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Different Routes for *Camellia Sinensis*-Mediated Synthesis of Iron Oxide Nanoparticles: Structural, Thermal, and Magnetic Properties

Jeferson Marques Santos¹  | Renzo Rueda-Vellasmin¹  | Juan A. Ramos-Guivar²  | Edson C. Passamani¹ 

¹Programa de Pós-Graduação em Física (PPGFis), Universidade Federal do Espírito Santo, Av. Fernando Ferrari, 514, Campus de Goiabeiras, Vitória, Espírito Santo, Brazil | ²Gupo De Investigación de Nanotecnología Aplicada Para Biorremediación Ambiental, Energía, Biomedicina y Agricultura (NANOTECH), Facultad De Ciencias Físicas, Universidad Nacional Mayor De San Marcos, Ciudad Universitaria, Lima, Peru

Correspondence: Edson C. Passamani (edson.caetano@ufes.br)

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ABSTRACT

Green-assisted iron oxide nanoparticles (NPs) were synthesized using *Camellia sinensis* extract (green tea, GT) at concentrations of 1%, 2%, 3%, 5%, and 10% w/v via three chemical routes: after-synthesis (ASR), subsequent synthesis (SSR), and in situ synthesis (ISSR). Rietveld refined X ray diffractograms and transmission electron microscopy results confirmed mostly γ -Fe₂O₃ NPs with mean sizes ranging from 8 to 25 nm depending on the synthesis route (Fe₃O₄ core was also observed in some of the ISSR samples). ⁵⁷Fe Mössbauer and magnetization data showed superparamagnetic behavior at 300 K for all NP ensembles. The saturation magnetization (*M_s*) value roughly scaled with GT concentrations and, for the 1% of GT sample synthesized by the ISSR-route, a 16% higher magnetization value (86 emu g⁻¹) was found when compared to the one measured for the control sample (74 emu g⁻¹), an effect attributed to the Fe₃O₄ phase initially stabilized. Fourier transform infrared and UV-vis spectroscopies showed polyphenols from the GT on the NP surface, a result that agrees with the thermogravimetric data. The 15 K ⁵⁷Fe Mössbauer data indicated that these polyphenols bind to surface iron ions, favoring spin canting and the formation of a “magnetically dead layer” on the NP surface, an effect associated with the functional (–OH) groups of GT polyphenols. Our findings demonstrate that the different routes produce functionalized Fe-oxide NPs with different crystallite sizes and polyphenol-layer thicknesses by simply using *Camellia sinensis* extract.

1 | Introduction

Iron oxide nanoparticles (IONPs) are a class of nanomaterials of major scientific and technological relevance, and are commonly classified according to their sizes, shapes, agglomeration state, surface properties, and related features [1, 2]. These characteristics directly affect their physical, chemical, optical, and electronic properties [1, 2]. One important application of IONPs is environmental remediation, which has strongly encouraged sustainable strategies for producing IONPs from natural sources

in place of harmful chemical compounds [1, 3, 4]. Such efforts are aligned with the broader transition toward renewable resources and the development of new materials for emerging technological demands.

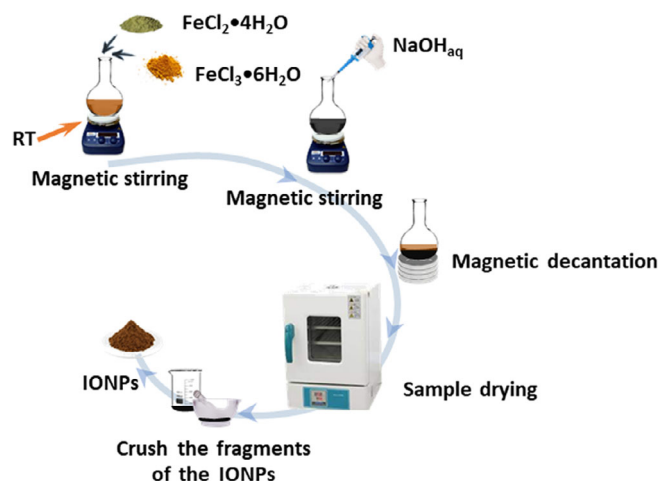
In this regard, green chemistry (GC) and its applications in nanotechnology involve the development of synthesis methods that rely on renewable materials, such as aqueous extracts from fruit peels and leaves, while employing non-hazardous reaction media and non-toxic solvents [5–7]. Indeed, the concept of green

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synthesis is rooted in the principles of GC, which promote the development of sustainable and environmentally benign chemical processes. A major milestone in this field was the publication of *GC: Theory and Practice* by Paul T. Anastas and John C. Warner in 1998, which established the foundations of the discipline [8]. Specifically, green synthesis generally employs biogenic materials under relatively mild conditions, such as lower temperatures and pressures, thus offering promising perspectives for scale-up and industrial applications [5]. The three main pillars of green synthesis of IONPs are the choice of solvent medium, the reducing agent, and the nontoxic stabilizing agent [2–4]. One of the main aims of the GC approaches to IONP synthesis is to minimize particle aggregation and ensure uniformity in size and morphology besides reducing the precipitating agents used during the syntheses. Overcoming this synthetic challenge requires the optimization of production parameters, such as plant extract concentration and reaction conditions, to achieve reproducible and standardized results [5].

Among the IONPs, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are two main Fe-oxide based phases that have been extensively investigated owing to their magnetic and biocompatibility properties, i.e., a set of features that allow them to be used in technological and biomedical applications [9]. Fe_3O_4 crystallizes in an inverse spinel structure with space group $\text{Fd}\bar{3}\text{m}$, and its chemical formula can be represented as $(\text{Fe}^{3+})[\text{Fe}^{2+}, \text{Fe}^{3+}]\text{O}_4$. Here, the square brackets denote octahedral sites (B-sites) that host one Fe^{2+} and one Fe^{3+} ion, while the parentheses indicate tetrahedral sites (A-sites) occupied by one Fe^{3+} ion. Oxygen anions (O^{2-}) form a close-packed cubic lattice located at the corners of the conventional cubic cell. This arrangement results in an average oxidation state of $+8/3$ per iron atom. Due to double exchange interactions, i.e., electron hopping between Fe^{2+} and Fe^{3+} ions mediated by the intervening O^{2-} anions, Fe_3O_4 exhibits, for instance, good magnetic properties and electrical conductivity, despite being a typical metal-like oxide [9]. However, this phase is chemically unstable to ambient conditions, an effect that is enhanced in nanomaterials. Thus, it often transforms into $\gamma\text{-Fe}_2\text{O}_3$ phase by oxidation of Fe^{2+} ions. More explicitly, it is formed through partial or complete oxidation of Fe^{2+} to Fe^{3+} at the octahedral sites leading to the transformation of Fe_3O_4 into $\gamma\text{-Fe}_2\text{O}_3$. Consequently, the $\gamma\text{-Fe}_2\text{O}_3$ phase has also the same inverse spinel structure as Fe_3O_4 but stabilized by ionic defects. The increased positive charge (Fe^{3+}) is compensated by the removal of iron ions from the octahedral structure, generating vacancies to preserve charge neutrality. When Fe_3O_4 is fully oxidized, the general formula of $\gamma\text{-Fe}_2\text{O}_3$ becomes $(\text{Fe}^{3+})[\text{Fe}_{5/3}^{3+}\square_{1/3}]\text{O}_4$. However, the vacancies may be partially distributed depending on the synthesis conditions. The oxidation process explains the lower conductivity and magnetization of $\gamma\text{-Fe}_2\text{O}_3$ compared to Fe_3O_4 [10]. With respect to the IONP synthesis, the green route, using plant extracts, has proven to be a promising approach, particularly for the synthesis of IONP ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$) with medical relevance. Bioactive compounds such as polyphenols, flavonoids, and tannins are abundant in plant-based raw materials and can be readily extracted. These substances act as both, reducing and stabilizing agents, modulating surface characteristics (e.g., acting as capping agents and enhancing biocompatibility) while also controlling the morphology and size of the IONPs [5]. Green tea (GT—*Camellia sinensis*) is an example of a plant rich in flavonoid-polyphenols, which often act as antioxidants and reducing agents.



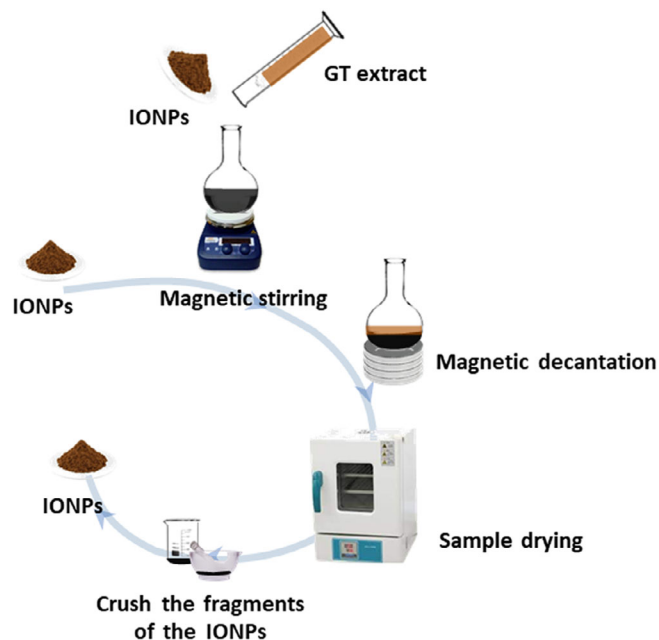
SCHEME 1 | Schematic procedure applied to the synthesis of the IONP control sample.



SCHEME 2 | Steps used to obtain the GT extract from the natural leaves.

Catechin is the most abundant flavonoid in the GT extract. These polyphenols are capable of reducing metal ions, promoting iron complexation and nucleation, and stabilizing the resulting IONPs [11, 12].

Regarding IONP synthesis, it is important to mention that IONPs ($\gamma\text{-Fe}_2\text{O}_3$) have recently been synthesized via green coprecipitation route using different iron salts, including Fe chlorides, and distinct precipitating agents such as ammonium hydroxide (NH_4OH) or sodium hydroxide (NaOH) [13]. In this previous work, the green intervention was implemented via post-synthesis and in situ routes. A systematic decrease in the effective magnetic anisotropy (K_{eff}) with increasing GT concentration was demonstrated, an effect that was basically attributed to the formation of an organic layer that mitigated interparticle dipolar interactions across all synthesized samples. Notably, IONPs obtained with NaOH , as the coprecipitating



SCHEME 3 | Procedure for the synthesis of the ASR sample using the CTL IONPs previously described.

agent, exhibited M_s values exceeding values typically found in γ - Fe_2O_3 NPs, and consequently, suggesting a partial preservation of Fe^{2+} ions at octahedral sites. These findings motivated the development of a systematic synthesis protocol for green-assisted IONPs using different chemical routes (or modes), aiming to provide further insights into Fe_3O_4 oxidation, particle size and magnetic behavior. In particular, considering the results reported in the literature on the green-assisted IONP formation [1, 2, 13], the correlation between the stage at which the GT extract is introduced during the synthesis process and its impact on the structural and magnetic properties of the IONPs should be systematically investigated; this highlights the importance of treating the moment of addition within the coprecipitation process as a key parameter influencing the final characteristics of the system.

Therefore, this work aims to carry out a systematic investigation of the synthesis of IONPs via complementary approaches such as: (i) the conventional coprecipitation route, relying solely on the precipitating agent without the use of reducing or stabilizing green-like compounds, and (ii) the green-assisted route with different GT concentrations (weight to volume percentage % w/v) while keeping the iron chloride precursors fixed. More specifically, the green-type intervention was carried out in three distinct modes: (a) after the formation of the IONPs (ASR), (b) after the interaction between the precursor reagents and the precipitating agents (SSR), and (c) simultaneously with the addition of the precursor reagents (ISSR). In this context, the GT extract acts simultaneously as a reducing and stabilizing agent for the IONPs. By applying the three chemical routes outlined above, which have been scarcely addressed in a systematic manner, this work helps to bridge gaps in the literature on the IONP formation; specifically, it advances the understanding of the relationship between structural and magnetic properties of IONPs and variations in GT extract concentration, the timing of its addition during

synthesis, and the effectiveness of the green functionalization process. Overall, structural and physical differences (particularly in the hyperfine and magnetic properties) arising from the distinct synthesis routes were systematically investigated by different experimental methods, and the oxidation of Fe_3O_4 to γ - Fe_2O_3 was found to depend on the synthesis route. In particular, X ray diffraction and transmission electron microscopy were used to determine the structural and morphological properties, while Fourier transform infrared, UV-vis, and ^{57}Fe Mössbauer spectroscopies to probe chemical and hyperfine properties of GT functionalized IONP compounds. Thermal and chemical stability of the functionalized IONPs were studied by thermogravimetric experiments and magnetic measurements provided information on the magnetic properties of the synthesized materials.

