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## Preparation and Characterization of Superparamagnetic Chitosan Coated Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) for Gene Delivery

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### Abstract

Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles have been synthesized successfully with controlled co-precipitation technique with ultrasonic. The crystal sizes determined by Debye - Scherrer equation with XRD data were found close to the particle sizes calculated from TEM images, and this indicates that the synthesized particles are nanocrystalline. FT-IR was used to characterize the chitosan coated nanoparticles, and it was found that chitosan coated maghemite nanoparticles were synthesized. The superparamagnetic behavior of nanoparticles was documented by the hysteresis loop measured with VSM spectrometer, and the magnetic saturation of about 67 emu/g and residual field of about 8.5 Oe were recorded for the nanoparticles. These synthesized core-shell nanoparticles have desired properties, which make them attractive for using in biomedical applications, such as gene delivery.

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*Keywords:* maghemite nanoparticles; chitosan; co-precipitation.

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### 1. Introduction

Recently, synthesis of magnetic material on the ultra nanoscale has been a field of intense study. Therefore, the development of uniform nanometer-sized particles has been intensively pursued because of their technological and fundamental importance. The nanoparticle materials often exhibit very interesting electrical, optical, magnetic, and chemical properties, which cannot be achieved by their bulk counterparts. Especially, ironoxide and ferrite attract a

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great deal of interest due to their technological importance in nanotechnologies in information storage, biotechnology, and ferrofluids, Lee et al. (2004).

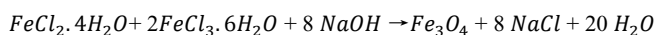
Chitosan-coated magnetic nanoparticles (CMNP) contain a core of magnetic material magnetite ( $Fe_3O_4$ ) and maghemite ( $\gamma - Fe_2O_3$ ). Their chitosan covering provides them with free amino and hydroxyl groups that enable the possibility to bind to a diversity of chemical groups and ions, leading to a number of applications such as protein and metal adsorption, guided drug and gene delivery, magnetic resonance imaging, tissue engineering, and enzyme immobilization, Julia and Rechtenbach (2008), Layek et al. (2010).

Iron oxide nanoparticles have been prepared by a variety of methods; the most popular one is coprecipitation from aqueous solutions. Welo and Bavdisch already in 1925 used an oxidative alkaline hydrolysis reaction to form magnetite and maghemite particles, a process that has been adapted later on. The precipitation with a base form a solution containing ferrous and ferric ions has often been used to prepare maghemite particles with about 10 nm in size. However, most studies were focused on the preparation of very small nanosized iron oxide particles with superparamagnetic properties, Niemirowicz et al. (2012).

In this study, we prepared superparamagnetic nanoparticles by controlled coprecipitation method with ultrasonic device. Then we characterized them with XRD, FT-IR, TEM, and VSM spectrometer.

## 2. Experimental

Ferrous chloride tetrahydrate ( $FeCl_2 \cdot 4H_2O$ ) and ferric chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ) (Merc chemical Co) were used for synthesis of iron oxide nanoparticles. The maghemite ( $\gamma - Fe_2O_3$ ) nanoparticles were synthesized by chemical coprecipitation technique.  $FeCl_3$  (Merc, purity > 99.9%) and  $FeCl_2$  (Merc, purity > 99.9%) taken in 2:1 ratio were dissolved in about 50ml redionized water, and this solution was stirred under strong ultrasonic agitation while heating solution to 70 °C. Next,  $NH_4OH$  was added drop-wise in to this iron solution source under strong ultrasonic agitation for 1 hour, at 70 °C, and bubbling  $N_2$  gas. The chemical reaction of  $Fe_3O_4$  precipitation is expected as follows:



