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Short communication

Optimizing co-precipitation parameters to achieve improved properties in  $CoFe_2O_4$  nanoparticles doped with  $Zn^{2+}$  and  $Dy^{3+}$  using the Taguchi method

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### ABSTRACT

This research focuses on optimizing critical process parameters in cobalt ferrite nanoparticles doped with  $Zn^{2+}$ and  $Dy^{3+}$ , synthesized using the co-precipitation method. Moreover, the combined effects of  $Zn^{2+}$  and  $Dy^{3+}$ content, OH concentration, calcination time and temperature, on the structural and magnetic properties of the synthesized nanoparticles were investigated. An L25 orthogonal Taguchi array was employed to design the required experiments and analyze these effects. Experimental results revealed a crystallite size ranging from 11 to 75 nm and saturation magnetization from 44.9 to 78.4 emu/g. Following the analysis of the experimental data, it has been established that the calcination temperature can be the predominant factor influencing both the crystallite size and saturation magnetization. Furthermore, the optimized sample identified through the Taguchi method exhibited the highest saturation magnetization value, a homogeneous morphology, and uniform particle distribution. These favorable characteristics make it a promising candidate for biomedical applications, where uniformity and homogeneity are important factors to consider. Moreover, the enhanced antibacterial activity of the free-doped sample, attributed to its smaller particle size, underscores the heightened impact of nanoparticles on gram-negative bacteria compared to gram-positive bacteria, likely due to structural variations in cell wall composition.

### 1. Introduction

Magnetic nanoparticles have attracted considerable interest among researchers and scientists in recent years, owing to their extraordinary potential in a wide range of applications [1]. Among these nanoparticles, spinel ferrites stand out for their exceptional optical, electrical, structural, and magnetic properties [2]. Spinel ferrites, represented by the general chemical formula MFe<sub>2</sub>O<sub>4</sub> (where M can represent Zn, Co, Mn, Ni, Mg, etc.) [3], have garnered widespread utilization in various industries, encompassing biotechnology [4,5], catalysis [6], energy storage devices [7], information storage systems [7], radar absorbing materials [8], and electronic circuits [9].

Cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>), classified as a spinel ferrite [10,11], has attracted considerable attention due to its remarkable characteristics, including high coercivity ( $H_c$ ), moderate saturation magnetization ( $M_s$ ),

chemical stability, and superior mechanical hardness [12].  $CoFe_2O_4$  exhibits an inverse spinel structure, characterized by a cubic crystal system. In this arrangement, oxide anions are arranged in a cubic close-packed configuration, while metal cations are coordinated by oxygen atoms in either tetragonal (A) or octahedral (B) sites. Each unit cell consists of 32 oxygen ions, 16 octahedral sites, and 8 tetrahedral sites. In Cobalt Ferrite,  $Fe^{3+}$  ions occupy the tetrahedral sites and half of the octahedral sites, while  $Co^{2+}$  ions occupy the remaining ones [13].

The properties of  $CoFe_2O_4$  nanoparticles are impacted by various factors, encompassing the purity of the phase, particle morphology, particle size, degree of crystallinity, and the distribution of cations within the A and B sublattices of the structure [14,15]. These parameters can be customized through the synthesis process [16]. Some of the common synthesis methods for the  $CoFe_2O_4$  nanoparticles include spray pyrolysis [17], hydrothermal [18], thermal decomposition [19], green

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synthesis [20], reverse micelle [21], sol–gel [22,23], and coprecipitation [24]. Among these methods, the co-precipitation method is a favored technique for synthesizing spinel ferrite nanoparticles due to its numerous advantages [25]. This method is renowned for its time efficiency, cost-effectiveness, simplicity, and reliability. The coprecipitation method yields a homogeneous powder with maximum efficiency, eliminating the requirement for organic fuels such as citric acid that make it as a more efficient and environmentally friendly process [26].

Notably, doping with elements of different valence states alters its magnetic, mechanical, electrical and thermal properties of  $CoFe_2O_4$  nanoparticles [27]. When divalent metal ions such as Zn [28], Cu [29], Ni [28], Mn [30], and Mg [31] are added as dopants to  $CoFe_2O_4$ , the characteristics of  $CoFe_2O_4$  undergo significant changes. The substitution of  $Zn^{2+}$  ions results in the formation of zinc-substituted cobalt ferrites ( $Co_{1-x}Zn_xFe_2O_4$ ) [32]. The introduction of non-magnetic zinc ions transforms  $CoFe_2O_4$  from ferromagnetic to superparamagnetic. Superparamagnetic materials exhibit unique magnetic behavior and find extensive applications in biomedical science, such as magnetic resonance imaging (MRI), targeted drug delivery, and further biomedical applications [33].

On the other hand, rare earth (RE) ions have diverse magnetic properties, with magnetic moments ranging from 0 ( $\text{La}^{3+}$ ) to 10.5  $\mu_B$  ( $\text{Dy}^{3+}$ ) [34]. Doping of RE ions into the spinel-type ferrites can improve the electrical and magnetic properties of ferrites [35,36]. For instance, doping by  $\text{La}^{3+}$  [37],  $\text{Ce}^{3+}$  [38], and  $\text{Gd}^{3+}$  [39] leads to notable changes in the crystallite size (*D*), lattice constant (*a*),  $M_s$ ,  $H_c$ , and magneto-crystalline anisotropy (*K*). Among the RE cations,  $\text{Dy}^{3+}$  exhibits the highest magnetic moment at 300 K, rendering it a favorable choice for fine-tuning the electrical, magnetic, and structural characteristics of magnetic materials [40]. The partial substitution of Fe<sup>3+</sup> with Dy<sup>3+</sup> ions in CoFe<sub>2</sub>O<sub>4</sub> nanoparticles is expected to enhance both magnetization and coercivity [41]. Furthermore, it is noteworthy that the Dy<sup>3+</sup> cation possesses a relatively large ionic radius of 0.91 Å [42]. This larger ionic radius can exert a substantial influence on the properties of nanoparticles incorporating this cation [43].

Although previous studies have explored the effects of  ${\rm Zn}^{2+}$  and  $\mathrm{Dy}^{3+}$  doping on the properties of CoFe<sub>2</sub>O<sub>4</sub>, there remains a gap in the research regarding the simultaneous doping of these two elements at various values. Hence, in this study, CoFe<sub>2</sub>O<sub>4</sub> nanoparticles doped with zinc and dysprosium were synthesized using the co-precipitation method. Notably, process parameters such as OH concentrations, time and temperature of calcination can also affect the properties, and their simultaneous effect was also considered in the present study. However, it should be noted that conducting studies with multiple variables can be challenging as it requires a considerable number of tests, which is often impractical. To achieve this objective, the Taguchi method, as the design of experiments (DOE) method, can be utilized to investigate the simultaneous effects of multiple parameters [44]. This approach offers numerous benefits, such as robustness, cost-effectiveness, ease of interpretation, and efficiency [45]. By utilizing orthogonal arrays, the method reduces the number of experiments and minimizes the impact of uncontrollable parameters [45]. The optimization process involves using the signal-to-noise (S/N) ratio as an objective function to determine the optimal conditions. Hence, in this particular study, the Taguchi method was utilized to optimize the processing parameters such as OH concentrations, time and temperature of the calcination process, as well as the amounts of dopants  $(Zn^{2+} and Dy^{3+})$ .

### 2. Materials and method

### 2.1. Materials

In this study, reagent-grade purity chemicals were used for the experiments. Cation sources, including cobalt (II) nitrate hexahydrate (Co  $(NO_3)_2$ ·6H<sub>2</sub>O,  $\geq$ 99 % from Merck), iron (III) nitrate nonahydrate (Fe

 $(NO_3)_3\cdot 9H_2O, \geq 99\%$  from Merck), zinc (II) nitrate tetrahydrate (Zn  $(NO_3)_2\cdot 4H_2O, \geq 99\%$  from Merck), and dysprosium (III) nitrate (Dy  $(NO_3)_3\cdot xH_2O, \geq 99\%$  from Sigma-Aldrich), were employed. Sodium hydroxide (NaOH) with a purity of 98\% was used as the alkaline agent, playing a crucial role in the synthesis process.

