

DEVELOPMENT OF OPTIMIZED-REVERSE CO-PRECIPIATION METHOD FOR THE SYNTHESIS OF MAGNETITE NANOPARTICLES

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Abstract

We have developed a simple and easy Optimized-Reverse-Co-Precipitation Method (ORCPM) for the synthesis of Magnetite-Nanoparticles. This technique decreases the chances of agglomeration, broad particle size distribution and provides better nanoparticles as compared to simple co-precipitation method. The effect of different variables such as the temperature, N₂-sparging, stirring rate, amount of capping agent and pH were studied and optimized for the synthesis of Magnetite-NPs by using the proposed method. Among these reactions each with varying parameters, we finally concluded that the best Optimized-Conditions for the synthesis of M-NPs were 0.2g Dextrin at 60 °C with 12 pH, stirring rate of 150 rpm and with the continuous nitrogen sparging, can give far better results than the existing co-precipitation technique. The synthesized M-NPs were characterized using Fourier Transform Infrared Spectroscopy, X-Ray Diffractometer, Scanning Electron Microscope and Zeta-Potential. It was found that synthesized Magnetite-NPs with current technique were of FCC-shape with an average particle size of 12.9nm.

Keywords: Optimized-Reverse-Co-Precipitation Method, Magnetite Nanoparticles, FTIR.

INTRODUCTION

When the materials are in their bulk, they show only their macroscopic physical characteristics. This character soon distinguishes as the material objects assume the Nanoscale size because of scientific fact that, the principles of classical physics are no longer capable for defining and describing the characters (Energy, Momentum etc) of such miniscule particles. Scientists have developed laws and principles of "Quantum Mechanics" to describe the behavior of atomic scale particles (Nanoscience and Nanotechnology, 2004). Nanotechnology has become one of the most tremendous and important forefront fields in Engineering, Environmental Sciences, Biology, Chemistry, Medicine, and Physics. (G. Burns, et al, 1985 : C. Kittel, et al, 1996). This emerging technology shows great promise for providing us in the near future with countless breakthroughs that will alter the direction of technological development with broad range applications (Charles P, et al, 2003). Nano Science is growing with a quite faster rate in contemporary research throughout world; the reason behind this immense attention is the wide spectrum applications of Nanoparticles to improve life quality. (Caruthers S.D, et al, 2007 : Cartaxo, et al, 2005). Nanoparticles are classified into various classes according to their physical, chemical, morphological and size based characteristics (Khan, et al, 2017). Each type of nanoparticles has its own applications. The magnetic iron oxide nanoparticles are of immense importance in various prominent research fields of natural, biological and as well as

environmental sciences (Gilchrist, et al, 1957). As there are eight types of iron oxides in our nature but among these, the most common and broadly used ones are magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and ($\gamma\text{-Fe}_2\text{O}_3$) maghemite (Cornell and Schwertmann, 2003).

Magnetite Nanoparticles are named in IUPAC system as Iron (II, III) Oxide with the chemical formula Fe_3O_4 (or $\text{FeO}\cdot\text{Fe}_2\text{O}_3$). It is a grayish black color mineral and sometimes found with its black color. When magnetite is in bulk form its saturation magnetization is about 90-92 emu/g at a temperature of 25 °C. The structural formula of magnetite shows that it has a tetrahedral magnetic sublattice as such $[\text{Fe}^{3+}]_{\text{Td}} [\text{Fe}^{3+}, \text{Fe}^{2+}]_{\text{Oh}} \text{O}^{2-}_4$, it is clear that it is containing Fe^{3+} -ions and an octahedral sublattice containing Fe^{3+} & Fe^{2+} -ions, these two sublattices have antiparallel spins (Baker, R.R., et al, 1983 : Klotz, et al, 2008). The surface area, surface energy, shape, surface charge, size of particles and that of temperature of iron-nanoparticles strongly influences the magnetic behavior of magnetite Fe-oxide and secondly it is quite dependent on the method used for their synthesis (Wu, et al, 2012b : Tronc, et al, 2000 : Wu, et al, 2012).

