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# Synthesis of Magnetic Nanoparticles Coated with Covalently Bonded Carboxymethyl Cellulose

Herrera A\*, Vela L, Morales G

Multifunctional Nanomaterials Research Group. Chemical Engineering Program.Faculty of Engineering.Universidad de Cartagena, Campus Piedra de Bolivar. Street 30 # 48-152. Office D-307. Cartagena, Colombia.Tel (575) 6752040 ext. 214

**Abstract :** Magnetite nanoparticles (MNP) were synthesized through the coprecipitation method and then modified with carboxymethylcellulose (CMC) by using carbodiimide chemistry. These nanoparticles exhibited a crystal size of  $30 \pm 20$  nm and a magnetization saturation of 48 emu/g. FTIR was used to determine the grafting of the CMC molecules, observing a peak at 1507 cm<sup>-1</sup>, which suggest the covalent bond of this hydrophilic polymer onto the magnetic nanoparticles. These nanoparticles exhibited a hydrodynamic size of about  $173\pm 53$  nm after suspension in distilled water, as estimated from DLS.Additionally from TGA, a 16% of organic material was estimated to be grafted onto the nanoparticles, indicating the possibility of a crosslink between a CMC molecule and several nanoparticles, as observed from SEM measurements. Despite agglomeration, modification of magnetic nanoparticles with CMC rendshigh hydrophilic nanoparticles that can be suspended in aqueous media forming a stable colloidal solution.

Keywords : Magnetite nanoparticles, carboxymethylcellulose, Carbodiimide chemistry.

# Introduction

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles belong to the group of nanomaterials that have received great acceptance within the scientific community due to their magnetic properties and their nano-scale size features. These properties make them highly attractive for a wide variety of applications, such as water treatment, biotechnology, ferrofluids, and biomedical applications, especially as agents for MRI and targeted drug delivery<sup>1-5</sup>.For these applications, it is important to modify the magnetic nanoparticles with functional molecules that allow their suspension in aqueous or organic media<sup>4-6</sup>. Among these materials, natural polymers, such as polysaccharides are considered the most popular ones due to the fact that they have a low cost, they are safe and biocompatible<sup>7-9</sup>.

Carboxymethyl cellulose (CMC) is a versatile natural polysaccharide that could be used for the modification of magnetite nanoparticles, because their functional carboxylate anions can be physically adsorbed onto the iron atoms present in the magnetic nanoparticles<sup>7</sup>. This methodology has the disadvantage that nanoparticles can be desorbed from the polymer matrix by changing the pH of the suspension media.

This research is focused on the synthesis of magnetite nanoparticles coated with covalently bonded CMC molecules. In this methodology, magnetite nanoparticles were first synthesized through the coprecipitation method, and then they were encapsulated on a polysiloxane matrix by condensation of aminopropyl silane molecules (APS). Afterwards, CMC molecules could be attached to the magnetic nanoparticles by linking the carboxylate anions present in the CMC molecule and the amine groups previously grafted around the nanoparticle's surface. This covalent bond is achieved by using carbodiimide chemistry in an acid aqueous media. The physical-chemical properties of the synthesized nanoparticles were characterized by different techniques, such as FTIR, TGA, dynamic light scattering, and scanning electron microscopy. Modification of magnetic nanoparticles with CMC rends high hydrophilic nanoparticles that can be suspended in aqueous media forming a stable colloidal suspension.

## Methodology

## Materials

All chemical reagents were used as supplied.Iron (II) chloride 99%, iron (III) chloride 97%, (3-aminopropyl)triethoxysilane (APS) 98%, sodium carboxymethyl cellulose (CMC) 90 kDa, dimethyl sulfoxide (DMSO) 99%, and ammonium hydroxide 29%v/v were acquired from Alfa Aesar.1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC)and N-hydroxysuccinimide (NHS) 98%were purchased from Sigma Aldrich.

#### Preparationof magnetic nanoparticles decorated with functional amine groups

Magnetite nanoparticles were synthetized by the co-precipitation method<sup>3</sup>. In a typical procedure, 30 mL of a ferric solution (0.36 M) was mixed with 30 mL of a ferroussolution (0.18 M). This mixture was stirred at 100 rpm and heated up to 70°C. Then, 9 mL of NH<sub>4</sub>OH were added, which produced a black coloration, indicative of magnetite formation. Synthesis was carried out at pH 8.0 for one hour at 80°C. Afterwards, nanoparticles were decanted using a magnet, washed four times with distilled water and dried at 80°C.