2 | Synthesis Methodology

The control sample and GT-assisted samples were successfully synthesized by modified coprecipitation method. All reagents were used as received, without further purification.

2.1 | Materials

IONPs were synthesized via the coprecipitation method. Stoichiometric amounts of the following reagents were used: ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $M_e = 198.8$ g/mol, 99.9%, Dinâmica, São Paulo, Brazil), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $M_e = 270.33$ g/mol, 99.9%, VETEC/Sigma-Aldrich, Rio de Janeiro, Brazil), and sodium hydroxide (NaOH , $M_e = 40$ g/mol, Êxodo Científica, São Paulo, Brazil) as the precipitating agent. The GT extract was prepared from leaves obtained from a natural-products store in Vitória, Espírito Santo, Brazil.

2.2 | Synthesis of Control Sample

The control sample of IONPs was synthesized using the conventional coprecipitation method, as schematically shown in Scheme 1.

Initially, the starting reagents, iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were stoichiometrically mixed in a molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+} = 1:2$, resulting in a final aqueous dispersion with a concentration of 0.6 M. This dispersion exhibited a dark orange color. Afterward, 5 mL of aqueous 1 M sodium hydroxide solution (NaOH_{aq}) was gradually added every 5 min, while maintaining vigorous stirring, until the pH reached an alkaline value of 10, resulting in a black-colored material. Then, the dispersion containing the formed IONPs was magnetically separated using a permanent magnet of neodymium, iron, and boron. At this moment, the supernatant was carefully discarded, and the pH of the dispersion was controlled to approach neutral pH 7. After the fifth supernatant was removed, the remaining wet solid material was dried for 24 h at 333 K in an oven. The resulting material was ground using a mortar and pestle until a fine powder was obtained, a condition that was necessary to perform ^{57}Fe Mössbauer experiments (to control the ^{57}Fe Mössbauer absorption cross-section). This sample was designated as the control and labeled CTL.

2.3 | Synthesis of Green Samples with *Camellia Sinensis*

To functionalize IONPs, a GT extract from *Camellia sinensis* was used in three distinct routes. First, the procedure to obtain the GT extract is displayed in Scheme 2.

Scheme 2 shows a series of steps for obtaining the GT extract from natural leaves. The leaves were first selected carefully and dried in an oven at 333 K for 12 h. Then, they were ground using a knife mill equipped with a bottom sieve of 0.5 mm mesh size, and immediately immersed in distilled water kept at 353 K (weight to volume concentration— w/v) for 15 min. In the next step, the GT extract, from each infusion, was vacuum filtered using three types of filter paper: initially fast filtration, followed by medium filtration, and finally slow-flow filter paper. The GT extract concentrations obtained (w/v) were 1%, 2%, 3%, 5%, and 10%. With these GT concentrations, green-synthesized samples were prepared using three distinct routes: After synthesis route (ASR), Subsequent synthesis route (SSR), and in situ synthesis route (ISSR), which are detailed in the following sections.

2.4 | Synthesis of after Synthesis Route (ASR) Samples

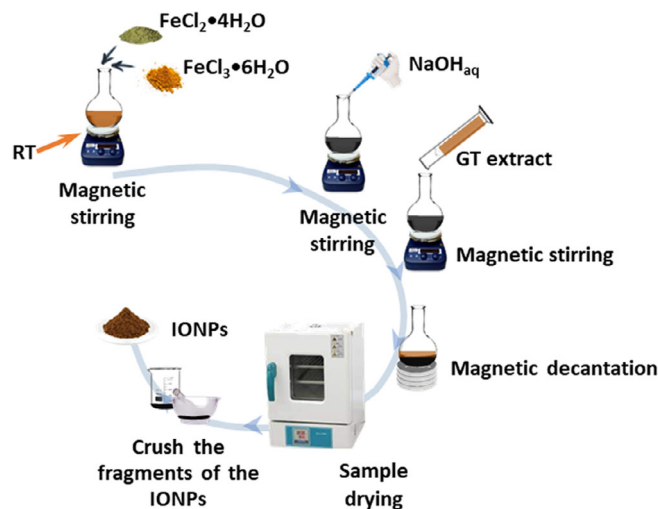
For the ASR samples, the CTL sample was dispersed in a GT extract of a specific concentration (w/v), as presented in Scheme 3.

Specifically, the ASR IONPs were synthesized by taking the CTL IONPs and immersing them in an excess of GT extract under vigorous stirring (at 30 rpm) for $\frac{1}{2}$ h. The resulting mixture was then magnetically decanted using the mentioned Nd-Fe-B magnet, and the supernatant was carefully discarded. The remaining wet solid material was transferred to an oven at 333 K and kept for 24 h. For clarity, these samples were designated as GCIA $n\%$ (IONPs synthesized via the GC method using *Camellia sinensis* in the ASR, where $n\%$ represents the GT concentrations equal to 1%, 2%, 3%, 5%, and 10% in w/v).

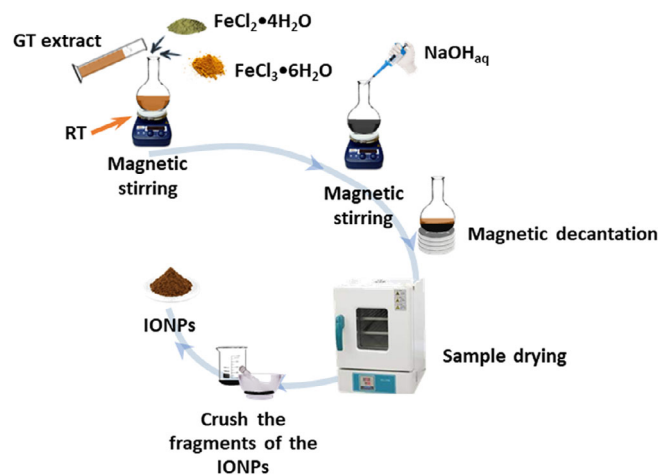
2.5 | Synthesis of Green Subsequent Samples (SSR)

For the SSR synthesis of IONPs, the green intervention was introduced at an intermediate stage of the synthesis process as represented in Scheme 4.

As can be seen, the steps shown in Scheme 4 are similar to those applied in the production of the CTL sample up to the completion of the addition of NaOH aq (1 M). At this stage, unlike in the CTL synthesis, the GT extract was added in a volume equal to that of the initial aqueous dispersion of the precursor reagents. The resulting mixture was homogenized for 1 h. Then, the material was washed five times using the Nd-Fe-B magnet to separate the IONPs, with the supernatant being discarded after each wash (pH approached neutral). The remaining wet solid material was dried in an oven at 333 K for 24 h. The resulting material was ground using a mortar and pestle until a fine powder was obtained, for



SCHEME 4 | Schematic steps of the synthesis of green samples using the Subsequent Synthesis Route (SSR).



SCHEME 5 | Schematic procedure for the synthesis of the green sample using ISSR.

the reason described above. These samples were designated as GCIS $n\%$ (IONPs synthesized via the GC method using *Camellia sinensis* in the SSR, where $n\%$ represents the GT concentration used, with $n\% = 1\%, 2\%, 3\%, 5\%$, and 10% in w/v).

2.6 | Synthesis of Green in situ (ISSR) Samples

In the synthesis of the ISSR IONPs, the GT extract was added simultaneously with the precursor reagents in distilled water, as shown in Scheme 5.

It shows that the starting reagents, iron (II— Fe^{2+}) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and iron (III— Fe^{3+}) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were stoichiometrically mixed at a molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+} = 1:2$. One-third of the total dispersion volume (comprising precursor reagents, distilled water, and GT extract) consisted of the GT extract, adjusted according to each concentration. However, the total volume was kept the same as that used in the synthesis of the CTL sample, with the molarity of the reagents in dispersion set at 0.6 M. The next steps were identical to those employed in the synthesis of the CTL sample.

The samples synthesized by ISSR were named according to the scheme GCI/n%—IONPs synthesized by GC method with *Camellia sinensis* ISSR (n% is the concentration of the used GT extract in which n% = 1%, 2%, 3%, 5%, and 10% in w/v).

Note that all samples synthesized with green intervention (CTL, ASR, SSR, and ISSR) using the GT extract (*Camellia sinensis*) were synthesized by the coprecipitation method. However, it should be stressed that the interaction between the reagents was carried out under magnetic stirring at an average speed of 3000 rpm for 2 h and 30 min for all samples (the entire synthesis process was conducted at RT). Decantation and washing of the samples were carried out magnetically, that is, an external magnetic field was applied to separate the magnetic particles from the supernatant. The resulting powder was then grounded, dried and subjected to structural, thermal, chemical, hyperfine, and magnetic characterization methods to identify the physical properties of the different functionalized IONPs.

3 | Experimental Methods

The physical characterization of the samples was performed using X ray diffraction (XRD), transmission electron microscopy (TEM), Attenuated total reflectance-fourier transform infrared (ATR-FTIR), and UV-visible (UV-vis) spectroscopies, thermal characterization by thermogravimetric (TG) analysis, magnetic, and hyperfine techniques by magnetometry and ^{57}Fe Mössbauer spectrometry, respectively. These techniques are described separately below.

3.1 | Structural Characterization by XRD

X ray diffraction (XRD) measurements of all samples were performed with a RIGAKU Ultima IV diffractometer operating with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) emitted by a Cu-anode operating at 30 mA and 40 kV under laboratory ambient conditions. XRD data were collected over the 2θ range from 10° to 80° , with an angular variation of $\Delta 2\theta = 0.02^\circ$ and 15 s per angular position using a Bragg-Brentano geometry, commonly used for polycrystalline samples. The crystallographic information #9006316 (obtained from the crystallographic database [14]) was found with the Match v3 software [15]. The refinements of the X ray diffractograms by the Rietveld method were carried out with the free software Fullprof suite. A standard cerium oxide sample was used to obtain the experimental line broadening, favoring an accurate determination of the mean crystallite sizes of Fe-oxide powders. The Cagliotti coefficients used were $U = 0.003$, $V = -0.001$, and $W = 0.008$.

3.2 | TEM

Particle size distribution (PSD) and morphology of the most representative IONP samples were analyzed using a JEOL 2100F TEM operating at 200 kV (JEOL Ltd., Tokyo, Japan), in both conventional transmission and high-resolution modes. PSD data were obtained by measuring approximately 300 particles from 30–35 micrographs. The resulting histogram-like plots were fitted using a log-normal distribution method, following the procedure described in the literature [16].

3.3 | ATR-FTIR Spectroscopy

ATR-FTIR measurements were performed using an Agilent Technologies Cary 630 FTIR Spectrometer equipped with an ATR module. The ATR-FTIR spectra were recorded over the spectral range of $4000\text{--}650 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . All measurements were carried out at RT, and no additional sample preparation was required due to the use of the ATR accessory.

3.4 | UV-vis Spectroscopy

UV-vis absorption spectra were recorded using a GTA-97 UV-vis Spectrophotometer from Global Analyzer. Measurements were performed in absorbance mode using a quartz cuvette with a path length of 10 mm and a volume of 4 mL. Spectra were collected over a wavelength range of 200–800 nm with a step size of 1.0 nm. Distilled water was used as the reference for baseline correction. The GT extract samples were prepared by infusing different concentrations of GT leaves (% w/v) in distilled water, followed by dilution to 1:100 (v/v) prior to measurement. For functionalized IONPs, a dispersion of 1 mg of sample per 10 mL of distilled water was prepared, and the suspension was immediately analysed after shaking to minimize sedimentation effects. All measurements were performed at RT under normal laboratory conditions.

