# Effect of Inorganic Ions on the Colloidal Stability of Magnetic Spinel Ferrite Nanoparticles Synthesized by dc Thermal plasma Arc Route

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Abstract

The $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles were synthesized by gas phase condensation method using dc thermal plasma arc method at plasma parameters of 500Torr and 6kW of dc power. Due to wide applications of magnetic nanoparticles in the field of biotechnology the colloidal stability of these nanoparticles for different inorganic ions with different ionic strength was systematically studied. The X-ray diffraction pattern confirms the single phase formation with highly crystalline spinel ferrite magnetic nanoparticles. The high saturation magnetization of 49.53 emu/gm and 46.52 emu/gm was obtained for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively. The maximum positive zeta potential of 62 mv and 61 mv (pH: 3.64) and negative zeta potential of -59 mv and -55 mv (pH: 9.66) was obtained for Co $Fe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively. The isolelctric point is obtained at pH 7.12 and pH 7.38 for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively. The effect of inorganic ions ($NaNO_3$, $CaCl_2$, $Na_2SO_4$) on the zeta potential of nanoparticles was also systematically studied. The divalent ions ($CaCl_2$ and $Na_2SO_4$) were observed to screen the electrostatic repulsive forces between the charged particles and reduce the zeta potential of nanoparticles. Further, since the cations/anions were not specifically adsorbed on the surfaces of nanoparticles, no shift in the isoelectric point was observed. The analogous results were obtained by observing the optical absorption of these suspensions. The minimum optical absorption was observed near the isoelectric point of these nanoparticles. The increase in the ionic strength of inorganic ions and ions of $CaCl_2$ and $Na_2SO_4$ further reduced the optical absorbance of these suspensions. All these effects were observed due to the agglomeration of nanoparticles caused by the reduction in the zeta potential.

## 1. Introduction

The magnetic nanoparticles are widely being used for applications in the biological seperations, targeted drug delivery, magnetic resonance imaging, enzyme and protein immobilization and cell sorting [1,2]. However the stability of these nanoparticle in the colloidal solution determines the adsorption capacity and interaction mechanism of different biomolecules. The nanoparticles with high stability has high adsorption capacity as they have less tendency to agglomerate. Therefore the recent studies are intended to understand their stability and ways of improving their colloidal properties inorder to enhance their applications in the biotechnology. Moreover the pH affects the charge distribution of the particle surface and hence understanding the effect of pH is very important in the analysis of electrokinteic properties of the nanoparticles. It is well reported that the stabilization of the nanoparticles is achieved by balancing the van

der Waals and magnetic dipolar interactions by introducing screened electrostatic repulsions that are created by the surface charge on the particles [3]. The surface charge on the particles arises from the inherent properties of the oxides on their surface. For metal oxides the hydrogen and hydroxyl ions has long being considered as potential-determining. Therefore the charges are positive at acidic pH and negative at alkaline pH and for the intermediate pH the charge on the particle reduces to zero which acts as the isoelectric point of that material. The particles have tendency to agglomerate if the charges on the particles are reduced and thus most of the aggregation process occurs at isoelectric point whereas the particles are stable for far away pH values.

The electrokinetic properties of nanoparticles is often described by the zeta potential which is the electrical potential developed at the solid-liquid interface in response to relative movement of nanoparticles and water. The zeta potential usually depends upon the magnitude of the surface charge of the particles, ionic strength and type of ionic ions in the colloidal solution [4]. Most of the ions are divided into three categories depending upon their effect on the electrokinetic properties. The potential determining ions, specifically adsorbed ions and the ions which are not specifically adsorbed. The ions which are not specifically adsorbed are termed as indifferent or inert electrolyte. Here the ions are mainly adsorbed by electrostatic forces onto the nanoparticles which affects the absolute value of zeta potential but does not affect the position of the isoelectric point. The inorganic ions usually interact with charged surfaces by both non-specific ion adsorption and specific adsorption process, however it further depends upon the type of charged surface.

