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# The influence of PEG 20,000 concentration on the size control and magnetic properties of functionalized bio-compatible magnetic nanoparticles

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#### ABSTRACT

Here in this paper, we report how the bio-compatible polymer poly ethylene glycol (PEG 20000) controls the size of the magnetite nanoparticles synthesized by the simple cost effective co-precipitation method. The size of the particles calculated by Scherrer formula from the Powder X-ray Diffraction (PXRD) reports clearly depicts this. The Fourier Transform Infrared spectroscopy (FT-IR) studies confirm the bonding of the PEG molecules with the magnetite nanoparticles. The Scanning Electron Microscope (SEM) and EDAX results confirm the surface morphology and the elemental composition. The saturation magnetization values of the particles also increases as seen from the Vibrating Sample Magnetometer (VSM) results. These particles can be very well used in various bio-medical applications.

Keywords: Magnetite, Iron Oxides, PEG, Hysteresis, Retentivity, Coercivity.

#### INTRODUCTION

Magnetic nanomaterials can be produced by a number of physical and chemical routes that differ in the final properties of the product. The direct products of the iron oxide nanoparticles obtained are organic soluble, which to some extent limits their applications in biological field. Therefore, it is essential to engineer the surface of iron oxide nanoparticles with hydrophilic molecules to minimize agglomeration of the particles [1]. Certain natural polymers have been employed to modify the surface of the particles to enhance their function. These polymers include starch, dextran, dendrimers, polyethylene glycol (PEG) and polyethylene oxide (PEO) all of which are known to be biocompatible [1]. The most successful development in the direction of nanocomposites was that of coated particles as both the kernel and coating material are distributed homogenously on a nanometer scale. The particles produced in the first reaction step are coated with the distance holder phase in a second reaction step [2]. The necessary perfect distribution of the two phases is obtained only by coating the particles of the active phase with the distance holder phase. This coating process will lead to the minimization of surface energy which is an important principle in nanomaterials [2]. The main objective in the preparation of magnetic nanoparticles consists in a strict control of particle size and colloid stability / dispersibility under physical conditions. These properties can be modulated by coating the particles in different ways: either the iron oxide nanoparticles are physically incorporated in a polymer matrix or their surface is functionalized with polymer molecules [3].

The main objective of our work is to synthesize biocompatible, water-soluble, soft iron oxide nanoparticles using the versatile, convenient and cheap co-precipitation method and to functionalize their surface with polyethylene glycol

(PEG 20,000) at various concentrations and to determine their properties. The polymer polyethylene glycol (PEG 20,000) has been chosen as the surfactant since it is found that the polyethylene glycol is known to be a biocompatible polymer [4] and the coating layer plays a key role in preventing the particles from agglomeration, also provide good water dispersibility by exposing hydrophilic PEG layer on the surface of magnetic nanoparticles. In addition, the PEG coated iron oxide nanoparticles are highly suitable and promising materials for biomedical applications such as magnetic drug targeting, MRI imaging [5,6], drug delivery [7] etc.

C L Cooper et al have synthesized PEG coated monodisperse iron oxide nanoparticles from organic solvents that are readily dispersed in aqueous solution and can be used for nanomedicine, it utilizes nanometer scale constructs to treat diseases at the cellular level [8]. Ja Young Park et al reported the synthesis of highly water dispersible PEG as surface modified ultra small superparamagnetic iron oxide nanoparticles by a simple one step synthesis and proved that the PEG surface modified ultra small superparamagnetic iron oxide nanoparticles can be used as MRI contrast agents [9]. Sheng Tong et al has reported the development of a versatile coating method combined with controllable core synthesis to generate an array of water soluble superparamagnetic iron oxide nanoparticles with different core size and core thicknesses [10]. For this study, polyethylene glycol was employed to improve the coating efficiency and size distribution of the particles.

W. Brullot et.al have obtained facile and versatile synthesis of broadly applicable ferrofluids based on polyethylene glycol coated iron oxide nanoparticles and found that by altering the mass percentage of the PEG coated iron oxide nanoparticles in a ferrofluid, important properties could be tuned [11]. Cole A. J et.al has reported polyethylene glycol modified, cross linked starch coated iron oxide nanoparticles and aimed to develop a long circulating magnetic iron oxide nanoparticles platform capable of sustained tumor exposure via the circulation and thus potentially enhanced magnetic tumor targeting [12]. Results indicated that the polyethylene glycol modified, cross linked starch coated is a promising platform for enhanced magnetic tumor targeting.

