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Insight to facile syntheses of iron oxide nanoparticles

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Abstract
Metal nanoparticles exhibit useful photonic, electronic and catalytic properties. Size requirements of nanoparticles are decided based on applications. Synthesizing magnetic nanoparticles with customized size and shape has always been a challenge. For iron oxide nanoparticles the objective of current article is to depict easy synthetic method without extraordinary requirements.

Keywords: metal nanoparticles, IONPs, co-precipitation

1. Introduction
Most commonly studied metal nanoparticles include gold, silver, titanium oxide and iron oxide nanoparticles. They have large surface area-to-volume ratio as compared to the bulk equivalents and large surface energies. Metal nanoparticles have quantitative as well as qualitative target-binding properties [1]. Due to their unique physicochemical properties, nanoparticles are used in sunscreens, toothpastes, sanitary ware coatings, and even food products. Metal nanoparticles are used in diagnosis and therapeutics due to their unique properties of high reactivity and translocation to the living cells. They also exhibit exceptional optical properties making them capable of producing quantum effects suitable for imaging applications [2].
Amongst nanomaterial, iron oxide nanoparticles (IONPs) are very popular. IONPs consist of cores made of iron oxides that can be targeted to the required area through external magnets. They show interesting properties such as super paramagnetism, high field irreversibility, high saturation field, extra anisotropy contributions or shifted loops after field cooling. IONPs magnetite and maghemite nanoparticles find applications in nanomedicine and biology, including magnetic resonance imaging, magnetic particle imaging, magnetic drug delivery systems, magnetic fluid hyperthermia, magnetic labeling and separation of cells [3]. Surface functionalized magnetic IONPs are a kind of novel functional materials, which have been widely used in the biotechnology and catalysis. Green protocol of synthesizing iron oxide nanoparticles has emerged as an alternative to overcome the limitation of conventional methods [4]. The raw materials for green synthesis of IONP are biomolecules from microorganisms and plants source [5].
For a beginner in the nano synthesis research there is no simplest and surest method of synthesis available. Herein we have discussed very basic methods to synthesize IONPs to get IONPs and then test their applications.

2. Materials and Methods
2.1 Materials
Hydrochloric acid, ferric chloride, ferrous chloride, sodium hydroxide, ammonium hydroxide solution, oleic acid, hydrochloric acid, hexane, acetone were purchased from MOLYCHEM Mumbai, India. Neem leaf extracts obtained as a gift sample from Apex Biotechnol Pvt. Ltd. Chandigarh, India.

2.2 Methods
Iron oxide nanoparticles are prepared by three different methods.

Method 1: Synthesis of nanometer size IONPs by co-precipitation Method
To a solution containing 0.85 ml of 12.1 N HCl and 25 ml of purified deoxygenated water, 5.2 grams of ferric chloride and 2 grams of ferrous chloride were added in portions.

The resulting solution added drop wise to 250 ml of 1.5 M NaOH under vigorous stirring. The black precipitate was isolated using magnet and supernatant was discarded. The precipitate was washed with 100 ml of purified deoxygenated water thrice. The anionic charge on the precipitate was neutralized by 500 ml of 0.01 N HCl solution. Cationic nanoparticles again separated by centrifugation at 4000 RPM and washed by adding water to pH 7. Finally a clear and transparent cationic colloidal solution was obtained [6, 7].

Fig 1: Difference between Magnetic NPs and Non- magnetic NPs

Method 2: Synthesis of iron oxide nanoparticles by polyol method:

In 20 ml of deoxygenated distilled water, 0.4 grams of ferric chloride and 1.1 grams of ferrous chloride were stirred till dissolution. To this 5ml of 6 N NH_4OH was added maintained at 80 ^{0}C for 1 hr. to obtain black precipitate. The solution was cooled down to room temperature followed by addition of 1.8 grams of oleic acid. The reaction product was neutralized by adding 1 N HCl drop wise to pH 7. The product was separated as a pasty precipitate. Decant out all the water by settling precipitate. To the precipitate 20 ml of hexane was added followed by 20 ml of acetone and the mixture centrifuged for 10 min. Precipitated particles separated out followed by addition of 20 ml of fresh hexane to precipitate and again dispersed [8].