3.5 | Thermal Characterization by Thermogravimetric (TG) Analysis

TG analyses of all samples were carried out using a Shimadzu TGA-50 instrument (Shimadzu Corporation, Kyoto, Japan) to evaluate the thermal stability of the materials and to quantitatively determine the amount of organic matter lost during heating. The measurements were performed under a continuous argon flow of 50 mL/min to avoid oxidative effects. A constant heating rate of 10°C/min was applied over a temperature range from 300 to 1173 K. This temperature range was selected to guarantee the complete removal of physically adsorbed species and thermally labile organic components.

3.6 | Magnetic Characterization by Vibrating Sample Magnetometry (VSM)

The $M(H)$ curves were recorded using a PPMS-Evercool II setup from Quantum Design Inc., USA, equipped with a Vibrating Sample Magnetometer (VSM). The $M(H)$ curves for all samples were measured in magnetic fields ranging from $\pm 3 \text{ T}$ at temperatures of 5 and 300 K. The magnetic parameters determined from the $M(H)$ curves include the remanent magnetization (M_R), the M_S , the coercive field (H_C), and the effective anisotropy coefficient (K_{eff}). To determine K_{eff} , the law of approach to saturation (LAS) was employed by fitting part of the positive quadrant of the $M(H)$ curve at high fields (2–3 T) of the low-temperature measurements, and the Langevin function was used to obtain M_S of measurements at RT, following a procedure described in the literature [17]. Indeed, the LAS approach allows the determination of both M_S and K_{eff} .

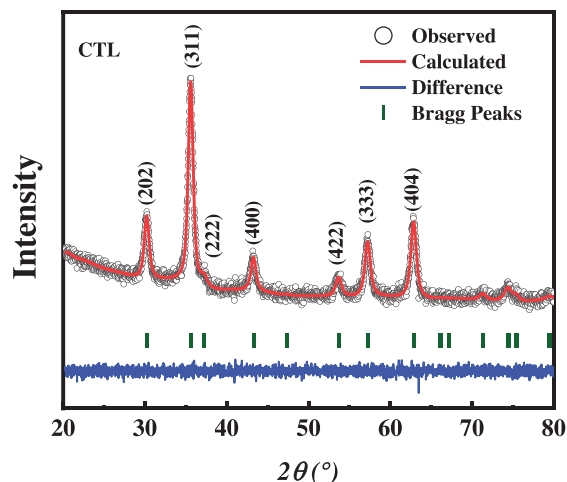


FIGURE 1 | Rietveld-refined X ray diffractogram of the CTL IONPs. Miller indices are labelled above the diffraction peaks.

3.7 | Hyperfine Properties by ^{57}Fe Mössbauer Spectrometry

300 and 15 K ^{57}Fe Mössbauer spectra for all samples were recorded in transmission geometry using a He-closed cycle setup from Janis Corporation Inc. The 25 mCi ^{57}Co :Rh source, mounted in a driver operating in a sinusoidal waveform, was synchronized with the sample holder, with both components mounted on an antivibration system and securely connected. The spectra were collected in a CMCA 550 WissEL multichannel operating with 512 channels. While the source was maintained at 300 K, the absorbers were either kept at 300 K or cooled down to 15 K to obtain low-temperature spectra. The energy change, due to the Doppler shift effect of 14.4 keV signal of ^{57}Fe decay, was calibrated using a 12.7 μm thick α -Fe foil. For each experiment, the sample powder was carefully distributed in a circular nylon holder of 1 cm^2 , yielding an effective thickness of approximately 0.1 mg of ^{57}Fe per cm^2 . The fittings of the ^{57}Fe Mössbauer spectra were performed using MossWinn 4.0i software [18].

4 | Results and Discussion

4.1 | Structural and Morphological Properties Measured by XRD and TEM

Structural properties of all samples were first obtained by refining the X ray diffractograms using the Rietveld method implemented in FullProf. Figure 1 exhibits the refined XRD pattern for the IONPs of the CTL sample, while Figure 2 displays the refined XRD patterns for a series of functionalized samples produced by ASR (GCIAn%), SSR (GCISn%), and ISSR (GCIIn%).

The XRD patterns (Figures 1 and 2) present a set of Bragg peaks that are assigned exclusively to the inverse spinel crystalline phase with symmetry defined by the $\text{Fd}\bar{3}\text{m}$ space group. However, it should first be mentioned that even by refining X ray diffractograms, it was not possible to determine the relative percentages (ratio) of magnetite and maghemite phases ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ ratio). Also, it has to be emphasized that Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ possess similar crystal structures, and in their bulk-

like phases, only small differences are observed (there is a slight shift in some Bragg peaks, for instance, those at $2\theta \approx 35.5^\circ$ (311), 63.5° (440) [19]). Consequently, these Fe-oxide phases are hardly distinguished by XRD experiments in nanomaterials [20]. In other words, the oxidation of iron ions at the octahedral sites (Fe^{2+} to Fe^{3+}) in Fe_3O_4 results in cation vacancies in the $\gamma\text{-Fe}_2\text{O}_3$ phase and the Fe cationic arrangements cannot be resolved by conventional XRD experiments in nanomaterials [10]. Table S1 presents the structural parameters of all analyzed samples. The lattice parameters (Table S1) range from 8.356 to 8.371 Å across the different samples and can be attributed to a combination of several structural effects [10]. Some of them are: (a) the reduction in crystallite size favors surface strain, particularly in particles below 10 nm, (b) oxidation of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ leads to a slight lattice contraction, and (c) surface functionalization and/or chemical inhomogeneity among the samples account for the observed changes in the lattice parameters. Overall, the measured lattice parameters fall within the expected range for partially oxidized Fe_3O_4 NPs or mixed-phase systems containing $\gamma\text{-Fe}_2\text{O}_3$ ($\text{Fe}_3\text{O}_4@ \gamma\text{-Fe}_2\text{O}_3$), consistent with the nanoscale nature and oxidation state of the crystallites/particles [10]

Regarding the particle sizes, it should be stressed that most of the green-functionalized samples exhibited crystallites below 15 nm, except the ISSR samples GCI/5% (17 nm) and GCI/10% (23 nm). These particle sizes were consistently confirmed by TEM images and/or PSD curves shown in Figure S1. TEM images also suggest that the particles exhibit predominantly circular-like shapes, with defined crystalline planes, indicating that the IONPs are well structured. Amorphous-like features are also observed on the IONP surfaces, features that are likely associated with the presence of organic-type compounds used for the surface functionalization of IONPs. In addition, the mean crystallite sizes of functionalized IONPs are larger than that of the CTL sample (8 nm), indicating that the functionalization with GT tends to increase the particle size when iron-chlorides are used as precursors. In other words, there is a general trend of increasing crystallite size with increasing GT concentration used in the synthesis.

Overall, it should be further mentioned that the samples synthesized via ASR, SSR, and ISSR exhibit crystallite sizes ca. 15 nm, a dimension that falls within the range typically found for a single-domain magnetic behavior of iron-oxide nanomaterials [21]. Therefore, depending on the K_{eff} values, the particles will behave in a superparamagnetic regime (their magnetic moments fluctuate rapidly and spontaneously under thermal energy at 300 K). To check this assumption, measurements at 300 K would depict non-pronounced $M(H)$ loops (i.e., loops with very low, often negligible, H_C and M_R values) and ^{57}Fe Mössbauer spectra dominated by paramagnetic components. Indeed, these features will be further demonstrated in the magnetic and hyperfine results through $M(H)$ and ^{57}Fe Mössbauer data.

4.2 | Chemical Properties by ATR-FTIR and UV-vis Spectroscopies

ATR-FTIR spectra of pure powdered GT and ASR, SSR, ISSR samples are shown in Figure 3a–d. First, it should be noted that the presence of phenolic compounds in GT extracts, typically

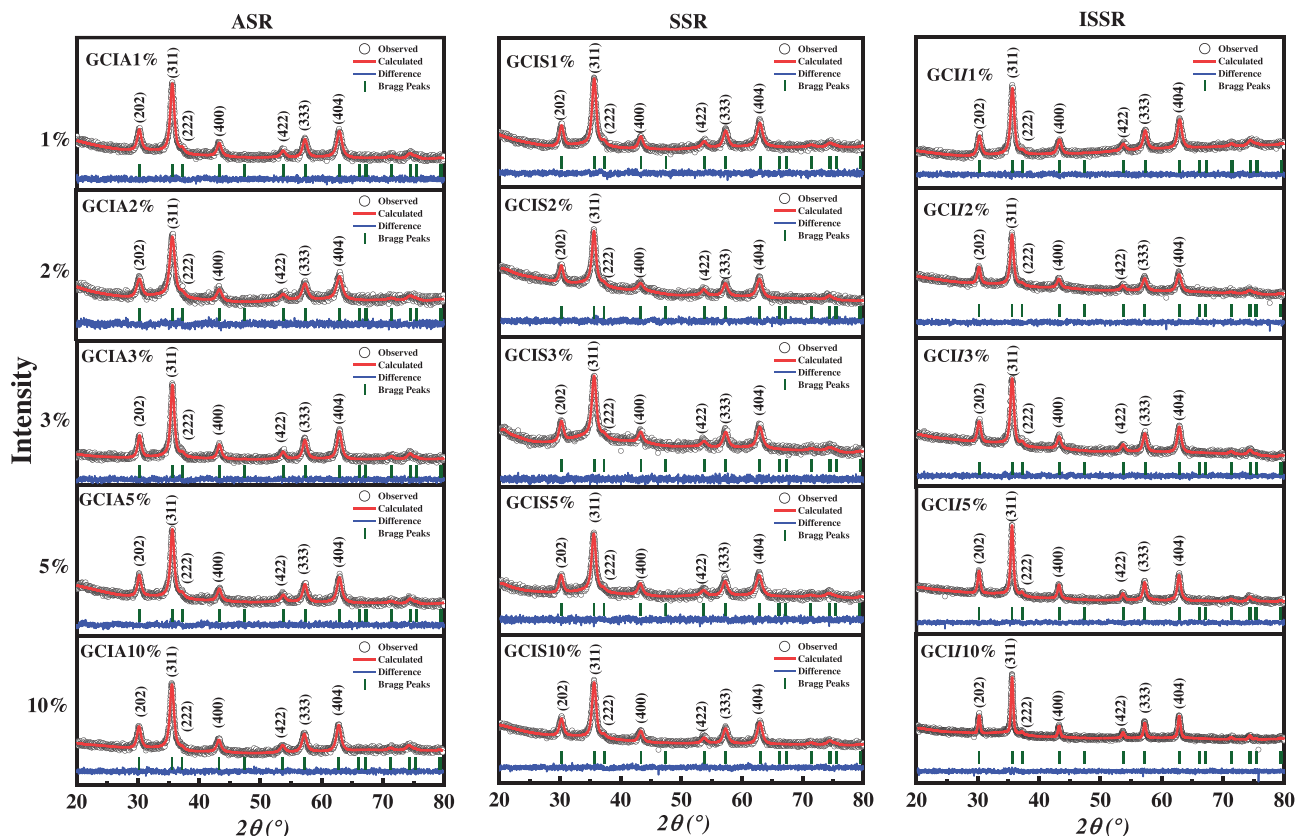


FIGURE 2 | Rietveld refined X ray diffractograms of functionalized IONPs obtained by green intervention through the ASR (GCIA n %); SSR (GCIS n %), and ISSR (GCI n %) routes at GT concentrations ' n ' of 1, 2, 3%, 5%, and 10%, respectively.

