# Structure and superparamagnetic behaviour of magnetite nanoparticles in cellulose beads

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ABSTRACT

Superparamagnetic magnetite nanoparticles were obtained starting from a mixture of iron(II) and iron(III) solutions in a preset total iron concentration from 0.04 to 0.8 mol l$^{-1}$ with ammonia at 25 and 70 °C. The regeneration of cellulose from viscose produces micrometrical spherical cellulose beads in which synthetic magnetite were embedded. The characterization of cellulose–magnetite beads by X-ray diffraction, Scanning and Transmission Electron Microscopy and magnetic measurement is reported. X-ray diffraction patterns indicate that the higher is the total iron concentration and temperature the higher is the crystal size of the magnetite obtained. Transmission Electron Microscopy studies of cellulose–magnetite beads revealed the distribution of magnetite nanoparticles inside pores of hundred nanometers. Magnetite as well as the cellulose–magnetite composites exhibit superparamagnetic characteristics. Field cooling and zero field cooling magnetic susceptibility measurements confirm the superparamagnetic behaviour and the blocking temperature for the magnetite with a mean size of 12.5 nm, which is 200 K.

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## 1. Introduction

The study of magnetite nanoparticles is particularly interesting because of their wide variety of technological applications in fields like recording devices, where the grains must be small and magnetically decoupled [1–4]; medicines supported by specific polymers [5–7]; pigments [8]; and biotechnology [9], they are also useful as a raw material in the synthesis of maghemite [10]. Recently, magnetite ferrofluids have become very attractive materials because they can be directed by the action of the magnetic field; they absorb electromagnetic energy with heat evolution and their physical properties may change with the application of a magnetic field [11,12].

Magnetite can be synthesized from several different paths, for example oxidation of $Fe(OH)_2$ precipitate via green rust [13] or through the reduction of hematite with hydrogen [14]. However, in order to obtain nanoparticles, only specific methods have been proven: iron complexes decomposition [15,16], mechanical alloy-ing [17], water/oil (w/o) microemulsion [18,19] and the Massart method [20]. Some of the reported difficulties are the wide particle size distribution and the large amount of solvent to spend [21]. The last two methods above are the most frequently employed and include Fe(II)/Fe(III) fast hydrolysis. In the original preparation reported by Massart, an aqueous mixture of ferric and ferrous chloride in hydrochloric acid is added to ammonia solution. The gelatinous precipitate is then isolated from the solution by centrifugation or magnetic decantation without washing with water. The synthesis of magnetite nanoparticles by this way has the advantages of operation simplicity, the use of economic reagents and it is still useful to study the influence of solution conditions in the size of the precipitated particles [22].

Superparamagnetic iron oxide nanoparticles (SPION) covered with a polymer have been used in medical research such as devices for cell isolation, immobilization of enzymes, controlled release systems and separation of biological materials [23]. Cellulose beads covering inorganic particles, a new kind of composite materials, can be used as organic support. Guo et al. reported the study of inorganic adsorbents inside cellulose beads in the elimination of arsenic from aqueous solutions [24]. Thus, cellulose beads could act as a column bed, suitable for liquid permeability.

Another way of using cellulose beads is to place a magnetic particle inside the structure and thus the new material could react as a magnetic actuator. Moreover, the synthesis of the magnetic cellulose [25] or polysaccharide like carboxymethyl-cellulose [26] and carrageenan [27] has generated a great attention in recent years due to their specific properties: non-toxic nature, biocompatibility, variable ionic permeability, combined with a high hydrophilicity and considerable mechanical strength.

The immobilization of α-amylase onto cellulose-coated magnetite nanoparticles has been reported in the starch degradation study [28]. Previous work describes the synthesis of cellulose beads bearing micrometric magnetite particles and papain immobilization study [29]. In this initial report, the covered micrometric magnetite in a cellulosic matrix results in a net reducing effect of magnetic coercive field with consequential formation of superparamagnetic cellulose composite. The synthesis of micrometric magnetite was performed by basic precipitation of ferrous ammonium sulfate to $Fe(OH)_2$ followed by $NO_3^-$ oxidation [30].

The aims of the present work are: (i) the synthesis of several samples of magnetite nanoparticles, with tuned sizes, using the Massart method at different initial conditions, followed by the synthesis of cellulose–magnetite beads; (ii) the characterization of the samples by means of several solid state techniques and the analysis of the effect of varying iron concentration and temperature in the mean size of magnetite nanoparticles; (iii) the study of the internal morphological structure and magnetic properties of the composite material via electron microscopy.

## 2. Experimental details

### 2.1. Synthesis

#### 2.1.1. Preparation of magnetite nanoparticles

Four samples of magnetite were obtained using the Massart method, with slight modifications [20]: a mixture of 500 ml of ammonium iron(II) sulphate hexahydrate and iron(III) chloride solutions (Fe(III)/Fe(II) 2:1) were added, in a preset total iron concentration of A: 0.04, B: 0.4 and C: 0.8 mol l$^{-1}$, over $NH_3$ (1.5 l, 1 mol l$^{-1}$) at 25 or 70 °C under stirring at 200 rpm and addition flow of 9.5 ml s$^{-1}$ during 20 min. The black suspension was filtered and washed with distilled water until sulphate and chloride ions were removed. All the reagents used were of analytical grade. Samples were labeled as total iron concentration and temperature reaction, i.e. A25 represents the sample precipitated from an iron solution of 0.04 mol l$^{-1}$ at 25 °C.