### 2.2. Synthesis process

The CoFe<sub>2</sub>O<sub>4</sub> nanoparticles with varying chemical compositions of Co<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2-y</sub>Dy<sub>y</sub>O<sub>4</sub> (where x = 0, 0.1, 0.2, 0.3, 0.4 and y = 0, 0.025, 0.05, 0.075, 0.1) were synthesized using the co-precipitation method at different OH concentrations (1, 2.5, 4, 5.5, and 7). The process flowchart is depicted in Fig. 1.

The synthesis process of nanoparticles is thoroughly described in the supplementary material (SI-I). The synthesized nanoparticles were calcined at different temperatures (600, 700, 800, 900, and 1000  $^{\circ}$ C) for varying times (1, 2, 3, 4, and 5 h) under an air atmosphere.

The chemical reaction for co-precipitation is described as follows [46,47]:

$$\begin{array}{rll} & \text{Co(NO}_{3})_{2}.6\text{H}_{2}\text{O} \xrightarrow{\text{H}_{2}\text{O}} \left[\text{Co(H}_{2}\text{O})_{6}\right]^{2\,+} & + \, 2\text{NO}_{3}^{-} \\ & \text{Fe(NO}_{3})_{3}.9\text{H}_{2}\text{O} \xrightarrow{\text{H}_{2}\text{O}} \left[\text{Fe(H}_{2}\text{O})_{6}\right]^{3\,+} & + \, 3\text{NO}_{3}^{-} & + \, 3\text{H}_{2}\text{O} \\ & \left[\text{Co(H}_{2}\text{O})_{6}\right]^{2\,+} & + \, \text{NaOH} {\rightarrow} \text{Co(OH)}^{3-} \\ & \left[\text{Fe(H}_{2}\text{O})_{6}\right]^{3\,+} & + \, \text{NaOH} {\rightarrow} \text{Fe(OH)}^{4-} \\ & \text{Co(OH)}^{3-} & + \, 2\text{Fe(OH)}^{4-} {\rightarrow} \text{CoFe}_{2}\text{O}_{4} & + \, 4\text{H}_{2}\text{O} & + \, 3\text{OH}^{-} \end{array}$$

As seen, the process begins with the dissolution of  $Co(NO_3)_2$ ·6H2O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in water, facilitating liquid phase synthesis. This is followed by the transformation of the resulting reactant solution through the addition of NaOH solution, leading to a homogeneous phase reaction between Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, which results in homogeneous precipitation.

#### 2.3. Design of experiments (DOE)

The Taguchi method is a valuable approach for analyzing the effects of individual design parameters and identifying the optimal condition of controllable parameters. This method uses S/N ratios to evaluate the influence of different designs. Based on the desired quality characteristics of the output, three commonly employed types of signal-to-noise ratios are employed: "larger is better", "smaller is better", and "nominal is better" [48].

In this specific study, the focus was on five parameters that significantly affect the properties of  $CoFe_2O_4$  nanoparticles synthesized through the co-precipitation process. These parameters include the amount of substitution of  $Zn^{2+}$  and  $Dy^{3+}$  ions, OH concentrations, and calcination time and temperature. Each parameter was varied across five levels (Table 1), allowing for a comprehensive analysis of their effects.

Different levels for each factor in this study were selected based on a combination of previous research, practical limitations, and the researchers' experiences. The range of OH concentration was determined from prior studies in this field, which indicated that crystal size increases with higher OH concentration [24]. Similarly, the temperature and duration of calcination were selected based on the thermal analysis results, the decomposition temperatures of the raw materials, and the conditions required to achieve the desired phase [49]. The incorporation of zinc and dysprosium was performed to enhance the magnetic properties, consistent with findings from earlier studies [34,50,51].

To efficiently optimize these parameters, the L25 orthogonal array, which is a specific design matrix, was utilized. This matrix aids in organizing the experiment by dividing the parameter combinations into 25 samples. In Table 1S, the L25 orthogonal array used in this study can be found, presenting the specific combinations of parameter levels assigned to each sample. As a result, 25 samples were synthesized and



Fig. 1. A schematic representation of the synthesized nanoparticles suing co-precipitation method.

Table 1
The controllable parameters and their selected levels.

Parameters	Symbol	Unit	Levels				
			1	2	3	4	5
Zn content	Х	_	0	0.1	0.2	0.3	0.4
Dy content	Y	_	0	0.025	0.05	0.075	0.1
Calcination temperature	Temp	°C	600	700	800	900	1000
Calcination time	Time	h	1	2	3	4	5
OH value	OH	Μ	1	2.5	4	5.5	7

meticulously analyzed. Through this extensive examination, valuable insights were gained into the influence of the chosen parameters on the properties of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles. By leveraging the power of the Taguchi method and the L25 orthogonal array, the best combination of parameter levels to achieve the desired output quality characteristics for CoFe<sub>2</sub>O<sub>4</sub> nanoparticles synthesized through the co-precipitation process was identified.

# 2.4. Characterization

The thermal behavior of the un-calcined nanoparticles was analyzed using thermogravimetry and differential thermal analyses (TG-DTA; Bahr STA 504). The analysis was conducted in an air atmosphere with a heating rate of 20  $^{\circ}$ C/min, from 25 to 1000  $^{\circ}$ C.

For the phase characterization of the synthesized nanoparticles, Xray diffraction (XRD) analysis was performed using a Bruker S4 instrument with a Cu target. The voltage and current used were 40 kV and 40 mA, respectively. The analysis covered a  $2\theta$  range of  $20-70^{\circ}$  with a step size of  $0.05^{\circ}$ . The obtained XRD data were analyzed using the Rietveld refinement method. The morphology of the nanoparticles was examined using both field emission scanning electron microscopy (FE-SEM; Mira3-Tescan-XMU instrument) and transmission electron microscopy (TEM; Talos L120C instrument).

Additionally, the average nanoparticle size was determined based on the FE-SEM and TEM micrographs. Fourier transform infrared (FTIR; L1600300 Spectrum TWO LITA) was performed to evaluate the functional groups in a wavenumber spectrum ranging from 400 to 4000  $\rm cm^{-1}$ . Furthermore, the magnetic characteristics were investigated using a vibrating sample magnetometer (VSM; Meghnatis Kavir Kashan) with a maximum field intensity of 1.5 T at room temperature.

### 2.5. In vitro antibacterial activity

The antibacterial activity of some synthesized nanoparticles was investigated using the minimum inhibitory concentration (MIC) technique. The MIC refers to the lowest concentration of an antimicrobial agent required to inhibit the visible growth of a microorganism after overnight incubation [52]. *Escherichia coli* (ATCC 11775) and *Staphylococcus aureus* (ATCC 12600) bacteria were donated by Shahid Sadoughi University of Pharmaceutical Sciences. The methodology and detailed protocol for the MIC test are thoroughly described in the supplementary information file (SI-III).

### 3. Result and discussion

### 3.1. Structural analysis

The XRD patterns of the calcined samples, illustrated in Fig. 2, reveal distinct peaks at 20 values of 30.2, 35.6, 37.3, 43.3, 53.7, 57.7, and  $62.9^{\circ}$ . These peaks align with crystallographic planes (220), (311), (222), (400), (422), (511), and (440), respectively. Their consistency with the JCPDS reference 96-591-0064 confirms the formation of a CoFe<sub>2</sub>O<sub>4</sub> cubic spinel-type structure within the Fd3m space group. Additionally, the XRD analysis indicates secondary phases in specific samples. Hematite (Fe<sub>2</sub>O<sub>3</sub>) peaks are observed in some samples, per the JCPDS reference 96-591-0083. Samples 4, 5, 15, and 19 exhibit peaks associated with dysprosium ferrite (DyFeO<sub>3</sub>), confirmed by the JCPDS reference 96-200-3126. Notably, sample 22 shows  $Co_3O_4$  peaks, identified by the JCPDS reference 96-900-5896.