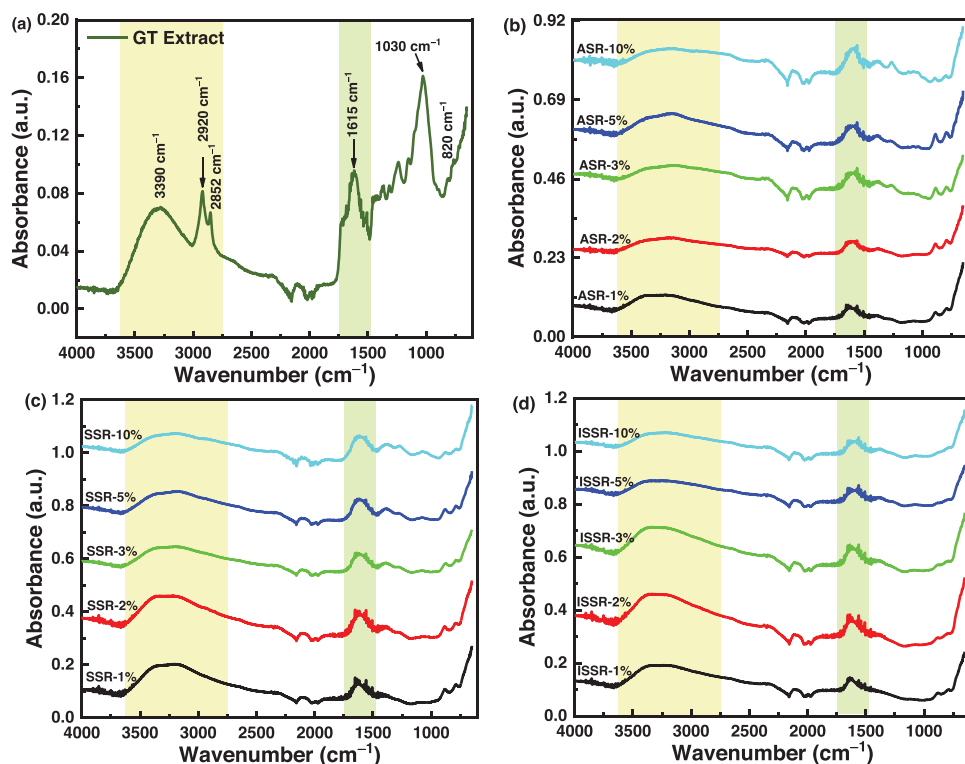


FIGURE 3 | ATR-FTIR spectrum of powdered GT in (a) and the ATR-FTIR spectra of the ASR in (b), SSR in (c) and ISSR in (d) samples synthesized at different GT concentrations. The yellow and green shadow areas of the spectra correspond to the optically active vibrational modes of the organic compounds belonging to the GT extract. The arrows in (a) indicate the most representative IR assignments.

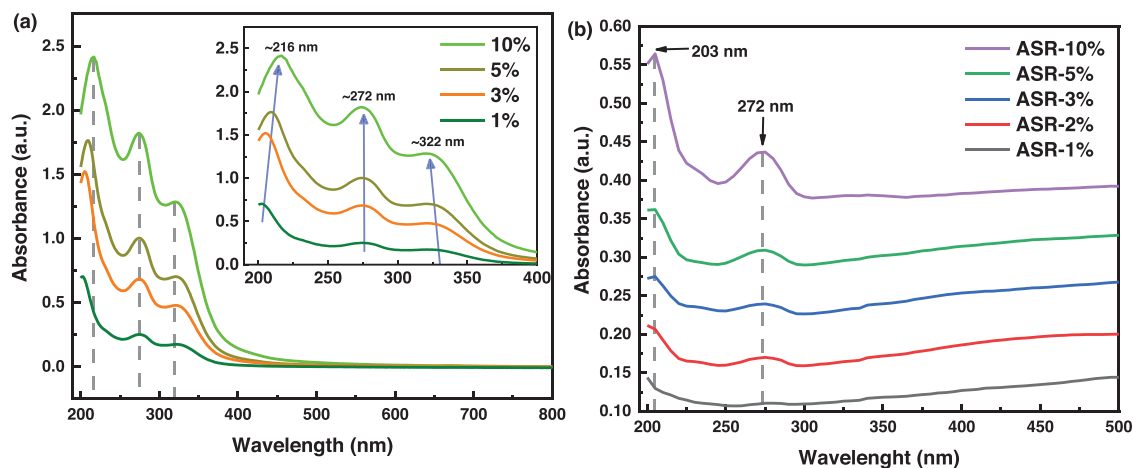


FIGURE 4 | (a) UV-vis spectra of the GT extract at different concentrations and (b) UV-vis spectra of the ASR samples prepared with different GT extract contents. The inset in panel (a) highlights the low-wavelength region.

associated with hydroxyl groups and aromatic rings, should appear in high wavenumber regions ($\nu > 1100 \text{ cm}^{-1}$) [22, 23]. In contrast, the functional groups related to Fe-oxides are generally observed in the low wavenumber region ($\nu < 900 \text{ cm}^{-1}$) [23]. Thus, first an ATR-FTIR experiment of the pure powdered GT was recorded and displayed in Figure 3a. It serves as a reference sample for identifying organic phases. As can be seen from this spectrum, it was not possible to resolve contributions from individual phenolic compounds, but it can be divided into two main regions: Region-I ($3700 < \nu < 2750 \text{ cm}^{-1}$) and Region-II ($1750 < \nu < 1450 \text{ cm}^{-1}$). Region-I contains two major bands, one centered at about 3390 cm^{-1} (yellow marked), which is attributed to O–H stretching modes from alcohols, as well as N–H stretching from amine groups. These functionalities are likely present in the polyphenolic constituents of the GT extract and also arise from residual water absorbed from the environment. The O–H stretching, from hydroxyl groups on the surface of Fe-oxides, also contributes to this band, reflecting interaction between the inorganic matrix and the organic coating. In the Region-II, the band ca. 1616 cm^{-1} (highlighted in green) corresponds to C=C stretching vibrations of aromatic rings in polyphenols [24]. Other notable features in this region include bands at approximately 1370 cm^{-1} and 1080 cm^{-1} , which are respectively attributed to C–O stretching and O–H bending vibrations (both in-plane and out-of-plane) [25]. Nearly all bands observed for the powdered GT are also seen in the ATR-FTIR spectra (Figure b–d of the ASR, SSR, and ISSR samples), indicating that the IONP surface are effectively functionalized by the organic-like compounds of the GT extract.

The UV-vis absorption spectra (Figure 4a) for the different concentrations in w/v (%) show three main absorption peaks at about 216, 272, and 322 nm. The peak at 216 nm can be attributed to the $\pi \rightarrow \pi^*$ electronic transition from the aromatic ring of the phenolic compounds, while the one at 272 nm can be associated with a conjugated π -electron system [26]. The weaker and broader peak at $\sim 322 \text{ nm}$ is assigned to $n \rightarrow \pi^*$ electronic transition from catechins [27]. Regarding the UV-vis spectra of the IONP samples shown in Figure 4b for the ASR samples, it can be first mentioned that the polyphenol bands found in the GT extract are also observed in the ASR samples and there is a relationship between

the intensity of the spectra and the w/v (%) used in the synthesis, as also reported in the literature [28]. In particular, Figure 4b displays the absorbance band at 272 nm and another one at about 203 nm, the latter associated with the 216 nm band shifted to lower wavelength region due to the Fe complexation. Thus, the presence and progressive increase of 272 nm band intensity in the spectra of the ASR samples and the shifting of 216 nm band indicate that polyphenolic species are effectively bounded to the IONP surface [29].

Overall, our FTIR and UV-vis spectra did not allow us to distinguish the different and fraction of polyphenol-type compounds and high-performance liquid chromatography (HPLC) would be an analytical method that could provide additional information (a method not available in our laboratory). On the other hand, the absence of quantitative information on polyphenols probably will not affect directly the properties here discussed, because it is assumed that all phases will participate on the IONP formation.

4.3 | Thermogravimetric (TG) Analysis: Weight Loss (W in %) Curves

The weight loss (W in %) curves of all synthesized samples were obtained by TG experiments and are shown in Figure 5 (left-hand side panel). The derivative of W with respect to T (dW/dT plots) are displayed in the right-hand panel of Figure 5.

For each green synthesis route (ASR, SSR and ISSR), the data of the CTL sample was also added in the same panel to enable direct route-to-route comparisons, which means, to show up the effect of the GT extract on the functionalization process of the IONPs. According to W(T) graphs (left-hand panel of Figure 5), the CTL sample exhibits a total low weight loss of 4% for all temperature range, where the major contribution (3%) occurs in a temperature range from 300 to 430 K (the derivative weight loss versus temperature (right-hand panel of Figure 5 clearly shows similarly greater variation in weight loss with temperature in this region). This observation in the sample weight loss of about 3% can be basically attributed to the extrinsic water and/or free water (adsorbed on the nanoparticle surface) released, as

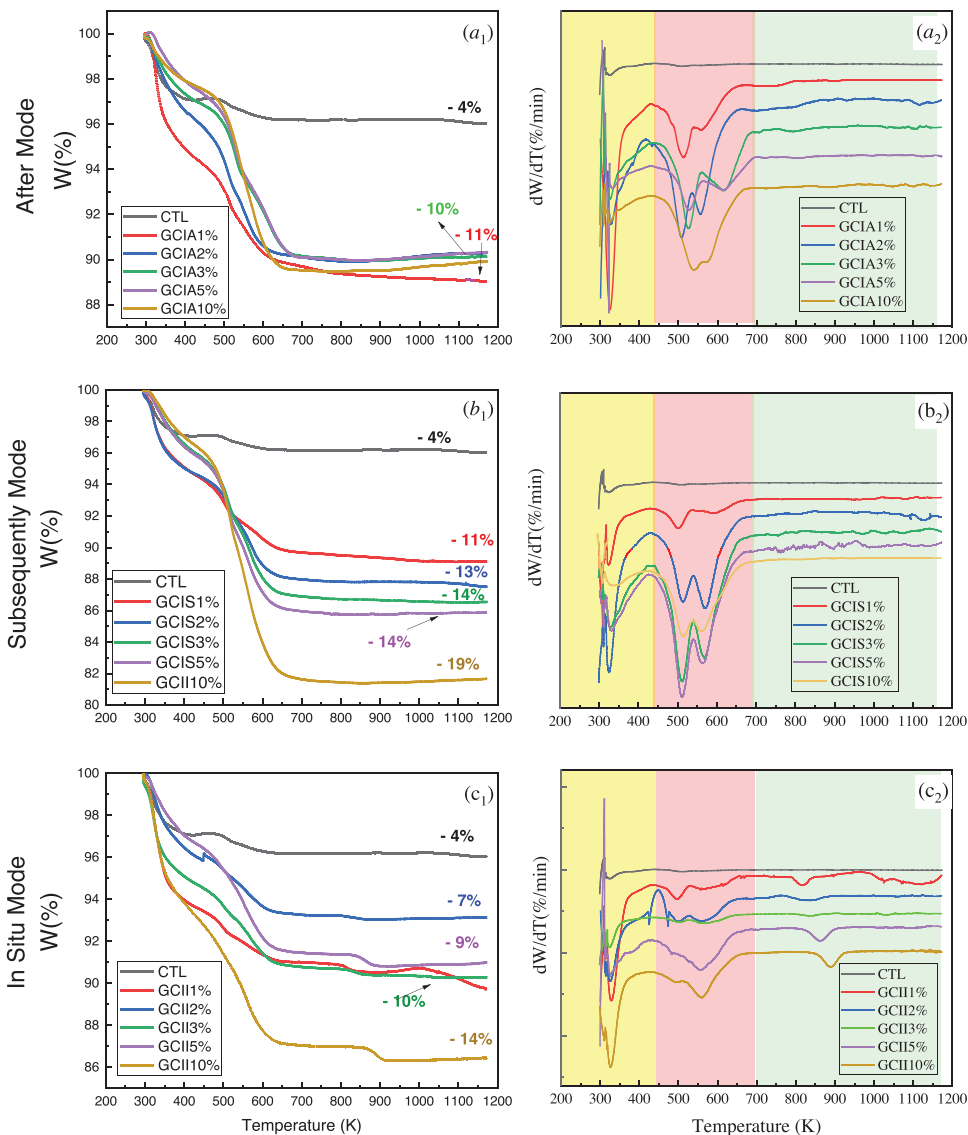


FIGURE 5 | Weight loss (W in %) versus temperature (T) curves obtained by thermogravimetric analysis are shown in the left-handpanel illustrations ‘ a_1 ’, ‘ b_1 ’ and ‘ c_1 ’ for the IONPs: CTL; ASR (GCIAn%), SSR (GCISn %) and ISSR (GCIIn %) for the concentrations ‘ $n\%$ ’ of 1%, 2%, 3%, 5%, and 10% in w/v. In the right-hand panel illustrations ‘ a_2 ’, ‘ b_2 ’ and ‘ c_2 ’, it is shown the derivative weight loss (dW/dT) curves from of each sample presented in the left-hand panel.