There are numerous synthesizing techniques for M-IONPs such as Sol-Gel-Pyrolysis, W/O-micro emulsion (or O/W-micro-emulsion), Hydrothermal Decomposition, Polyol, Co-Precipitation, Thermal Decomposition of organic precursor, Gas Deposition etc (Sun, X.H., et al, 2009). Every preparing method has its own advantages and characteristics with specific performance, procedure and conditions (Park, J., et al, 2004 : Tartaj, P., et al, 2006). In every technique, we get different properties of nanoparticles as like shape, dispersity, crystallinity, average size, magnetic properties, size distribution etc. Among this vast class of preparation methods, we only briefly discuss Co-Precipitation technique because we have brought certain changes in this method by optimizing some important reaction parameters. Co-Precipitation method was first time initiated by "Massart" more than 39 years ago (Massart, R., 1981). This method has been applied in various ways & routes and resulted in broad variety of modifications but amazing fact is that, its main Chemistry did not change yet. In the presence of a basic (alkaline) solution (with controlled pH 8-14) the ferrous and ferric ions (Fe^{2+} & Fe^{3+}) with molar ratio of 1:2 precipitate out to yield magnetite-NPs (Sasaki, et al, 1999). The co-precipitation method is simple to be implemented while the structure, morphology, size & magnetic properties of nanoparticles can be controlled by the variation of certain parameters as such pH of solution, reaction time, ionic strength of media and most importantly the types of salts being used (mostly Ferrous and Ferric chlorides are used). Due to these factors, the simple co-precipitation technique suffers from such limitations where broad particle size distribution, agglomeration and many morphological issues are associated with this method.

However, in our simple and easy optimized Reverse Co-Precipitation technique we have worked on the parameters to overcome these limitations to a greater extent. In present work, we have minimized these limitations by altering almost every parameter of the experiments and concluded the final findings, which include the reverse of co-precipitation technique pH, temperature, amount of capping agent and stirring rate.

EXPERIMENTAL

Development of Reverse-Co-Precipitation Technique

In our simple and easy Optimized-Reverse-Co-Precipitation Method (ORCPM), we have prepared ferrous and ferric (Fe^{2+} / Fe^{3+}) salt solutions from ferrous chloride tetrahydrate and ferric

chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ & FeCl_3) (Purchased from Merck Suppliers, in collaboration with NCEAC, Jamshoro, Sindh) with 2:1 (molar ratio) ferrous 0.06M & ferric 0.03M. These both solutions were prepared for five different reactions each with different parameters was performed several times. Fe-Salt solutions were sonicated separately for 10, 15, 20, 25 and 30 minutes at varying temperatures of 45, 50, 55 60 and 65°C for the complete dissolving of these Fe-salts. These iron salt solutions were putted on the DIAB (MS-H380 pro) hot plate connected to the accurate electric stirrer for 10, 15, 20, 25 and 30 minutes. While at the same time, N_2 -sparging was initiated for 10, 15, 20, 25 and 30 minutes to create an inert gas environment, in a series of reactions for obtaining the optimized value for our new method.

Agglomeration is a common phenomenon in the synthesis of Magnetite-Nanoparticles, for avoiding this, we used 0.1g, 0.2g, 0.3g, 0.4g and 0.5g dextrin separately in a 100ml beaker and each was labelled and dissolved in 20ml of distilled water and sonicated for 5 minutes. These solutions were also transferred in the five different reacting media and the parameters (temperature, pH & stirring rate) were altered simultaneously. The temperature was maintained for each reaction differently as such 30°C, 40°C, 50°C, 60°C and 70°C. The pH was likely altered to obtain optimized value, for which we used 0.1M NaOH and 0.1M HCl solution to obtain required pH, the solutions were prepared in such a manner, 9pH, 10pH, 11pH, 12pH and 13pH and labelled as S1, S2, S3, S4 and S5 respectively. The stirring rate was also kept on changing in every reaction as, 90rpm, 110rpm, 130rpm, 150rpm and 170rpm respectively, shown in table 1.1. These all reacting media's were continued separately in different working days each with different parameters as mentioned above with continuous Nitrogen-gas-sparging, unless for our desired goal of achieving a condition where we could minimize the large particle size distribution, agglomeration and other short comings of Co-Precipitation technique. After these all, we have taken NH_4OH 20ml and transferred into the reaction mixture drop wise (40 drops per minute) with the help of burette. When basic solution started reduction of Fe-ions into Fe-Nanoparticles, within short duration of time the pale yellow/light orange colour of ferrous/ferric salts solution present in two naked-round Bottom-flask turned into the dark brownish colour, which was indication for the synthesis of magnetite-nanoparticles. This process was continued for 20 minutes until the entire basic solution was transferred into the reaction media. Even after the complete transfer of NH_4OH , the solution was kept at constant stirring and temperature for 60 minutes (1 hour) for the complete growth and capping magnetite-NPs.

