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# Design and characterization of colloidal solution of manganese ferrite nanostructure coated with carboxymethyl chitosan

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## HIGHLIGHTS

- Colloidal solution of $MnFe_2O_4$ nanostructures were fabricated in presence of CMC.
- XRD patterns showed the spinel structure for the both bare and CMC coated NPs.
- TEM results revealed a spherical shaped morphology.
- The presence of CMC content of 3 wt% showed the optimum uniformity and stability.

## ARTICLE INFO

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## ABSTRACT

In this study, colloidal solution of superparamagnetic $MnFe_2O_4$ nanostructure was fabricated in presence of carboxymethyl chitosan. Different content of polymer and manganese-iron concentrations were examined and the physical and chemical properties of magnetic nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR), x-ray diffraction pattern (XRD), transmission electron microscopy (TEM) zeta-potential and vibrating sample magnetometer (VSM). XRD pattern showed the spinel structure for the both bare and polymer coated nanoparticles. FTIR spectra demonstrated that the carboxyl methyl chitosan binds to the surface of magnetic nanoparticles via a hydrogen bond and it was supposed that the mechanism of CMC stabilizing the suspension is electrostatic repulsion. Furthermore, the stability evaluation by zeta potential presented the optimum value of 50 mV for CMC concentration of 3 wt%. TEM results revealed a spherical shaped morphology with an average diameter of 9 nm and narrow size distribution for the optimum polymer concentration of 3 wt%. Both naked and CMC-$MnFe_2O_4$ nanostructures demonstrated super-paramagnetic behavior, as confirmed by zero coercivity and remanence on the magnetization loops. Moreover, the presence of low (10%) manganese content revealed the optimum net magnetization of 37.80 emu/g.

## 1. Introduction

Multi-functional nanoparticles (NPs) are now became alternative system with great potential in technological, biological and medical applications [1]. Among different types of nanoparticles, magnetic nanoparticles have attracted particular interest because of their tunable thermal properties useful for therapeutic purposes as well as their intrinsic performance as contrast agents in magnetic resonance imaging (MRI) [2]. Today, superparamagnetic iron oxide (SPION) particles such as magnetite ($Fe_3O_4$) or its oxidized form maghemite ($\gamma$-$Fe_2O_3$) with appropriate surface chemistry are the most commonly employed in biomedical applications as their biocompatibility has already been confirmed [3]. The elemental doping of iron oxide provides possibility of achievement the high performance magnetic agents which may hold a great potential for biomedical applications and highlight the necessity of careful effort to enhance the library of functional doped-SPIONs [2,4–6]. So, careful studies correlated to the stability and control of particle size are critical because the properties of the nanocrystals strongly rely on the dimension of the nanoparticles [7]. It is known that the polymer coating not only inhibits aggregation and increases stability but also leads to the creation of more hydrophilic nanostructures and provides a variety of surface functional groups to bind drug molecules [4]. Among different polymeric stabilizers, chitosan (CTS), a cationic copolymer of glucosamine and N-acetylglucosamine is widely studied for its useful characteristics such as biorenewabilty, biodegradability, biocompatibility, bioadhesivity and non toxicity [8–12]. Chitosan, as a natural polysaccharide is one of the most abundant carbohydrates in nature and is mostly derived from the exoskeleton of

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crustaceans [10]. The main challenges facing with chitosan is its limited solubility and lack of effectiveness as absorption enhancer at neutral pH values [13,14]. Thus, chitosan is chemically modified so as to improve the solubility and the ability to interact with other substances. Carboxymethyl chitosan (CMC) is a water-soluble chitosan derivative in which the $–CH_2OH$ group of each monomer substituted by –COOH group. The amphiphilic, blood compatibility and effective membrane penetrable properties of CMC provide the possibilities of ample of applications [15–17]. The current study has been designed the synthesis of colloidal solution of carboxymethyl chitosan bound manganese ferrite nanostructure. As-synthesized $MnFe_2O_4$ nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Zeta potential, transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM).

## 2. Materials and method

Carboxymethyl chitosan (deacetylation degree 90%, Molecular weight: (249.12)n) was purchased from Santa Cruz Biotechnology, Inc., Dallas, TX, USA. Iron chlorides ($FeCl_2$& $FeCl_3$), Manganese chloride ($MnCl_2$) and sodium hydroxide (NaOH) of analytical grades were supplied by Merck Inc. (Billerica MA, USA) and were used without further purification.

The manganese ferrite nanostructures were synthesized by a modified co-precipitation technique from the reported by Sanjai et al. [18]. Briefly, an appropriate amount of iron salts and manganese chloride were dissolved in double distill water (50 ml), where the mole fraction of $Fe^{2+}$ to $Fe^{3+}$ was adjusted to 1:2 for all samples. A mixture of iron and manganese was continuously stirred for 30 min under nitrogen atmosphere. Next a solution of polymer (carboxymethyl chitosan (20 ml)) dissolved in double distill water was added slowly to metal ions solution and stirred for further 30 min to form a homogeneous mixture. Following the stirring, 3 ml of 1.5 M sodium hydroxide was added drop wise and the mixture heated up to 60 °C and kept stirring for 2 h at this temperature in order to complete the reaction. Finally, the colloidal black-brown suspension was obtained and stored at 4 °C in the dark until further use. Polymer concentration was changed from 0 to 5 wt% and the ratio of metal ions of Mn and Fe was varied in the range of 0.1–0.9 mol% according to this formula: $Fe_{1-x}$ $Mn_x$ (x = 0.1,0.3,0.5,0.7,0.9).