typically reported in the literature for IONPs ($\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$) [30]. A residual weight loss of about 1% was still detected beyond this temperature range (from 430 K onward), which still can be attributed to intrinsic water or bound water, as already reported in the literature due to the hydroxyl groups incorporated into the crystal structure or on the nanoparticle surface. Notice that close to 871 K, a phase transition from $\gamma\text{-Fe}_2\text{O}_3$ to hematite ($\alpha\text{-Fe}_2\text{O}_3$) is clearly seen by a peak in the TG curve [30]. Above 871 K, the sample residue consists solely of crystalline oxide phase (probably dominated by $\alpha\text{-Fe}_2\text{O}_3$ phase), with no further weight loss detected by the TG analyzer. On the other hand, the TG analysis of the different functionalized IONP samples shows one strong dependence on the GT concentrations independently of used route, i.e., ASR, SSR, ISSR. More specifically, from the TG analysis (left-hand panel of Figure 5) and differential thermal analysis (right-hand panel of Figure 5) indicate that the green intervention samples (note that the differential curves segmented

in three regions—yellow, red, and green) are slightly different, i.e., the intensity of weight loss variation with temperature is different among the functionalization with different routes (ASR, SSR, ISSR). For example, the ASR functionalized samples show a weight loss between 10% and 11%, while those obtained by SSR and ISSR display a weight loss that seems to scale with GT concentration, being more effective in the SSR samples where the weight loss reached 19%, suggesting a higher organic layer covering the IONPs. Thus, while the ASR sample exhibited losses of approximately 10% across all GT extract concentrations, the SSR samples showed losses ranged from 11% to 19% and ISSR samples displayed a variation between 10% and 14%. Also, the samples prepared with 10% GT concentration exhibited the highest mass losses among all groups, with the greatest loss observed in SSR. No significant differences were found for the other concentrations. Therefore, it can be inferred that the functionalized samples exhibited greater weight losses compared to those observed

for the CTL sample due to the organic-like compounds that functionalized the IONP surfaces, and also, the weight loss, in general, gradually increases with the GT concentration for all routes, a result and assumption that are consistent with the ATR-FTIR and UV-vis results above discussed.

It should also be emphasized that up to about 325 K, the $W(T)$ curves of the functionalized samples are very similar to that of the CTL sample, as also evidenced by the derivative signal. This behavior is mainly associated with the loss of volatile organic compounds and physically adsorbed or free water at the IONP surface [30, 31]. However, examining the full TG measurement range, the most significant weight losses are observed between 420 and 873 K, where compounds such as polyphenols (catechins) and bulky molecules undergo to a thermal decomposition process. These events correspond to the high-loss region highlighted in red in the right-hand panel in Figure 5, as well as the residual losses in the green-highlighted area in the derivative weight loss versus temperature plot in the right-hand panel of Figure 5. Above this temperature range, the sample weights remain virtually unchanged. In general, the weight losses, that are intensified for temperatures above 325 K (also confirmed by dW/dT plots Figure 5, highlighted in red) are associated with a set of multiple peaks observed for a temperature range between 425 and 690 K. Dippong et al. [31] suggested to be mainly due to the decomposition of organic compounds such as fatty acids, polyphenols (including catechins), varying amounts of polymeric and macromolecular compounds. All these results indicate that there is a thickness difference of organic layers from the GT extract that covers the IONPs and, this layer thickness is certainly different for the different synthesis procedure, i.e., ASR, SSR and ISSR as experimentally demonstrated by our TG results. This organic surface layer is not detectable by XRD because it is essentially amorphous from the X ray diffraction standpoint, but its presence becomes evident in the ^{57}Fe Mössbauer analysis discussed below.

4.4 | Magnetic Analysis

The mean particle sizes of the IONPs in this work are, in general, below 15 nm, assuming a roughly spherical particle geometry, as suggested by the TEM images (Figure S1). It is well established that superparamagnetic behavior in IONPs depends strongly on particle size. For Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ IONPs, the critical diameter typically lies at or below 20 nm. However, depending on other factors, such as particle shape, agglomeration (dipolar interaction) and surface effects, superparamagnetic behavior can still be observed in IONPs with sizes up to 50 nm [32, 33]. In special, it is important to emphasize that the superparamagnetic behavior in IONPs is of particular relevance on magnetic hyperthermia treatments, since the samples do not retain remanent magnetization and their superparamagnetic behavior often enhancing heating releasing under alternating magnetic fields (a feature that can be applied in medical treatments and also in oil viscosity changes, e.g.) [34]. Based on these considerations, magnetic analyses were performed by measuring $M(H)$ curves at 300 and 5 K for all synthesized samples. These parameters were numerically extracted from the $M(H)$ curves to characterize magnetic properties and the possible superparamagnetic behavior found in our ensemble of IONPs. Specifically, the main extracted parameters

include M_R , H_C , M_S , and K_{eff} . Figure 6 presents the $M(H)$ curves for both, the CTL and green-intervention samples using the three protocols (ASR, SSR, and ISSR) with different GT concentrations. Each plot of Figure 6 contains six $M(H)$ loops, i.e., the one for the CTL and five $M(H)$ curves representing each percentage used for green intervention (1%, 2%, 3%, 5%, and 10%) of samples prepared by ASR, SSR, and ISSR. Table 1 presents the magnetic parameters obtained at 5 K directly by fitting the $M(H)$ loops, as will be discussed later on (Table S2 shows the magnetic properties obtained at 300 K).

According to the magnetic data presented in Table 1, it can be inferred that, depending on the temperature at which the $M(H)$ loop was recorded, the synthesized IONPs exhibit either magnetically blocked (at 5 K) or unblocked (at 300 K) characteristics. Starting with analysis of the H_C field (Table 1), it is noticed that the H_C field at 5 K ranges from 220 to 350 Oe, indicating that all samples display magnetically blocked state for the particle magnetic moments. This H_C field range matches with those values found in soft magnetic materials. At 300 K (Table S2), however the H_C field values drop to values smaller than 40 Oe. Their M_R values follow similar trend, i.e., at 5 K, M_R values vary between 13 and 24 emu g^{-1} , while at 300 K, they are remarkably low and smaller than 4 emu g^{-1} . The squareness ratio ($\text{SQR} = M_R/M_S$), which reflects the degree of magnetic remanence in magnetic IONPs, ranges from 0.22 to 0.33 at 5 K. These values are found in an ensemble of superparamagnetic IONPs having a significant interparticle interactions, a relative broad particle size distribution, and an associated distribution of magnetic anisotropies. In contrast, at 300 K, M_R/M_S values range from 0 to 0.06 clearly indicate a strong superparamagnetic regime at this temperature, which means most of IONPs have magnetic anisotropy energy lower than the thermal energy at 300 K (≈ 25 meV). Although there are variations in H_C and M_R values found for the CTL, ASR, SSR, and ISSR samples (the later considering the different GT concentrations), no significant and systematic magnetic differences were found that would distinguish them. We would just like to point out that the observed superparamagnetic behavior would be particularly suitable for magnetic hyperthermia, since it suppresses permanent aggregation driven by residual magnetic interactions and facilitates effective heat release during exposure to alternating magnetic fields [35].

Regarding specifically on magnetic properties at 300 K and considering that the magnetization exhibits a tendency to gradually reach the saturation regime (no saturation regime is obtained), the Langevin model Equation (1) was used to determine M_S [36]. In Equation (1), the term linear χH allows to account for paramagnetic-like contributions from inter and intraparticles. The other parameters are μ the magnetic moment of the particle, k_B Boltzmann constant, H the applied field and T the temperature (χ is the magnetic susceptibility of PM contribution).

$$M(H) = M_S [\coth \mu H / k_B T - k_B T / \mu H] + \chi H, \quad (1)$$

Additional parameters can be obtained by fitting the high-field region of the $M(H)$ curves, that is, the range in which complete saturation is not reached (between +2 and +3 T), using the law of approach to saturation (LAS) [17]. For example, it is possible to observe surface effects and/or interparticle interactions using the

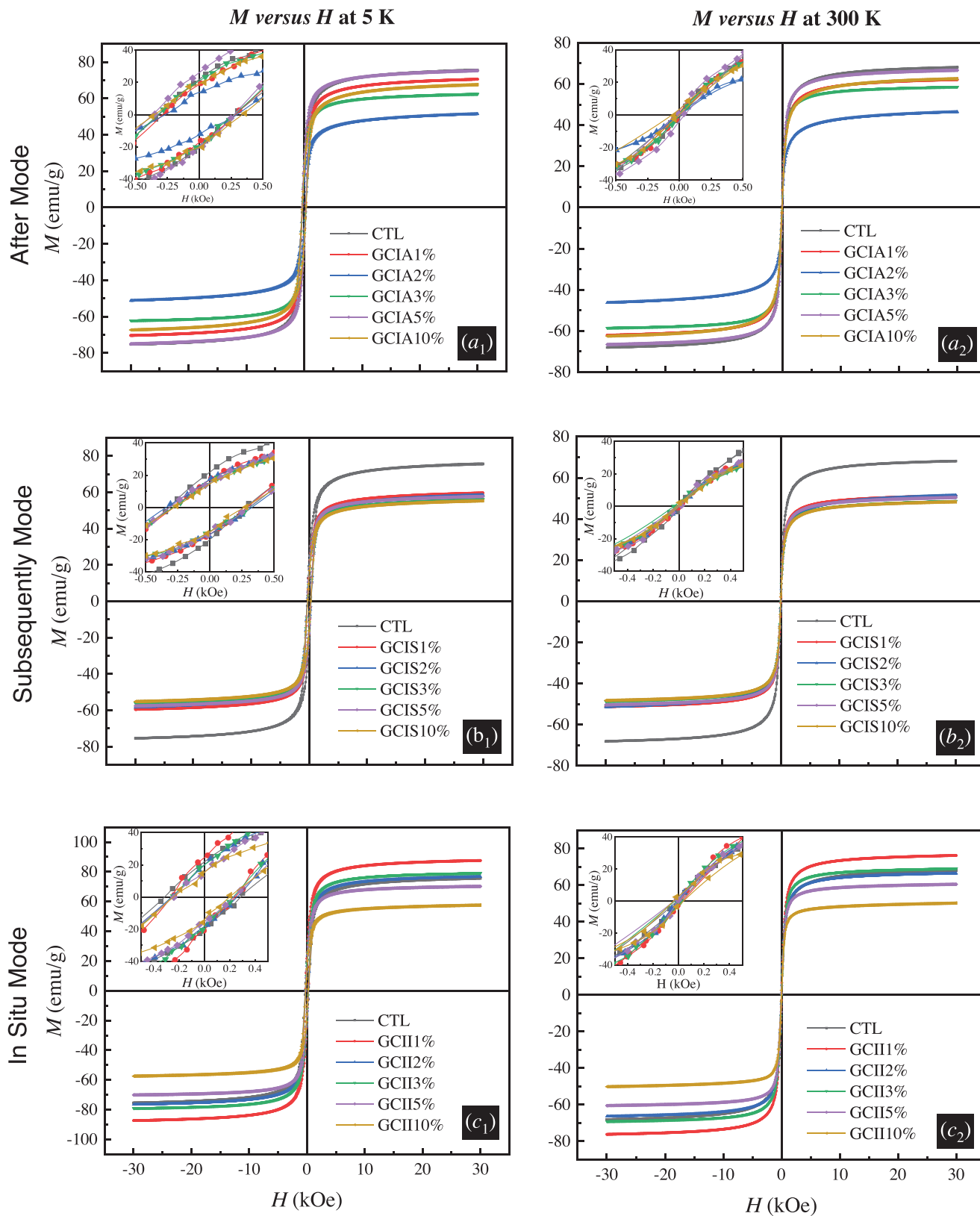


FIGURE 6 | $M(H)$ loops measured at 5 K (left-hand column illustration 'a₁', 'b₁' and 'c₁') and at 300 K (right-hand column in illustration 'a₂', 'b₂' and 'c₂') for IONP samples: CTL IONPs and ASR (GCIA_n%), SSR (GCIS_n%), and ISSR (GCII_n%) samples, with GT concentration 'n%' of 1%, 2%, 3%, 5%, and 10%.