In this paper, the synthesis of magnetite  $(Fe_3O_4)$  nanoparticles and magnetite  $(Fe_3O_4)$  nanoparticles surface functionalized with bio-compatible polymer PEG 20,000 using the simple and cost effective co-precipitation method at various concentration has been described. The synthesized particles are characterized by various characterization techniques such as X-ray powder diffraction (XRD) analysis, fourier transform infra red spectrometer (FT-IR), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) analysis.

#### MATERIALS AND METHODS

#### 2. Synthesis

#### 2.1 Synthesis of pure Fe<sub>3</sub>O<sub>4</sub>

For the synthesis of pure  $Fe_3O_4$  nanoparticles, initially 1.99 gm of  $FeCl_2.4H_2O$  and 3.24 gm of  $FeCl_3$  were dissolved in 50 ml of millipore water and 30 ml of  $NH_4OH$  was also dissolved in 50 ml of millipore water separately. Both the solutions in the beaker were allowed to stir for about half an hour, to achieve uniform mixing of the particles. Then, the  $NH_4OH$  solution was added dropwise into the first solution till a pH of 9 is obtained. After the required pH is reached, the solution was kept under stirring.

After thorough mixing of the solution, the solution was kept under sonication for about half an hour and the precipitates were obtained by repeated cycles of centrifuging in millipore water. The obtained precipitate was dried at  $120^{\circ}$  C for about two hours and then grinded. The iron oxide nanoparticles were finally obtained. The assynthesized particles are named as sample A. The chemical reaction for Fe<sub>3</sub>O<sub>4</sub> formation may be written as,

# $Fe^{2+} + Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$

#### 2.2 Synthesis of Fe<sub>3</sub>O<sub>4</sub> surface modified with PEG 20,000

For the functionalisation of the magnetite nanoparticles with the polymer polyethylene glycol (PEG) of molecular weight 20,000 ; 1.99 gm of FeCl<sub>2</sub>.4H<sub>2</sub>O and 3.24 gm of FeCl<sub>3</sub> were dissolved in 50 ml of millipore water and 30 ml of NH<sub>4</sub>OH was also dissolved in 50 ml of millipore water separately. Then 2.5 gm of PEG 20,000 was taken and dissolved in 100 ml of Millipore water and the solution was allowed to stir. After a few hours of stirring, nearly 25 ml of the surfactant solution was added to the two beaker solutions separately and were allowed to stir for uniform mixing. The remaining 50 ml of the solution was kept aside.

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Then, the surfactant mixed NH<sub>4</sub>OH solution was added dropwise to beaker I until the pH of 9 was obtained. The formation of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles was identified by the colour change. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained by centrifuging the precipitate in Millipore water for several times. The obtained precipitate was made to dry at room temperature for 24 hours. The dried powder was then dissolved in the remaining 50 ml of the surfactant solution. The obtained solution was kept in sonicator for about half an hour and again centrifuged in Millipore water for several times to obtain the PEG coated Fe<sub>3</sub>O<sub>4</sub> nanopaticles. The particles were dried at 120° C for two hours and then powdered. The particles were taken as and sample B. The same procedure was repeated for various concentrations of PEG 20,000 taken in 5 gm, 7.5 gm and 10 gm.

#### **RESULTS AND DISCUSSION**

#### 3.1 X-ray diffraction study

The powder XRD pattern for the as-prepared magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles was recorded by a Rich Secifer, X-ray diffractometer using monochromatic nickel filtered CuK<sub> $\alpha$ </sub> ( $\lambda$ = 1.5416 Å) radiation. The crystal structure and the phase purity of the synthesized pure magnetite (Fe<sub>3</sub>O<sub>4</sub>) and different concentrations of PEG coated magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were examined. Fig. 1 displays the typical XRD pattern of the magnetite (Fe<sub>3</sub>O<sub>4</sub>) samples. The stronger peaks reveal the high purity, good crystallinity and the peak broadening indicates the formation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. For Fe<sub>3</sub>O<sub>4</sub> nanoparticles and for the PEG surface modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles various peaks corresponding to planes (220), (311), (400), (422), (511) and (440) are observed. The crystal structure is found to be face centered cubic with lattice constant a = 8.4272 Å and this matches well with JCPDS (89-3854) data (a=8.393 Å).

