Exploring the effect of Co concentration on magnetic hyperthermia properties of CoₓFe₃₋ₓO₄ nanoparticles

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Abstract

Although enhanced ferrite nanoparticles (NPs) have been envisioned for use in future biomedical applications, less attempt has been made to tailoring and optimizing their detailed magnetic properties and specific loss power (SLP) values. Herein, CoₓFe₃₋ₓO₄ (0 ≤ x ≤ 1) NPs are synthesized using a co-precipitation method at 80 °C in the presence of air atmosphere. The effect of varying Co concentration on crystalline, morphological, magnetic and hyperthermia properties is also investigated in detail. Hysteresis loop measurements showed an increase in coercivity (Hc) from 7.75 to 340.50 Oe, and a decrease in saturation magnetization (Ms) from 59.10 to 32.70 emu g⁻¹ with increasing x = 0 (pure magnetite) to x = 1 (pure Co ferrite), respectively. In addition to confirming the hysteresis loop results, first-order reversal curve (FORC) analysis estimated a 52% decrease in superparamagnetic (SP) fraction. Hyperthermia measurements carried out under an alternating magnetic field with intensity of 400 Oe and a frequency of 400 kHz showed an increase in SLP from x = 0 to x = 0.4, and a decrease in SLP for 0.4 < x ≤ 1. SLP was maximized at 395 W g⁻¹ for the intermediate concentration of x = 0.4. The optimized heat generation of Co₀.₄Fe₂.₆O₄ NPs comprising approximately 50%–50% SP–ferromagnetic fractions may result from the simultaneous contribution of the three following mechanisms: hysteresis loop loss, Brownian and Neel relaxation together with relatively high Hc and moderate Ms.

Abbreviations

(NPs) Nanoparticles
(SLP) specific loss power
(FORC) first-order reversal curve
(SP) superparamagnetic
(FESEM) field-emission scanning electron microscopy
(Hc) coercivity
(Ms) saturation magnetization
(K) anisotropy constant

1. Introduction

Nowadays, magnetic nanoparticles (NPs) have attracted attention of researchers in various fields due to their useful and unique features. Among them, spinel ferrite NPs with ferrimagnetic properties and general formula of MOFe₂O₄ or MFe₂O₄ (in which M represents one or a combination of two-valence cations such as Co²⁺, Fe²⁺...
The spinel ferrite structure is a cubic close-packed arrangement of oxygen atoms, where $M^{2+}$ and $Fe^{3+}$ ions occupy either tetrahedral (A) or octahedral (B) sites [5]. Magnetite ($Fe_3O_4$) and cation-substituted magnetite ($M_{x}Fe_{3−x}O_4; M = Co, Fe, Ni, Mn, etc$) are among the most commonly investigated magnetic inverse spinel ferrites [6–9]. Higher anisotropic character of $Co^{3+}$ ions than both $Fe^{3+}$ and $Fe^{2+}$ ions has been revealed in octahedral sites of a cubic spinel structure [10, 11]. These groups of materials can be suitable candidates for different magnetic and biomedical applications such as data storage, microwave absorbers, magnetic photocatalysts, drug delivery, magnetic resonance imaging and magnetic hyperthermia [12–16]. One of the most interesting properties of magnetic NPs is their ability to convert the electromagnetic energy absorbed to heat under an alternating magnetic field so that the energy loss in the form of heat occurs when inverting the magnetization [17–21]. This ability of NPs has paved the way for their use in the field of biomedicine and magnetic hyperthermia, involving supplementary treatments in chemotherapy and radiotherapy [22, 23]. Accordingly, magnetic hyperthermia has been considered an efficient approach to combat cancer due to its high potential applications [24, 25].

In the magnetic hyperthermia treatment, NPs prepared in the form of ferrofluids can be directly injected into the tumor location and/or carefully delivered toward the specified location through blood circulation under the influence of a magnetic field. After exposing the specified location to an alternating magnetic field, NPs lose the electromagnetic energy absorbed from the applied magnetic field and consequently convert it to heat through different mechanisms.