Fig 2: Pasty mass of IONPs formed by Polyol method

Method: 3 Method for the Synthesis of iron oxide nanoparticles using Neem leaf extract (Green method)

Neem leaf extract stock: 20 grams of Neem leaf extract was taken in a beaker and added a sufficient quantity of distilled water to make a final volume of 100 ml. The resulting solution was boiled for 30 min. cooled filtered and stored at 0 ^{0}C.

Preparation of IONPs solution: 0.1M Ferric chloride was prepared by using mixture of distilled water: methanol in ratio of (1:1). The resulting solution was added to the 20% w/v of Neem leaf extract stock. The mixture was stirred for 30 min till a colour change indicating formation of IONPs [9, 10].

Fig 3: IONPs by green method

3. Results and Discussion

The characterization studies on size and shape of IONPs were performed by transmission electron microscopy (Make: JEOL JEM2100 TEM). To determine the size distribution of nanoparticles colloidal solution was analyzed by the particle size analyzer [Horiba]. The biosynthesized IONPs were examined using FTIR spectroscopy (Shimadzu FT-IR Spectrometer). The crystalline nature of particles was evaluated by using X-ray diffraction method (XRD). (Panlytical X`pertPro).

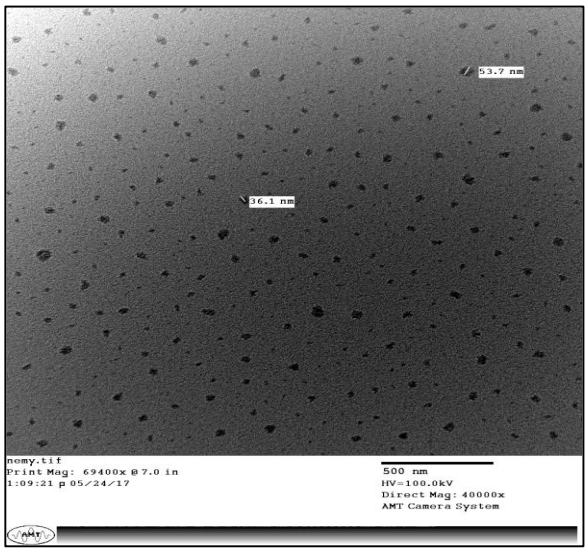
3.1 TEM and particle size Analysis:

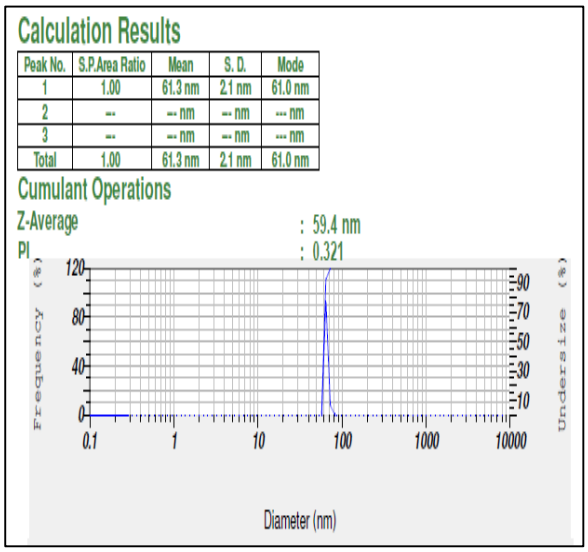
Nanoparticle from Method I: The morphology and structure of IONPs are shown in fig.4 The TEM images of IONPs particle by Method I have diameter ranging from 36.1 nm to 53.7 nm. The TEM image discloses the spherical Fe_3O_4 particles with an average size of about 44.9 nm. These nanoparticles find uses as MRI contrast agent.

Nanoparticle from Method II: Polyol method gives particles of very small size. TEM image of IONPs have diameter 4.04 nm, 4.78 nm and 5.77 nm. Particles are not aggregated and uniformly distributed and round in shape recommended for electronic or gene delivery applications.