Similar studies were carried out by Y. Shih et al. (2012) where the effect of ionic composition and the ionic strength of inorganic ions on the stability of $TiO_2$ nanoparticls was reported [5]. Also B. Mukherjee et al. (2010) reported that the $Ca^{2+}$ induced higher aggregation than $Na^+$ and co-ions $SO_4^{2-}$ and $Cl^-$affected the surface charge of the $TiO_2$ nanoparticles [6]. Presently the influence of these inorganic ions on the zeta potential of $NiFe_2O_4$ and $CoFe_2O_4$ nanoparticls is least reported. Moreover the spinel ferrite nanoparticles synthesized buy gas phase condensation method using dc thermal plasma arc route is of interest to us as we have obtained high zeta potential values for these particles as compared to chemical methods. These particles showed good stability with less tendency to agglomerate in the colloidal solution. However more study is required to understand their electrokinetic properties under different environments. Therefore in the present study we have used three different inorganic ions namely $NaNO_3$, $CaCl_2$ and $Na_2SO_4$ for studying their effect on the electrokinetic properties of magnetic spinel ferrite ($CoFe_2O_4$ and $NiFe_2O_4$) nanoparticles synthesized by gas phase condensation method using dc thermal plasma arc.

## 2. Experimental methods

The nanoparticles of $CoFe_2O_4$ and $NiFe_2O_4$ were synthesized by gas phase condensation method using dc thermal plasma arc reactor and assigned the terms CFOTP and NFOTP respectively throughout this manuscript. The detail of the dc thermal plasma arc reactor is reported in our earlier publication [7]. Argon was used as plasma forming gas and both the nanoparticles were obtained at optimized plasma parameters of 500Torr and 6kW of dc power. Here initially the pellets were prepared by mixing the micron sized powder of Ni:Fe and Co:Fe in the ratio of 1:2 and then compressing it with hydraulic press at 120 kg/m$^2$ of pressure.

These pellets were placed on the graphite anode where the plasma plume was made to strike. The evaporated species then reacted with the available oxygen in the chamber to form pure phase of cobalt and nickel ferrite nanoparticles. The steep temperature gradient of $10^6$ K/m restricts the further growth to obtain the particles in the nano-range. The high yield of 20gm/hr can be obtained by using dc thermal plasma arc reactor.

The zeta potential values were obtained by suspending 0.2 mg/ml of as-synthesized magnetic nanoparticles in already prepared buffer solutions of different pH values. The buffer solutions of pH 3.64, 4.59 and 5.58 were prepared with 0.02 M acetic acid and 0.02 M sodium acetate, 0.02 M $Na_2HPO_4$ and 0.02 M $KH_2PO_4$ were used for pH 6.49, 6.86 and 7.86 and those corresponding to pH 8.40, 8.96 and 9.66 were prepared with 0.02 M of tris-HCl. For studying the effect of different electrolytes on the zeta potential of nanoparticles, inorganic ions with 0.001M concentration was added to the as prepared solution. Further the electrolyte with different concentration was added to the solution in order to understand its effect on the zeta potential. Finally the suspensions were sonicated for 30 min before the readings were actually taken. Each experiment was repeated six times in order to ensure the reproducibility of the measurements. The mean value of six readings was used to plot the graphs of pH versus zeta potential and log C versus zeta potential.

Because both the nanoparticles had the tendency to sediment fast we have used the method of optical absorbance measurements. Here the nanoparticles were initially sonicated for 30 min, then allowed to sediment and finally re-dispersed manually before taking the readings. Thus the state of aggregation at different pH value for different electrolyte and electrolyte concentration was studied by carrying out the absorbance measurements using UV-Vis spectrophotometer at a wavelength of 540 nm. The quartz cuvette with dimensions of 1cm x 1cm was used for the measurements. Finally the mean value of three readings was used to plot the final data point. Thus in order to obtain the qualitative information about the stability of the suspensions and compare the results with the zeta potential curves, we have used the method of optical absorbance.

The as-synthesized nanoparticles were characterized by X-Ray Diffraction (XRD: Bruker D8 advance) technique at wavelength of 1.54 Å. The morphology of the particles was recorded using Field Emission Scanning Electron Microscopy (FE-SEM: JEOL Model JSM-6360). Vibrating Sample Magnetometer (VSM: Model 7307, LakeShore) was used to record the magnetic properties at room temperature (300 K). The zeta potential of the nanoparticle was recorded using Brookhaven Zeta Plus 90 Analyzer using the principle of electrophoretic light scattering (ELS).

## 3. Results and discussion

The XRD pattern was obtained for of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles synthesized by gas phase condensation method at plasma parameter of 500T and 6kW is shown in Fig.1. From XRD pattern the diffraction peaks were indexed by comparing the interplanar distance “d” with the JCPDS data for $CoFe_2O_4$ (File No. 22-1086) and for $NiFe_2O_4$ (File No. 74-2081). The prominent peaks of (220), (311), (222), (400), (511) and (440) are observed which corresponds to the characteristic cubic spinel ferrite structure (space group: Fd3m) and confirms the single phase formation. The average crystallite size calculated by using the Debye Scherrer formula was 29 nm and 28 nm for CFOTP and NFOTP nanoparticles respectively.

