SYNTHESIS AND CHARACTERIZATION OF OLIVE OIL MEDIATED IRON OXIDE NANOPARTICLES

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A non-toxic chemical synthesis method for preparing iron oxide nanoparticles has been developed by adopting olive oil as capping and stabilizing agent. Olive oil is a fatty acid which is used for controlling the tendency of precipitation and agglomeration of the hydroxide precursors on the morphology of the iron oxide nanoparticles. The purpose of natural olive oil is to enhance the biocompatibility. The characterization of iron oxide nanoparticles was performed by X-ray powder diffraction (XRD) analysis, Transmission electron microscopy (TEM), Particle size analyzer (PSA), Vibrating sample magnetometer (VSM) and Ultraviolet –Visible Spectroscopy (UV-Vis) studies.

1.Introduction

The methods of synthesis of nanoparticles under non-toxic conditions with phosphine free are increasingly used for chemical synthesis. The co-precipitation technique is the most widely used for preparing Metal oxide nanoparticles. The nanoparticles of iron oxide such as Magnetite (Fe_3O_4) and Maghemite (γ- Fe_2O_3) are very prominent material in biomedical applications [1-2]. Since these iron oxide nanoparticles are biocompatible and inexpensive, they find very attractive role in cell separator, drug delivery in cancer therapy, contrast agent in MRI imaging system, hyperthermia, etc.,

Co-precipitation method is the conventional method to prepare metal oxide nanoparticles [3-7].This process consists of dissolving a metal salt precursor, normally a chloride, oxychloride or nitrate, and the particular metal hydroxides form and precipitate in de-ionized water by adding a base solution such as NaOH or NH_3OH in the precursor solution. The resultant chloride salts, ie., NaCl or NH_4Cl are washed away by using de-ionized water or ethanol. Then the hydroxide is calcined after filtration and washing to obtain the final oxide powder. This method often uses trioctylphosphine(TOP), tributylphosphine(TBP), trioctylphosphine oxide(TOPO) or Oleylamine (OA) and other long chain amines as solvents and capping agents to avoid the uncontrolled precipitation. But the reactions with TOP and TBP are quite hazardous and unstable in the synthesis of nanoparticles.

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The iron oxide nanoparticles are excreted through the liver after the treatment, hence the nanoparticles of iron oxides should have to be a non-toxic is an added advantage in biomedical applications. The usage of olive oil as a capping agent and as a stabilizer eliminates the need of for the use of air-sensitive, toxic and expensive chemicals such as TOP,TBP or amines and leads to highly dispersed and high quality nanoparticles with good biocompatibility and smaller particle size. It has been reported that these iron oxide nanoparticles have been stabilized with different biocompatible stabilizing agents such as polyethyleneglycol(PEG) (Suzuki et al.,1995), polyvinyl alcohol(PVA) (Lee et al., 1996), polylactic acid(PLA) (Gomez-Lopera et al.,2001), polyethylene (Chatterjee et al., 2002), block copolymer (Harris et al., 2003),dextran (Paul et al.,2004), chitosan (Hassan et al.,1992) starch (Veiga et al., 2000), oleic acid(Chun-Yu Wang et al.,2009). But all these stabilizing agents are being derived by chemical treatment and have been used for biomedical applications. Hence there may be chance of harmfulness to the biological system.

The olive oil used here is a natural stabilizer and which is derived without any chemical reaction. The olive oil is unlikely to cause allergic reactions, and as such can be used in preparations for lipophilic drug ingredients. Further the olive oil is very effective in controlling of heart disease, stroke, cholesteral level and the usage of iron oxide nanoparticles with its coating during the treatment may have the advantage to the blood cells. Olive oil is predominantly a triacylglyceride of long chain fatty acids with free fatty acids (FFA), Polyphenols (Antioxidants), Peroxides, Polycyclic Aromatic Hydrocarbons (PAHs),vitamin K and vitamin E. The Primary fatty acids in olive oil are oleic acid [8], linoleic acid and linoolenic acid. Oleic acid is monosaturated and makes up 85% of olive oil ($C_{17}H_{35}COOH$) or $CH_3-(CH_2)_7 - CH = CH - (CH_2)_7 - COOH$ and linoleic acid is polyunsaturated which makes up 15% of olive oil [9-11] . The olive oil mediated synthesis of particles were successfully demonstrated and shows that the nanoparticles were stable for several months without any decomposition and favours particles homogeneity (Javeed Akhtar et al, J.mat.Chem,2010).

2. Experimental

2.1 Materials

Ferrous sulphate ($FeSO_4$, 99%), ferric chloride ($FeCl_3$, 99%) and Sodium hydroxide (NaOH) were obtained from Merck (India) and used as received. The olive oil (Rivera type with 1% acidity) was received from local market. Double distilled water was used for the reactions at all stages of the synthesis.