TABLE 1 | Magnetic properties obtained from the fittings the 5 K $M(H)$ loops with the LAS model for the CTL sample and the functionalized ASR (GCIA $n\%$), SSR (GCIS $n\%$), and ISSR (GCI $n\%$) samples synthesized at GT concentrations ($n\%$) of 1%, 2%, 3%, 5%, and 10%.

Samples		H_C (kOe)	M_R (emu g ⁻¹)	M_S (emu g ⁻¹)	SQR M_R/M_S	K_{eff} (± 1 kJ/m ³)
Control—CTL		0.31	21	74	0.28	36
ASR	GCIA1%	0.29	18	69	0.26	33
	GCIA2%	0.28	13	50	0.27	28ss
	GCIA3%	0.30	20	61	0.33	26
	GCIA5%	0.32	24	74	0.32	22
	GCIA10%	0.35	20	66	0.30	10
SSR	GCIS1%	0.29	17	58	0.29	27
	GCIS2%	0.33	17	57	0.30	29
	GCIS3%	0.30	15	55	0.28	25
	GCIS5%	0.31	15	56	0.27	24
	GCIS10%	0.27	15	54	0.27	26
ISSR	GCI1%	0.25	23	86	0.26	36
	GCI2%	0.26	19	76	0.25	33
	GCI3%	0.24	19	78	0.25	31
	GCI5%	0.25	15	69	0.22	26
	GCI10%	0.22	14	56	0.26	26

Equation (2):

$$M(H) = M_S \left(1 - \frac{b}{H^2} \right) + \chi H \quad (2)$$

In Equation (2), the b parameter is related to K_{eff} as described in Equation (3).

$$b = \frac{4}{15} \frac{K_{eff}^2}{M_S^2} \quad (3)$$

K_{eff} values were then obtained and also shown in Table 1 with other important magnetic parameters. In Table S2, the data obtained from fittings $M(H)$ data recorded at 300 K.

Regarding the M_S value of the samples, the CTL sample exhibited a value of 74 emu g⁻¹. Considering values reported in the literature for bulk Fe₃O₄ (98 emu g⁻¹) and γ -Fe₂O₃ (84 emu g⁻¹) at cryogenic temperatures [21], the smaller measured value of 74 emu g⁻¹ for the bare IONPs can be explained by surface spin effects. The high surface-to-volume ratio (s/v) found in IONPs favors a magnetic dead-like layer on the particle surface [37]. It should be punctually stressed that 3d-based magnetic oxides with a spinel-type structure have often ferrimagnetic (FI) ordering in bulk-like state. However, in nanoparticle state, due to the finite size effect, spin canting phenomenon naturally occurs at the particle surfaces due to the partial misalignment of the magnetic moments (spins) of the ions not perfectly oriented in an antiparallel configuration. In other words, a small angle between spins is established at the particle surface (particle core remains FI), leading to a modification of the resultant magnetization of the system [38]. In IONPs of Fe₃O₄ and γ -

Fe₂O₃, it has been demonstrated that the breakdown of crystal coordination leads to the weakening and/or magnetic frustration of exchange interactions, favoring a magnetically disordered layer with a zero-magnetization contribution [39]. Thus, the GT extract (a materials that exhibits a high content of flavonoids) will act as reducing agents, partially promoting the conversion of Fe³⁺ to Fe²⁺, complexing (chelating) the particle surfaces via coordination with hydroxyl (–OH) and carbonyl (C=O) groups, consequently stabilizing a capping layer on the particle surface. This coating organic-layer and its interface with the IONP surface (IONP/Organic-layer) contribute to a higher specific surface area and increased structural disorder due to the enhancement of exchange interactions at the IONP/Organic-layer interface. Thus, magnetic exchange interactions are modified due to the local disruption of Fe – O – Fe superexchange interactions, favoring the spin misalignment as shown recently in the literature [13]. This assumption is also supported by results reported in the literature for ensembles of IONPs with a mean diameter of ~ 10 nm, edge and surface effects that show significantly reduction of magnetization up to 20% [40], i.e., it goes from 92 emu g⁻¹ from bulk to 88–78 emu g⁻¹ for Fe₃O₄ samples and to 76–67 emu g⁻¹ for γ -Fe₂O₃ samples.

Therefore, the synthesis using effective dispersing agents (e.g., surfactants, polymers, organic ligands) promotes the surface functionalization of the IONPs [41]. In this regard, the GT extract was used to replace conventional chemical compounds (given their potential ecological hazards), to reduce particle agglomeration and to enhance particle surface protection. By looking at the M_S values, it was observed that the ASR samples present M_S with quite heterogeneous values, with the lowest magnetization found for the GCIA2% sample (50 emu g⁻¹), while

the highest one occur for the GCIA5% sample (74 emu g^{-1}), the latter in turn showing a value practically equal to that of the CTL sample. No correlation between the M_S values and the GT concentrations was found for samples synthesized by ASR route, but their M_S values are similar to those found in an ensemble of $\gamma\text{-Fe}_2\text{O}_3$ NPs [21, 40]. Therefore, the ASR green intervention did not promote the stabilization of Fe_3O_4 , leading to a transformation into $\gamma\text{-Fe}_2\text{O}_3$ for all GT concentrations. On the other hand, the SSR samples showed homogeneous and closely related M_S values (average of 56 emu g^{-1} , a value that is 15% lower than that found for the CTL sample). These samples apparently display M_S values outside of typical values found for $\gamma\text{-Fe}_2\text{O}_3$ NPs [21, 40]. However, it can be understood by a large contribution from the organic layer on the particle surface that is not magnetic (reduction of magnetic mass of the sample). The SSR green intervention did not also promote the Fe_3O_4 stability, as also found in ASR. But when we took the ISSR sample, an inverse relationship between the GT concentration and the M_S was found; that is, the lower the GT concentration, the greater the M_S displayed in the sample. Particularly, the samples synthesized with GT concentrations of 1 and 3% (GCII1% and GCII3%) exhibit M_S values decreasing from 86 emu g^{-1} and 78 emu g^{-1} , respectively. This set of M_S values obtained for the ISSR samples are higher than that found in the CTL sample (74 emu g^{-1}), even in the case where the IONPs have their surfaces functionalized by polyphenols from the GT extract. Notably, the sample synthesized with 1% GT concentration shows a M_S more than 16% higher than that of the CTL sample. For IONPs with diameters close to 10 nm, the M_S would be expected to range between 67 and 74 emu g^{-1} [21, 37–40], values significantly lower than that observed for GCII1% sample, which was 86 emu g^{-1} . This result suggests that the 1% green intervention in this synthesis modality promotes stability by reducing the oxidation of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ within the magnetic domains of the particles. Therefore, it can be assumed that the low ISSR samples can behave as a core@double-shell materials ($\text{Fe}_3\text{O}_4@ \gamma\text{-Fe}_2\text{O}_3@ \text{organic layer}$), while the other syntheses (ASR and SSR) always showed single magnetic $\gamma\text{-Fe}_2\text{O}_3$ IONPs covered by an organic layer ($\gamma\text{-Fe}_2\text{O}_3@ \text{organic layer}$).

At this stage, a more detailed analysis of the key magnetic features of the IONP samples can be undertaken. First, it should be mentioned that in the laboratory systems, the shape, distribution, and dispersion of IONPs are strongly influenced by auxiliary factors related to the synthesis method. Nevertheless, an inherent degree of heterogeneity is unavoidable, and in some cases, the systems are challenging to control. These issues provoke big difference on effective magnetic anisotropy K_{eff} [42]. Considering that this parameter is extremely relevant from magnetic point of view and accounts for collective effects and/or strong dipolar magnetic interactions, which contribute positively to the blocking temperature (T_B) [21] as displayed by data in Table 1 for a set of K_{eff} obtained for the CTL and functionalized samples. Specifically, the values range from 10 (GCIA10%) to 36 kJ/m^3 (GCII1%), while the H_C field varied from 220 to 350 Oe and M_R between 13 and 23 emu g^{-1} , all these values indicate that the ensemble of IONPs are well-below T_B at 5 K. Comparing the K_{eff} of the CTL sample with those functionalized samples, it is noticed that the ASR, SSR, and ISSR samples exhibit lower K_{eff} . Specifically, the green-assisted ASR and ISSR samples show a decreasing behavior of K_{eff} value with the increasing of the GT concentration. This observation is attributed to the formation of

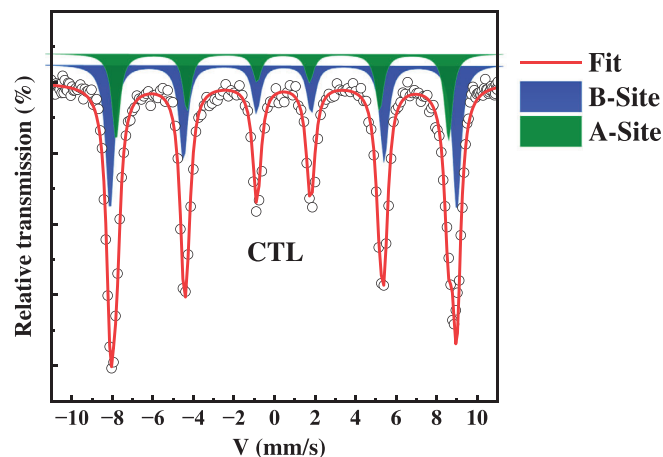


FIGURE 7 | 15 K ^{57}Fe Mössbauer spectrum of the CTL IONPs. The two subspectra used to fit it are also displayed: green associated with the tetrahedral Fe^{3+} configuration, whereas the blue one is due to Fe^{3+} in octahedral symmetry.

organic layers that reduced interparticle dipolar interactions in all functionalized samples. Even so, no correlation was found between SSR samples, indicating that the functionalized process with organic layer is more complex in this synthesis. Magnetic parameters obtained at 300 K are shown in Table S2, and no systematic behavior was obtained, a fact attributed to the different particle size distributions, organic layer thicknesses and other intrinsic effects. However, since the samples characterized in this study contain IONPs with sizes smaller than 20 nm (ca. 11–13 nm), consequently they have a high surface/volume ratio, this different K_{eff} values can be primarily related to the broad size distribution, a condition that affects surface spin disorder contribution, interparticle interactions, particle morphology, and surface coating, a set of effects that collectively change K_{eff} values. Overall, these factors contribute to a partial magnetically blocked state even at 300 K, despite a pure superparamagnetic-like behavior inferred from the near-zero values of H_C and M_R . Residual hysteresis and an elevated T_B are plausibly attributed to strong dipolar and collective magnetic interactions within the IONP ensemble. Thus, considering all the magnetic properties highlighted here, it is evident that they seem to converge toward predominantly superparamagnetic behavior at 300 K. Under these conditions, our IONPs can be employed in specific applications such as magnetic hyperthermia in biological [34].

4.5 | Hyperfine Properties: ^{57}Fe Mössbauer Analysis

Figure 7 shows the Mössbauer spectrum of the CTL sample, while Figure 8 presents the 15 K ^{57}Fe spectra of the ASR, SSR, and ISSR samples synthesized with the GT concentration of 1%, 2%, 3%, 5%, and 10%.