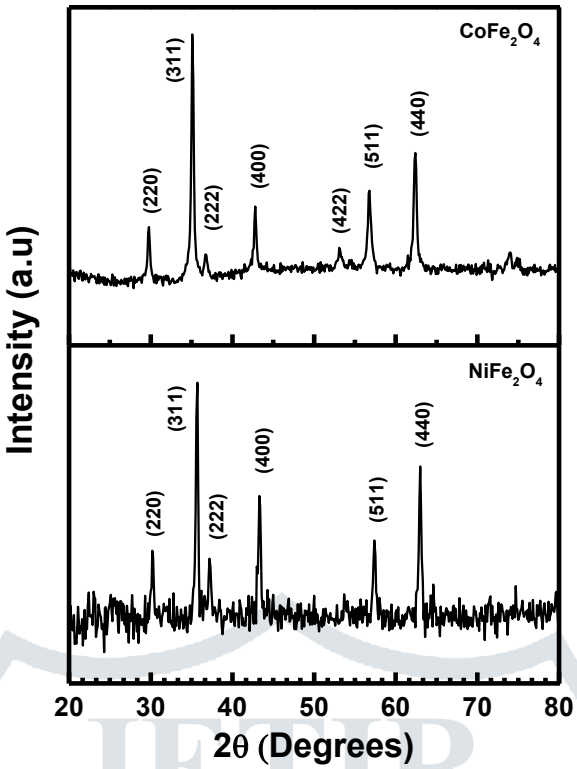


Fig.1 The XRD pattern for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles synthesized at plasma parameters of 500 Torr and 6 kW of dc power.

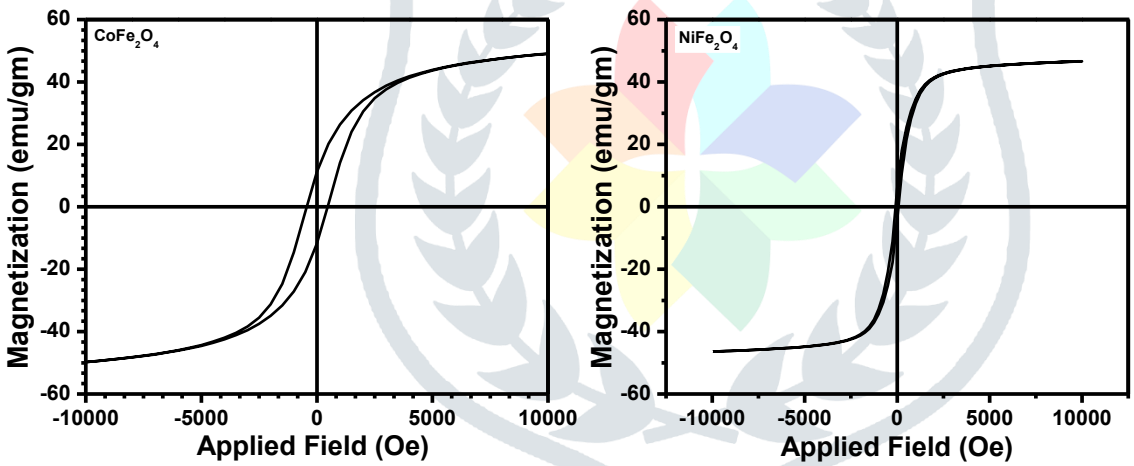


Fig.2 The M-H curve for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles for the maximum applied field of ±10KOe

The M-H curve obtained for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles is shown in Fig.2 and the magnetic data obtained is further summarized in Table 1. It can be observed that both the particles had high values of saturation magnetization with high coercivity value for $CoFe_2O_4$ nanoparticles as should be for the hard magnets. The high value of saturation magnetization for both the particles is attributed to the wider particle size distribution, cation redistribution and high crystallinity which is expected in high temperature thermal plasma synthesis process [7,8].

Table 1 Magnetic data for Cobalt Ferrite and Nickel Ferrite nanoparticles synthesized at plasma parameters of 500T and 6kW

| Sample | Saturation Magnetization (emu/g) | Coercivity (Gauss) | Retentivity (emu/g) | Squareness |
|---|---|---|---|---|
| $CoFe_2O_4$ | 49.53 | 448.98 | 11.46 | 0.23 |
| $NiFe_2O_4$ | 46.52 | 79.89 | 5.15 | 0.11 |

The FESEM images of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles along with the histograms of particle size distribution are shown in Fig 2. The FESEM images reveals that both the particles exhibit spherical shape with log-normal particle size distribution in the range from 10 nm -150 nm. The average particle size determined from the FESEM data is 34 nm and 33 nm for CFOTP and NFOTP nanoparticles respectively.