2.2 Synthesis and Characterization

Iron oxide nanoparticles were prepared by the method of co-precipitation with the addition of olive oil as a surfactant. 50 ml of 1 mol/L solution $FeCl_3$ and 50 ml of 2 mol/L $FeSO_4$ were mixed and dissolved in deionized water. Then 3 mol/L Sodium hydroxide was added into the above solution and the pH value was maintained between 10-11 with continuous stirring using a magnetic stirrer for 30 minutes and a dark precipitation was formed immediately. Olive oil of 10 ml was heated to 70°C and added in precipitated solution with continuous stirring for 48 hr. The resulting ferrosoferric hydroxide dehydrates yielded precipitation of the iron oxide particles and they were washed several times with double distilled deionized water and then filtered. Finally it was dried at 150°C for 2 hr and grinded to fine powder.

The X-ray diffraction characterization of the nanoparticles was carried out using PANalytical - X'per PRO model and TEM photograph was taken by Philips CM12 model. VSM studies carried out by Lakeshore, USA; Model 7404,particle size analysis was done by Malvern (U.K.) Make 2000E model and UV-Vis spectrum was analyzed by Carry 500 Varian model.

3. Results and discussion

The iron oxide powder sample with olive oil as surfactant is prepared and characterized by XRD studies. The XRD patterns reveal that the powders are in nanosize and the nanoparticles of iron oxide prepared by wet chemical route are crystalline. The fine particles nature of the sample is reflected in the X-ray line broadening. The X-ray diffraction analysis shows that the sample prepared by the co-precipitation method resulted the formation of mixed phase of Fe_3O_4 and γ- Fe_2O_3 nanoparticles. The presence of γ-Fe_2O_3 nanoparticles is due to the oxidation of Fe_3O_4 nanoparticles during synthesis. The eight characteristic peaks for (220), (221), (311), (400), (422), (511), (440) and (533) correspond to iron oxide spinel structure of magnetite and maghemite. Fig.1 shows the XRD pattern of the mixed phase of nanocrystalline iron oxide (Fe_3O_4 and γ- Fe_2O_3) and it matches well with the JCPDS data (JCPDS cards #75-0033 (Fe_3O_4), # 39-1346 (γ- Fe_2O_3).The application of Debye- Scherrer's formula to the major peak intensities reveals the information of Fe_3O_4 and γ- Fe_2O_3 nanoparticles are with average size of 19.2 nm [12-17].
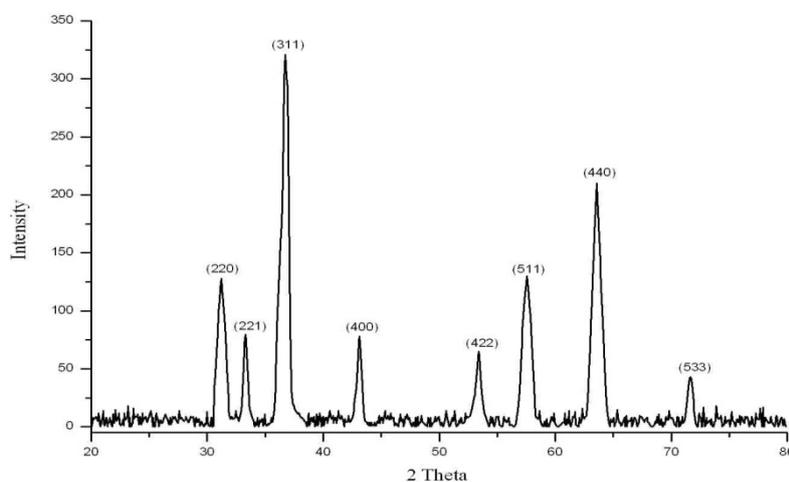
Fig. 1. XRD of nano particles of Magnetite(Fe_3O_4) and Maghemite (γ- Fe_2O_3)

