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RESEARCH ARTICLE

One-step synthesis of modified Fe₃O₄ nanoparticles with enhanced magnetic property.

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Manuscript Info Abstract

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A novel *one-step* synthesis protocol has been developed to reduce the modification reaction time while preserving the saturation magnetization of the Fe₃O₄ magnetic nanoparticles (MNPs). A modified co-precipitation method was employed to synthesize Fe₃O₄MNPs in an aqueous solution. Surface modification was carried out using citric acid and polyethylene glycol and their dendrimers as biocompatible modifier. Vibrating sample magnetometry ensured a higher saturated magnetization of modified MNPs compared with unmodified MNPs. The spinel structure of Fe₃O₄MNPs remained intact, verified using X-ray Diffractometry.

Surface morphology and the size of modified particles were examined using Transmission Electron Microscopy and X-ray Diffractometry. It was observed that the proposed synthesis method reduced the modification reaction time dramatically with high magnetic saturation level. The proposed method eliminated the post modification steps such as particle separation, purification, dispersion of synthesized nanoparticles in the reaction media used in conventional procedures.

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Introduction:-

Nanoparticles gain a lot of attention in academic studies and industrial applications. Magnetic nanoparticles can be utilized in various ways, very similar to those of nanoparticles in general. However the magnetic properties of these particles add a new dimension. MNPs were used in variety of applications such as drug delivery agents (Mu, 2011), image contrast agents in MRI (Masoudi, 2012), efficient hyperthermia for cancer therapy (Kumar, 2011), heavy metal removal (Xin, 2012), dye removal (Yan, 2013) and many other applications. So far, many protocols have been developed for Fe₃O₄MNPs preparation, including hydrothermal (Zhang, 2012), pyrolysis (Chen, 2011), microwave hydrothermal synthesis (Kholam, 2002), γ -ray radiation (Wang, 1997) and thermal decomposition of organic precursors (Aslibeiki, 2011). It is well-known that Fe₃O₄MNPs have a poor dispersion in water and organic solvents due to their large specific surface area, high surface energy and magnetization; therefore, there is a tendency to modify MNPs surface. Conventionally, surface modification was carried out on already synthesized nanoparticles (Zhang, 2013; Ge, 2012; Mahdavian, 2010). These multistep procedures are time consuming and require lots of solvent for purification. However, finding new or even improved synthetic methods which reduce the reaction time and/or production costs are of demand in prospering technologies. Therefore, there is a great interest in producing modified nanoparticles by *one-step* or even *one-pot* methods; for instance, *one-pot* synthesis of modified silica nanoparticles was studied by Pourabbas and et. al. (Marini, 2008; Pourabbas, 2010; Effati, 2012) and *one-step* production of modified silica nanoparticles was studied as well (Wang, 2008). In order to duplicate the similar idea in the synthesis of modified Fe₃O₄MNPs, co-precipitation method was opted with regard to its ease and simplicity. In the chemical co-precipitation approach, the Fe₃O₄MNPs are formed by reaction of Fe³⁺/Fe²⁺ at a pH of around 10 to 11. But, the pH value of the original ferrite solution containing Fe²⁺ and Fe³⁺ is around 1–2. Hence, a base

solution such as NaOH, KOH or NH₄OH solution is necessarily added to the ferrite solution by pouring or titrating. This base solution also can act as a catalyst in subsequent reactions between surface hydroxyl groups and modifying agents. Regarding to the aqueous media of reaction, molecules with carboxylic end functional groups are soluble in the reaction media, therefore coprecipitation method has distinct advantages. Citric acid (CA) and dendrimer of polyethylene glycol-co-citric acid were used as the biocompatible surface modifying agents (Sun, 2007; Wan, 2007). Biocompatibility of this dendrimer was thoroughly examined by Namazi et al. (2005). Therefore, citric acid (CA) and dendrimer of citric acid-polyethylene glycol (CA-PEG) were selected with regard to their biocompatibility, nontoxicity and water solubility for subsequent possible applications.

Materials and methods:-

Materials:-

Ferric chloride hexahydrate (FeCl₃·6H₂O, >99%), ferrous chloride tetrahydrate (FeCl₂·4H₂O, >99%), Citric acid and sodium hydroxide were purchased from Merck and used without further purification. Citric acid-ethylene glycol polymer with citric acid end functional groups (6840 Mw) was purchased from Kimiaexir.