One of these mechanisms is the hysteresis loop loss taking place for ferromagnetic and ferrimagnetic materials as they have a relatively wide hysteresis loop due to their considerable saturation magnetization ($M_s$) and coercivity ($H_c$). The area inside a hysteresis loop is proportional to the loss energy converted to heat, which is defined by equation (1):

$$P = \mu_0 f \int M \, dH$$

where $P$ is the heat per unit volume generated by ferromagnetic and ferrimagnetic particles, $\mu_0$ is the permeability of free space, $f$ is the frequency and $M$ is the sample magnetization [26].

Other mechanisms mostly involved in superparamagnetic (SP) NPs are the Brownian and Neel relaxation mechanisms. In these cases, the area inside the hysteresis loop is very small and approximates to zero. In the Brownian mechanism, the electromagnetic energy absorbed is converted to heat by the physical rotation of particles and the friction with their surrounding ferrofluid. In the Neel mechanism, the rotation of magnetic moment inside each particle acts as a converter of the absorbed electromagnetic energy to heat. Characteristic times of Brownian and Neel relaxation mechanisms, $\tau_B$ and $\tau_N$, respectively, are defined in equations (2) and (3) [27]:

$$\tau_B = \frac{3 \eta V_{H}}{k_B T}$$

$$\tau_N = \tau_0 \exp \left( \frac{K V_m}{k_B T} \right)$$

where $\eta$ is the viscosity of the suspension fluid, $V_{H}$ is the hydrodynamic volume of the magnetic NPs, $k_B$ is the Boltzmann constant, $T$ is the temperature in Kelvin, $\tau_0$ is the attempt time of $\approx 10^{-9}$ s, $K$ is the magnetocrystalline anisotropy constant, and $V_m$ is the volume of the magnetic core. Due to the possibility of having a combination of Brownian and Neel relaxation mechanisms, the effective characteristic time, $\tau_{eff}$, can be defined as given in equation (4). This indicates that the smaller relaxation time has a predominant role and can control $\tau_{eff}$ [28, 29].

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_N} + \frac{1}{\tau_B}$$

Therefore, the Brownian relaxation is mainly responsible for heat generation of low viscosity ferrofluids comprising NPs with large sizes [30]. The heat generated by NPs (heat efficiency) arising from each of the aforementioned mechanisms or their coincidental combination is defined by a quantity called specific loss power (SLP) as expressed in equation (5) [31–35]:

$$SLP(f, H) = \frac{P(f, H)}{\rho}$$

where $P(f, H)$ is the loss power of NPs under the effect of the magnetic field, $H$ is the maximum intensity, $f$ is the frequency ($\omega = 2\pi f$) and $\rho$ is the magnetic material density. By substituting the magnetic parameters into equation (5), it is possible to rewrite it as follows:
2.1. Synthesis (materials and methods)

As a simple, inexpensive and efficient approach, a co-precipitation method in the air atmosphere was used to synthesize Co$_x$Fe$_{3-x}$O$_4$ (0 ≤ x ≤ 1) NPs. In this respect, iron chloride salts (FeCl$_3$·6H$_2$O, FeCl$_2$·4H$_2$O and CoCl$_2$·4H$_2$O) were used as precursors. Also, NaOH and cetyltrimethylammonium bromide (CTAB) acted as precipitating agent and surface modifier agent, respectively.
The CoxFe$_{3-x}$O$_4$ NP precipitates were obtained from the two following starting solutions: a mixture of metallic salts with proper stoichiometric proportion, and the alkali hydroxide. Under intense stirring, the chemical reaction was performed using a molar ratio of 1:2 of Fe$^{2+}$:Fe$^{3+}$ at 80 °C. Under continuous stirring, 1 M NaOH was added dropwise to the solution until reaching a pH value of ∼12. The heating continued while keeping the solution temperature at 80 °C for 30 min until forming a black precipitation, representing the desired magnetic phase. The black mixture was then cooled down to room temperature and separated via centrifugation (6 000 rpm, 5 min). Finally, the precipitates were thoroughly washed with distilled water and methanol to eliminate chloride ions, and dried in an oven at 60 °C overnight. Accordingly, six NP samples (labeled as S1–S6) of CoxFe$_{3-x}$O$_4$ compound with different Co concentrations were prepared as listed in table 1.

