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Size selected synthesis of magnetite nanoparticles in chitosan matrix

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ABSTRACT

We report a new method to prepare magnetite nanoparticles with narrow size distribution and controlled particle size. Magnetite nanoparticles were prepared in the pores of the biopolymer chitosan. To develop pores with different sizes, chitosan was gellified with several concentrations of the crosslinker glutaraldehyde. X-ray diffraction studies showed pattern characteristic for magnetite particles with diameters varying from 4 to 12.7 nm. Mössbauer spectra at room temperature showed only paramagnetic component for the smaller particles, and magnetic and paramagnetic components for the bigger particles, indicating the transition from superparamagnetic to blocked magnetic regime as the particle size increases. The zero field cooling (ZFC) magnetization measurements showed peak temperatures varying from 55 to 151.4 K. The ZFC peak temperatures showed a trend in agreement with the size of the particles. Considering the different experimental time window between Mössbauer spectroscopy and magnetometry, the results obtained from both techniques are in agreement.

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1. Introduction

Chitosan, a polysaccharide biopolymer derived from naturally occurring chitin, displays unique polycationic, chelating, and film-forming properties due to the presence of active amino and hydroxyl functional groups. Chitosan also exhibits a number of interesting biological activities, including antimicrobial activity and diverse stimulating or inhibiting activities toward a number of human cell types. For these reasons, chitosan is widely used in many fields, including medicine, food and chemical engineering, pharmaceuticals, nutrition, and agriculture [1]. The synthesis of biocompatible magnetic nanomaterials has long been of interest in biomedical applications including magnetic resonance imaging, magnetic drug targeting, hyperthermia anti-cancer strategy, and enzyme immobilization [2], the efficacy depends on their particle size. Iron oxides, such as magnetite and maghemite have been used for these technological applications because of its biocompatibility and magnetic properties [3].

Several works were reported on the covalent binding of chitosan onto the surface of previously prepared magnetite nanoparticles to study its thermal properties [4], to produce a magnetic composite for heavy metal ions removal from aqueous solution [5,6], for hyperthermia [7,8]. A few works were reported on the synthesis of

magnetite nanoparticles in chitosan matrix. Magnetite nanoparticles of 13 nm with narrow size distribution were prepared in cross-linked chitosan beads [9] and magnetite with 10 nm of particle size was prepared without a cross-linker [10]. In the first work [9], the crosslinked chitosan was soaked for 30 min in solutions containing ions of Fe^{3+} or Fe^{2+} to produce Fe–chitosan complexes, after each step the Fe–chitosan hydrogel was subsequently washed with water. This process was repeated three times, then the composite was soaked in a NaOH solution for 12 h and the magnetite composite was achieved. In the second work [10] the authors showed the increase in the viscoelastic modulus of chitosan ferrogels, the magnetite nanoparticles had a wide size distribution. In this paper we report a new method for the synthesis of size-selected magnetite nanoparticles in porous chitosan with several degrees of crosslinking, we varied the amount of the crosslinker to modify the polymer porous structure. The crosslinked-chitosan was used as a framework to produce monodispersed magnetite nanoparticles with controlled size and narrow size distribution.

2. Materials and methods

The samples were prepared by in situ coprecipitation of iron salts in a polymer template. The method consists of the reaction at room temperature of reagents entrapped in the porous network of the polymer matrix. Chitosan biopolymer with a deacetylation degree of 85% was obtained from Polymar, Ceará-Brazil. Glutaraldehyde solution, iron nitrate, iron sulfate, citric acid and sodium

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hydroxide were obtained from Sigma–Aldrich. Stock chitosan solution was prepared as follows 10 g of chitosan was dissolved in 500 mL of a 20 w% citric acid solution. Structural and magnetic characterizations were performed using an X-ray diffractometer from Rigaku Miniflex-II (Japan) with a Cu target, Mössbauer spectra were recorded at room temperature in a spectrometer from Wiessel (Germany) with a $^{57}\text{Co:Rh}$ source and activity of 25 mCi, the measurements were performed under the transmission mode. Magnetization measurements were done using a squid magnetometer from Quantum Design (USA).

3. Sample preparation

All the samples were prepared with the same amount of total iron and the chitosan solution. The 7.4×10^{-4} moles of iron nitrate and 3.7×10^{-4} moles of iron sulfate were added to a 10 mL of chitosan solution at room temperature. After stirring at 2000 RPM for 5 min, a given volume of glutaraldehyde was added and stirred for 5 min, then, kept under rest for 5 h. The volumes of the glutaraldehyde solution added were 0.1, 0.3, 0.4, 0.5, 1.0 and 2.0 mL. Since commercial glutaraldehyde has a concentration of 25 v%, glutaraldehyde had a final concentration of 0.25, 0.75, 1.0, 1.25, 2.5 and 5.0 v% in the chitosan solution. After polymerization, the solid gel was gently smashed and then transferred to a 50 mL of a 20 w% NaOH solution. Immediately, the brownish gel changed to a black color. The samples were washed with deionized water and centrifuged until a pH=8, then, dried in the oven for 1 h at 80 °C and grounded to obtain a powder.