Modified Fe₃O₄ preparation:-

1.99 g (0.01 Mol) FeCl₂·4H₂O, 5.41 g (0.02 Mol) FeCl₃·6H₂O were dissolved in 40 ml deionized water in a two neck round bottom flask. A solution of 1 g CA (for citric acid modified MNPs) and 5 g CA-PEG polymer (for polymer modified MNPs) in 20 ml deionized water was then added to the ferrite solution with vigorous magnetic stirring under nitrogen flux. A solution of 6 g NaOH in 50mL deionized water was then added to the above mixtures slowly under nitrogen flux in ambient temperature. After an hour, obtained black colored precipitates were separated from the mixture using a permanent magnet, rinsed for several times and then dried under reduced pressure at room temperature.

Characterization:-

Surface chemistry of modified Fe₃O₄MNPs was investigated using FTIR (Bruker Alpha). Phase composition, particle size and structure were examined by X-ray powder diffraction (XRD, philips X' Pert PRO). TEM (Philips EM208S) was used to study the surface morphology and also particle size. Magnetic properties of the MNPs were examined by a vibrating sample magnetometer (VSM) (EG&G Model 4500).

Result and discussion:-

Surface chemistry:-

Fig. 1 compares the FTIR spectra of unmodified Fe₃O₄ MNPs (a), CA-PEG modified Fe₃O₄ MNPs (b) and citric acid modified Fe₃O₄ MNPs (c). The characteristic peaks at 579 and 630 cm⁻¹ are attributed to Fe-O bonds in Fe₃O₄ MNPs. These peaks are observed in all samples. The broad peak at 3425 cm⁻¹ is assigned to surface O-H bending vibration or adsorbed water molecules on Fe₃O₄ MNPs surface. These peaks are also detectable in all samples. The peak at 1620 cm⁻¹ is due to asymmetric vibrations of H-O-H. Peaks at around 1700, 1100 cm⁻¹ are attributed to stretching vibration of C=O and C-C(O)-C respectively. Peaks at about 3400 and 1339 cm⁻¹ are due to O-H bending vibration and C-O stretching vibration respectively. Peaks around 852 and 2960 cm⁻¹ are assigned to out of plane bending and stretching vibration of C-H bonds respectively. These peaks reveal that citric acid and polymeric chains are successfully grafted onto the surface of Fe₃O₄ MNPs, and also some of carboxylic groups remain free, which is integral for subsequent reactions such as absorbing or drug attachment.

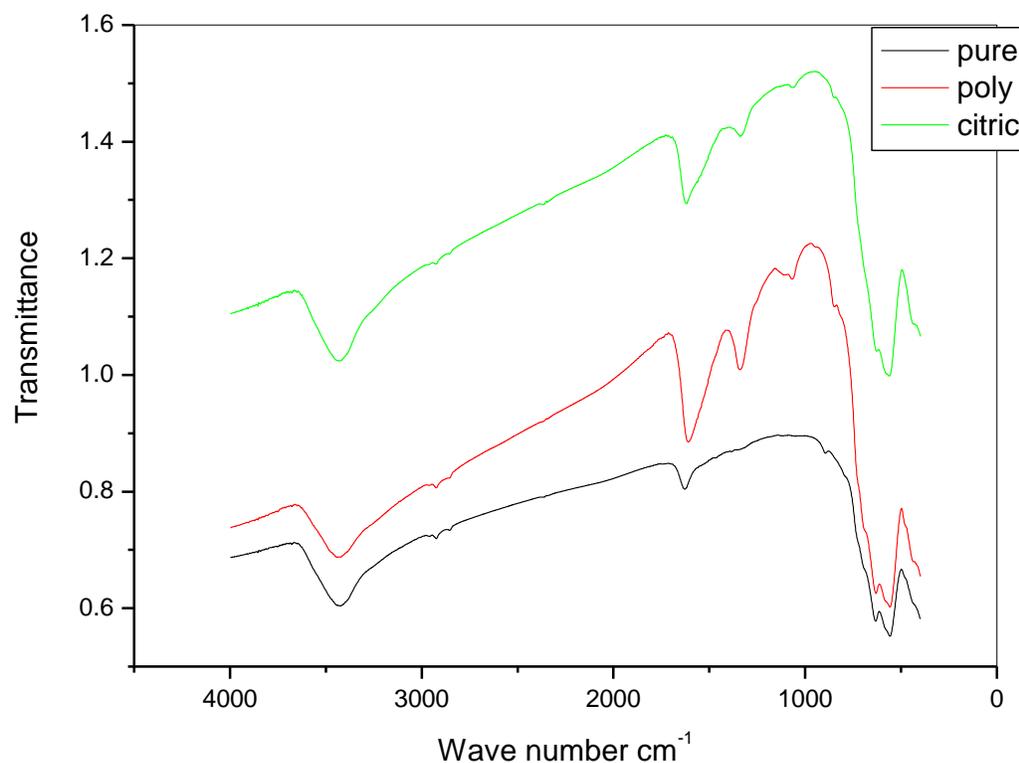


Fig 1. FTIR spectrums of unmodified Fe₃O₄ MNPs (a), polymer modified Fe₃O₄ MNPs (b) and citric acid modified Fe₃O₄ MNPs (c).

