a double shell magnetite/silica/adipic acid in order to study the effect of cobalt on the degradation in a simulated body fluid. The results indicate that cobalt delays the hydrolytic degradation when silica shell is used in magnetite nanoparticles, but when adipic acid is used the degradation rate is increased.

Keywords: nanoparticles, magnetite, cobalt

1 INTRODUCTION

Magnetite Nanoparticles (Fe_3O_4) are the most used magnetic material for biomedical applications such as cell separation, magnetic resonance imaging, drug delivery and hyperthermia, due to its properties like high enough saturation magnetization that allows its manipulation with an external field (Sun et al., 2004)

The surface of the nanoparticles can be modified with a biocompatible or/and biodegradable polymeric coating in order to acquire the ability to bond with biological entities (Berry, 2009). In vivo applications, the biological fluid degrades the polymeric shell and in this way the biological entities are delivered. Recent publications have emphasized the importance to control the magnetite particles size, because under some critical value, the material exhibits a superparamagnetic behavior. This means that there is no hysteresis in the magnetization curves, which implies that the coercivity is zero (Cullity and Graham, 2009; Neuberger et al., 2005), but only few researches have focused in the effect that this property has in the magnetite nanoparticles stability.

2 EXPERIMENTAL PROCEDURE

2.1 Functionalized Magnetite Synthesis

Synthesis of magnetite was obtained by dissolution of 6.756g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3.426g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 30ml of distilled water, and then NH_4OH were added abruptly in a rapid injection process to increase the pH value to 12. A black precipitate was formed; it was washed several times by magnetic separation until the supernatant reached a pH value of 7. The powder was dried at $30 \pm 5^\circ \text{C}$ during 24 h. In the case of the doped magnetite ($\text{Fe}_{3-x}\text{Co}_x\text{O}_4$), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ partially. Fe^{+3} , Fe^{+2} and Co^{+3} were precipitated in the same conditions. The cobalt content value was between 0.02 to 0.16.

Silica-magnetite nanoparticles was obtained by the hydrolysis of sodium methasilicate follow the procedure of Escobar (2010). Nanoparticles were added to a solution of sodium silicate with sonication at 80°C , the pH was rise at 6.5 using chlorohydric acid (HCl).

In order to obtain acid adipic-magnetite nanoparticles, 150 mg of adipic acid were dissolved in ethanol, the pH was modified with HCl until 1, then 50 mg of magnetite nanoparticles was added, sonication was used for 30 minutes in order to deagglomerate the nanoparticles, then the pH was lowered until 5, after 24 hour the nanoparticles were separated and washed with distilled water until $\text{pH}=7$.

2.2 Stability of Nanoparticles in a Simulated Body Fluid

Phosphate buffer solution (PBS) was obtained through dissolution of the 8 g of NaCl, 0.2 g de KCl, 1.44 g de Na_2HPO_4 and 0.24g de KH_2PO_4 in 800 ml of distilled water. The pH of the solution was adjusted to 7.4 and then the solution was placed in autoclave in order to be sterilized. 50 mg of nanoparticles were added to 0.5 ml of PBS stored at 37°C during 6 and 18 hours, then the nanoparticles were separated and washed with distilled water. The powder was dried at 27°C , after the water was completely evaporated, the nanoparticles were weighed.

X ray diffraction was used in order to study the crystalline structure of the pure and doped magnetite. Cationic substitution in the structures and the functionalization of the nanoparticles were confirmed using infrared spectroscopy (FTIR).

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of cobalt doped magnetite is shown in figure 1. Cobalt content does not change the crystalline structure because all patterns have the six characteristic peak of the inverse spinel structure of the pure magnetite. However, FTIR spectra show that cobalt modify the intensity of the band at 400 cm^{-1} , this band is due to Fe-O bond in octahedral sites of this magnetite structure. The band at 650 cm^{-1} due to the tetrahedral sites of the magnetite structure remains without changes.

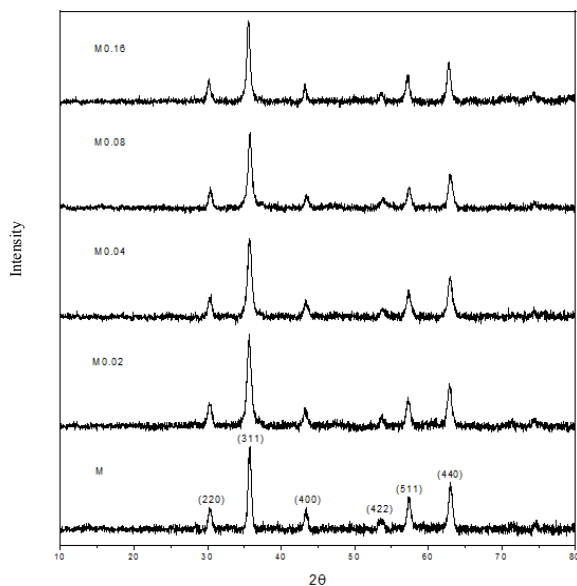


Figure 1. X ray pattern of the cobalt doped magnetite.