Magnetic nanoparticles (1.5 g) were peptized with nitric acid (2 M)and then suspended in 80 mL of DMSO. To graft the amine (NH<sub>2</sub>) groups onto the magnetic nanoparticle surface, 5 mL of APS, 1.25 mL of deionized water and 0.1 mL of acetic acid were added to the magnetic nanoparticle suspension<sup>9</sup>. Reaction was carried out at room temperature using a shaker at 125 rpm for 3 days. It has been reported that long agitation times ensure the hydrolysis/condensation mechanism of the APS molecules, allowing the encapsulation of the magnetic nanoparticles in a siloxane (Si-O) matrix, which exhibits functional amine groups<sup>9</sup>. Afterwards, functionalized nanoparticles were removed from magnetic decantation, washed twice with ethanol, and dried at room temperature. Finally, magnetic-APS nanoparticles (0.1 g) were suspended in 10 mL of deionized water at pH 4.0 using an ultrasonic bath for 15 minutes. This colloidal suspension was stored at 4 °C for further modification with CMC molecules.

#### Modification of magnetic-APS nanoparticles with covalently bonded CMC

Commercial CMC was acquired with a degree of substitution DS of 0.7 carboxymethyl groups per anhydroglucose unit. Number of carboxylate anions(COO<sup>-</sup>) present per CMC chain can be estimated by (10):

$$\frac{COO^{-}}{CMC \ chain} = OS\left(\frac{M_{W-CMC}}{M_{W-AGU}}\right) (1)$$

where,  $M_{w-CMC}$  is the molecular weight of the CMC (90,000 g/mol) and  $M_{w-AGU}$  is the molecular weight of an anhydroglucose unit (162 g/mol). From this relationship, a number of ~388 COO<sup>-</sup>/CMC chain were estimated. These carboxylate anionscan be used to covalently attach the CMC molecules onto the magnetic nanoparticles through a link with the amine groups (NH<sub>2</sub>) previously grafted around the nanoparticle surface<sup>11</sup>.

To this end, 0.1 g of CMC was suspended in 7.5 mL of deionized water at pH 5.0. Then, 12.5 mg of EDC and 7.5 mg of NHS were added. The activated carboxylic solution was subsequently mixed with the aqueous suspension of magnetic-APS nanoparticles prepared at 4°C. This reaction mixture was shaken at 125 rpm for 2 days at room temperature. Afterwards, modified magnetite-APS-CMC nanoparticles were separated by magnetic decantation, washed twice with ethanol, and dried at room temperature.

Size and crystalline structure were characterized through X-ray diffraction using an X'Pert PRO equipped with a PW3050/60 goniometer. Magnetic properties were determined from a Vibration Sample Magnetometer VSM-7400.An FTIR NICOLET 6700 was used to determine the functional groups grafted around the nanoparticles. Thermogravimetric analysis (TGA) was performed to determine the amount of CMC attached onto the nanoparticle's surface. This measurement was performed using the TGA Q500 V20.8 Build 43 equipment under air with a heating rate of 20°C/min. The hydrodynamic diameter of the CMC coated magnetic nanoparticles was determined by dynamic light scattering DLS using the HORIBA LB-550 equipment. Additionally, images of the functionalized nanoparticles were recorded by scanning electron microscope SEM using the JEOL JSM-6490LV equipment coupled to an energy dispersive spectroscopy (EDS).

## **Results and discussion**

#### Crystal size and magnetic properties

Figure 1.ashows the diffraction pattern obtained for the synthesized magnetite nanoparticles, which exhibited an inverse cubic spline crystalline structure in accordance with the information reported in literature<sup>11</sup>. An average crystal size of  $30 \pm 20$  nm was determined from the Scherrer's equation<sup>12</sup>:

$$D = \frac{K\lambda}{(\beta\cos\theta)(2)}$$

Where D represents the crystal size, K is a constant (0.9),  $\lambda$  is the X-ray wavelength (0.154 nm),  $\beta$  is the full width at the half maximum intensity, and  $\theta$  is the Bragg angle.

Magnetic properties were determined by measuring the magnetization of the sample M as a function of the applied magnetic field  $H^{12}$ . Figure 1.b displays this measurement, from which a magnetization saturation  $M_s$  of 48 emu/g was established. This value is in agreement with the one reported for magnetic nanoparticles (46.7 emu/g)<sup>12</sup>. The magnetic core size was determined from the Langevin function and the magnetic response of the nanoparticles at low and high magnetic fields<sup>9</sup>. From this analysis, a magnetic core size of  $4.0 \pm 1.0$  nm was estimated for the synthesized magnetite nanoparticles.



Figure 1. X-ray diffraction pattern (a) and magnetization response (b) displayed for magnetite nanoparticles synthesized from the co-precipitation method.

#### Modification with CMC molecules

Figure 2.a shows the FTIR spectra recorded for magnetite nanoparticles coated with APS and modified with CMC molecules. From these measurements, vibrations peaks were observed at 2900, 1645, and 1100 cm<sup>-1</sup>, for the sample of magnetite-APS nanoparticles, which correspond to the functional groups CH<sub>2</sub>, NH<sub>2</sub>, and Si-O-Si, present in the chemical structure of the APS molecule<sup>11</sup>. In the case of magnetite-CMC nanoparticles the

presence of peaks at 3600 cm<sup>-1</sup> and 1700 cm<sup>-1</sup>was observed. These peaks are related to the vibrations of the functional groups OH and C=O, respectively, which form part of the hydrophilic CMC polymer. Additionally, a peak at 1507 cm<sup>-1</sup>was observed for the magnetite-CMC nanoparticles, suggesting the covalent bond between carboxylates and amines after activation with the carbodiimide agent EDC in presence of NHS<sup>11</sup>.