Surface morphology:-

Fig. 2 (a) and (b) shows the TEM images of Fe₃O₄MNPs modified with citric acid and CA-PEG polymer respectively. As it can be seen, modifying agents are successfully attached to the surface of MNPs and a likely core-shell structure is observed. This result was confirmed by FTIR spectra which were discussed in the previous section. The effect of molecular size of modifying agent on particle size, can be understood when Figures 2 (a) and 2 (b) are compared. Synthesized Fe₃O₄MNPs in the presence of the CA-PEG polymeric chain, have bigger and more uniform size distribution than those of synthesized in the presence of citric acid. Average sizes of obtained MNPs were measured using image analyzer software (Image J). Mean particle sizes are 23 and 19 nm for CA-PEG modified Fe₃O₄ MNPs and CA modified Fe₃O₄MNPs respectively. These values will be confirmed by XRD data as well.

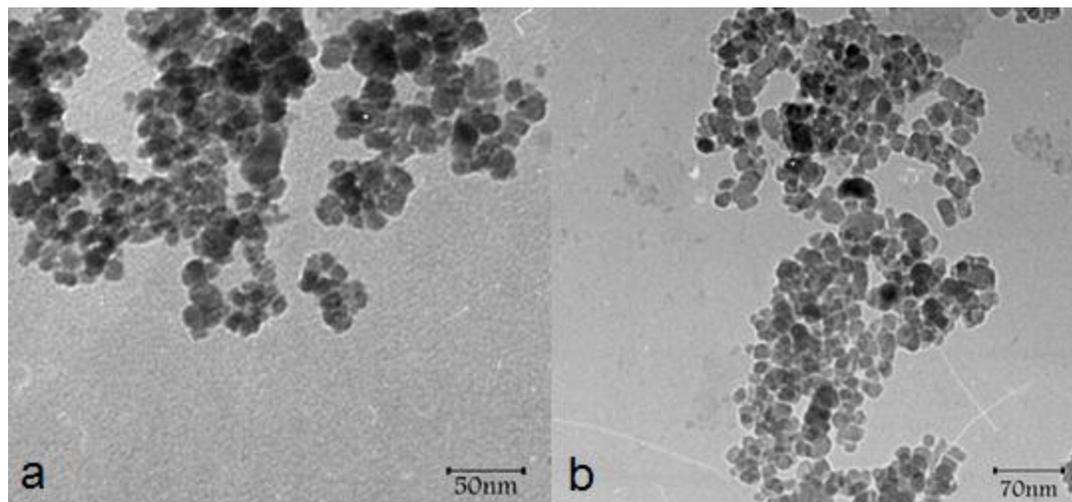


Fig 2. TEM images of Fe₃O₄ MNPs modified with citric acid (a), and TEM images of modified Fe₃O₄ MNPs modified with polymer (b).

XRD analysis:-

XRD graphs are utilized to investigate structure, phase composition and particle size. Fig. 3 (a), (b) and (c) shows the XRD patterns of pure Fe₃O₄MNPs, citric acid modified Fe₃O₄MNPs and modified Fe₃O₄ MNPs with CA-PEG polymer respectively. In each sample only the phase of Fe₃O₄ is detectable. Other phases which are the usual co-products in the chemical coprecipitation procedure are not observed here. Moreover the XRD patterns clearly depict that the presence of CA or CA-PEG in the reaction media has no interference in the magnetite phase formation. Average particle sizes are calculated from Scherer equation:

$$D_c = K\lambda / b \cos 2\theta$$

Where λ is the X-ray wave length (1.54060 Å), b is the width of the XRD reference peak at half height, K is a shape factor which is about 0.89 for magnetite and 2θ is the reference peak center. The results are summarized in table 1. The calculated average size of the modified particles is slightly different from those obtained from TEM. TEM images show a larger size than XRD results for modified particles because non crystalline layers at the particle surface are not detectable in XRD analysis.