Recognizing that these secondary phases can affect the material's properties, further investigation and optimization of synthesis conditions are crucial to minimize their formation.

Based on previous studies [34,53], the doping of RE elements into the spinel lattice has induced phase segregation and the migration of RE ions towards grain boundaries, even at low concentrations. This phenomenon often results in the formation of additional amorphous or



Fig. 2. XRD patterns related to some synthesized samples.

crystalline phases, such as orthoferrites (REFeO<sub>3</sub>) [54,55], hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [56,57], and metal monoxides [58]. The presence of secondary phases significantly affects the structural and magnetic properties of cobalt ferrite. Dysprosium ferrite and hematite are two impurities detected in the samples. Dysprosium ferrite exhibits antiferromagnetic behavior, which reduces the magnetic response of the samples [59].

In contrast, hematite acts as a secondary phase that affects coercivity. The removal of the hematite phase, along with a reduction in grain boundaries significantly decreases the complex phase and also increases the proportion of superparamagnetic nanoparticles with high interactions.

Interestingly, the presence of hematite can also be beneficial for tuning the desired magnetic properties. The varying current during the

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addition of an alkaline solution in the co-precipitation process is a key factor influencing hematite concentration and, consequently, the magnetic properties [60]. Furthermore, studies have shown that samples without a secondary phase exhibit a spherical morphology with well-defined boundaries [61]. Therefore, in general, by carefully controlling the amount of impurities in the samples, the magnetic and structural properties can be controlled, thereby optimizing them for various applications.

In the context of this study, the ionic radius of  $Dy^{3+}$  ions (0.91 Å) is larger than that of  $Fe^{3+}$  ions (0.67 Å), limiting the substitution of  $Fe^{3+}$ ions with  $Dy^{3+}$  ions. Consequently, the excess amount of  $Dy^{3+}$  ions tends to accumulate at the grain boundaries, ultimately leading to the formation of impurity phases.

The crystallite size, lattice parameter, X-ray density, average particle size, strain, and specific surface area ( $S_{SA}$ ) of synthesized samples are calculated and listed in Table 2.

The Debye-Scherrer equation was employed to calculate the average crystallite size of the synthesized magnetic nanoparticles for the high-intensity (311) plane, represented as follows [62]:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where *D* represents the average crystallite size, *K* is the instrumental constant (0.98),  $\lambda$  denotes the wavelength of Cu-K $\alpha$  radiation (1.5406 Å),  $\theta$  represents the Bragg angle, and  $\beta$  refers to the full width at half maximum (FWHM).

Furthermore, the lattice parameter can be estimated using the following equation [62]:

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$
(2)

where in this equation, a represents the lattice parameter, d denotes the interlinear distance, and (hkl) indicates the Miller indices for the diffraction peaks.

Also, the unit cell volume of the samples was calculated using the lattice parameters derived from the Rietveld refinement technique, with the results presented in Table 2.

#### Table 2

The structural	parameters	calculated	using	the XRE	) data
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Sample No.	Crystallite size (nm)		Particle (nm)	size	Lattice parameter (Å)		Volume (Å <sup>3</sup> )	X-ray density	S <sub>SA</sub> (m <sup>2</sup> / g)	Strain $(\times 10^{-4})$
	Debye-Scherrer's formula	Rietveld analysis	FE- SEM	TEM	Calculated by Eq. (2)	Rietveld		(g/cm <sup>3</sup> )		
1	18	16	25	21	8.3572	8.3934	591.3080	5.2699	70.67	22.00
2	20	23	_	_	8.3313	8.3790	588.2698	5.3574	48.12	20.00
3	23	25	_	38	8.3490	8.3904	590.6741	5.3955	43.60	13.00
4	31	43	_	_	8.3220	8.3925	591.1178	5.4514	25.65	4.03
5	48	72	_	_	8.3460	8.3891	590.3996	5.5180	15.02	2.25
6	35	39	_	_	8.3572	8.3969	592.0480	5.2778	29.47	1.90
7	31	45	_	_	8.3490	8.3973	592.1326	5.3369	25.14	12.00
8	38	69	_	_	8.3218	8.4020	593.1274	5.3877	16.13	7.48
9	18	14	28	25	8.2974	8.4043	593.6146	5.4429	81.65	13.00
10	19	18	_	_	8.3353	8.4013	592.9792	5.5085	59.84	14.00
11	47	69	-	_	8.3572	8.4099	594.8021	5.2678	16.45	2.60
12	14	14	_	_	8.3873	8.3764	587.7223	5.3916	78.53	27.00
13	17	18	_	_	8.3544	8.3915	590.9065	5.4224	62.83	21.00
14	22	22	_	_	8.3517	8.4067	594.1233	5.4527	50.17	17.00
15	26	33	_	_	8.3681	8.4107	594.9718	5.5044	33.05	16.00
16	23	30	_	_	8.3654	8.3984	592.3653	5.3040	37.54	17.71
17	23	27	_	_	8.3218	8.4098	594.7808	5.3420	42.27	12.26
18	31	39	_	37	8.3544	8.4160	596.0973	5.3896	28.45	10.96
19	43	75	155	_	8.3764	8.4130	595.4601	5.4549	14.59	9.95
20	14	12	_	_	8.3791	8.3923	591.0755	5.5552	88.96	30.00
21	45	63	_	_	8.3818	8.4210	597.1604	5.2758	18.04	4.42
22	48	46	_	_	8.3984	8.3984	592.3653	5.3783	24.26	4.59
23	11	11	24	20	8.3490	8.3952	591.6885	5.4443	100.00	27.03
24	14	15	_	_	8.3435	8.4047	593.6994	5.4855	73.40	26.30
25	16	18	-	_	8.4039	8.4325	599.6102	5.4905	59.16	20.19

The Rietveld refinement technique involves a least-squares fitting process that compares measured X-ray diffraction patterns with simulated ones. This method has proven successful in determining structural parameters for both single-phase and multi-phase materials [63]. To validate the results obtained from Eqs. (1) and (2), and to obtain additional structural parameters, Rietveld refinement analysis was performed in this study. Fig. 1S presents the XRD patterns obtained through the Rietveld refinement technique for multiple samples.

The average crystallite size and lattice parameter values were calculated using Eqs. (1) and (2), along with the Rietveld refinements, are listed in Table 2. As seen, the lattice parameter increases from 8.3934 Å in sample 1 to 8.4325 Å in sample 25, corresponding to the increasing values of Zn and Dy. As indicated in Table 2, the results demonstrate that as the substitution of  $Dy^{3+}$  increases in samples 2 to 5, there is a corresponding increase in the average crystallite size. Additionally, it is observed that the lattice constant decreases with higher concentrations of Dy in the lattice. This decrease in lattice constants can be attributed to the distribution of cations and the variation in cation sizes [64].  $Co^{2+}$  (0.79 Å) and  $Fe^{3+}$  (0.67 Å) ions are found in both A- and B-sites. However, replacing the smaller Fe<sup>3+</sup> ions in the B-sites with larger Dy<sup>3+</sup> ions results in the localized structural disorder and lattice strains. In response to this strain, the larger cation  $Co^{2+}$  migrates from the B-sites to the A-sites, leading to a slight contraction in the lattice. These findings align with previous studies conducted on the subject [65-67]. Contrarily, when  $Zn^{2+}$  is substituted in samples 6, 11, 16, and 21, it leads to an augmentation in both the average crystallite size and the lattice parameter. This increase in the lattice parameter can be attributed to replacing smaller  $\text{Co}^{2+}$  ions with larger  $\text{Zn}^{2+}$  ions (0.83 Å). As a result of this substitution, the lattice expands, leading to an increase in the lattice parameter. These findings are in line with prior studies [32,68]. The data suggest that the average crystallite increases with higher calcination temperatures and longer durations. This trend can be attributed to the decrease in surface energy as calcination progresses [63]. Moreover, an increase in the concentrations of NaOH solutions corresponds to larger average crystallite sizes [24].