The 15 K spectrum of the CTL sample shows six absorption lines characteristic of nuclear Zeeman interaction with magnetic hyperfine fields (B_{hf}). It was well fitted using only the two Fe^{3+} sites (A—tetragonal and B—octahedral) found in the cubic spinel structure of the $\gamma\text{-Fe}_2\text{O}_3$ phase [43]. The two subspectra (A—green and B—blue) have slightly different hyperfine parameters,

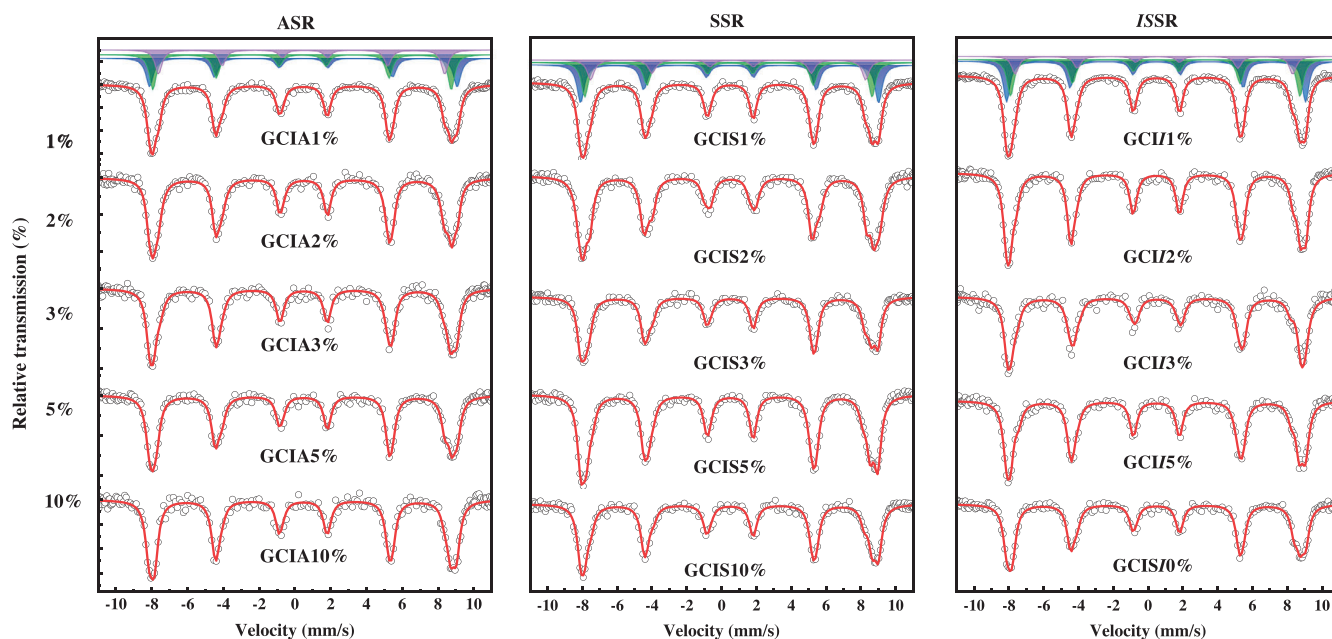


FIGURE 8 | 15 K ^{57}Fe Mössbauer spectra of IONPs synthesized using the following protocols. ASR (GCIAn%), SSR (GCISn%), and ISSR (GCIIn%) for GT concentrations of 1%, 2%, 3%, 5%, and 10%. The spectra were fitted with three components: A (green subspectrum) and B (blue subspectrum) Fe^{3+} sites found in the spinel-type structure, consequently attributed to the $\gamma\text{-Fe}_2\text{O}_3$ grain cores and the C-component (violet subspectrum) associated with the Fe bound to the organic layer composed of GT-derived phenolic species.

such as isomer shift (δ_a and δ_b) and magnetic hyperfine field (B_{hf}^A and B_{hf}^B), as summarized in Table S3.

In contrast, the 15 K spectra of the functionalized samples synthesized by ASR, SSR, and ISSR shown in Figure 8 are only well-fitted with three magnetic subspectra (data displayed in Table S3). The two components due to the A and B sites of the spinel structures previously observed for the bare IONPs (Figure 7), plus a third component (C) with a reduced B_{hf} value. The C component has also hyperfine parameters similar to Fe^{3+} ions in octahedral symmetry. Thus, considering the functionalization process observed by ATR-FTIR, UV-vis, and TG results and the effect of crystallite size with increasing GT content previously discussed, the C-component (not observed in bare IONP sample) can be easily attributed to the Fe^{3+} ions bound to an organic layer from the GT extract, i.e., associated with an Fe–organic capping layer that covers the IONP surfaces. Although the thickness of this organic layer cannot be directly determined from the present experiments, it is expected to increase with GT concentration, as suggested by the weight-loss data in Figure 5. Moreover, XRD results for the GCIIn% series provide clear evidence of the impact of the synthesis method, showing a systematic increase in crystallite size from 11 nm (GCI 1%) to 23 nm (GCI 10%). This behavior stands in sharp contrast to the GCIAn% and GCISn% series, in which the crystallite size remains roughly unchanged. Thus, the different values of quadrupole shifting of the C-component indicate that the GT polyphenols in the GCIIn% do not merely act as passive coating agents. On the contrary, it is highly likely that they behave as chelating agents, complexing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in the dispersion during the synthesis. This observation leads to the formation of a superficial layer on the IONP surfaces in which the magnetic spins are magnetically disordered. Such spin disorder, known as spin canting or a “magnetically dead layer,” originates from the

incomplete coordination of surface Fe atoms and their strong interaction with the functional (–OH) groups of the polyphenols in the extract [44]. This magnetically disordered layer contributes little, if at all, to the total magnetization aligned with the external field [45]. It occurs in all IONPs (bare or functionalized), but it seems to increase its effect in the functionalized samples of $\gamma\text{-Fe}_2\text{O}_3$ NPs. Although a correlation with the ATR-FTIR and TG data is expected in principle, the complexity arising from functionalization and diverse synthesis routes precludes the identification of a clear systematic trend, except for an increase with GT content.

As expected, 300 K ^{57}Fe Mössbauer spectra revealed (Figure S2 to the CTL sample and Figure S3 to the GT functionalized IONP samples) a more complex shape and they cannot be simply fitted using a limited number of idealized sextets. Consequently, they were fitted using both a magnetic hyperfine field distribution (MHFD) and a quadrupole splitting field distribution (QSFD) components to account for the broad distribution of particles sizes with different spin relaxation times, i.e., the fraction that is magnetically blocked and the one in magnetically unblocked regime. The parameters extracted from the ^{57}Fe Mössbauer spectra of the standard sample and the samples functionalized with GT extract at 300 K are presented in Table S4. Thus, the superparamagnetic regime (QSFD component) can be distinguished by spin relaxation of magnetically blocked state of bigger IONPs, which was fitted with MHFD [46]. As would be expected, for particles with sizes ranging from 8 to 13 nm, as determined by XRD data, a significant fraction of the Fe species should exhibit superparamagnetic behavior [37]. Specifically, it should be pointed out that the GCIIn% samples combine a significant increase in the organic layer in the samples (up to 14%), showing an exceptional magnetic stability that is reflected by a QSFD fraction smaller than 10% of total spectrum area. This observation

confirms that the ISSR produces functionalized IONPs with large and well-ordered magnetic cores (responsible for stability and the high B_{hf}) even when these particles are embedded in an organic matrix or coating layer, while in the other two routes (ASR and SSR), the IONPs are not well protected by the organic layer and oxidation occurs rapidly transforming Fe_3O_4 into $\gamma\text{-Fe}_2\text{O}_3$ phase. On the other hand, it is precisely this organic layer, indirectly quantified by TG data, that accounts for the reduction in the overall M_s , thereby resolving the apparent contradiction between the high quality of the magnetic core of ISSR samples and their macroscopic magnetic responses, since the others routes are expected to have fully oxidation of Fe^{2+} , while the ISSR may preserve partially the Fe_3O_4 phase for a longer time.

In brief, a comparative analysis of the three green-assisted synthesis routes helps to clarify their distinct roles in the final properties of the IONPs. The ASR route, in which the GT extract is added after nanoparticle formation, behaves predominantly as a post-synthesis surface functionalization strategy. This is consistent with the small variation in crystallite size observed by XRD and with the absence of a clear correlation between GT concentration and M_s , indicating that this route has limited influence on the magnetic core and mainly modifies the particle surface. The SSR route, where the extract is introduced after coprecipitation but before washing and drying, leads to a stronger organic contribution, as supported by the larger weight losses observed by TG and by the relatively homogeneous but reduced M_s values. Thus, SSR appears to be the most effective route for increasing the amount of organic material associated with the particles, although without evidence of Fe_3O_4 stabilization. In contrast, the ISSR route produces the most significant structural and magnetic changes. In this case, the GT extract is present together with the iron precursors from the beginning of the synthesis, favoring direct interaction with Fe_3O_4 species, systematic crystallite growth, and, at low GT concentrations, higher M_s values than the control sample. This behavior indicates that ISSR is the most promising route for tuning the balance between crystallite growth, surface functionalization, and partial preservation of a Fe_3O_4 -rich core. Therefore, from a practical point of view, ASR may be preferred when a simpler post-synthesis surface coating is desired, SSR when a thicker organic layer is advantageous, and ISSR when the objective is to more strongly modulate both structural and magnetic properties. Since all routes ultimately yield IONPs with predominantly superparamagnetic behavior at RT, these materials remain attractive for applications such as magnetic hyperthermia and other magnetically responsive systems.

More specifically, from the structural point of view, the Rietveld results showed that the GT-assisted synthesis generally increases the crystallite size relative to the control sample, although the magnitude of this effect depends strongly on the synthesis route. This trend is particularly evident in the ISSR series, where the crystallite size increases from 11 nm to 23 nm as the GT concentration rises, while the ASR samples exhibit only a minor size variation. In parallel, the TG data showed progressively larger weight losses for the functionalized samples, indicating a higher amount of organic material associated with the IONPs as the GT concentration increases. Therefore, the GT concentration affects not only particle growth, but also the amount of organic coating bound to the particle surface. This correlation is further

supported by the ^{57}Fe Mössbauer results. At low temperature, the appearance of the additional C-component in the functionalized samples was assigned to Fe ions interacting with GT-derived polyphenolic species on the nanoparticle surface. Thus, increasing GT concentration favors a thicker or more effective organic surface layer, which enhances surface disorder and spin canting. Magnetically, this explains why some samples, especially in the ISSR route, may exhibit larger crystallite sizes but lower macroscopic M_s at higher GT concentrations: the magnetic core remains well ordered, but the polyphenol-rich surface layer contributes to a magnetically disordered shell or “magnetically dead layer,” reducing the net magnetic response. At the same time, the high M_s value observed for GCII1% suggests that, at low GT concentration in the in situ route, the extract can also help stabilize a less oxidized Fe_3O_4 -rich core. Therefore, the final magnetic behavior results from a balance between two competing effects induced by the extract: partial preservation of the magnetic core and formation of an increasingly disordered organic-functionalized surface layer. Although ATR-FTIR and UV-vis spectroscopies do not allow us to quantify each individual polyphenolic compound separately, they do provide sufficient evidence to support a qualitative interpretation in which the GT concentration controls the extent of surface functionalization and, consequently, the crystallite growth, oxidation state stability, and IONPs magnetic response. This interpretation has been clarified in the revised manuscript.

5 | Conclusion

IONPs of control and green-type samples were systematically synthesized via coprecipitation routes using different protocols: ASR, SSR, and ISSR. This study goes beyond the notion of the GT as a simple passive coating, but as an important parameter that modifies structural and magnetic properties of IONPs when the insertion of GT extract is performed under the three above routes. XRD data revealed a polycrystalline structure indexed to the $\text{Fd}\bar{3}m$ space group, with crystallite sizes ranging from 8 to 23 nm, a crystallite size that depends primarily on the protocol and the GT concentration. TG analyses showed that the CTL sample exhibited negligible mass loss ($\sim 4\%$ w/v), whereas GT-functionalized samples presented progressively higher weight losses that are roughly proportional to the GT concentration. Magnetization data displayed almost negligible hysteresis loop at 300 K, suggesting soft-like magnetic character and superparamagnetic-like behavior for the ensemble of IONPs here studied. The effective magnetic anisotropy K_{eff} showed a decrease in its value with the GT increasing for the ASR and ISSR samples, an observation mainly attributed to the formation of an organic layer that suppressed interparticle dipolar interactions (no significant correlation of K_{eff} parameter was found for the SSR samples). The increase of the GT concentration resulted in lower M_s values for the ISSR samples, but, in contrast, no clear similar correlation was found for the ASR and SSR samples. In addition, the ISSR samples exhibited M_s higher than the value found for the CTL sample (it reached 86 emu g^{-1} for the GCII1% sample), suggesting a reduced degree of structural oxidation and partial preservation of the Fe_3O_4 phase. Thus, the samples with GT extract up to 3% showed chemical stability with a core-double-shell features ($\text{Fe}_3\text{O}_4@ \gamma\text{-Fe}_2\text{O}_3@ \text{organic layer}$). ^{57}Fe Mössbauer data supported the assumption of core-shell model, since the 15 K spectra of

the functionalized systems are fitted with three components: two assigned to the A (octahedral) and B (tetrahedral) sites, with hyperfine parameters typically found in Fe^{3+} of an ordered spinel lattice, and the third sextet (C) associated with the iron ions bounded to the GT polyphenols. Thus, the C-component supports the formation of a superficial layer in which the magnetic spins are magnetically disordered, known as spin canting or a “magnetically dead layer,” originates from functional ($-\text{OH}$) groups of the polyphenols in the extract. 300 K ^{57}Fe Mössbauer data also showed superparamagnetic components associated with the superparamagnetic contribution of the samples (its fraction depends on the synthesis route and GT concentration). In general, it can be inferred that although the organic coating decreases the M_s , the grain cores retain high structural quality and magnetic stability, evidencing a clear correlation between larger crystallite size, enhanced magnetic ordering, and the reduced macroscopic magnetic response. Therefore, our findings showed that the different routes can yield functionalized Fe-oxide NPs with different crystallite sizes and thickness of polyphenols just by using *Camellia sinensis* extract and these unfunctionalized IONPs can be applied in applications where hyperthermia are needed, for instance, in biological, since these IONPs are suitable to alternating magnetic field due to its superparamagnetic behavior.