In our Optimized-Reverse-Co-Precipitation technique, we finally approached desired parameters for synthesis of Magnetite-Nanoparticles by following methodology:

- i. We found that, initial sonication either carried for 10-25 minutes has no direct effects on the formation of particles at the time of reduction of Fe^{2+} & Fe^{3+} into M-NPs.
- ii. The temperature along with initial sonication for complete dissolving of Fe-salts has found to be attained rapidly at higher T (60°C) within 5 minutes of sonication.
- iii. It is notable that, greater the rate of stirring along with N_2 -sparging decreases the chances of agglomeration and minimizes the risk of oxidation of M-NPs.
- iv. The FTIR & XRD data show that, the addition of dextrin before formation of nanoparticles avoids agglomeration while the amount of dextrin used is dependent on Concentration of Fe-salts, in our recent study only 0.2g was found to be sufficient.
- v. The temperature at the time of formation of particles was varied in every observed reaction, good results from XRD and SEM images was shown at 60°C.

vi. The pH was found best at 12 during our current study when the temperature for this reaction was 60°C.

vii. The stirring rate for every reaction was varied and kept fixed during reaction; we noted 150rpm was satisfactory for result-4 (Fe₃O₄-labelled-4 best nanoparticles among rest of the particles, in other reactions with respect to size and applications).

When all the Nanoparticles were settled down at the bottom of beaker, the supernatant was decanted, further distill, water was added into the beaker to wash the Nanoparticles several times up to the mark and pH was again tested. This procedure was repeated for several times until neutral pH was attained as shown in the Figure-1. (a). The newly obtained Magnetite-Nanoparticles were drawn into the petry-dishes and covered with aluminum-foil and shifted to oven for 1 night to dry at 60°C (Figure-1. (b) and removed from petry dishes. After this all, we scratched our nanoparticles from the glass surface of petry dishes, drawn them into small plastic Epin-drops and labelled them as Fe₃O₄-1, Fe₃O₄-2, Fe₃O₄-3, Fe₃O₄-4 and Fe₃O₄-5 respectively and used them for further characterization and applications as shown in below Figure 1.(c).

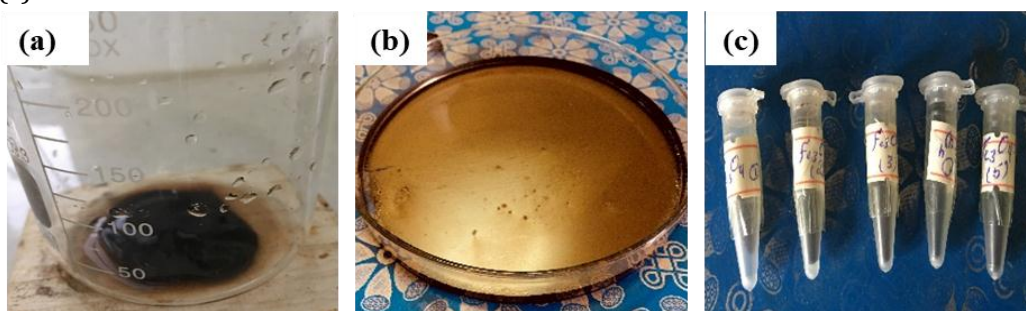


Figure-1.1 (a) Neutralized Nanoparticles after several washes. (b) The overnight Oven dried M-NPs in Petry Dish. (c) Stored Nanoparticles into Epin-drops, labelled them likewise for characterization and applications.

Table: 1.1. Showing five different reactions with various parameters.