As evident from the findings in Table 2, it can be concluded that lattice strain and crystallite size exhibit an inverse relationship, as the lattice strain decreases, the crystallite size tends to increase, and vice versa (SII-II, Fig. 2S).

The X-ray density can be determined using the following equation [69]:

$$\rho_{th} = \frac{8M}{N_a a^3} \tag{3}$$

where, in the given equation,  $\rho_{th}$  represents the X-ray density, *M* represents the molecular mass, *a* signifies the lattice parameters, and  $N_a$  refers to Avogadro's number. The calculated results for this parameter are detailed in Table 2. Notably, the values of X-ray density exhibit an increase with higher  $Zn^{2+}$  and  $Dy^{3+}$  contents. This phenomenon can be attributed to the rise in the molecular weight exceeding the expansion of the unit cell volume. Consequently, the overall effect is an increase in X-ray density as the content of  $Dy^{3+}$  increases (Fig. 3S) [33].

Nanoparticles characterized by a substantial specific surface area  $(S_{SA})$  play a pivotal role in various biomedical applications, particularly in drug delivery. The expansive surface area facilitates heightened drug loading and release capabilities, along with enhanced interactions with biological systems. This, in turn, enables targeted drug delivery, thereby augmenting treatment efficacy. Overall, the  $S_{SA}$  stands out as a crucial parameter that significantly influences the effectiveness of nanoparticles in biomedical applications [70,71].

This parameter can be determined using the following equation [72]:

$$S_{SA} = \frac{K_{sf}}{D\rho_{th}} \tag{4}$$

where  $S_{SA}$  represents the specific surface area,  $K_{sf}$  is the shape factor

(assuming all nanoparticles are spherical,  $K_{sf} = 6$ ), D represents the average crystallite size, and  $\rho_{th}$  represents the X-ray density of the nanoparticle. As presented in Table 3, the  $S_{SA}$  values range from 15.02 to 100 m<sup>2</sup>/gm. Notably, sample 23 exhibits the highest  $S_{SA}$ , along with having the finest average crystallite size. Generally, a greater  $S_{SA}$  corresponds to an increased number of active surface sites. This attribute can be advantageous in various applications as it enhances the reactivity and potential interactions of the nanoparticles with their surroundings.

The distribution of cations within nanoparticles is a critical factor that significantly influences their properties [73].

The cation distribution data for some samples (Table 2S), revealing that  $Zn^{2+}$  ions are predominantly located on the B site and both Fe<sup>3+</sup> and Co<sup>2+</sup> cations can occupy both the A and B sites. Nevertheless, owing to their larger ionic radii, Dy<sup>3+</sup> cations are predominantly situated in the B-sites. In contrast, zinc cations possess the flexibility to occupy both the A and B sites.

### 3.2. Thermal analysis

The typical TG-DTA curves of the uncalcined nanoparticles are depicted in Fig. 3. The results suggest that processes such as water removal, metal hydroxide decomposition, and the formation of spinel ferrite can be achieved at temperatures below 600 °C. This observation is consistent with findings in the literature [32]. During the heating process up to 600 °C, several sequential events take place. Initially, at temperatures below 150 °C, there is water desorption, where any physically absorbed water is released as the material undergoes further drying. Subsequently, the decomposition of organic templates occurs in the temperature range of 150-350 °C. During this stage, multiple processes take place. Initially, chemically absorbed water and OH species are desorbed from the particle surface. Furthermore, any residual nitrate groups from the precursors are eliminated. Subsequently, nonstoichiometric oxygen species are released. This is succeeded by the crystallization of the final product and the formation of the ferrite phase. These transformations occur gradually as the temperature increases to 600 °C [53,74,75]. TG curves depict the observed mass loss in samples 1, 5, and 18. The variation in mass loss among these samples can be elucidated by considering the strength of the ionic bonds between the cation and anion at both the A-and B-sites, along with the enthalpy of formation  $(\Delta H_f)$  of the compound. In this context, Pauling's equation can be employed to calculate the ionic bond strength as follows [76]:

$$I_{AB} = \left(1 - \exp\left[-\left(X_A - X_B\right)^2/4\right]\right)$$
(5)

where the average electronegativity of the cation and anion is represented as ( $X_A$ ) and ( $X_B$ ), respectively. The electronegativity values of the cations Co<sup>2+</sup>, Zn<sup>2+</sup>, and Dy<sup>3+</sup>, and the anion O<sup>2-</sup> are 1.88 [77], 1.65 [78], 1.22 [79], and 3.44 [80], respectively. By substituting these values into Eq. (5), the ionic bond strengths of the Co–O, Zn–O, and Dy–O bonds can be determined. The calculated values are as follows:  $I_{\text{Co-O}} =$ 0.4558,  $I_{\text{Zn-O}} = 0.5511$ , and  $I_{\text{Dy-O}} = 0.7083$ . These findings unequivocally demonstrate that the ionic bond strength of the Co–O bond is lower than that of both the Zn–O and Dy–O bonds. Consequently, the  $\Delta H_f$  for the doped CoFe<sub>2</sub>O<sub>4</sub> compound exhibits a more negative value than undoped CoFe<sub>2</sub>O<sub>4</sub>.

Based on the relationship between the free energy of formation  $(\Delta G_f)$ and  $\Delta H_f$ , given by  $\Delta G_f = -\Delta H_f - T\Delta S_f$ , a more negative enthalpy of formation results in a more negative free energy of formation. This implies that the doped CoFe<sub>2</sub>O<sub>4</sub> phase is more stable compared to the undoped CoFe<sub>2</sub>O<sub>4</sub> phase and potentially even more stable than secondary phases that may be present, which aligns well with existing literature [81]. Alternatively, the DTA curve displays a small endothermic peak at 150 °C, attributed to dehydration. An exothermic peak at 250 °C indicates the decomposition of the metal nitrates and hydroxides. Another exothermic peak at 550 °C signifies the formation of spinel ferrite, and these results are consistent with the observed mass

Table 3				
Magnetic	properties	of all	synthesized	samples.