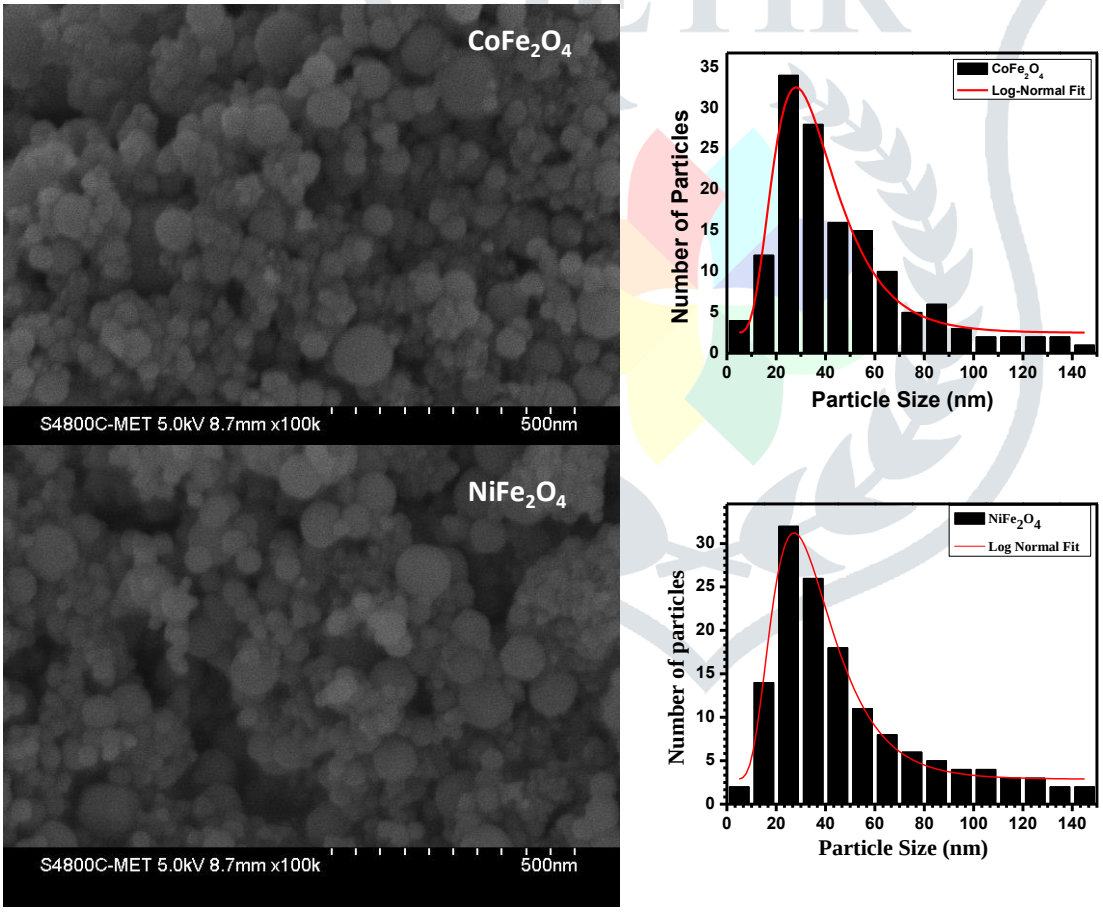


Fig. 3 FESEM image of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles along with their histograms synthesized at plasma parameter of 500 Torr and 6 kW of dc power

**Zeta Potential Analysis**

The effect of inorganic ions on the zeta potential of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles for wide range of pH values is shown in the Fig. 3. It is observed that the maximum positive zeta potential of 62 mv and 61 mv

(pH: 3.64) and negative zeta potential of -59 mv and -55 mv (pH: 9.66) is obtained for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively at ionic strength of 0.001M $NaNO_3$. These high values of zeta potential obtained for these particles can be analyzed by understanding the role of different parameters determining the zeta potential. The zeta potential and isoelectric point has been observed to be very sensitive to the heterogeneity of the oxide surfaces (degree of crystallinity) together with the surface topology (roughness, steps/corners ratio) and structural relaxation phenomena (bond length and edge variation, crystalline plane or molecular cluster) [9]

Thus this high value of zeta potential observed in thermal plasma synthesized nanoparticles is attributed to the steep temperature gradient involved during the synthesis process which produces highly crystalline nanoparticles with surface defects.