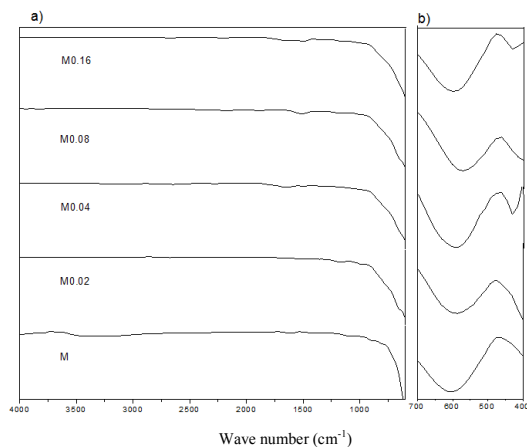


Figure 2. FTIR spectra of cobalt doped magnetite

The coating with silica (MS) and adipic acid (MA) was follow with a FTIR spectroscopy. In Figure 3, all samples of the cobalt doped magnetite show the characteristic band

of Si-O interaction about 1100 cm^{-1} . The band at 650 cm^{-1} due to the tetrahedral sites of the magnetite, is shown at the end of the spectra.

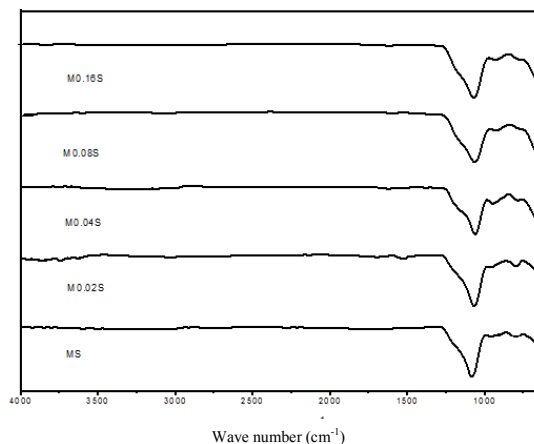


Figure 3. FTIR spectra of silica-magnetite nanoparticles

When adipic acid is used like a coating, the FTIR spectra (figure 4) show the band at 1415 y 1550 cm^{-1} due to symmetric and asymmetric carboxylate functional group (COO^-) (Dolamic y Bürgi, 2007).

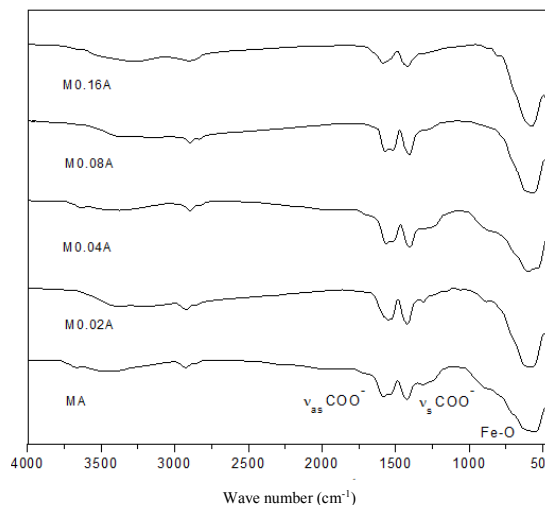


Figure 4. FTIR spectra of adipic acid-magnetite nanoparticles

The weight loss of the functionalized nanoparticles after 6 hours in the simulated body fluid in function of the coercivity is show in the figure 5. In the pure magnetite and silica-magnetite nanoparticles when the coercivity increased the weight loss decreased, so the degradation of the polymeric shell decreased with the cobalt content, because the increment in the coercivity is due to the cobalt content. In the case of the adipic acid-magnetite

nanoparticles the degradation rate of the polymeric shell increase when the coercivity is increased.

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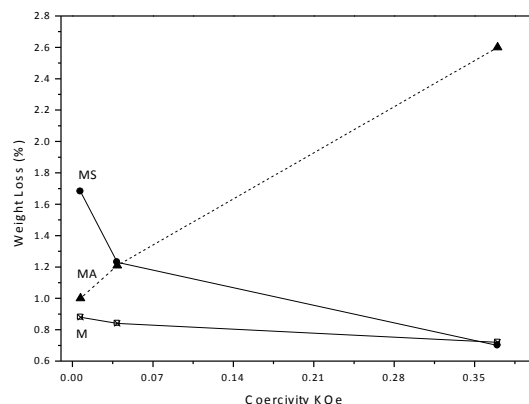


Figure 5. Weight loss of nanoparticles after 6 hour in simulate body fluid.

4. CONCLUSIONS

Cobalt doped magnetite nanoparticles were synthesized by chemical coprecipitation and functionalized with silica and adipic acid. The polymeric coating was degraded by the PBS and the results indicate that cobalt delays the hydrolytic degradation when silica shell is used in magnetite nanoparticles, but when adipic acid is used the degradation is accelerated.

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