Sample No.	$M_s$ (emu/g)	$M_r$ (emu/g)	<i>H</i> <sub>c</sub> (Oe)	$K \times 10^5 ({\rm erg/cm^3})$	<i>n<sub>B</sub></i> (μ <sub>B</sub> )	$M_r/M_s$	$H_m$ (Oe)	$\chi = dM/dH$ (er $H \rightarrow H_m$	nu/gOe) $H \rightarrow 0$
1	54.62	20.96	913.60	1.314	2.294	0.3837	809	0.0268	0.0162
2	54.85	25.88	1033.20	1.518	2.330	0.4718	918	0.0306	0.0150
3	57.35	29.25	1310.01	2.026	2.464	0.5100	1233	0.0266	0.0137
4	65.18	32.26	951.18	1.689	2.831	0.4949	798	0.0419	0.0216
5	65.26	23.34	536.26	0.965	2.866	0.3576	460	0.0534	0.0307
6	73.54	26.63	450.47	0.874	3.098	0.3621	406	0.0676	0.0454
7	71.23	26.73	531.92	1.011	3.034	0.3753	602	0.0622	0.0363
8	73.48	24.18	383.44	0.758	3.165	0.3291	399	0.0819	0.0496
9	50.07	15.55	404.88	0.552	2.181	0.3106	355	0.0418	0.0323
10	54.17	18.07	484.47	0.723	2.385	0.3336	349	0.0448	0.0293
11	78.40	17.75	185.53	0.383	3.311	0.2264	148	0.1050	0.0863
12	52.25	8.12	137.81	0.194	2.232	0.1554	98	0.0644	0.0549
13	58.62	13.04	203.88	0.324	2.532	0.2224	206	0.0722	0.0574
14	60.59	14.76	229.73	0.379	2.646	0.2436	233	0.0725	0.0565
15	67.48	18.54	247.29	0.459	2.979	0.2747	253	0.0871	0.0659
16	63.49	11.94	147.13	0.248	2.689	0.1881	162	0.0897	0.0754
17	68.89	14.43	160.98	0.296	2.951	0.2095	201	0.0992	0.0805
18	74.14	16.03	154.48	0.309	3.211	0.2162	155	0.1204	0.0987
19	74.49	11.03	94.92	0.193	3.262	0.1481	58	0.1211	0.1136
20	50.41	2.57	29.74	0.042	2.231	0.0509	0.56	0.0866	0.0837
21	72.22	6.56	55.88	0.106	3.067	0.0908	0.38	0.1178	0.1124
22	70.98	6.50	53.86	0.103	3.048	0.0916	51.8	0.1228	0.1001
23	44.91	0.78	9.30	0.011	1.950	0.0174	2.2	0.074	0.0730
24	50.14	3.05	32.49	0.044	2.202	0.0608	4.61	0.0942	0.0902
25	49.88	4.77	53.04	0.073	2.214	0.0956	49.2	0.0916	0.0884



Fig. 3. TG-DTA curves of the uncalcined samples 1, 5, 18, and 21.

loss by others [82]. The discrepancy in the DTA curves between sample 5 and samples 1 and 18 can be attributed to the variation of crystallite size in these samples. As highlighted in the data presented in Table 1, the crystal size of sample 5 is noticeably larger compared to samples 1 and 18. This difference results in a more pronounced exothermic peak in sample 5 within the temperature range of 550 °C. In general, in the coprecipitation method for synthesizing CoFe<sub>2</sub>O<sub>4</sub>, the percentage of dopants (Zn and Dy) impacts the associated water content. This is because changes in the concentration of Zn and Dy can alter the particle size and affect the rate of ferrite formation [83].

In the DTA curve of sample 5, an intriguing endothermic peak is discernible within the temperature range of 950 °C. This peak is caused by the presence of DyFeO<sub>3</sub> impurity within this specific sample. Consequently, at this temperature, the dysprosium ferrite transforms, leading to the formation of dysprosium iron garnet [84].

### 3.3. FT-IR analysis

The FTIR spectrum of sample 1 was recorded both before and after calcination, covering a frequency range from 4000 to 400 cm<sup>-1</sup>, as illustrated in Fig. 4.

Generally, two peaks were identified, attributed to metal–oxygen (M–O) bond vibrations corresponding to the A and B sites in the spinel ferrite sub-lattice [85], which can be observed in Fig. 4(a).

In Fig. 4(a), the peak observed at approximately  $1640 \text{ cm}^{-1}$  can be attributed to the stretching mode vibration of surface-adsorbed H–O–H molecules. On the other hand, the peak at around 3236 cm<sup>-1</sup> corresponds to the bending vibration mode of H–O–H in free or absorbed water molecules [85,86]. Additionally, a peak at approximately 1108 cm<sup>-1</sup> is exhibited, likely attributed to residual FeOOH, indicating the presence of iron oxyhydroxide in the sample [87]. Additionally, the spectrum displays a prominent peak at around 916 cm<sup>-1</sup>, a



Fig. 4. FT-IR spectra of sample 1 (a) before, and (b) after the calcination process.

characteristic feature often linked to the Fe–Co system. Furthermore, a band observed at 1348 cm<sup>-1</sup> is attributed to the symmetric vibration of the NO<sub>3</sub> group [88]. As seen in Fig. 4(b), the intensity of O–H, N–H, and N–O bonds noticeably decreases after the calcination process. This observation indicates that organic compounds are being eliminated during this process stage. These results align with the findings from the thermal analysis (Fig. 3). For instance, in Sample 1, the reaction does not reach completion prior to calcination, as evidenced by the peaks associated with water removal and the decomposition of metal hydroxides in the TG-DTA diagram. This observation is further supported by the FTIR spectrum of the sample before calcination, which displays peaks corresponding to organic groups, such as O–H groups. Notably, these peaks disappear in the FTIR spectrum of the sample after calcination, indicating the removal of these organic components.

Fig. 5 illustrates the FT-IR spectra of the calcined samples 1, 11, 17, 18, and 21. In the spectra, two distinct peaks are observed. The lower frequency peak, typically found in the range of 472–474 cm<sup>-1</sup> ( $v_I$ ), corresponds to the intrinsic vibration of the M–O bond at the B-sites. Conversely, the higher frequency peak, ranging from 559 to 570 cm<sup>-1</sup> ( $v_2$ ), is attributed to the A-sites. The presence of these well-defined peaks offers further evidence for forming the spinel ferrite structure with the space group of Fd3m [63]. The higher wavenumber observed in the spectrum corresponds to the vibrations of the oxygen ions and the metal ions located at the A-sites within the spinel ferrite structure.

On the other hand, the lower wavenumber corresponds to the vibrations involving the oxygen ions and the metal ions at the B-sites. The difference in the location of these peaks can be attributed to the variation in bond length among the metal ions and the oxygen ions at the respective sites. The shorter bond lengths between the metal and oxygen ions at the A-sites result in higher wave numbers, while the longer bond lengths at the B-sites lead to lower wave numbers [89].

Notably, previous research [63] has shown that the peaks shifting corresponding to metal cations ( $v_1$  and  $v_2$ ) in the FT-IR spectra indicate changes in the lattice parameter and cation distribution. It is important to consider factors such as calcination temperature and grain size, as they can influence these shifts [90]. Understanding the relationship between these variables and the observed peak shifts can provide valuable insights into the structural changes and properties of the sample. The observed variation in M–O peak intensity, as the Dy<sup>3+</sup> and Zn<sup>2+</sup> content increases, can be attributed to the perturbation in the M–O bonds. This perturbation arises from the substitution of Dy<sup>3+</sup> and Zn<sup>2+</sup> ions, as well as the redistribution of Co<sup>2+</sup> and Fe<sup>3+</sup> ions at the A and B sites [34].

Fig. 6 illustrates the variations in the stretching vibrations of the  $v_2$ 





Fig. 6. The displacement of the stretching vibration bands in the A sites for the some samples.

peak, adopted from the spectra presented in Fig. 5. In the spectrum of sample 17, a shift in the absorption bands at the A-sites is observed compared to sample 11. This shift results from an increase in the concentration of doped zinc and the introduction of dysprosium into the CoFe<sub>2</sub>O<sub>4</sub> structure. The larger ionic radius of zinc compared to cobalt causes the bond length to increase when zinc occupies the A-sites, leading to a shift towards lower wavelengths in the peak corresponding to the tetrahedral M-O bond [91]. Additionally, the presence of dysprosium in the structure may also contribute to this observed shift. This phenomenon is also observed in samples 1 and 21, as well as samples 11 and 21. As the concentration of doped zinc increases, the peak corresponding to the tetrahedral M-O bond undergoes a shift towards lower wavelengths, attributed to the increased presence of doped zinc in the A-sites. Additionally, the higher atomic weight of the dopants can lead to a transfer in the absorption band towards a lower frequency. Therefore, in the case of samples 17 and 21 compared to sample 1, the total atomic weight, including the dopants, could be the reason for the shift towards a lower frequency [62].

Moreover, in sample 18 compared to sample 17, there is an increase in the concentration of zinc in A-sites (as presented in Table 2S). This would typically lead to a decrease in the wavelength of the tetrahedral M–O in sample 18. However, contrary to expectations, the results show the opposite. This difference can be attributed to an increase in the bond length at the B-sites and the presence of network distortions, aligning well with the findings reported by other researchers [92].