Black  $Fe_3O_4$  particles were separated by permanent magnet. They were then washed gradually with  $HNO_3$  (400 ml, 0.1M) and  $HNO_3$  (200ml, 0.01M) before being suspended in  $HNO_3$  (100ml, 0.01M). This solution turned a brown-red colour. After cooling, the particles were washed 3 times with dionized water and separated from the solution using a permanent magnet, for preparation  $\gamma - Fe_2O_3$ - chitosan NPs, chitosan (0.5 g) in 100ml of 0.2 wt% acetic acid solution, amount of colloidal nanoparticles in water were added to the chitosan solution. The mixture was treated with ultrasonic device for 10 min., then 5ml of 25 wt%  $NH_4OH$  was added and the mixture was treated with ultrasonic for 10min. again. After the reaction, the composites were separated by centrifuge and were washed by dionized water for several times. At the last step, the products were floated in 0.5% v/v acetic acid solution.

The powder sample of  $\gamma - Fe_2O_3$  was subjected to X-ray diffraction (XRD) on a BURRKER X-ray powder diffractometer using Cu-K $\alpha$  radiation in order to check the phase purity and average crystallite size. IR spectra were recorded from 400 to 4000 cm<sup>-1</sup> using a BURUKER- DECTOR FT-IR spectrometer. Room temperature magnetization was done by using a vibrating sample magnetometer (VSM, MDK6). The transmission electron microscopy (TEM) study was carried out on electron microscopy instrument (EM 900, Zeiss).

## 3. Results

### 3.1. XRD analysis

Figure 1 shows the XRD pattern of maghemite particles synthesized by co-precipitation technique. The XRD diffraction peaks correspond well to maghemite ( $\gamma - Fe_2O_3$ ). An estimation of the magnetite nanoparticles size has been performed from the Scherrer formula, Teodor et al. (2009).

Where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum;  $\theta$  is corresponding Bragg angle,  $K$  is the Debye-scherrer constant. According to the Debye-scherrer equation, the average crystallite size of the chitosan coated  $\gamma - Fe_2O_3$  nanoparticles is 15nm. XRD result was confirmed by the results of Layek et al. (2010), Laurent et al. (2008).

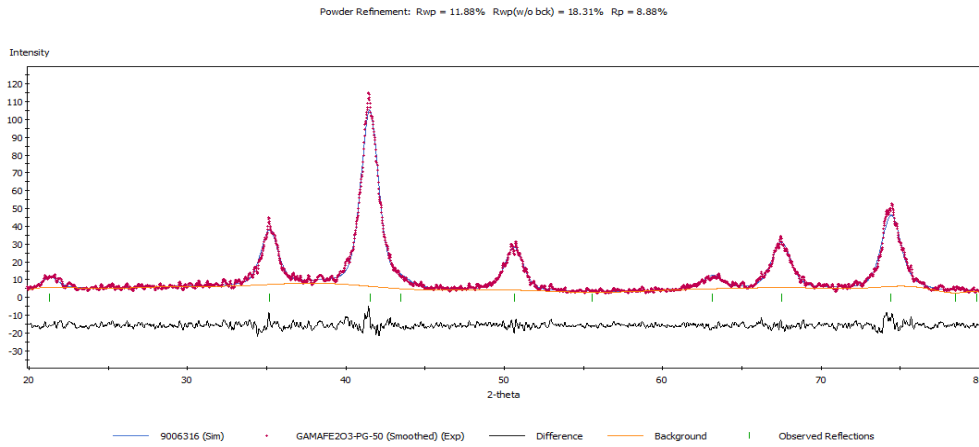


Fig. 1. XRD pattern of maghemite nanoparticles.

### 3.2. FT-IR Spectra

To confirm the structure of the samples FT-IR spectrum was recorded at room temperature. In Fig. 2 a strong absorption band at  $581\text{ cm}^{-1}$  is assigned to vibration of the  $Fe - O$  functional groups. The peak around  $3388\text{ cm}^{-1}$  observed in curve indicates to the  $OH$  group, peak at about  $1620\text{ cm}^{-1}$  can be assigned to  $N - H$  binding vibration, and peak  $1381\text{ cm}^{-1}$  operated to  $C - O$  stretching of primary alcoholic group in chitosan.