### Table 1. NP samples of Co$_x$Fe$_{3-x}$O$_4$ compound with different Co concentrations.

| Sample | Co concentration (x) | Chemical formula (Theo.) | Chemical formula (Exp.) |
|--------|----------------------|--------------------------|-------------------------|
| S1     | 0                    | Fe$_3$O$_4$ (Pure iron oxide II, III) | Fe$_{2.89}$O$_4$ |
| S2     | 0.2                  | Co$_{0.2}$Fe$_{2.8}$O$_4$ | Co$_{0.14}$Fe$_{2.86}$O$_4$ |
| S3     | 0.4                  | Co$_{0.4}$Fe$_{2.6}$O$_4$ | Co$_{0.33}$Fe$_{2.67}$O$_4$ |
| S4     | 0.6                  | Co$_{0.6}$Fe$_{2.4}$O$_4$ | Co$_{0.41}$Fe$_{2.59}$O$_4$ |
| S5     | 0.8                  | Co$_{0.8}$Fe$_{2.2}$O$_4$ | Co$_{0.69}$Fe$_{2.31}$O$_4$ |
| S6     | 1                    | CoFe$_2$O$_4$ (Pure cobalt ferrite) | Co$_{0.97}$Fe$_{2.03}$O$_4$ |

The Co$_x$Fe$_{3-x}$O$_4$ NP precipitates were obtained from the two following starting solutions: a mixture of metallic salts with proper stoichiometric proportion, and the alkali hydroxide. Under intense stirring, the chemical reaction was performed using a molar ratio of 1:2 of Fe$^{2+}$:Co$^{3+}$:Fe$^{3+}$ at 80 °C. Under continuous stirring, 1 M NaOH was added dropwise to the solution until reaching a pH value of ∼12. The heating continued while keeping the solution temperature at 80 °C for 30 min until forming a black precipitation, representing the desired magnetic phase. The black mixture was then cooled down to room temperature and separated via centrifugation (6 000 rpm, 5 min). Finally, the precipitates were thoroughly washed with distilled water and methanol to eliminate chloride ions, and dried in an oven at 60 °C overnight. Accordingly, six NP samples (labeled as S1–S6) of Co$_x$Fe$_{3-x}$O$_4$ compound with different Co concentrations were prepared as listed in table 1.

2.2. Structural characterizations

2.2.1. Phase identification

Crystalline characteristic and phase purity of all NP samples were determined by x-ray diffraction (XRD; Philips, model X’Pert Pro; Cu K$\alpha$ radiation with $\lambda = 0.154$ nm) analysis. The average crystallite size ($d_{XRD}$) of the resulting NPs was estimated using the Scherrer equation [47]:

$$d_{XRD} = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $\lambda$ is the X-ray wavelength, $\beta$ (in radians) is the full width at half maximum of the main peak [i.e., the (311) plane] and $\theta$ is the Bragg diffraction angle.

2.2.2. Morphology and composition identification

Morphology, mean diameter, size distribution and composition of the NPs were determined by using a field-emission scanning electron microscope (FESEM; MIRA3 TESCAN) equipped with energy dispersive spectroscopy (EDS). Dynamic light scattering (DLS, Vasco/Cordouan Technologies/France) measurements were also performed to identify NP size distribution.

2.3. Magnetic characterizations

2.3.1. Hysteresis loop measurements

Magnetic properties were obtained by measuring hysteresis loops using a vibrating sample magnetometer (VSM; Magnetic DaneshPajoh Kashan Co.) at room temperature.