### 3.4. Microstructural observations

The morphology and size distribution of the synthesized nanoparticles were examined using FE-SEM and TEM techniques. Fig. 7 specifically presents the FE-SEM micrographs of selected samples. The FE-SEM micrographs reveal the homogeneous morphology of the ferrite nanoparticles, characterized by the presence of spherical refined grains. However, some agglomeration is also observed, which can be attributed to the interactions between the magnetic nanoparticles. On the other hand, it can be seen that the substitution of dysprosium and zinc cations has a minimal impact on the morphology of the particles. The micrographs demonstrate that the overall particles morphology remain relatively consistent. However, there is a discernible effect on the particle size, indicating that substituting these cations subtly influences the size distribution.



Fig. 7. FE-SEM micrographs in the combination of the particle size distribution diagrams for samples; (a) 1, (b) 9, (c) 19, and (d) 23.

Consequently, the doping of these cations in the particle structure leads to a slight increase in particle size. On a contrasting note, it is crucial to highlight that samples 1, 9, and 23 exhibit particle sizes within a similar range of 24–28 nm, while sample 19 stands out with significantly larger particles, averaging around 155 nm. This observation highlights the significant effect of calcination temperature on particle size. Specifically, a higher calcination temperature leads to the formation of larger nanoparticles.

The particle size, as determined from FE-SEM micrographs (refer to Table 2), is notably larger than the estimate obtained from XRD patterns. This finding implies that each particle comprises a significant aggregation of individual crystals or grains [34].

For a more detailed examination of the morphology, Fig. 8 provides TEM micrographs of selected samples. As observed, nanoparticles typically exhibit a spherical or semi-spherical shape. Moreover, the average particle size was evaluated by analyzing TEM micrographs, and the results are presented in Table 2. It is clear from the data that there is a significant increase in the average particle size of sample 3 compared to sample 1. This can be attributed to two contributing factors: an increase in the quantity of dysprosium cation and an increase in the calcination temperature for sample 3. These factors contribute to the growth and agglomeration of particles, resulting in larger particle size. Notably, this observation aligns with the outcomes derived from the SEM analysis.

Moreover, the TEM images reveal a significant level of agglomeration in samples 18 and 19. This agglomeration could be attributed to various factors, including variations in the amount of zinc and dysprosium cations, along with the calcination temperature. Also, as illustrated in Table 3, there is a clear similarity between the average particle size determined from TEM and FE-SEM micrographs. In conclusion, incorporating  $Dy^{3+}$  and  $Zn^{2+}$  as dopants, along with modifications to the synthesis parameters, can influence the morphology and size of  $CoFe_2O_4$  nanoparticles. Nevertheless, it has been discerned that under optimized conditions, the production of exceedingly fine nanoparticles with a uniform morphology is achievable.

# 3.5. VSM analysis

Fig. 9 illustrates the M–H hysteresis loops of various synthesized samples, enabling the extraction of key magnetic properties. The magnetic characteristics, such as  $M_s$ , remanent magnetization ( $M_r$ ), coercive field ( $H_c$ ), squareness ratio (SQR), magnetic moment ( $n_B$ ), and K, can be determined using the VSM loops. Detailed values for these properties can be found in Table 3.

The synthesized ferrites exhibit a range of  $M_s$  values, ranging from 44.91 to 78.4 emu/g, while  $M_r$  values fall within the intervals of 0.78 to 32.26 emu/g. Additionally, the  $H_c$  varies from 9.3 to 1310 Oe for different samples. The  $M_s$  value of undoped CoFe<sub>2</sub>O<sub>4</sub> nanoparticles is lower than that of bulk CoFe<sub>2</sub>O<sub>4</sub>, typically around 80 emu/g [34]. This decrease in  $M_s$  is primarily attributed to the smaller size of the nanoparticles crystallites, leading to structural disorder on their surfaces. Several factors contribute to the low  $M_s$  values in nanoparticles, including the presence of a magnetic dead layer, the disorderly distribution of cations on the nanoparticles' surfaces, the spin canting effect resulting from competing antiferromagnetic interactions, and other



Fig. 8. TEM micrographs of the synthesized samples; (a) 1, (b) 3, (c) 9, (d) 18, (e) 19, and (f) 23.

factors [93]. The magnetic properties of spinel ferrites are influenced by various factors such as changes in crystallite size, variations in magnetic moments, the favored occupation of different ions at particular sites, and the existence of local strains.

Furthermore, super-exchange interactions between different ions and disordered cation distributions can also impact the magnetic properties [93]. Room temperature magnetic measurements for samples 1–5 reveal that the  $H_c$  initially increases and then decreases with higher calcination temperatures beyond 800 °C, while  $M_s$  exhibits a continuous linear increase. The rise in  $M_s$  and  $H_c$  can be attributed to the enhancement of magnetic anisotropy in the ferrite particles, hindering the alignment of the magnetic moment in response to an applied field. It is noteworthy that, in general, magnetic parameter values tend to decrease as the average grain size decreases, and conversely, they increase as the average grain size increases [93]. As seen in Table 2, as the particle size increases, the  $M_s$  also increases (Fig. 4S), with the calcination temperature having a direct influence on this relationship. In other words, as the calcination temperature rises, the particle size also increases, resulting in a corresponding increase in the  $M_s$  of the samples.

In general, it can be observed that the sample with the lowest  $M_s$  is sample 23, calcined at 600 °C, possessing the smallest crystal size. On the other hand, sample 11, calcined at 1000 °C, displays the highest  $M_s$ , attributed to its larger crystal size. The decrease in  $H_c$  observed after calcination beyond 800 °C can be attributed to the development of multi-domains beyond the critical size, exceeding the single-domain size limit of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles [94]. Furthermore, the increase in  $M_s$ with higher Dy<sup>3+</sup> concentration is due to incorporating higher magnetization entities in the form of Dy<sup>3+</sup> ions within the CoFe<sub>2</sub>O<sub>4</sub> lattice [51]. The substitution of non-zero angular momentum ions (Co<sup>2+</sup>) with zero angular momentum ions (Zn<sup>2+</sup>) results in a reduction of spin–orbit coupling in the ferrite particle system, reducing both the magnetocrystalline anisotropy and  $H_c$ . This behavior has been consistently



Fig. 9. Hysteresis loops of several synthesized samples.

observed in another study [95]. Generally, in ferrite structures,  $Dy^{3+}$  and  $Zn^{2+}$  ions occupy B sites, leading to the migration of  $Co^{2+}$  ions from B to A sites. Through this redistribution, the difference in magnetic moment between the A and B sublattices is modified, leading to a notable effect on the magnetic properties [34,95]. The magnetic moment's dependence on dopant concentration can be estimated by evaluating the magnetic moment per formula unit in terms of Bohr magneton, calculated using the equation [63]:

$$n_B = \frac{M_s M}{5585} \tag{6}$$

where  $n_B$  represents the magnetic moment, M denotes the molecular weight, and  $M_s$  represents the saturation magnetization. The magnetic moment varies due to changes in both the  $M_s$  and the dopant content, as observed in Table 3. It is well-established that variations in superexchange interactions between A and B sites can result in alterations in the magnetic moment values. In this investigation, a relationship between the  $M_s$  values of the samples and their corresponding magnetic moments was identified. Notably, the samples with the highest  $M_s$ demonstrated the highest magnetic moments, whereas those with the lowest  $M_s$  displayed the lowest magnetic moment. For the synthesized samples, the squareness ratio (SQR) falls within the range of 0.0174-0.5100, indicating uniaxial anisotropy. Notably, these values are below 0.500, confirming uniaxial anisotropy. Low SQR values could be attributed to surface spin disorder, affecting the magnetic properties [93]. According to the data provided in Table 3, sample 3 exhibits the highest SQR value, while sample 23 demonstrates the lowest SQR value. Moreover, the magnetocrystalline anisotropy impacts coercivity. The relationship between K and  $H_c$  is described by [63]:

$$K = \frac{H_c M_s \mu_0}{2} \tag{7}$$

where  $\mu_0$  represents the vacuum permeability.