Figure 2. (a) FTIR spectra for magnetite nanoparticles coated with APS and CMC molecules; and(b) TGA analysis for magnetite nanoparticles after modification with CMC.

A TGA analysis was performed to determine the organic content of the hydrophilic polymer attached onto the magnetite nanoparticles. Figure 2.b displays this measurement, in which three significant weight loss stages can be observed. The first one occurs at 50°C, and corresponds to the loss of humidity contained in the sample (4%). The other weight loss stages were observed at 261°C and 300°C, which can be attributed mainly to the decomposition of CMC molecules ( $M_{w-CMC}$  90,000 g/mol), as the APS is a very small organic molecule ( $M_{w-APS}$  221 g/mol). This weight loss corresponds to a 16% of the initial sample weight. Therefore, it is inferred that the remaining 80% can be associated to the weight of the inorganic iron oxide material present in the magnetite nanoparticles.

## Hydrodynamic size and size distribution

The hydrodynamic size distribution of the magnetite nanoparticles coated with carboxymethylcellulose was determined by dynamic light scattering (DLS). For this measurement a sample of the MNP-CMC nanoparticles was suspended in distilled water at room temperature. Figure 3 shows this result, from which it was possible to calculate an average hydrodynamic diameter of  $173 \pm 53$  nm by:

$$D_{\mathbf{h}} = \frac{\sum DG_d}{\sum G_d}, \sigma = \left(\frac{\sum [G_d (D_{\mathbf{h}} - D)^2]}{\sum G_d}\right)^{0.5} (3)$$

where *D* is the particle size obtained from the multimodal size distribution (MSD) function of the instrument,  $G_d$  is the relative intensity showed in the histogram, and  $\sigma$ is the standard deviation of the data<sup>11</sup>.



Figure 3. DLS measurement for magnetite-CMC nanoparticles suspended in distilled water.

The wide size distribution observed from DLS can be attributed to the fact that magnetite nanoparticles were synthesized by means of the co-precipitation method, which has been reported to produce small

agglomerates instead of monodisperse nanoparticles<sup>9</sup>. This feature, along with the few amount of CMC that was found to be grafted onto the surface of the nanoparticles (16% according to TGA), can be explained by two proposed case scenarios: (*i*) a single chain of CMC was grafted around a cluster of agglomerated nanoparticles by linking its carboxylate anions (COO<sup>-</sup>) to the previously condensed amine (NH<sub>2</sub>)groups present in the magnetite-APS nanoparticles; or (*ii*) CMC moleculescan form a crosslink between clusters of magnetite nanoparticles, by connecting them through their amine groups, building a much bigger structure, as an amount of approximately 388 carboxylic groups per CMC chain was estimated. Figure 4 illustrates both possible scenarios.



Figure 4. Possible spatial configuration of a CMC chain around magnetic nanoparticles.(a) A single CMC chain surrounding a cluster of MNPs; and (b) Crosslink of CMC and clusters of MNPs.

Scanning electron microscopy (SEM) was used to obtain images of the magnetite nanoparticles after modification with CMC molecules. Figure 5 shows these photographs, and there agglomeration of the magnetite nanoparticles coated with the CMC can be observed, as previously hypothesized. In addition, EDS spectroscopy indicated an elemental composition for magnetite-CMC nanoparticles of about 15.4% of carbon, 39.4% of oxygen, 1.3% of silicon, and 43.9% of iron. This suggests a low content of CMC molecules as compared with the magnetite nanoparticles. This result is in agreement with the results obtained from TGA measurements, which showed an inorganic content of about 80% related to the iron oxide material present in the magnetite nanoparticles. Moreover, it endorses the possible second scenario proposed to explain the spatial configuration of the CMC molecules forming a crosslink with several clusters of magnetite nanoparticles.



Figure 5. SEM images of magnetic nanoparticles coated with covalently bonded CMC.(a) magnification at X20,000; and (b) magnification at X50,000

# Conclusions

An easy and economical method to obtain magnetite nanoparticles modified with covalently bonded CMC was presented. This hydrophilic polymer allows the suspension of magnetic nanoparticles in aqueous media, rendering high stable colloidal solutions. In addition, CMC is a natural polymer that exhibits a high density of carboxylate ions per chain. These functional groups could be used for further modifications to graft other molecules of interest, such as proteins or antibodies. From this point, it could be possible to design a smart platform for different applications, such as biomedicine, sensors, and magnetic actuators.

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