Nanoparticle from Method III: using Neem leaves extract mediated synthesized IONPs showed in fig.3, the particle size of nanoparticles have diameter 7.50 nm, 10.6 nm and 65.7 nm and particles exhibit a typical aggregates ion of the nanoparticles induced by the sample preparation method.

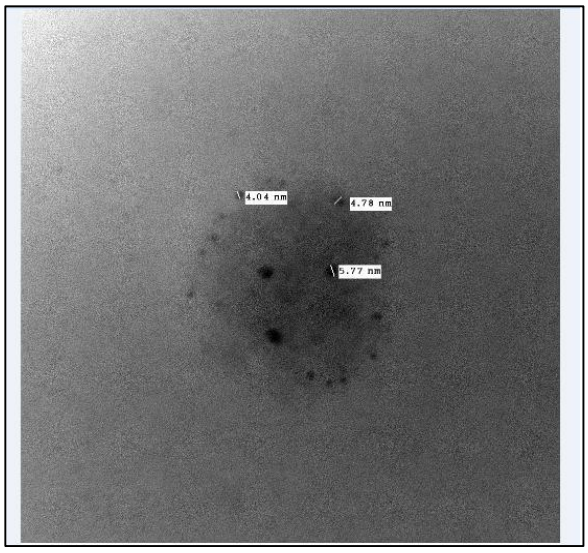
Based on TEM size as large as 189.1 nm was reported and has irregular shape. Comparative study of two methods can help us to select the method of synthesis based on applications. Polyol method has resulted into small size particles as compared to co-precipitation without surfactant method. IONPs in this range are recommended for contrast agent in MRI.