The calculated anisotropy values are presented in Table 3. As seen, sample 3 has the highest, and sample 23 has the lowest magnetocrystalline anisotropy. Changes in anisotropy are directly associated with magnetization reorienting from the easy axis to the hard axis. Numerical values of dM/dH provide insights into magnetic susceptibility ( $\chi$ ).

The curves of dM/dH vs. H (Fig. 5S) display symmetric peaks around  $H \sim 0$ , with a clear separation of  $2H_m$ . The extracted values of  $H_m$  and the corresponding dM/dH at  $H_m$  and H = 0 are compiled in Table 3 for further analysis. The finite values of dM/dH at  $H \sim 0$  for the synthesized samples confirm their pseudo-single and multi-domain characteristics.

Analyzing the data provided in Table 3, it is evident that the  $H_m$  values consistently exhibit lower values in comparison to  $H_c$ , suggesting the absence of a distribution of the switching field. This trend is typically associated with nanoparticles that possess a well-ordered core–shell structure. In contrast, nanoparticles with a disordered shell structure often exhibit a broader distribution of switching fields, leading to higher  $H_m$  values. The decrease in  $H_m$  indicates a higher  $\chi$  to external magnetic influences and a more superparamagnetic behavior in the samples. This observation highlights the influence of  $Dy^{3+}$  and  $Zn^{2+}$  concentrations on the magnetic characteristics of  $CoFe_2O_4$  [96]. The increased peak height and reduced peak spacing observed with an increase in temperature suggest that the samples are in a well-ordered and favorable magnetic state, consistent with the pertinent literature [97].

# 3.6. The best process condition based on each response variable

In this section, the objective was to determine the optimum properties of the synthesized nanoparticles. For this purpose, according to the processed response variables in Tables 2 and 3. A "smaller is better" strategy was employed to minimize both the crystallite size and impurity percentage in the study. Conversely, a "larger is better" approach was adopted to identify the maximum values of  $H_c$ ,  $M_s$ , and  $M_r$ .

Table 4 presents the results derived from the S/N ratio plots (Fig. 6S), which helps to identify the optimal values for the process parameters. It is observed that to achieve the optimal *D* value, it is essential to set the amount of  $Zn^{2+}$ , OH, and the calcination temperature and time at 0.1, 7, 1000 °C, and 3 h, respectively. The lowest impurity level is obtained when the OH value is set at 7, along with a calcination temperature of 700 °C and a duration of 2 h. To achieve the highest  $M_s$ , the optimum values for OH,  $Zn^{2+}$ , calcination temperature, and time are 7, 0.3, 1000 °C, and 4 h, respectively. Similarly, the maximum  $M_r$  is achieved when OH is set at 1, with a calcination temperature of 900 °C and a duration of 2 h. Finally, to achieve the highest  $H_c$ , the amount of  $Dy^{3+}$ , OH, and the calcination temperature and time should be set at 0.025, 1, 800 °C, and 2 h, respectively.

The results in Table 5 demonstrate the relationship between the target variable and the content of  $Zn^{2+}$  and  $Dy^{3+}$ , OH concentration, and calcination temperature and time for S/N Ratios. These data allow us to identify the most influential factor on each target variable. The calcination temperature has the greatest impact on the crystallite size. As seen, higher temperatures during the calcination process lead to the formation of nanoparticles with larger crystallite size. Additionally, calcination temperature and time significantly affect the percentage of impurities in the samples. Concerning  $M_s$ , the most influential factors are the calcination temperature and the amount of  $Dy^{3+}$ . On the other hand, the  $Zn^{2+}$  emerges as the key influencing factor on  $M_r$  and  $H_c$ .

# 3.7. The best process condition based on the combined variable

To optimize the process parameters, a combined variable is created that incorporates five response variables: the impurity percentage, D,  $H_c$ ,  $M_s$ , and  $M_r$ . Given that these variables have different units and scales, Min-Max normalization is applied to transform them into decimal values that lie within the range of 0-1. Additionally, coefficients are assigned to each response variable to reflect their relative significance in the

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Та

The optimal value of the processing parameters for each variable.

Target variable	Type of optimization	Х	Y	OH	Temp (°C)	Time (hr)
D	Minimize	0.1	0	7	1000	3
Impurity percentage	Minimize	0.0	0	7	700	2
Ms	Maximize	0.3	0	7	1000	4
$M_r$	Maximize	0.0	0	1	900	2
$H_c$	Maximize	0.0	0.025	1	800	2

#### Table 5

Response table of S/N ratio for target variable versus X, Y,OH, calcination temperature and time.

Target variable	Response	Х	Y	ОН	Time (hr)	Temp (°C)
D	Delta	2.11	3.69	1.59	1.33	13.85
	Rank	3	2	4	5	1
Impurity	Delta	3.22	4.94	7.58	8.39	8.36
percentage	Rank	5	4	3	1	2
$M_s$	Delta	1.30	1.53	0.32	0.41	3.15
	Rank	3	2	5	4	1
$M_r$	Delta	17.57	3.63	2.91	3.22	10.00
	Rank	1	3	5	4	2
$H_c$	Delta	28.47	3.25	3.68	3.40	7.66
	Rank	1	5	3	4	2

combined variable. In this case, the coefficients 0.1, 0.35, 0.05, 0.4, and 0.1 were considered for the impurity percentage, D,  $H_c$ ,  $M_s$ , and  $M_r$ , respectively (Table 6).

Based on the S/N ratio plots, the calculation of the combined variable (CV) was performed to determine the optimal condition. The findings are presented in Fig. 10 and Table 6, showcasing the results of this analysis. According to the results, the optimal values for  $Zn^{2+}$ ,  $Dy^{3+}$ , OH, calcination temperature, and time are 0.1, 0.025, 1, 900 °C, and 4 h, respectively. These values are identified as they lead to the maximum value of the CV, indicating the most favorable conditions.

Furthermore, the results outlined in Table 3S indicate that the properties mentioned earlier are predominantly influenced by the  $Zn^{2+}$  content when considering the combined variable. Based on these results, sample 26 is the preferred candidate for additional analysis and experimentation.

### 3.8. Optimized sample results

Fig. 11 displays the XRD patterns of samples 1 and 26 (the optimized sample). The XRD pattern of the optimized sample reveals a single-phase cubic spinel of  $CoFe_2O_4$ . Through the optimization of the synthesis process, impurities have been effectively eliminated, resulting in the production of an impurity-free sample. Furthermore, the optimized sample demonstrates larger values for both *D* (38.89 nm) and *a* (8.397 Å) compared to sample 1. As previously highlighted, the calcination temperature is known as the primary factor influencing *D*. In the case of sample 26, the larger *D* value can be attributed to the utilization of higher calcination temperature and longer calcination time during its preparation, contrasting the conditions applied to sample 1.

Fig. 12 presents the FT-IR spectra of samples 1 and 26. As seen, the presence of M–O peaks in both samples indicates the formation of spinel CoFe<sub>2</sub>O<sub>4</sub>. However, in the optimized sample, the absorption bands of the M–O shift to higher positions. This shift in absorption bands can be attributed to changes in the cation distribution and synthesis parameters.

Sample 26 was examined for morphology and particle size distribution using FE-SEM, as depicted in Fig. 13. It is evident that sample 26 exhibits nanoparticles with a semi-spherical morphology, displaying a

### Table 6

Description	of the	combined	variable.
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Target variable	CV					
	Type of optimization	Weight				
D	Minimize	-0.35				
Impurity percentage (I)	Minimize	-0.10				
$M_s$	Maximize	0.40				
$M_r$	Maximize	0.10				
H <sub>c</sub>	Maximize	0.05				
Combined variable	$CV = 0.4 \times M_s + 0.1 \times M_s$	$M_r + 0.05 \times H_c - 0.35 \times D - 0.1 \times D_r$				



Fig. 10. The main effect plots for S/N ratio for the combined variable depicted by Minitab.