The XRD patterns of pure magnetite (Fe<sub>3</sub>O<sub>4</sub>) and PEG 20,000 surface modified magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles are similar and there is a small difference in the intensity of the various peaks obtained. The diffraction pattern and the relative intensities of all the diffraction peaks match well with those of magnetite (JCPDS No. 19-0629). The average particle size of the samples was obtained using the Scherer formula and the results are presented in table 1. From the results, it is clear that there is a gradual decrease in the average particle size when the concentration of the PEG 20,000 in the samples has been increased. This ascertains that the addition of the polymer PEG 20,000 plays a major role in controlling the size of the magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles.







Table 1: Average particle size of the different samples

Sample	Average particle size	
Pure Fe <sub>3</sub> O <sub>4</sub>	18 nm	
Fe <sub>3</sub> O <sub>4</sub> /PEG2.5	16 nm	
Fe <sub>3</sub> O <sub>4</sub> /PEG5	15 nm	
Fe <sub>3</sub> O <sub>4</sub> /PEG7.5	13 nm	
Fe <sub>3</sub> O <sub>4</sub> /PEG10	12 nm	

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#### 3.2 FT-IR analysis

The FT-IR spectra of the pure  $Fe_3O_4$  and the PEG coated  $Fe_3O_4$  nanoparticles are shown in Fig 2. For the pure  $Fe_3O_4$  nanoparticles, the peak at broad vibration band between 3600 and 3200 cm<sup>-1</sup> is associated with the OH stretching vibrations of water molecules which is assigned to -OH absorbed by  $Fe_3O_4$  nanoparticles. The peak at ~2925 cm<sup>-1</sup> corresponds to the stretching vibration of  $-CH_2$ , the peak at ~1406 cm<sup>-1</sup> is attributed to the vibration of -CH and the peak at ~582 cm<sup>-1</sup> corresponds to the Fe-O bond vibration of  $Fe_3O_4$  nanoparticles.

For the case of PEG coated magnetite nanoparticles, it has been observed that there is a slight shift in the peaks obtained compared to the pure magnetite nanoparticles. For all the synthesized PEG coated  $Fe_3O_4$  nanoparticles at various concentrations, the peaks were obtained at ~2924 cm<sup>-1</sup> which corresponds to the stretching vibration of – CH<sub>2</sub>, the peak at ~1619 cm<sup>-1</sup> is assigned to the carboxylate (COO<sup>-</sup>) stretching vibration, the peak at ~1406 cm<sup>-1</sup> is attributed to the vibration of –CH and the strong peak at ~579 cm<sup>-1</sup> is assigned to the Fe-O bond, which confirms the presence of magnetite nanoparticles. The peaks corresponding to the bonds CH<sub>2</sub>, -CH and -COO<sup>-</sup> are the strong evidence to show that the synthesized magnetite nanoparticles surface has been coated with PEG.



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#### 3.3 SEM analysis

Scanning electron microscope (SEM) was employed for morphological study using a JEOL JSM 6310 operated at 10 kV. The SEM images of the pure  $Fe_3O_4$  and the PEG coated  $Fe_3O_4$  nanoparticles are shown in Fig 3. The SEM studies reveal the structure and surface morphology of the synthesized pure  $Fe_3O_4$  nanoparticles and the PEG coated  $Fe_3O_4$  nanoparticles. An even distribution of the magnetite nanoparticles was observed in all the images. The agglomeration of the synthesized nanoparticles has been highly reduced when the concentration of the PEG is increased. In the case of drug delivery, when the magnetic nanoparticles are coated with PEG, it is believed that their circulation time in the blood stream, their stability and permeability through body tissues is increased [1].