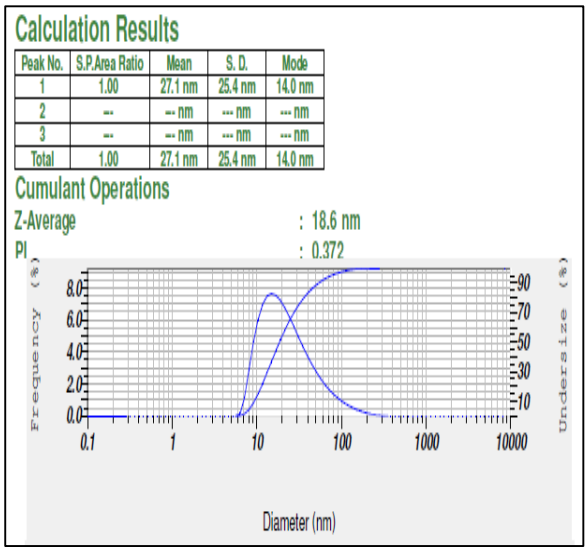




a) TEM b) Particle size analysis

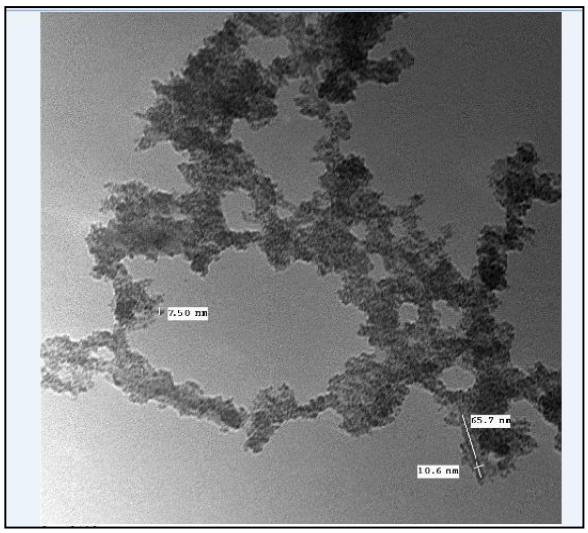
Method I

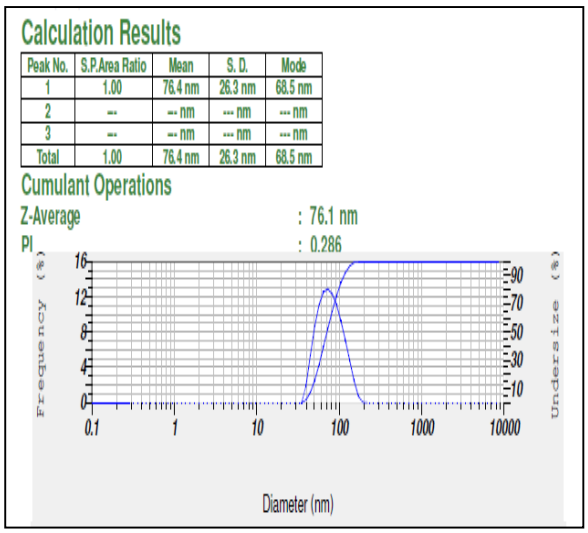




a) TEM b) Particle size analysis

Method II





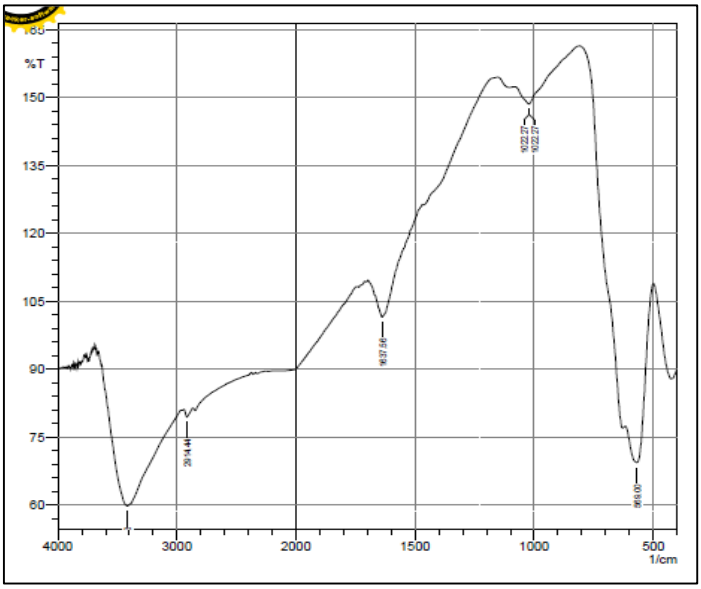
a) TEM b) Particle size analysis

Method III

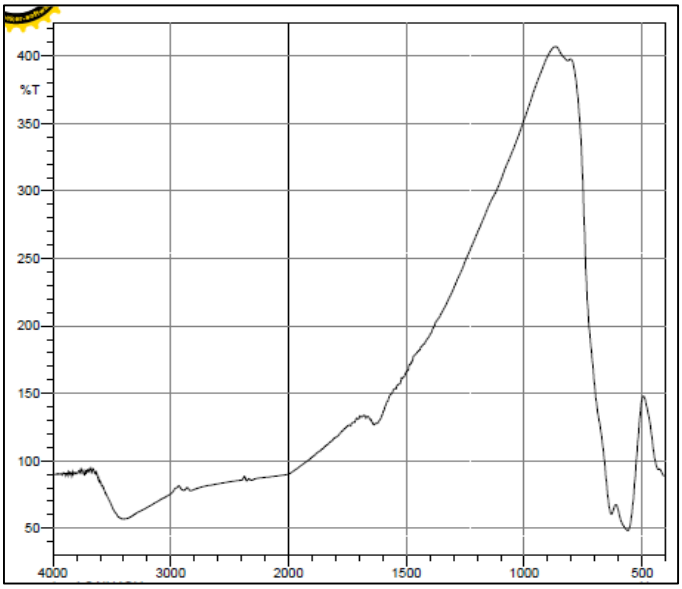
Fig 4: TEM and Particle size analysis of IONPs