Fig. 11. XRD patterns of samples 1 and 26.



Fig. 12. FT-IR spectra corresponding to samples 1 and 26.



Fig. 13. FE-SEM micrograph related to sample 26.

narrow particle size distribution. Upon comparing the FE-SEM images of sample 26 (Fig. 13) and sample 1 (Fig. 7(a)), it is apparent that the particle size is larger in sample 26. This increase in particle size can be attributed to the presence of substituted elements such as  $Dy^{3+}$  and  $Zn^{2+}$  in sample 26. Additionally, the calcination temperature and time of sample 26 can be attributed to this increment. In contrast, sample 26 demonstrates a higher degree of particle agglomeration than sample 1. This increased agglomeration can change the magnetic properties.

Fig. 14 displays the M–H hysteresis curves for both samples 1 and 26. The magnetic parameters derived from these curves are presented in Table 4S. Notably, the magnetic properties of sample 26 exhibit an



Fig. 14. Hysteresis loops related to samples 1and 26.

improvement compared to sample 1. The optimized sample demonstrates a  $\chi$  of 0.0801 emu/gOe at  $H_m$  and a value of 0.044 emu/gOe for H  $\rightarrow$  0. Moreover, the optimized sample exhibits a  $H_c$  of 497 Oe. These findings signify the favorable magnetic characteristics of the optimized sample, suggesting improved magnetization behavior and stability.

Furthermore, a comparison of the synthesized CoFe<sub>2</sub>O<sub>4</sub> nanoparticles in this study with findings from other studies [32,64,98,99] is presented in Table 7. As shown, it is evident that the CoFe<sub>2</sub>O<sub>4</sub> nanoparticles produced in this research demonstrate desirable magnetic properties.

### 3.9. In vitro antibacterial activity

The antibacterial activity of sample 1 and the optimized sample against gram-negative and gram-positive bacteria was evaluated using the liquid broth dilution method, and the outcomes are detailed in Table 8.

According to Table 8, it was found that sample 1 demonstrated

### Table 7

Comparison of the properties of the synthesized samples with those reported in other research studies [32,64,98,99].

Chemical composition	Synthesis method	Ms (emu∕ g)	H <sub>c</sub> (Oe)	SQR	Ref.
$Co_{0.9}Zn_{0.1}Fe_{1.975}Dy_{0.025}O_4$	Co- precipitation	78.43	497	0.3952	This work
$Co_{0.7}Zn_{0.3}Tm_{0.01}Fe_{1.99}O_4$	Ultrasonic irradiation	28.90	19	0.026	[98]
$CoDy_{0.02}Fe_{1.98}O_4$	Sol-gel auto- combustion	77.62	1108	0.52	[64]
$\mathrm{Co}_{0.7}\mathrm{Zn}_{0.3}\mathrm{Fe}_{2}\mathrm{O}_{4}$	Co- precipitation	56.66	2680	0.72	[32]
Co <sub>0.5</sub> Ni <sub>0.5</sub> CrFeO <sub>4</sub>	Sol–gel	40.60	365	-	[99]

#### Table 8

Antibacterial activity of gram positive and negative bacterial after MIC test.

Bacteria	MIC (mg/ml)	
	CoFe <sub>2</sub> O <sub>4</sub>	Co <sub>0.9</sub> Zn <sub>0.1</sub> Fe <sub>1.975</sub> Dy <sub>0.025</sub> O <sub>4</sub>
Escherichia coli (E. coli)	1.56	50
Staphylococcus aureus (S. aureus)	50	_

greater antibacterial activity compared to the optimized sample that the MIC values of sample 1 were found to be 1.56 mg/ml for *E. coli* and 50 mg/ml for *S. aureus* versus the optimized sample with a MIC value of 50 mg/ml for *E. coli*.

The antibacterial activity of the investigated nanoparticles can be attributed to various mechanisms [100]:

- (i) Production of reactive oxygen species (ROS): Nanoparticles may generate reactive oxygen species, which can induce oxidative stress and damage bacterial cells.
- (ii) Release of metal ions: When nanoparticles interact with bacteria, nanoparticles can release metal ions such as Co<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>3+</sup>. These metal ions can form bonds with sulfhydryl groups in bacterial proteins, altering their structure and function.
- (iii) Attachment of nanoparticles to bacteria surface: Nanoparticles might adhere to the surface of bacteria, leading to damage or disruption of the bacterial membrane or cell wall.

The antibacterial activity of nanoparticles is resulted of one or some of the mentioned mechanisms.

On the other hand, the antibacterial activity of nanoparticles is influenced by various factors such as size, morphology, surface area, and others [101]. Research indicates that ROS production is influenced by particle size as important role, with smaller particles leading to increased ROS production due to increased particle defects and specific surface area [101].

The superior antibacterial activity of sample 1 compared to the optimized sample can be attributed to the smaller particle size. It should be noted that the influence of nanoparticles on antibacterial efficacy is more pronounced in gram-negative bacteria than in gram-positive bacteria, which can be resulted of the structural differences in their cell walls. Gram-negative bacteria possess thinner and less sturdy cell walls, along with an outer layer rich in lipopolysaccharides that carry negative charges [102].

On the other hand, according to beneficial effects of human microbiotum, such as gut bacteria, on body health, using of metallic nanoparticles with antibacterial activity is ambiguous. So, in this investigation, development of nanoparticle with low antibacterial activity (50 mg/ml) can be safer for the body's normal flora.

# 4. Conclusion

In this study, the synthesis of the Co<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2-y</sub>Dy<sub>y</sub>O<sub>4</sub> nanoparticles with optimal structural and magnetic properties was effectively accomplished using the co-precipitation method. The L25 orthogonal Taguchi array was employed to investigate the effects of different parameters and identify the best process condition, including the content of Zn<sup>2+</sup> and Dy<sup>3+</sup>, the OH concentration, and the duration and temperature of calcination. The optimal values for achieving high  $M_s$  were identified as follows: X = 0.1, Y = 0.025, OH = 1, time = 4 h, and temperature = 900 °C. It is noteworthy that the Zn<sup>2+</sup> content had the most significant influence on the properties of the optimal sample, whereas the OH concentration had the least impact. On the other hand, the synthesized CoFe<sub>2</sub>O<sub>4</sub> nanoparticles exhibited a *D* of 38.89 nm,  $M_s$  of 78.43 emu/g,  $M_r$  of 31 emu/g, and  $H_c$  of 497 Oe, demonstrating excellent structural and magnetic properties. In general, this research successfully optimized process parameters for synthesizing CoFe<sub>2</sub>O<sub>4</sub>

nanoparticles with superior structural and magnetic properties, holding great potential for various applications, including biomedical and magnetic storage applications, where high-quality materials with excellent structural and magnetic properties are highly sought after. Moreover, the assessment of the antibacterial properties exhibited by the synthesized nanoparticles has confirmed their significant potential for a wide range of biomedical applications. In other words, the results indicated that the synthesized nanoparticles exhibit low antibacterial activity (50 mg/ml), making them potentially safer for the body's normal flora.

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### CRediT authorship contribution statement

Leila Rakhsha: Writing – original draft, Software, Methodology, Formal analysis, Data curation. Saeed Hasani: Writing – review & editing, Validation, Supervision, Project administration, Methodology. Amir Seifoddini: Validation, Supervision, Methodology. Mohammad Taghi Rezvan: Writing – review & editing, Software, Methodology, Data curation. Vahid Ramezani: Writing – review & editing, Validation, Supervision, Methodology, Data curation.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2024.113568.

### Data availability

No data was used for the research described in the article.

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