Parameters	Reaction-1 (S1)	Reaction-2 (S2)	Reaction-3 (S3)	Reaction-4 (S4)	Reaction-5 (S5)
Amount of Dextrin (g)	0.1	0.3	0.4	0.2	0.5
Temperature (°C)	30	40	50	60	70
Ph	9	10	11	12	13
Stirring Rate (rpm)	90	110	130	150	170

RESULTS AND DISCUSSION

Characterization of Fe₃O₄-NPs Coated with Dextrin

The Fourier Transform Infrared (FTIR) Analysis Study

The Fourier Transform Infrared Spectroscopy (FTIR) confirmed the functionalization of magnetite-Nanoparticles with dextrin. (Figure-2 (Dx) and (1-5) shows the FTIR-spectra of dextrin and magnetite-NPs coated with dextrin in the range of 4000-400 cm⁻¹ Wavenumber range. The magnetite-NPs show a high intensity band spectrum at 576 cm⁻¹ which corresponds to the stretching vibration of Fe-O from Fe₃O₄ (Z.P. Yang et al., 2010). The stretching modes of O-H are found at 1630 cm⁻¹. Dextrin showed a broad peak at 3446 cm⁻¹, which is due to the O-H stretching. The association due to -OH-groups is actually indicated by this broad band shown in Fig-4.1. The aliphatic C-H stretching peak was observed at 2924 cm⁻¹. C-O-C stretching peak was

observed between 1028-1160 cm^{-1} (H.R.Wang and K.M. Chen., 2006). The symmetric and asymmetric carboxylic stretch peak was found at 1384 cm^{-1} and 1630 cm^{-1} respectively (Rajesh C. and Sukumaran V., 2012).

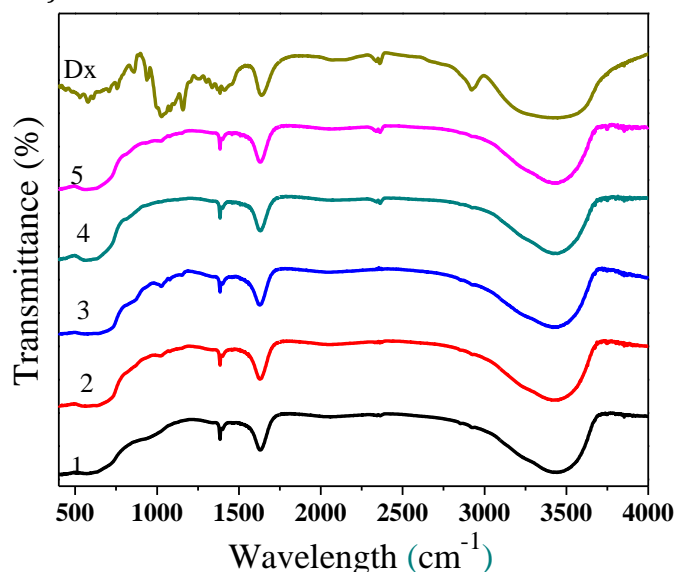


Figure-2 (Dx) FTIR of Dextrin. (1-5) FTIR of Fe_3O_4 coated with Dextrin for all five reactions.

The dextrin FTIR-spectra shows differences as compared to the dextrin-coated-Magnetite-NPs, which indicates the intermolecular interaction between the Fe_3O_4 -NPs and dextrin, showing a successful surface functionalization of newly synthesized Nanoparticles with our Optimized Reverse-Co-Precipitation Method. The first five-patterns (From 1 to 5) show the FTIR-Spectra for our five-different experimental reaction conditions carried out at laboratory. It is clearly evident from above all figures that there is no direct effect of addition of Dextrin on the surface-functionalization process during the synthesis of Magnetite Nanoparticles.

Thus, we can conclude from the FTIR-data that, (i) the addition of dextrin before the formation of nanoparticles can only avoid the aggregation without altering the functionalization. (ii) The addition of Dextrin after the formation of M-NPs also shows good surface functionalization. (iii) The amount of dextrin used is dependent on Concentration of Fe-salts. In our recent study only 0.2g was found to be sufficient (e.g. 0.3g, 0.4g etc has no effects further).