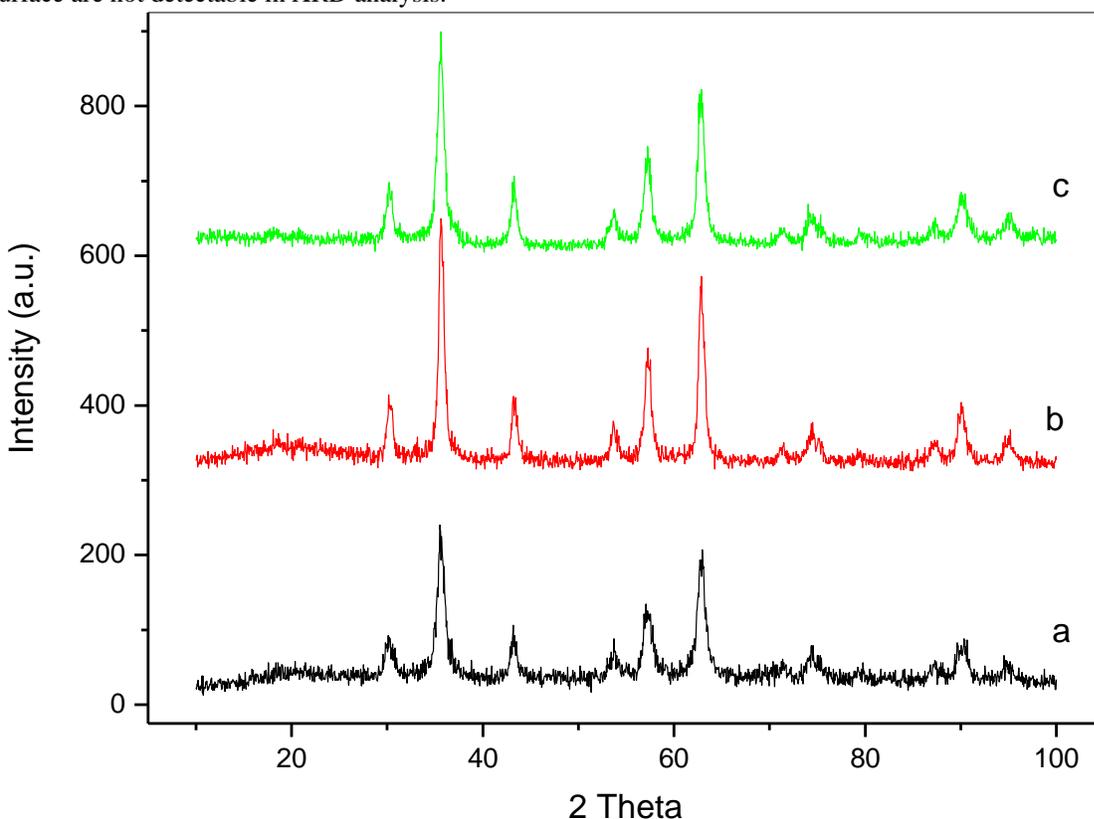


Fig 3. XRD patterns of unmodified Fe₃O₄ MNPs (a), polymer modified Fe₃O₄ MNPs (b) citric acid modified Fe₃O₄MNPs (c).

Table 1 Fe₃O₄ MNPs average particle size determined by XRD and TEM.

Samples	Particle mean size Measured from XRD (nm)	Particle mean size Measured from TEM (nm)
Pure Fe ₃ O ₄	16	-
Citric Acid Modified	17	19
Polymer modified	19	22

Magnetic properties:-

Saturation magnetization of the modified and unmodified samples was measured using a vibrating sample magnetometer (VSM). The magnetic hysteresis curves for all particles (modified and unmodified) exhibit super paramagnetic behavior, Fig 4. It is observed that the saturation magnetizations of modified particles are higher than unmodified Fe₃O₄MNPs whereas a significant decrease was reported in previous studies (Zhang, 2012; Hong, 2009; Kim, 2007; Qu, 2010; Bach, 2012; Hasanpour, 2012; Du, 2012; Dai, 2013).