### 2.1. Characterization

The structural properties of the synthesized samples were recorded by powder X-ray diffraction (explorer, company GNR Italy) with copper target (Cu-K$\alpha_1$ line, $\lambda = 1.54056$ Å) at an interval of 20–70°. Morphology of nanoparticles was characterized using Transmission Electron Microscope (CM120, Philips& Leo 912 AB) operating at an accelerating voltage of 200 kV; by depositing the suspension on carbon coated 100 mesh size copper grids. Fourier transform infrared spectra were recorded on a Thermo Nicolet spectrometer (AVATAR 370, USA) at 25 °C.

Magnetic properties were measured at room temperature by vibrating sample magnetometer (VSM, Magnetic Danesh Pajoh Inst.) in a maximum field of 15 kOe. The hysteresis of the magnetization was obtained by changing outside fields (H) between −10,000 and + 10,000 G and operating at 300 K. The stability of the nanoparticles in an aqueous solution (pH 10.8) was investigated by zeta-potential (Zeta Compact model, CAD Company, France) of the particles as a function of time at 25°.

## 3. Results and discussion

### 3.1. X-ray diffraction

The formation of crystal structure of manganese ferrite nanoparticles was confirmed by x-ray diffraction. Fig. 1 presents the peak positions at 30.49°, 35.83°, 43.72°, 57.47°, 63.01° matching with (220), (311), (400), (511) and (440) crystal planes of spinal cubic structure of $MnFe_2O_4$-NPs reported in ICDD PDF 01-075-0449. It can be observed that the peak position of capped nanoparticles slightly shifted towards lower 2θ values. This may attributed to internal stress and a lower degree of crystallinity, which clearly explain the interaction of polymer and metal ions [19,20].

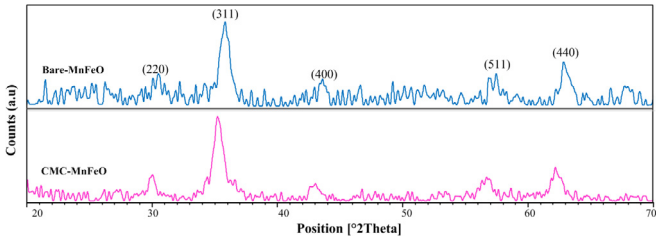


**Fig. 1.** X-ray diffraction patterns of Bare and CMC coated $MnFe_2O_4$ nanoparticles.

Fig. 2 shows the XRD pattern of synthesized NPs at various concentrations of metal ions. It was found that the higher manganese concentration (0.9 mol%) entirely changed the crystal structure from cubic to tetragonal and the peak positions at 29.19°, 30.78°, 33.10°, 35.90°, 39.26°, 44.04°, 52.48°, 58.05°, 60.42°, 64.00° matching with (112), (200), (222), (211), (004), (420), (321), (224), (116) crystal planes of $Mn_3O_4$ mostly highlighted.

### 3.2. TEM

To further assess the role of CMC in the synthesis of $MnFe_2O_4$-NPs, the polymer concentration was varied from 0 to 5 wt% during the fabrication and the samples were subjected to TEM analysis (Figs. 3–7 & Table 1). Morphological evaluation of the TEM images demonstrated that the CMC concentration of 0–3 wt% lead to the formation of generally spherical shaped nanoparticles and further increase of CMC formed polyhedral particles. As depicted in TEM images, naked $MnFe_2O_4$ NPs have a significant degree of agglomeration with the mean size of 12 nm (Fig. 3), while the presence of CMC lead to formation of relatively discrete $MnFe_2O_4$ nanoparticles. As shown in Table 1, there is not much difference in mean particle size of bare and 0.5 wt% CMC concentration (11 nm), while the presence of polymer conducted a narrower size distribution (5.8 nm). It seems that in both cases, rate and number of nucleation did not much alter but the presence of CMC in

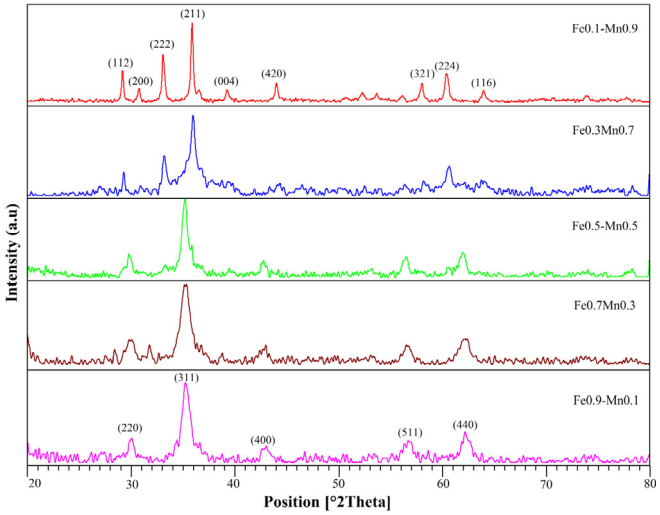


**Fig. 2.** X-ray diffraction patterns of different Fe-Mn oxide mixtures ($Fe_{1-x}Mn_x$) (x = 0.1,0.3,0.5,0.7,0.9).