2.3.2. FORC analysis

The procedure to perform the FORC analysis was as follows: A magnetic field ($H_{max}$) was initially applied to positively saturate the sample. This field was then reduced to a reversal field $H_r$ ($H_r < H_{max}$) with certain steps and swept back to $H_{max}$, resulting in the first reversal curve of the NP sample. Meanwhile, magnetization $M$ ($H, H_r$) was measured at each step. By continuing this procedure, sets of minor FORCs were obtained. The FORC distribution $\rho$ is defined as given in equation (11):

$$\rho(H_r, H) = -\frac{1}{2} \frac{\partial^2 M(H_r, H)}{\partial H \partial H_r}$$

Moreover, $H_c$ and $H_u$ axes are defined by equations (12) and (13) as follows:

$$H_c = \frac{H - H_r}{2}$$

$$H_u = \frac{H + H_r}{2}$$

The $H_c$ axis specifies the coercive field distribution of magnetic domains, and the $H_u$ axis indicates the presence or absence of magnetic interactions between constituent domains of NPs [48–50]. In this study, 30 step
fields of 133 Oe ($H_{\text{max}} \approx 4000 \text{ Oe}$), 233 Oe ($H_{\text{max}} \approx 7000 \text{ Oe}$) and 266 Oe ($H_{\text{max}} \approx 8000 \text{ Oe}$) were used to perform the FORC analysis of samples S1–S4, S5 and S6, respectively.

2.4. Magnetic hyperthermia study
Prior to performing magnetic hyperthermia measurements, 15 mg dried powder of each NP sample (S1–S6) was dissolved in 5 ml distilled water to obtain a ferrofluid with a concentration of 3 mg ml$^{-1}$.

An ultrasonic bath at frequency of 50 Hz was used for 30 min to disperse and homogenize the ferrofluid. After applying an alternating magnetic field with intensity of 400 Oe and a frequency of 400 kHz to the vials containing ferrofluids, hyperthermia measurements were carried out by a home-made system (MDKHP, Magnetic DaneshPajoh Kashan). The temperature rise (arising from the heat released from each NP sample) was recorded within a span of 300 s for time steps of 60 s. The corresponding temperature rise-time diagram of each sample was plotted, and SLP value was obtained after calculating the slope of the diagram (at the first 60 s) and inserting it in equation (9). The specific heat capacity of distilled water and the starting temperature were set to 4.185 J g$^{-1}$°C and 20°C, respectively.

3. Results and discussion

3.1. Compositional and structural characteristics
Table 1 shows theoretical and experimental chemical formulas expected from stoichiometric amounts and obtained from EDS analysis (not shown here) of Co$_x$Fe$_{3-x}$O$_4$ compound with different Co concentrations (samples S1–S6), respectively. As inferred, the actual chemical compositions are similar to the expected stoichiometric amounts, indicating the successful substitution of Co ions.

Figure 1 shows XRD patterns of as-synthesized Co$_x$Fe$_{3-x}$O$_4$ (0 $\leq x \leq 1$) NP samples S1–S6. The diffraction peaks of all samples agree well with standard ICDD data (ICDD file No. 01-075-0449 for sample S1 and 00-01-1121 for samples S2–S6), indicating the formation of a spinel Co ferrite phase. Moreover, the peaks before (220) and (400) planes show the partial presence of Fe$_3$O$_4$ and CoO phases, respectively. Using equation (10), $d_{\text{XRD}}$ was estimated from the main (311) peak, and the results are given in table 2. It is found that, $d_{\text{XRD}}$ increases from 8.4 to 15.3 nm with increasing Co concentration ($x$) from 0 to 1, respectively.