3.2 FTIR Analysis

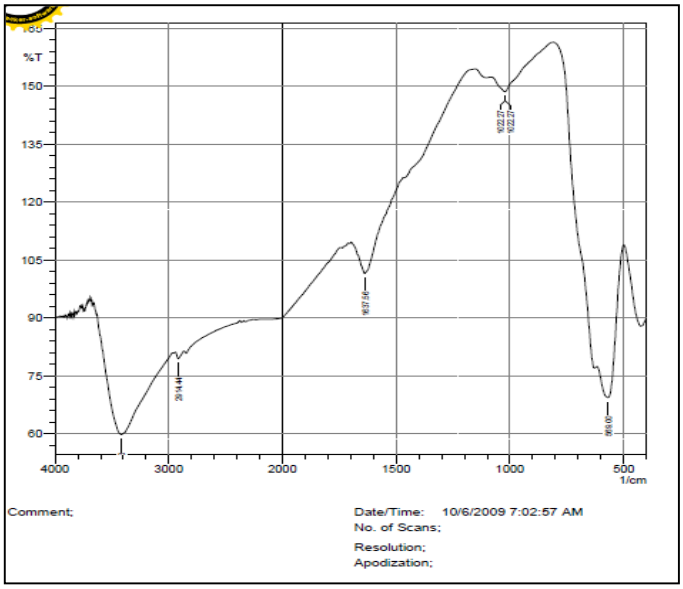
Fig: 5 shows FT-IR spectra of synthesized IONPs. The FTIR peak at 3415.93 cm^{-1}, 3400.99cm^{-1} and 3415.93 cm^{-1} are attributed to the stretching vibrations of O-H suggesting water absorbed by IONPs. By method I,II and III respectively. All three FTIR show peaks around 550-570 cm^{-1} the absorbance band at 569 cm^{-1}characterized by the Fe-O stretching vibrations, consistent with the reported value [11]. The peak exhibited at 1637.56 cm^{-1} for IONP of method 1and method 3 is attributed FeO-H_2O stretching. This peak is not observed in method 2 because of a longer organic solvent treatment to IONPs.



a) Method IIONP FT-IR



b) Method II IONP FT-IR



c) Method III IONP FT-IR

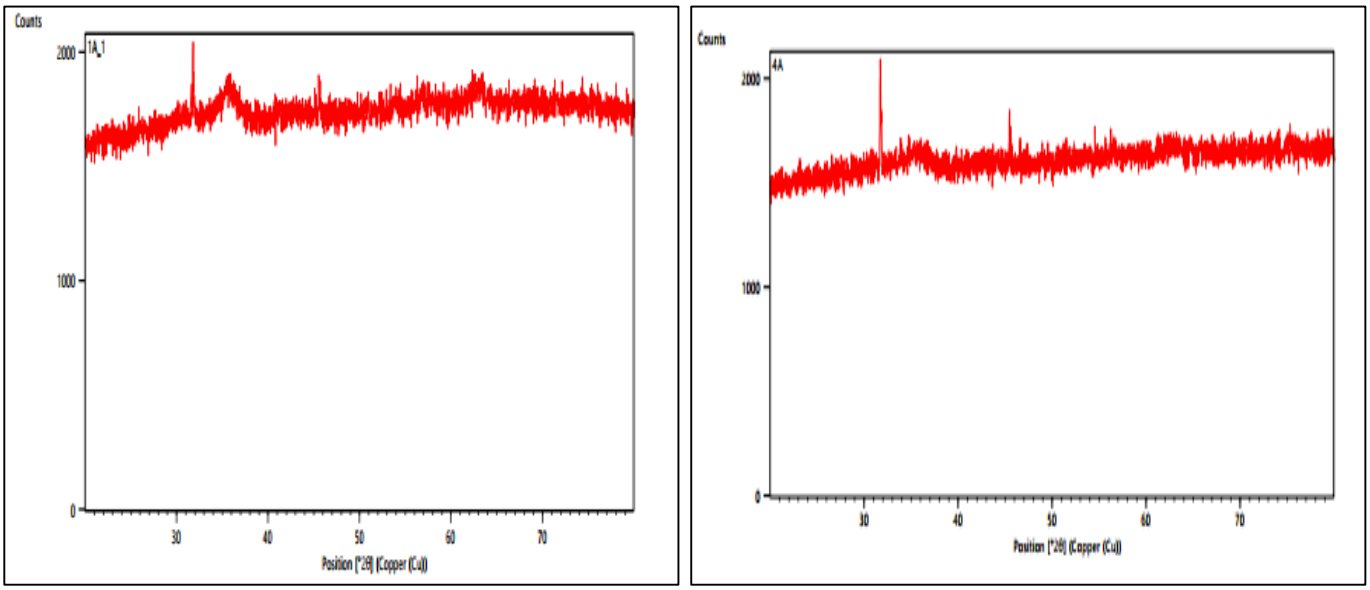
Fig 5: FT-IR Spectra of IONPs of IONPs for Method I, Method II and Method III