THE STUDY OF POWDER X-RAY DIFFRACTION (XRD)

It is one of efficient analytical-techniques used to detect and characterize diverse class of unknown crystalline-materials. X-ray Diffraction-spectrometers use monochromatic x-rays for the determination of the interplanar spacings of the unknown materials. In the working mechanism of XRD, the samples are being analyzed as powders with grains in unsystematic alignments to insure that all crystallographic directions are "sampled" by the beam. When the Bragg-conditions for constructive interference are obtained as a result of "reflection" is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation.

The best results we obtained in our optimized-reverse-co-precipitation method as follows that, the powder X-Ray-Diffraction revealed the diffraction peaks at 30.1° , 35.4° , 43.3° , 53.4° , 57.3° and 62.9° , respectively these diffraction peaks were indexed to (220), (311), (400), (422), (511),

and (440) planes. The obtained planes clearly show that our synthesized Magnetite-Nanoparticles have “Face-Centered-Cubic Crystalline phase”. The confirmed crystalline nature of our newly synthesized M-NPs via Optimized Reverse-Co-Precipitation method is shown in Figure-3 pattern 4.

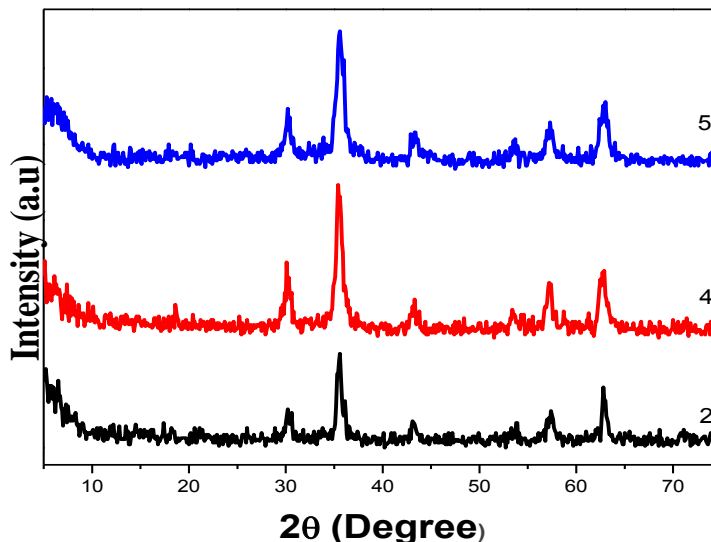


Figure-3. X-Ray Diffraction Patterns of Magnetite-Nanoparticles.

The size of M-Nanoparticles was calculated by using the Scherrer-Equation, which follows as:

$$D = \frac{0.9 * \lambda}{\Delta \cos \theta}$$

Where! D = the crystalline size of Nanoparticles, 0.9 (k) = It is the Scherrer Constant, λ = The Wavelength of X-Ray used (1.54 Å), θ = It is the Bragg's Angle, Δ = It is our FWHM (Full Width at Half Maximum).

The data was inserted into the Debye-Scherrer-Equation, which helped to calculate the average particle size, which was 12.9 nm.

Here we have chosen best results among all five reactions. In Figure-3 bottom-pattern (2) shows the results of reaction-2, which was carried with the following parameters and was labelled as S2. The temperature was maintained at 40°C, amount of dextrin was 0.3g, the pH was kept constant at 10 during entire reaction and the stirring rate was 110rpm respectively. In this case, the obtained results from XRD-data show clearly that, there is no homogeneous particle size distribution; minimum particle size was 0.18nm and maximum more than 25nm calculated using Scherrer-Equation, but it is showing large particle size distribution. The obtained diffraction peaks were found to be 30.2°, 30.8°, 35.6°, 43°, 54°, 57.5° and 62.8° respectively. Which again shows little deviation from our optimized results of reaction four (S4), surely with little change in structure from FCC-Crystalline phase. The images are shown in SEM-results in coming sections to be irregular and somehow cylindrical in shape.