3.2. Morphological characteristics
Figures 2(a)–(f) show FESEM images of as-synthesized Co$_x$Fe$_{3-x}$O$_4$ (0 $\leq x \leq 1$) NP samples S1–S6, respectively. FESEM observations reveal a nearly spherical morphology of the NP samples. The corresponding size distribution histogram of each sample fitted by a log-normal function is depicted in the top-right inset. The corresponding mean diameter values obtained from FESEM images ($d_{\text{FESEM}}$) are also inserted in table 2. As can
be seen, $d_{\text{FESEM}}$ increases from 16 to 30 nm with increasing $x$ from 0 to 1, being similar to the increasing trend of $d_{\text{XR}}$. This variation behavior of $d_{\text{XR}}$ and $d_{\text{FESEM}}$ has been previously reported in other studies \[34, 51\]. To identify NP size distribution, DLS measurements (not shown here) were performed in addition to the FESEM analysis. Since the synthetic approach for the different samples was the same, the DLS analysis was obtained for sample S3 ($x = 0.4$). The mean NP diameter was found to be about 89 nm. Since the NP size obtained from the DLS analysis is the hydrodynamic size, and also due to the agglomeration of NP, the resulting mean diameter of the NP is an acceptable value. Overall, the above-mentioned factors (hydrodynamic size and agglomeration) cause the NP size obtained from DLS analysis to be larger than its corresponding from FESEM analysis.

### 3.3. Magnetic characteristics

#### 3.3.1. Hysteresis loop measurements

Room-temperature magnetic properties of different NP samples were investigated using VSM with an applied magnetic field of up to 15 kOe. Figure 3 shows the hysteresis loops of Co$_x$Fe$_{3-x}$O$_4$ NP samples S1–S6. The inset reveals details of the hysteresis loops at a lower magnetic field range (±400 Oe). Moreover, $M_s$ and $H_c$ values of each sample extracted from the hysteresis loops are shown in figure 4. As inferred, increasing the Co concentration from $x = 0$ to $x = 1$ decreases the respective $M_s$ from 59.10 to 32.70 emu g$^{-1}$. This decreasing trend in $M_s$ value can be related to the smaller magnetic moment of Co$^{2+}$ than that of Fe$^{2+}$ \[34, 52\].

From another aspect, the NP size increases with increasing $x$, indicating an increase in the number of magnetic moments per volume. Therefore, $M_s$ is expected to increase with increasing $x$. On the other hand, it is expected to have a decreasing trend for $M_s$ when taking into account the smaller magnetic moment of Co$^{2+}$ ions.
than that of Fe$^{2+}$ ions ($4\mu_B$). Overall, it appears that the magnetic moment effect dominates the NP size effect so that $M_s$ shows a decreasing trend as a function of Co concentration (figure 4).

Additionally, increasing $x$ from 0 to 1 increases the respective $H_c$ from 7.75 to 340.50 Oe, indicating a transition from SP to ferromagnetic state. Similar results to $M_s$ and $H_c$ of the present study have been obtained in previous reports [34, 35, 40, 53]. The enhancement of $H_c$ due to the increase in the Co concentration can be related to the considerably high intrinsic anisotropy of Co. In other words, it can be stated that the Co ferrite anisotropy with different origination (e.g., intrinsic magnetocrystalline anisotropy) induces $H_c$. The anisotropy constant ($K$) can be simply estimated from equation (14) as follows [42, 54]:

$$K = \frac{H_c M_s}{0.96}$$

The $K$ values calculated for samples S1–S6 are shown in table 2, and figure 5 depicts the corresponding variation of $K$. As can be seen, increasing $x$ from 0 to 1 increases $K$ from 458.64 to 11598.28 erg g$^{-1}$, respectively.