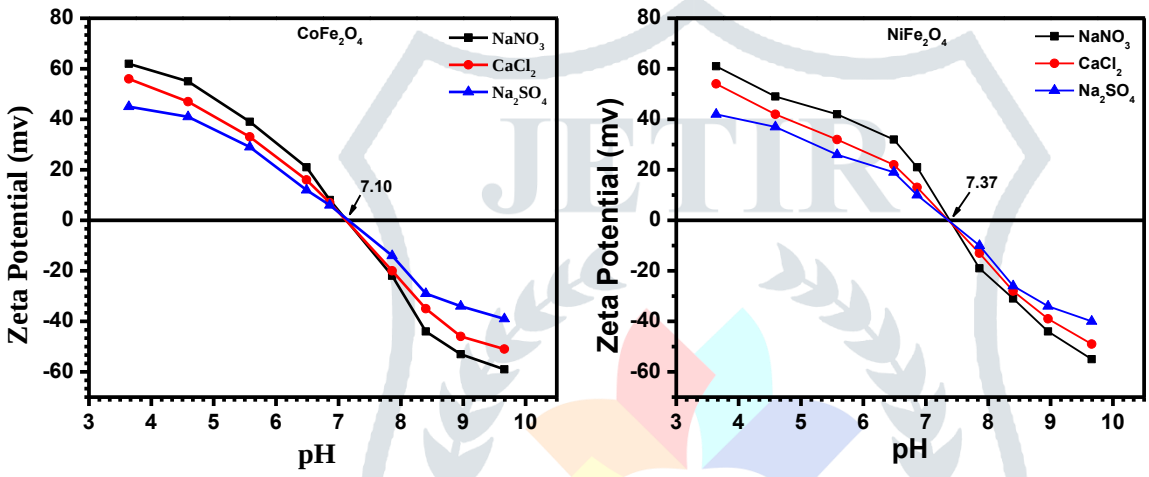


Fig. 4 Effect of different inorganic ions (fixed concentration: 0.001M) on the zeta potential for $CoFe_2O_4$ and $NiFe_2O_4$ Nanoparticles for wide range of pH values.

From Fig. 4 it is also observed that the isoelectric point for both the nanoparticles remains unaltered by the presence of different inorganic ions. This implies that there is no specific adsorption of cations and anions (inert/indifferent electrolyte) by the $CoFe_2O_4$ and Ni $Fe_2O_4$ nanoparticles. It is also known that in some cases of metal oxides the alkali cations and nitrate and sulfate anions appear to be surface inactive. Moreover the counteracting effect of adsorbed cations ($Na^+$,$Ca_2^+$, $Na_2^+$ ) and anions ($No_3^-$, $Cl^-$, $SO_4^{2-}$) does not change the isoelectric point as they only accumulate as counterions in the electrical double layer (EDL) on the charged particles just by coulombic attractive forces [ 10,11].

The effect of electrolyte concentration on the zeta potential of both the nanoparticles is shown in Fig. 4. It is observed that ions (cations and anions) of $CaCl_2$ and $Na_2SO_4$ results in the reduction of the zeta potential for both the particles. At lower pH values below the isoelectric point both the particles are positively charged and favor the ion pair formation between $NO_3^-$ and $SO_4^{2-}$ anions. At higher pH values above isoelectric point the particles favor ion pair formation with the $Na^+$ and $Ca^{2+}$ cations. Since the $Ca^{2+}$ is divalent cation, the resulting ionic strength of the solution is increased relative to $NaNO_3$ for the same concentration [8]. This is because $NaNO_3$ belongs to 1:1 type of electrolyte whereas $CaCl_2$ and $Na_2SO_4$ belongs to 2:1 type of electrolyte. For 2:1 type of electrolytes the ionic strength is more than its molarity. This results in the compression of electrical double layer and further decrease in the zeta potential. But for the solutions with

the same ionic strength ($CaCl_2$ and $Na_2SO_4$)) the counter ions with smaller hydrated radius more effectively neutralize the negative surface charge thus reducing the zeta potential of the nanoparticles. Also the sulfates provide better neutralization effect than chloride ions causing the reduction in the zeta potential [5].