The TEM image and particle size distribution of the olive oil coated iron oxide nanoparticles are shown in fig.2. The TEM samples were prepared by placing a drop of dilute suspension of iron oxide nanoparticles in ethanol on a carbon coated copper grid and allowed the solvent to evaporate slowly at room temperature. It reveals that the particles are in spherical shape and its average size obtained from TEM analysis is almost same as it is estimated from XRD analysis.
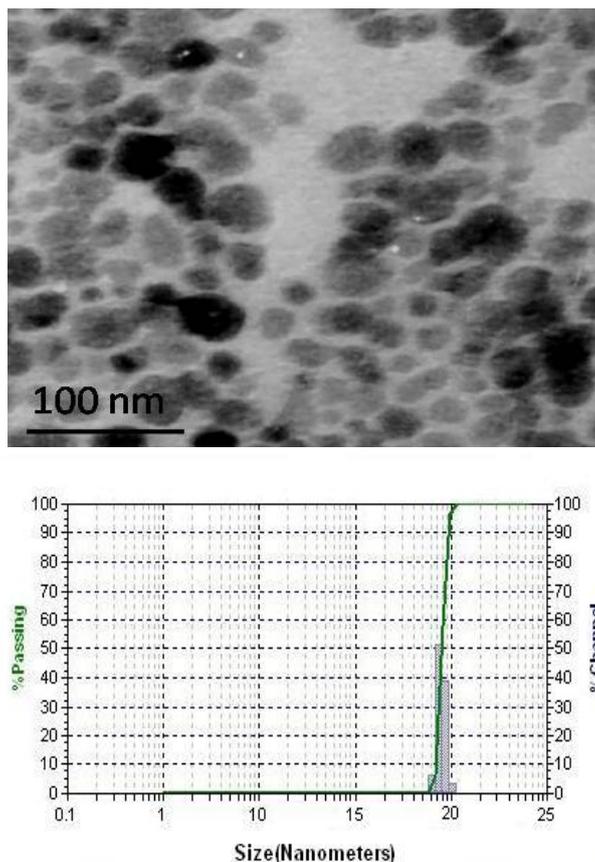
Fig. 2. TEM image and Particle Size distribution of olive oil mediated iron oxide nanoparticles

The magnetic properties of the olive oil coated iron oxide nanoparticles was measured by Vibrating-sample magnetometer. Fig.3 shows the magnetization of the coated iron oxide nanoparticles with reference to the external field at room temperature. Its saturation magnetization is predicted as 40 emu/g and it exhibits superparamagnetic behavior [18-20].
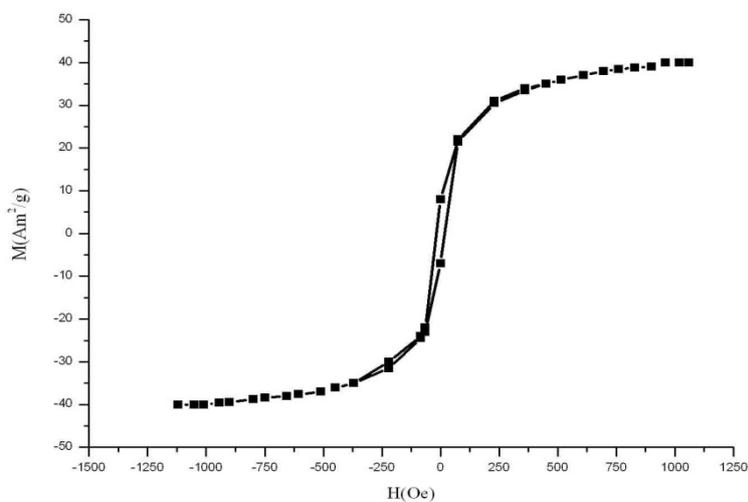
Fig.3 Magnetization curve at room temperature for olive oil encapsulated iron oxide nanoparticles.

UV –VIS absorption spectra measures the wavelength of the light that the nanoparticles absorb. Fig.4 shows the absorption spectrum of as-synthesized nanoparticles and the absorption band is observed at 297 nm for this iron oxide nanoparticles. Band gap energy is calculated on the basis of the maximum absorption band (297nm) of this mixed phase of iron oxide nanomaterials is 4.17 eV, according to the following equation.

$$E_g = \frac{h\,v}{\lambda_{max}} = \frac{1240}{\lambda_{max}}\,eV$$

Where E_g is the band-gap energy and λ_{max} is the wavelength (297nm) of the nanoparticles, h is planck's constant and v is the frequency .
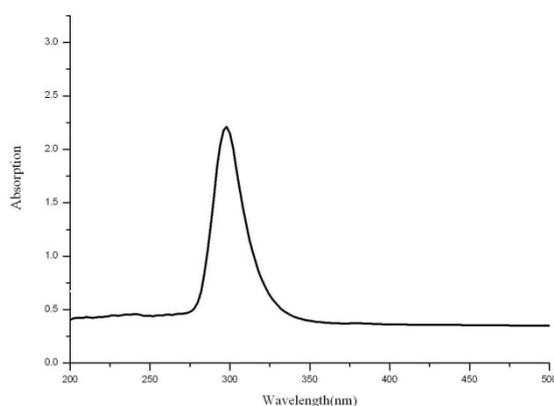
Fig.4 Absorption spectrum for the iron oxide nanoparticles.

4. Conclusion

A non-toxic chemical synthesis of iron oxide nanoparticles has been developed by olive oil as capping and stabilizing agent. It has been shown that the as-prepared nanoparticles are in good homogeneity with mixed phases of iron oxides from the results of XRD. TEM photograph shows that the resulting particles are spherical with diameters of about 20 nm and M-H characteristics shows the super paramagnetic behavior at room temperature of the iron oxide nanocrystallites.

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