#### 2.1.2. Preparation of superparamagnetic spherical cellulose beads (SCB)

In order to precipitate the cellulose beads, three sizes of synthetic magnetite, ranging from 6.5 to 12.5 nm in diameter, were used. The composite was obtained by dispersing 0.18 g of $Fe_3O_4$ nanoparticles in water, followed by mixing the previous suspension in 50 g of viscose (9%, w/w of cellulose in the viscose) during 5 min. The mixture was then dispersed in 124 ml of kerosene and 9 ml of oleic acid, maintaining the stirring 10 min at 1700 rpm and room temperature, then was heated to 88–90 °C. The product was filtered and washed with hot water to regenerate the cellulose; finally it was washed in situ with ethanol, acetone and cold water. The concentration of magnetite in cellulose beads was 4% (w/w).

### 2.2. Characterization

For the characterization of the samples, the following techniques and equipment were used: Infrared spectroscopy (IR): The infrared spectra were registered in an Atimattson Genesis Unicam FTIR spectrometer. In the disk preparation, 95.5 mg of KBr and 0.5 mg of sample were mixed, and infrared spectra were recorded in the range between 4000 and 400 cm$^{-1}$.

X-ray diffraction (XRD): The powder diffraction patterns were recorded using a Siemens D500-1 diffractometer with a Daco-MP microprocessor. Recording conditions were Cu monochromatic Kα radiation, at 45 kV and 40 mA.

Scanning and Transmission Electron Microscopy (SEM and TEM): For SEM characterization, a JEOL JSM 6335F microscope operating at 5 kV was used. Each sample was dispersed into butanol by means of ultrasonic stirring and a drop evaporated to dryness on a bronze cylinder. In the case of TEM microscopy, a Philips CM200 FEG electron microscope operating at 200 kV was used. Samples were ultrasonically dispersed in butanol and then dropped on a Cu grid covered with carbon. The thin sections of cellulose–iron oxide composites were prepared by fixing samples on an epoxy resin and foiled with quartz cuter in an ultramicrotome. The particle size was estimated measuring the diameters directly on the micrograph with an error of ±0.2 nm. Image analyses on micrographs were performed using Digital Micrograph Computer Software.

Magnetometry: Magnetic susceptibility measurements were performed in a MPMS-Xl Quantum Design Squid magnetometer. The magnetic susceptibility data were obtained by heating the sample from 2 to 300 K, with an applied field of 0.1 T. First the data were obtained by cooling down the sample to 2 K without any applied field, i.e. zero field cooling measurements (ZFC); then the data were collected after cooling down the sample from 300 to 2 K with an applied field of 0.1 T, i.e. field cooling measurements (FC). Magnetization measurements versus applied field were performed up to 5 T at 5 K and 300 K, respectively.

## 3. Results and discussion

### 3.1. Study of synthesis and crystalline evolution of magnetite nanoparticles

X-ray diffraction patterns recorded for magnetite samples are shown in Fig. 1(a–d). In all of the patterns, the Bragg maxima are indexed to $Fe_3O_4$ (JCPDS 88-0315) which is the only phase present. The results from XRD indicate that the higher the concentration in total iron, the higher the crystallinity of the magnetite precipitate, i.e. at the same reaction temperature of 25 °C, from Fig. 1(a)–(c), the FWHM (full width at half maximum) function reduces while peak maxima enhance. This effect of increasing the crystallite size is also observed when the precipitate is obtained at total iron concentration of 0.4 mol l$^{-1}$, with a temperature increasing from 25 to 70 °C (comparing Fig. 1(b) and (d)).

IR spectrum of a selected magnetite precipitate, in the range from 1000 to 400 cm$^{-1}$, exhibits a typical strong band at 570 cm$^{-1}$, shown in Fig. 2, related to the $\nu_1(F_{1u})$ stretching mode Fe–O [31]. No bands associated with hematite nor iron oxyhydroxide phases are present, which is indicative of a single pure phase.

TEM micrographs of magnetite are presented in Fig. 3, from (a) to (f). The magnetite crystals appeared as quasi-spherical nanoparticles, property which is related to the high nucleation speed during the precipitation. At higher iron concentrations, magnetite nanocrystals also appear better crystallized in accordance with some reported crystalline habits [32], as can be seen in Fig. 3(b and c). The mean particle diameters (MPD) of the magnetite precipitate, as well as other characteristics are shown in Table 1. In the studied total iron concentration range, there is a linear correspondence between the mean particle diameter and the total iron concentration, represented as follows:

$$MPD = 6.1 + 7.9c(Fe)_{tot} \tag{1}$$