The Figure-3 middle pattern (4) is showing the results of reaction four labelled S4 with following parameters. The temperature was set at 60°C, pH was kept constant at 12, the amount of dextrin taken was 0.2g and the stirring rate was 150rpm respectively. The results obtained in this reaction were found to be best among rest of the reactions, due to their homogeneous particle

size distribution between 8-15.5nm. The obtained diffraction peaks were noted on graph at 30.1°, 35.4°, 43.3°, 53.4°, 57.3° & 62.9° and indexed as 220, 311, 400, 422, 511 and 440 planes respectively. The results obtained in this case were considered our best-optimized results among rest and the crystalline structures were found to be FCC with average particle size 12.9nm. The SEM images are also found to be best among rest of the synthesized NPs. The Figure-3 top pattern (5), shows the result of our last reaction, where we set our parameters as follows. The temperature at 70°C, pH at 13, amount of dextrin 0.5g and the stirring rate at 170rpm respectively. The results in this case were again found to show large particle size distribution between 0.6nm to 40.7nm and diffraction peaks at 30.2°, 35.6°, 43.5°, 53.7°, 57.3° and 63°, with irregular shapes.

In these all reactions mentioned above with different XRD-data and graphical representation, we concluded the best results according to data revealed in reaction four (namely-S4), we referred it to be the best-optimized reaction which we carried out during our research.

SCANNING ELECTRON MICROSCOPY (SEM) STUDY OF M-NANOPARTICLES

The SEM observations of magnetite-NPs were carried out with an available low magnification scanning electron microscopy. The amount of dextrin, temperature, pH and stirring rate was altered according to the Table: 1.1. The SEM images show that dextrin coated nanoparticles are agglomerated to some extent.

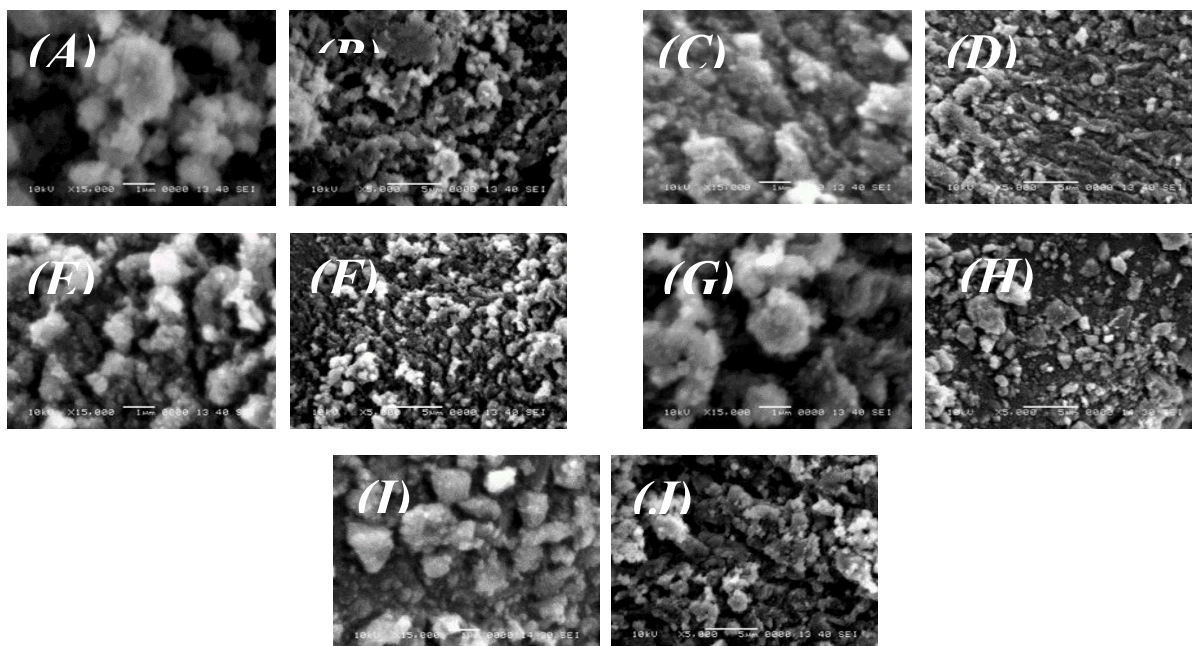


Figure-4: SEM-Images of all five reactions (1µm-5µm) carried out with various parameters.