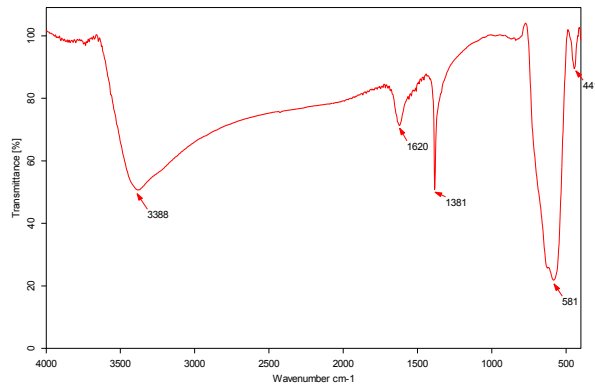


Fig. 2. FT-IR spectrum of maghemite nanoparticles.

### 3.3. VSM analysis

Magnetic materials having around a dozen nanometers in size are used to show a superparamagnetic behavior in which coercivity has below 150 Oe value. The hysteresis loop of chitosan -  $\gamma - Fe_2O_3$  nanoparticles at room temperature is showed in Fig. 3. This phenomenon proved that magnetic nanoparticles made in this study are superparamagnetic because coercivity value is 8.5 Oe. Also in Fig. 3, saturated magnetization  $M_S$  of magnetic nanoparticles is 67 emu/g, and is lower than that of the bulk and naked  $\gamma - Fe_2O_3$  (73.5 emu/g).

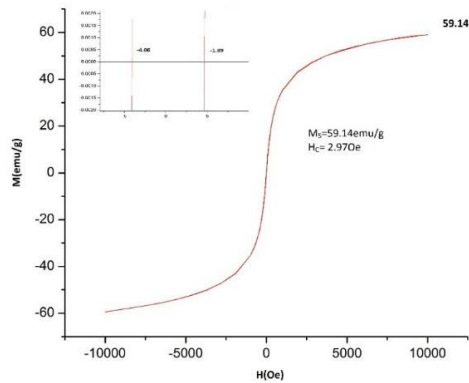


Fig. 3. Magnetization (M–H) curves of nanoparticles.

### 3.4. TEM image

The size and shape of chitosan-maghemite nanoparticles were investigated using TEM. The TEM image of chitosan- $\gamma - Fe_2O_3$  nanoparticles, shown in Fig. 4, was proved that nanoparticles were monodisperse and had a mean diameter of 10nm. In addition, by comparison with the work of Way et al their particles size is reported 10-15 nm(Search et al. n.d.).

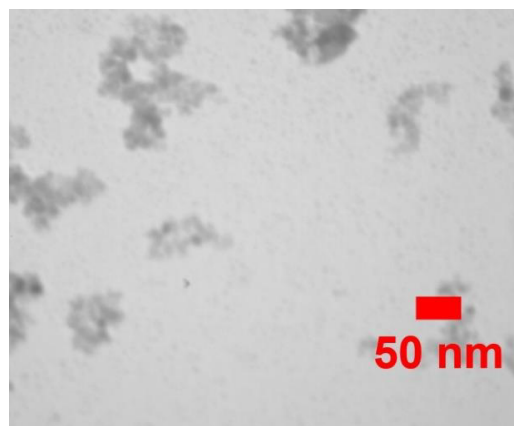


Fig. 4. The TEM images of thechitosan- $\gamma$ -Fe2O3 nanoparticles.

#### 4. Conclusions

High purity chitosan coated maghemite nanoparticles with dimensions of 10nm were synthesized by controlled chemical co-precipitation method. The magnetization of nanoparticles at room temperature was 67 emu/g at the magnetic field. Due to small mean size and low coercivity, the obtained nanoparticles were super-paramagnetic. The nanoparticles which were prepared by these method have a good potential to be applied as bio-materials applications such as gene delivery.

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