4. Results and discussion

4.1. Structural and morphology characterization

X-ray diffraction (XRD) patterns were analyzed using the Rietveld method. The patterns in Fig. 1 show peaks due to magnetite and a broad peak at 20° due to the crosslinked chitosan. The average lattice parameter obtained from the Rietveld refinement was of 0.839 nm. This value is in close agreement with the reported value for stoichiometric magnetite [11]. The magnetite particle size obtained from XRD changed with the amount of glutaraldehyde in two ways: for glutaraldehyde concentration from 0.25 to 1.25 v%, the size of the particles increased from 4.0 to 12.7 nm and above this concentration the particle size decreased to 6 nm. Fig. 2 shows the transmission electron microscopy (TEM) picture for the sample prepared with 1.25 v% glutaraldehyde, the picture shows

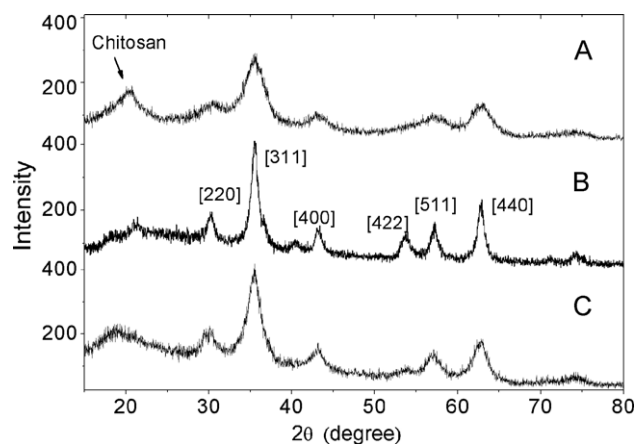


Fig. 1. XRD patterns for magnetite nanoparticles prepared in the chitosan frame and crosslinked with several glutaraldehyde concentrations: (A) 0 v%, (B) 1.25 v% and (C) 5.0 v%.

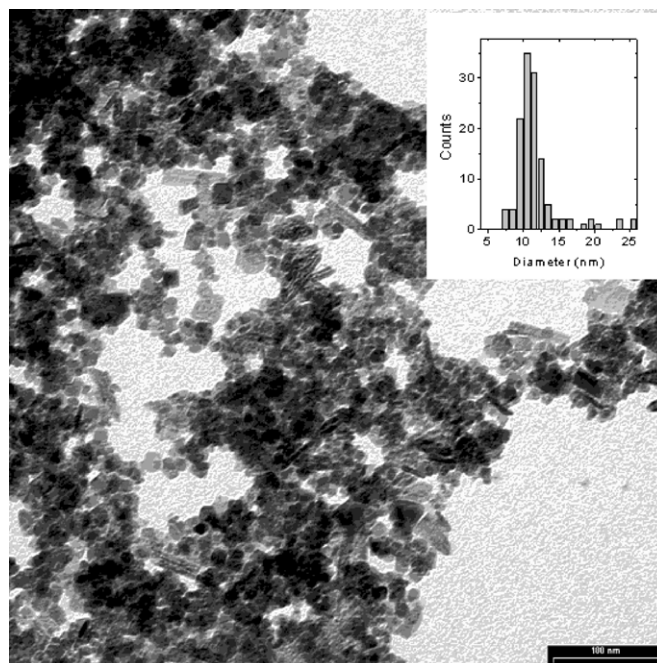


Fig. 2. TEM picture for sample prepared with 1.25 v% glutaraldehyde, scale bar of 100 nm. The inset shows the histogram of the particle size distribution.

monodisperse particles with narrow size distribution, the inset show an histogram with a main particle size at 12 nm. This result supports the value obtained from the XRD analysis.

4.2. Magnetic characterization

The magnetization versus field measurements shown in Fig. 3a were performed at 300 K for the samples prepared in crosslinked-chitosan with the smaller and the bigger magnetite particles size, the loops showed no coercivity indicating that the particles are superparamagnetic. The low magnetization value is related to the total mass that includes the magnetite and the crosslinked polymer mass. Zero field cooling (ZFC) magnetization measurements were performed under a field of 50 Oe for the samples prepared with glutaraldehyde concentration ranging from 0 to 2.5 v%. Fig. 3b shows these measurements. The low intensity of the ZFC peak temperature for the smaller particles prepared with 0.0 and 2.5 v% of glutaraldehyde is related to the large amount of atoms located on the particles surface and to the total mass that includes the crosslinked-polymer mass. The ZFC peak temperatures for the samples showed increasing values ranging from 71.3 to 151.4 K when the particle size increased from 4 to 12.7 nm and the ZFC peak temperature decreased to 54.9 K for magnetite with particle sizes of 6 nm. Fig. 4 shows the trend observed for the ZFC peak temperature and the particle size as a function of the glutaraldehyde concentration. At any temperature, the bigger particles have large magnetic anisotropy energy and should block at higher temperatures when compared to smaller particles. One can determine the blocking temperatures (T_B) by using the Néel-Arrhenius relaxation law, $\tau_m = \tau_0 e^{K_1 V_C / K_B T_B}$, where τ_0 is a constant of the order of 10^{-9} seg, V_C is the critical particle volume for superparamagnetic behavior, K_1 is the magnetic anisotropy constant [12] and τ_m is the measuring time for the Mössbauer (10^{-7} s) and VSM (100 s) techniques. By using the VSM measuring time, the calculated T_B values were of 75 and 14 K for the samples with 12.5 and 6 nm, respectively. The observed peaks in the ZFC appeared at higher temperatures, these results indicate that the particles are experiencing dipolar magnetic interactions due to the proximity among them.

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