It is observed from Fig. 4 that the zeta potential of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles decreases with the increase in the ionic strength of the colloidal solution. The positive /negative zeta potential reduces by +9 mv/-7 mv and +10 mv/-8 mv for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively with increase in the concentration of $NaNO_3$ electrolyte. And with increase in the concentration of $CaCl_2$ electrolyte the zeta potential reduces by +8 mv/-7 mv and +6mv/-5mv respectively. Similarly with increase in the concentration of $Na_2SO_4$ electrolyte the zeta potential reduces by +8mv/-8mv and +5mv/-5mv for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles respectively.

At higher concentrations, the decay constant is faster which results in the smaller double layer thickness. Therefore the zeta potential decreases when the concentration of the ions increases. Further in aqueous solutions the anions ($Cl^-$, $SO_4^{2-}$) are less hydrated than cations ($Na^+$, $Ca^{2+}$) which help them in closely approaching the nanoparticle surfaces. Due to this the reduction in the positive zeta potential is usually more than the negative zeta potential for $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles. The fact that the ionic strength effect was not same for different electrolytes is due to the different binding affinities for cations/anions [12].

Hence it is concluded that the $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles synthesized by gas phase condensation using dc thermal plasma arc has high values of zeta potential for wide range of pH values, however the inorganic ions ($CaCl_2$ and $Na_2SO_4$) are observed to screen the electrostatic repulsive forces between the charged particles in the solution thus enhancing the short range van der Waals interactions which promotes the rate of agglomeration.