Among these images obtained from SEM, G & H are found to be best due to low agglomeration, small particle size and minimum chances of large particle size distribution etc revealed from both SEM and XRD.

ZETA-POTENTIAL OF M-NANOPARTICLES COATED WITH DEXTRIN

Malvern Zeta sizer-Nano-Zs (UK) was used to determine the Zeta-Potential of the Magnetite-Nanoparticles by the method of “Electrophoretic-Light-Scattering”. When the beam of laser

(5Mw, 635nm) is passed through aqueous sample containing particles inside the cuvette and reference laser beam outside cuvette by detecting the “Doppler Shift” between this passing & reference beam.

The Zeta-Potential of all reactions are reported except for last one due to null results obtained for zeta-potential distribution. All the results given in the graphs are showing the mean values. The Zeta-Potential-Distribution-Plots of all M-NPs formed during different reactions as follows +8mV(S1), +4mV(S2), +5mV(S3) and +9mV(S4) for our best-optimized reaction (S4) respectively according to Figure-5 pattern 1 to -4.

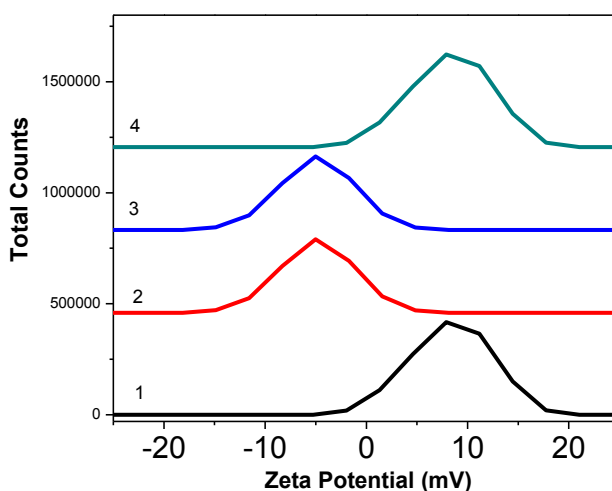


Figure-5: Zeta-Potential-Distribution of four reactions from 1-4.

All the results confirm that the M-Nanoparticles surfaces are positively charged. The dextrin molecules are polarized into OH⁻ and H⁺. Thus, the OH⁻ part of dextrin associates/coordinates with Fe²⁺/Fe³⁺ of Magnetite-NPs, this was already confirmed by FTIR results in initial sections. The H⁺-ion are associated with NPs along with OH⁻ and as a result surface of the Fe₃O₄-NPs becomes +vely charged. Due to these ionic factors, steric and electrostatic interactions occur in between nanoparticle and this reason could be considered the higher solubility of Magnetite-Nanoparticles in water.

CONCLUSION

The main goal of this research work was to synthesis magnetite-NPs with a method, which could minimize the limitations of co-precipitation technique by avoiding broad particle size distribution and simultaneously avoiding agglomeration. We developed a simple and easy Optimized-Reverse-Co-Precipitation-Method (ORCPM), for the synthesis of Magnetite Nanoparticles. The method was developed after carrying out many experiments and each was tested several times to understand the optimized conditions, properties and acknowledge certain factors, which influence the synthesis of magnetite-Nanoparticles.. In our research, we concluded the optimized conditions that sonication has no effect on formation of particles, higher stirring rate can avoid agglomeration along with constant N₂ -Sparging can lead us to avoid risks of oxidation of M-NPs. The synthesized NPs in each reaction were characterized using Fourier transform infrared spectroscopy; X-ray-diffraction, Scanning electron microscopy and Zeta-potential studies are carried out to understand their crystalline structure, morphological properties, particle size and surface charges of M-NPs.

After this all, I can conclude that synthesizing the Magnetite-Nanoparticles with our simple and easy Optimized-Reverse-Co-precipitation technique would be better than existing co-precipitation method due to less time consuming and resulting in low energy consumption, avoiding agglomeration and most importantly minimizing broad particle size distribution. This supports their best efficiency and other important properties regarding their size, structure, magnetic properties, easily separation with strong magnets and cost effective.

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