Fig. 3 (a) SEM images of pure Fe<sub>3</sub>O<sub>4</sub>

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Fig. 3 (b) SEM images of Fe<sub>3</sub>O<sub>4</sub>/PEG2.5



Fig. 3 (c) SEM images of Fe<sub>3</sub>O<sub>4</sub>/PEG5



Fig. 3 (d) SEM images of Fe<sub>3</sub>O<sub>4</sub>/PEG7.5



Fig. 3 (e) SEM images of Fe<sub>3</sub>O<sub>4</sub>/PEG10

#### **3.4 Magnetic studies**

To study the magnetic properties of the as prepared  $Fe_3O_4$  and PEG 20,000 functionalized  $Fe_3O_4$  nanoparticles, the room temperature (300K) magnetization hysteresis curves are measured using Lakeshore Vibrating Sample Magnetometer (VSM) 7410.

The room temperature (300 K) magnetization curves i.e the graphs for M vs. H has been plotted for the pure magnetite (Fe<sub>3</sub>O<sub>4</sub>) and PEG functionalized magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles and is shown in Fig 4. From the hysteresis curves, the saturation magnetization, coercivity and retentivity values were obtained (Table 2). The hysteresis curves are steep with low retetivity and coercivity thus confirms that the synthesized particles are soft magnetic. Also, the very small area of the hysteresis curves indicates that the particles are very close to the superparamagnetic state. It may be due to the slight larger particle size over the domain size values. From the values tabulated, the saturation magnetization value for the synthesized pure Fe<sub>3</sub>O<sub>4</sub> nanoparticles is found to be 45.364 emu/g. This magnetization value was found to be greatly reduced when compared with the bulk material's value of 92 emu/g. The reduction in  $M_s$  (saturation magnetisation) value compared to the bulk value is due to the decrease in

particle size. The large surface to volume ratio may also be another factor that leads to the reduction in  $M_s$  value. It is clearly seen that the saturation magnetization values has been increased for the PEG surface functionalized magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles as compared to the pure magnetite (Fe<sub>3</sub>O<sub>4</sub>) value. This increasing tendency of  $M_s$  is consistent with the growth of the particle size and enhancement in crystallinity.





(e) Fig. 4 Magnetic hysteresis curve of (a) pure Fe<sub>3</sub>O<sub>4</sub> (b) Fe<sub>3</sub>O<sub>4</sub>/PEG 2.5 (c) Fe<sub>3</sub>O<sub>4</sub>/PEG 5 (d) Fe<sub>3</sub>O<sub>4</sub>/PEG 7.5 and (e) Fe<sub>3</sub>O<sub>4</sub>/PEG 10

Table 2: Saturation magnetization, coercivity and retentivity values of the different samples measured at 300 K

Sample	Magnetisation	Coercivity	Retentivity
	(emu/gm)	(Oer)	(emu/gm)
PURE Fe <sub>3</sub> O <sub>4</sub>	45.364	315.15	14.649
Fe <sub>3</sub> O <sub>4</sub> /PEG 2.5	60.604	328.25	15.909
Fe <sub>3</sub> O <sub>4</sub> /PEG 5	33.613	325.08	9.5744
Fe <sub>3</sub> O <sub>4</sub> /PEG 7.5	52.363	329.86	14.813
Fe <sub>3</sub> O <sub>4</sub> /PEG 10	57.043	326.72	15.704

#### CONCLUSION

The magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were successfully synthesized by a facile co-precipitaion technique and their surface has been engineered by coating with non-toxic, eco-friendly and biodegradable polyethylene glycol (PEG 20,000) at varied concentrations. X-ray diffraction analysis shows the crystal structure and the phase purity of the synthesized magnetite nanoparticles. The average particle size of the synthesized magnetite nanoparticles confirms that there is a gradual decrease in the size of the particles when the concentration of the PEG 20,000 has been increased. Fourier Transform Infrared Spectroscopy studies explain the vibration modes of the synthesized Fe<sub>3</sub>O<sub>4</sub> and the bond confirms the presence of PEG 20,000 in the synthesized magnetite nanoparticles. SEM studies reveal the structure and surface morphology of the synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The magnetization value is found to increase for the PEG 20,000 coated nanoparticles when compared to the pure magnetite nanoparticles. Thus, the surface functionalistaion of the as-synthesized magnetite nanoparticles with PEG 20,000 effectively controls the particle size and show enhanced magnetization values. The present study demonstrates the synthesis of water solvable magnetic nanoparticles with promise for various applications including biomedicine.

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