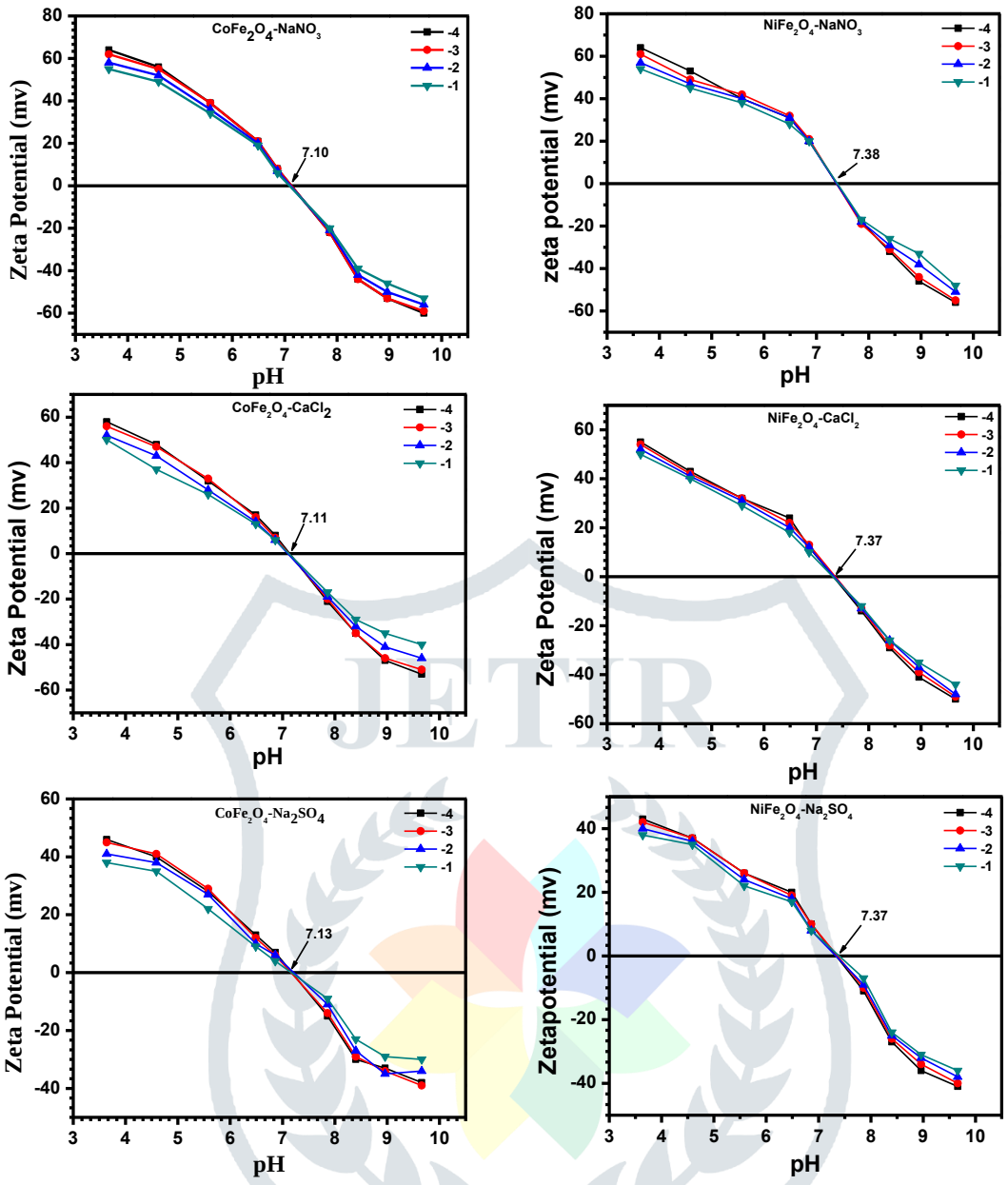


Fig. 4 The effect of electrolyte concentration on the zeta potential of nanoparticles at different pH values. The log values of electrolyte concentration are given in the inset of each plot.

**Absorbance as a function of pH for different electrolytes**

The effect of different electrolytes on the aggregation of $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles is shown in Fig. 5. The samples were prepared by adding the requisite amount of nanoparticles in the already prepared buffer solution of different pH values to obtain the solid phase concentration of 1mg/ml. It can be observed that for both kinds of nanoparticles the absorbance is smaller when the pH is close to the isoelectric point. The same trend is observed for the solutions with different electrolytic solution. This is due to the fact that the value of zeta potential near isoelectric point reduces to zero which further helps in the formation of stable agglomerates. On the contrary, the absorbance is larger at higher acidic and basic pH values due to the availability well dispersed particles in the solution. However it can be observed that the absorbance intensity decreases when the electrolyte of the solution is $CaCl_2$ and further for $Na_2SO_4$. This is due to the fact that

these electrolytes reduce the zeta potential of the nanoparticles which results in the formation of agglomerates and further reduction in the absorbance intesity. This result is analogous with the results obtained in the earlier section. Similar results were reported by de Vicente et el. and R.C. Plaza et al. regarding the colloidal stability of cobalt ferrite and nickel ferrite nanoparticles [13, 14].

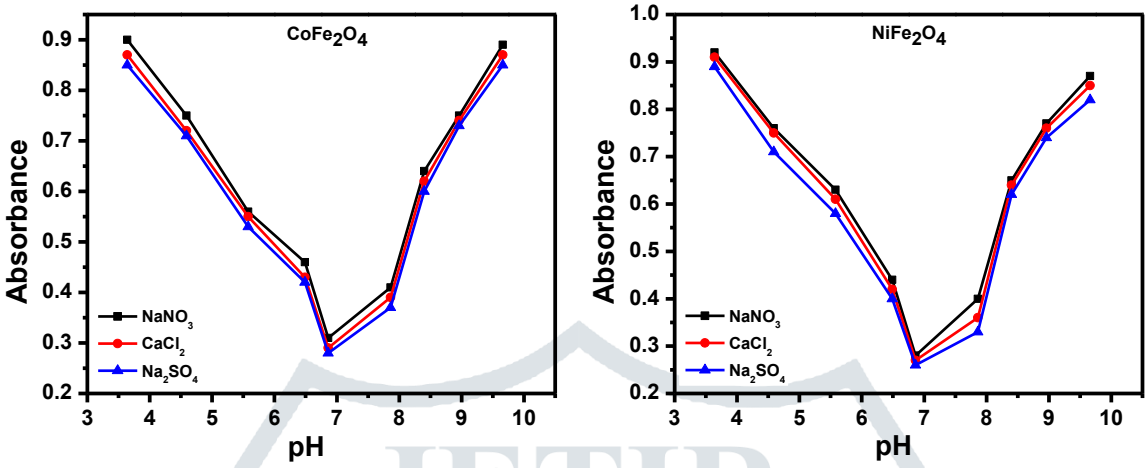


Fig. 5 Absorbance of nanoparticle dispersions at different pH values for different electrolytes in the solution. (0.001M electrolyte concentration; 25 $^{o}$C temperature; 1mg/ml solid phase concentration)

**Absorbance as a function of electrolyte concentration**

The absorbance of re-dispersed suspensions as a function of electrolyte concentration is shown in Fig. 6. The trend for all the electrolytes is that as we increase the ionic concentration the absorbance decreases for both the particles. This means that more aggregate are formed causing the suspensions to be unstable. This happens because the increase in the ionic strength results in a more effective screening of the electrostatic repulsive interaction between the particles thus decreasing the zeta potential. These results are in analogous with the results obtained for the zeta potential in the earlier section.