3.3 X-RAY Diffraction Analysis

XRD pattern of the synthesized IONP shown in Fig: 6 Sample have the characteristics peak at 2ɵ value of 31.8169, 35.6065, 45.6207, 62.9530 and 74.4490 were indicated as diffractions angles. Which were almost the same as the standard diffraction spectrum of Fe_3O_4 in term of reflection peak position. It implies that resultant nanoparticles synthesized pure Fe_3O_4 with given spinal structure.

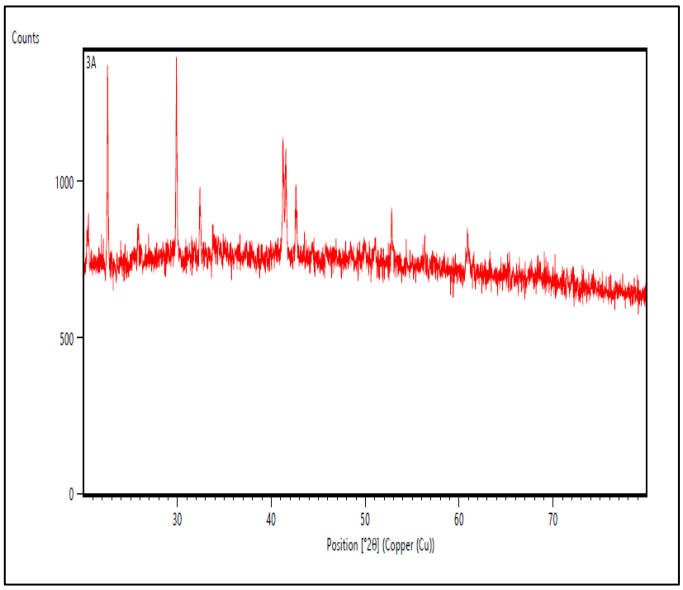
XRD pattern of the IONPs synthesized by polyol method showed the characteristics peak at 2ɵ Values of 31.7255, 35.8338, 45.4759, 62.6408 and 75.2842. Which was almost same as the diffraction spectrum of the reported standard Fe_2O_3 NP

XRD pattern of the IONPs synthesized by green method, shows, characteristic additional 2ɵ values. Neem leaves extracts contains traces of alkaloids, flavonoids and tannins hence the XRD pattern shown the characteristics peaks for leaves traces and from the IONPs. Here characteristics peaks for IONPs have 2ɵ value of 32.3938, 42.5211, 60.9404 and 72.0671, whereas the characteristics peaks of Neem leaves constituents shown at 2ɵ value of 20.5247, 22.5731, 25.8167, 29.8906, 41.2391, and 41.5211 [12, 13].



a) XRD-Method I

b) XRD-Method II



c) XRD-Method III

Fig 6: X-RAY Diffraction Analysis of IONPs for method I, Method II and Method III

4. Conclusion

The major focus of current research work have been on synthetic aspects of IONPs with optimum surface charge, shape, size and colloidal stability. We were successful in obtaining IONPs with different size to suit tailor-made applications by co-precipitation method, polyol method and green method. All three of these methods are simple methods for the synthesis of IONPs and generating fully oxidized form of iron as confirmed by FTIR and XRD analysis.

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