For better clarity, $H_c$, $K$, remanence magnetization ($M_r$) and squareness ($S_q$) of the Co$\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) NP samples S1–S6 are depicted together in figure 6. The variation behavior of the magnetic quantities is similar to each other, demonstrating increasing trends. Especially, the important role of $K$ in $H_c$ is revealed as they follow each other. The reduction in $M_s$ and the increase in $M_r$ may lead to the increasing trend of $S_q$ from 0.01 to 0.25 when increasing $x$ from 0 to 1, respectively.
3.3.2. FORC investigations
To obtain comprehensive, detailed and precise information about the magnetic behavior of the NP samples, FORC analysis was used. FORC diagrams of samples S1–S6 are shown in figures 7(a)–(f), respectively. The FORC diagrams indicate and confirm that the variation behavior of $H_c$ matches the hysteresis loops of samples (figure 5). For example, in the particular case of sample S1, FORC distribution is located around the origin of the diagram ($H_c = 0$ Oe and $H_u = 0$ Oe) with high density, evidencing its low coercive field and estimating a SP.
behavior. Moreover, the comparison between FORC diagrams of other samples (S2–S6) indicates that the high density distributions are distanced from the origin, and broaden toward higher values along the $H_c$ axis. This gives rise to higher coercive field values obtained from hysteresis loop measurements (see figure 4). Furthermore, since the dispersion and elongation of each FORC diagram along the $H_c$ axis may represent the particle size distribution [51] sample S6 has higher NP size distribution than that of other samples. Cross-sectional profiles of the FORC diagrams along $H_c$ axis are shown in figure 8.

As expected, the higher FORC density of NPs with low coercive field magnetic domains is observed for Sample S1, evidencing its low $H_c$ obtained from the hysteresis loop measurements. It is worth noting that the particle size standard deviation ($\sigma$) of sample S1 is the lowest ($\sigma = 3.8$), according to FESEM results in figure 2. The reduction in FORC density of samples S4–S6 occurs with a smaller slope compared to that of samples S2 and S6.
S3. FORC analysis is also capable of determining the SP fraction of NPs by distinguishing between reversible and irreversible component fractions [55]. Table 2 and figure 9 (for simpler comparison) show the corresponding SP fraction of each sample. As can be seen, the SP fraction is reduced from 77% in sample S1 to 25% in sample S6, indicating a 52% decrease. This trend shows a transition from SP to ferromagnetic state quantitatively.

3.4. Magnetic hyperthermia investigations

Figure 10 shows bar graphs of temperature rise ($\Delta T$) in terms of time (heating curve) for all NP samples at a time interval of 300 s with time steps of 60 s. As seen, sample S3 with a compound containing a middle concentration of Co i.e. Co$_{0.4}$Fe$_{2.6}$O$_4$ has the highest $\Delta T = 35$ °C. On the contrary, samples S1 and S6 have lower values of $\Delta T = 15$ °C and 17 °C, respectively.

$\Delta T$ amount at a certain time interval for sample S3 is approximately 2.3 and 2 times larger than that of samples S1 and S6, respectively. In turn, this may be reflected in SLP value. Figure 11 shows SLP values of all NP
samples. As expected, sample S3 has the highest SLP value which is equal to 395 W g\(^{-1}\). Moreover, SLP value of sample S1 (Fe\(_3\)O\(_4\)) and sample S6 (CoFe\(_2\)O\(_4\)) is found to be 127 and 150 W g\(^{-1}\), respectively. Similar results on SLP maximization of ferrite NPs with a middle concentration of Co have been reported in previous studies [30, 35]. From the point of view of magnetic anisotropy, the increasing trend of K with increasing Co concentration (figure 5) is observed in the SLP enhancement from samples S1 to S3 so that the SLP is maximized at 395 W g\(^{-1}\) for x = 0.4. Although K once again increases from sample S4 to S6, the respective SLP value decreases from 210 to 150 W g\(^{-1}\). In this case, although K values of NPs (being larger than their corresponding bulk values) play a key role in magnetic hyperthermia, one can conclude that they do not necessarily increase SLP.