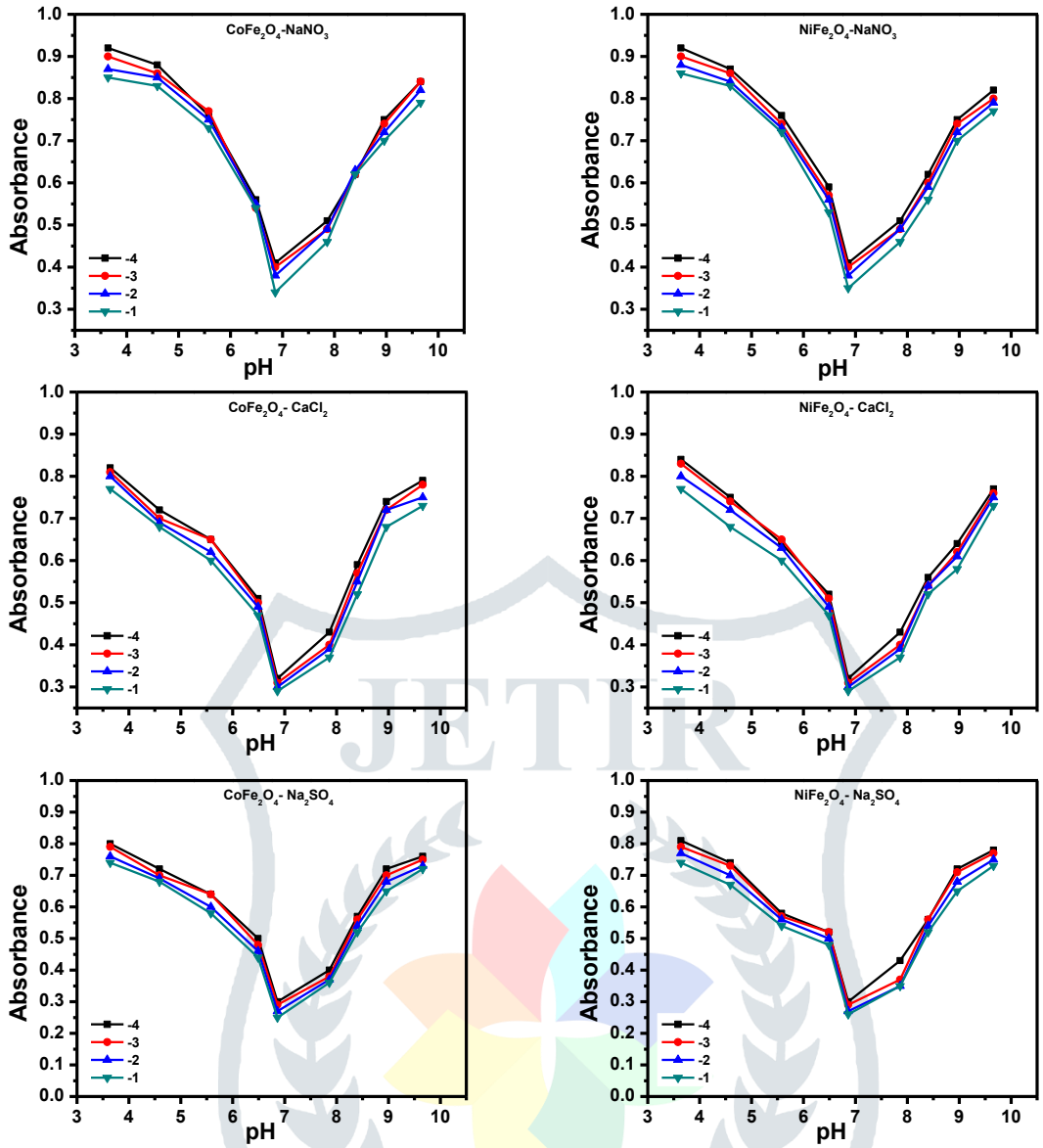


Fig. 6 Absorbance of nanoparticles dispersions for different concentrations of electrolyte as a function of pH

## 4. Conclusions

Hence it is concluded that the $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles synthesized by gas phase condensation using dc thermal plasma arc has high values of zeta potential for wide range of pH values however the inorganic ions ($CaCl_2$ and $Na_2SO_4$) are observed to screen the electrostatic repulsive forces between the charged particles in the solution thus enhancing the short range van der Waals interactions which promotes the rate of agglomeration. These results were confirmed by observing the optical absorption of these suspensions.

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