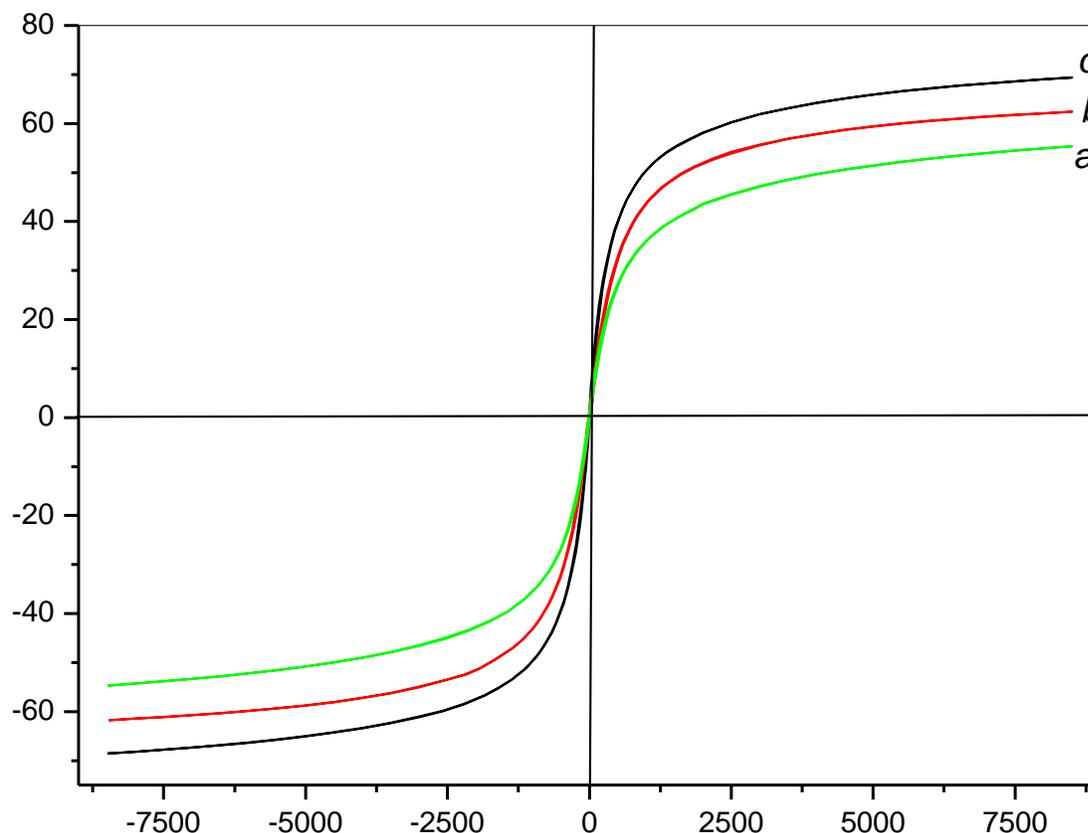


Fig 4. Magnetization loops of the unmodified Fe₃O₄ MNPs (a), citric acid modified Fe₃O₄ MNPs (b) and polymer modified Fe₃O₄ MNPs (c).

The magnetic data on the unmodified and functionalized Fe₃O₄MNPs revealed an increase in the magnetization. The simultaneous synthesis and modification has no impact on the structure of the Fe₃O₄MNPs, as confirmed by XRD. It is thus hypothesized that the CA and CA-PEG functionalization processes change the surface magnetic state of the particles - magnetic dead layer- (Borges, 2001; Oguz, 2008). Similar observations have been reported for thiol modified Au NPs (Crespo, 2004) and Fe₃O₄MNPs (Daou, 2008) which magnetic saturation increased in the presence of certain functional groups. The strong covalent bonding between CA/CA-PEG with reactive groups on Fe₃O₄ surface assumed to be the origin of the improvement in the magnetic properties of the Fe₃O₄ MNPs upon functionalization. The current findings are of significance because biomedical devices employing magnetic Fe₃O₄ MNPs (Radisic, 2006) are more sensitive and more efficient with higher magnetization values while Fe₃O₄MNPs have biocompatible surface with regard to functional groups on the surface. The presented results here introduce a novel procedure to synthesize and modify Fe₃O₄MNPs toward optimal production method and usage for biomedical applications.

Conclusion:-

According to their applications, Fe₃O₄MNPs have been intensely investigated however *one-step* synthesis/modification of the nanoparticles has never been studied so far. This was examined in this work. The success of *one-step* synthesis of modified MNPs was confirmed by XRD, FTIR, TEM and VSM. XRD patterns showed only pure phase of Fe₃O₄ and FTIR results along with TEM images confirmed surface modification. VSM results showed that both modified and unmodified MNPs have super paramagnetic behavior. This data also revealed another important feature of *one-step* modified MNPs. They showed higher magnetic saturation which is crucial in subsequent applications of MNPs. *One-step* synthesis of modified Fe₃O₄MNPs reduced reaction time, production cost and contamination level of modified MNPs by elimination of post modification requirements, including separation, purification, dispersion of already synthesized nanoparticles in reaction media and a new catalyst for the modification reaction. It can be a step toward industrial production of modified MNPs.

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