In fact, the SLP is maximized at a specific K, and decreases for higher and lower values of that K [56]. In other words, the magnetic anisotropy can be considered a controlling parameter for SLP. Such correlation of SLP with anisotropy can be justified based on the type of dependency between SLP and anisotropy. With regard to equations (6) and (7), since the maximization of \(\chi''\) leads to a maximum SLP, it is necessary to have \(\omega\tau_{\text{eff}} = 1\). Therefore, it is concluded that, a specific \(\tau_{\text{eff}}\) (resulting in a specific K value) can cause \(\omega\tau_{\text{eff}}\) to be maximized at a certain frequency, thus maximizing SLP. It should be noted that, among different sources for inducing anisotropy in materials, shape anisotropy and magnetocrystalline anisotropy are of particular importance for NPs. Taking into account the approximately spherical shape of the NPs in the present study, the magnetocrystalline anisotropy plays the major role, arising from spin-orbit interaction and energy consideration in ordering of magnetic moments for a specific crystalline direction (i.e., the easy axis) [31].

With a suitable combination of relatively high H\(_c\) and moderate M\(_s\) in sample S3, a considerable area inside its hysteresis loop can be found, strengthening the heat generation by the hysteresis loop loss mechanism. Apart from rapid and strong reaction between magnetic moments in the presence of magnetic field and thus heat generation in the inverse magnetization stage, the moderate M\(_s\) of sample S3 can enhance the capability of careful delivery of NPs when displacing them through blood circulation to reach the desired location.

On the other hand, the Brownian and Neel relaxation mechanisms can have a role since sample S3 has an SP fraction of about 50%. Therefore, the simultaneous presence of each of the three mechanisms together can generate a considerable amount of heat and cause SLP to be maximized for sample S3. Note that, despite its low H\(_c\) with an SP fraction of 77%, sample S1 has a lower SLP than that of sample S3. This is because the heat generation in sample S1 mainly arises from the Brownian and Neel relaxation mechanisms and the role of hysteresis loss is very small. In fact, figure 8 indicates that different mechanisms are simultaneously involved in heat generation in sample S3 since its coercive field distribution curve has acted as a boundary of samples S1 and S2 with samples S4-S6.

By comparing between SLPs of sample S1 and S6 while also considering the noticeable difference in their H\(_c\) and SP fraction, it appears that the hysteresis loss mechanism is dominant in competition between hysteresis loss and Brownian and Neel relaxations mechanisms for sample S6. On the contrary, this competition is opposite for sample S1.
As a matter of fact, decreasing the ferrofluid concentration and increasing the magnetic field intensity increase the corresponding SLP. Compared to the study by Mohapatra et al in which the optimum SLP was found at the concentration of 2 mg ml$^{-1}$ and field intensity of 491 Oe, the present study results in a relatively high SLP (395 W g$^{-1}$) for ferrite NPs at a higher concentration (3 mg ml$^{-1}$) and lower field intensity.

4. Conclusions

Using a co-precipitation method, CoxFe$_{3-x}$O$_4$ (0 $\leq x \leq 1$) NPs with a spinel ferrite phase were successfully synthesized. FESEM images indicated the formation of NPs with spherical morphology and sizes ranging from 16 to 30 nm for 0 $\leq x \leq 1$. Increasing Co concentration from $x = 0$ to 1 increased and decreased the respective $H_c$ and $M_s$ from 7.75 to 340.50 Oe and 59.10 to 32.70 emu g$^{-1}$, respectively. FORC analysis indicated the presence of low coercive field NPs with high density distributions. In this case, SP fraction of NPs decreased from 77% to 25% with increasing x from 0 to 1, respectively. Magnetic hyperthermia properties of the CoxFe$_{3-x}$O$_4$ compound were found to strongly depend on the Co concentration, NP size and magnetic properties including $H_c$, $M_s$, and K. The SLP of ferrofluids (having a concentration of 3 mg ml$^{-1}$) increased from 127 to 395 W g$^{-1}$ with increasing x from 0 to 0.4, thus increasing the corresponding SLP. Compared to the study by Mohapatra et al the optimum SLP was found at the concentration of 2 mg ml$^{-1}$ and field intensity of 491 Oe, the present study results in a relatively high SLP (395 W g$^{-1}$) for ferrite NPs at a higher concentration (3 mg ml$^{-1}$) and lower field intensity.

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