Supplementary Materials

The following supporting information can be downloaded at: xxxxx, Figure S1. Histograms of particle size distribution (main) and TEM images (inset in the main panel) for a series of IONP samples: (a) CTL, (b) ASR10%, (c) SSR10%, (d) ISSR10%, (e) ISSR3%, (f) ISSR2%, and (g) ISSR1%. The PSD curves were constructed from 300 particles measured from different images, and the histograms were fitted with a log-normal function (blue line); Figure S2. ^{57}Fe Mössbauer spectra at 300 K of the CTL IONPs. The experimental data (open circles) were fitted using a magnetic hyperfine field distribution (MHFD); Figure S3. 300 K ^{57}Fe Mössbauer spectra at 300 K of the ASR (GCIAn%), SSR (GCISn%), and ISSR (GCIIn%), at GT concentrations of 1, 2, 3%, 5%, and 10%. The experimental data (open circles) were fitted using a MHFD. Table S1. Structural parameters obtained from Rietveld refinement of the X-ray diffractograms of the samples: CTL and IONPs in the ASR (GCIAn%); SSR (GCISn%), and ISSR (GCIIn%) at GT concentrations ‘n%’ of 1%, 2%, 3%, 5%, and 10% in w/v, respectively. Table S2. Magnetic properties obtained from fitting the 300 K $M(H)$ loops with the LAS model. The data are from IONP CTL samples as well the functionalized IONPs obtained in the ASR (GCIAn%); SSR (GCISn%), and ISSR (GCIIn%) at GT concentrations ‘n%’ of 1%, 2%, 3%, 5%, and 10%. Table S3. Hyperfine parameters extracted from fits to the ^{57}Fe Mössbauer spectra recorded at 15 K for the IONP samples synthesized by ASR (GCIAn%), SSR (GCISn%), and ISSR (GCIIn%), respectively at GT concentration ‘n%’ of 1%, 2%, 3%, 5%, and 10%. $\langle IS \rangle$ is the mean isomer shift, $\langle 2\epsilon \rangle$ the quadrupolar shifting, the linewidth Γ was obtained from the Lorentzian fitting of the ^{57}Fe Mössbauer spectra and B_{hf} the maximum value of the MHFD. Table S4. Hyperfine parameters extracted from fits to the ^{57}Fe Mössbauer spectra recorded at 300 K for the IONP samples synthesized by ASR(GCIAn%), SSR (GCISn%), and ISSR (GCIIn%), respectively at GT concentration ‘n%’ of 1%, 2%, 3%, 5%, and 10%. $\langle IS \rangle$ is the mean isomer shift, $\langle 2\epsilon \rangle$ the quadrupolar

shifting, the linewidth Γ was obtained from the Lorentzian fitting of the ^{57}Fe Mössbauer spectra and B_{hf} the maximum value of the MHFD (magnetic hyperfine field distribution).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. K. K. Brar, S. Magdouli, A. Othmani, et al., “Green Route for Recycling of Low-cost Waste Resources for the Biosynthesis of Nanoparticles (NPs) and Nanomaterials (NMs)-A Review,” *Environmental Research* 207 (2022): 112202, <https://doi.org/10.1016/j.envres.2021.112202>.
2. P. Raveendran, J. Fu, and S. L. Wallen, “Completely “Green” Synthesis and Stabilization of Metal Nanoparticles,” *Journal of the American Chemical Society* 125 (2003): 13940–13941, <https://doi.org/10.1021/ja029267j>.
3. A. I. Osman, Y. Zhang, M. Farghali, et al., “Synthesis of Green Nanoparticles for Energy, Biomedical, Environmental, Agricultural, and Food Applications: A Review,” *Environmental Chemistry Letters* 22 (2024): 841–887, <https://doi.org/10.1007/s10311-023-01682-3>.
4. M. Naseer, S. H. Siyal, T. Najam, et al., “Engineering of Metal Oxide Integrated Metal Organic Frameworks (MO@ MOF) Composites for Energy and Environment Sector,” *Materials Science and Engineering: B* 313 (2025): 117909, <https://doi.org/10.1016/j.mseb.2024.117909>.
5. R. Soomro, M. Abdelmonem, A. D. Meli, M. Panhwar, and C. A. Che Abdullah, “A Novel Plant-based Approach for Synthesis of Iron Oxide Nanoparticles and Cancer Therapy,” *Discover Chemistry* 2 (2025): 25, <https://doi.org/10.1007/s44371-025-00091-5>.
6. L. M. De Souza, P. S. da, S. Porto, and E. P. Muniz, “A Utilização da síntese verde na Produção de Nanopartículas Magnéticas de Óxido de Ferro: Uma análise bibliométrica,” *Research, Society and Development* 8 (2019): e1081518, <https://doi.org/10.33448/rsd-v8i1.518>.
7. S. Ying, Z. Guan, P. C. Ofoegbu, et al., “Green Synthesis of Nanoparticles: Current Developments and Limitations,” *Environmental Technology & Innovation* 26 (2022): 102336, <https://doi.org/10.1016/j.eti.2022.102336>.
8. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and practice* (Oxford University Press/Oxford, 2000), <https://doi.org/10.1093/oso/9780198506980.001.0001>.
9. M. Vinícius-Araújo, J. V. R. Rocha, and A. F. Bakuzis, “Nanopartículas Magnéticas à Base de Óxido de Ferro: Propriedades Magnéticas e Apli-

- cações na Medicina,” *Revista Brasileira de Ensino de Física* 46 (2024): e20240187, <https://doi.org/10.1590/1806-9126-rbef-2024-0187>.
10. R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structures, Properties, Reactions, Occurrences and Uses, Second* (John Wiley & Sons WILEY-VCH GmbH & Co. KGaA, 2003), <https://doi.org/10.1002/3527602097>.
 11. S. Laurent, D. Forge, M. Port, et al., “Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications,” *Chemical Reviews* 108 (2008): 2064–2110, <https://doi.org/10.1021/cr068445e>.
 12. H. Liang, W. Wang, Y. Huang, S. Zhang, H. Wei, and H. Xu, “Controlled Synthesis of Uniform Silver Nanospheres,” *The Journal of Physical Chemistry C* 114 (2010): 7427–7431, <https://doi.org/10.1021/jp9105713>.
 13. R. Rueda-Vellasmin, J. A. Ramos-Guivar, J. M. Santos, N. Checca-Huaman, and E. C. Passamani, “Tuning the Fe-Oxide Nanoparticle Properties by Playing With Salt Precursors and Camellia sinensis Extract Concentrations,” *Chemphyschem* 26 (2025): e202500226, <https://doi.org/10.1002/cphc.202500226>.
 14. C. Pecharrmán, T. González-Carreño, and J. E. Iglesias, “The Infrared Dielectric Properties of Maghemite, γ -Fe₂O₃, From Reflectance Measurement on Pressed Powders,” *Physics and Chemistry of Minerals* 22 (1995): 21–29.
 15. H. Putz and K. Brandeburg, *Match!—Phase Identification from Powder Diffraction* (Crystal Impact GbR, 2024).
 16. M. Y. Huertas-Chambilla, M. F. Moyano-Arocutipa, J. Y. Zarria-Romero, et al., “In-Field 57Fe Mössbauer Study of Maghemite Nanoparticles Functionalized Multiwall Carbon Nanotubes and Their Ecotoxicological Properties in Young Daphnia Magna,” *Hyperfine Interact* 243 (2022): 24, <https://doi.org/10.1007/s10751-022-01807-0>.
 17. J. A. R. Guivar, E. A. Sanches, F. Bruns, et al., “Vacancy ordered γ -Fe₂O₃ nanoparticles functionalized With nanohydroxyapatite: XRD, FTIR, TEM, XPS and Mössbauer studies,” *Applied Surface Science* 389 (2016): 721–734, <https://doi.org/10.1016/j.apsusc.2016.07.157>.
 18. Z. Klencsár, MossWinn 4.0i, <http://Www.MossWinn.Hu/> (July 2023).
 19. W. Kim, C. Y. Suh, S. W. Cho, et al., “A New Method for the Identification and Quantification of Magnetite–maghemite Mixture Using Conventional X-ray Diffraction Technique,” *Talanta* 94 (2012): 348–352, <https://doi.org/10.1016/j.talanta.2012.03.001>.
 20. J. A. Ramos-Guivar, D. A. Flores-Cano, and E. C. Passamani, “Differentiating Nanomaghemite and Nanomagnetite and Discussing Their Importance in Arsenic and Lead Removal From Contaminated Effluents: A Critical Review,” *Nanomaterials* 11 (2021): 2310, <https://doi.org/10.3390/nano11092310>.
 21. B. D. Cullity and C. D. Graham, *Introduction to Magnetic Materials* (Wiley, 2008), <https://doi.org/10.1002/9780470386323>.
 22. J. Xia, D. Wang, P. Liang, et al., “Vibrational (FT-IR, Raman) analysis of tea catechins based on both theoretical calculations and experiments,” *Biophysical Chemistry* 256 (2020): 106282, <https://doi.org/10.1016/j.bpc.2019.106282>.
 23. E. Giorgini, V. Notarstefano, R. Foligni, P. Carloni, and E. Damiani, “First ATR-FTIR Characterization of Black, Green and White Teas (Camellia sinensis) From European Tea Gardens: A PCA Analysis to Differentiate Leaves From the in-Cup Infusion,” *Foods* 13 (2023): 109, <https://doi.org/10.3390/foods13010109>.
 24. K. K. Singh, K. K. Senapati, and K. C. Sarma, “Synthesis of Superparamagnetic Fe₃O₄ Nanoparticles Coated With Green Tea Polyphenols and Their Use for Removal of Dye Pollutant From Aqueous Solution,” *Journal of Environmental Chemical Engineering* 5 (2017): 2214–2221, <https://doi.org/10.1016/j.jece.2017.04.022>.
 25. G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Third Edition (John Wiley & Sons, 2001).
 26. J. A. H. Kaeswurm, A. Scharinger, J. Teipel, and M. Buchweitz, “Absorption Coefficients of Phenolic Structures in Different Solvents Routinely Used for Experiments,” *Molecules* 26 (2021): 4656, <https://doi.org/10.3390/molecules26154656>.
 27. X. Wang, J. Huang, W. Fan, and H. Lu, “Identification of Green Tea Varieties and Fast Quantification of Total Polyphenols by near-infrared Spectroscopy and Ultraviolet-visible Spectroscopy With Chemometric Algorithms,” *Analytical Methods* 7 (2015): 787–792, <https://doi.org/10.1039/C4AY02106A>.
 28. S. Çentinkaya and N. Kütük, “Rapid Synthesis of PbO-NPs Photocatalysts, Investigation of Methylene Blue Degradation Kinetics,” *Gazi University Journal of Science* 36 (2023): 511–527, <https://doi.org/10.35378/gujs.1001825>.
 29. Z. Markova, P. Novak, J. Kaslik, et al., “Iron(II,III)–Polyphenol Complex Nanoparticles Derived From Green Tea With Remarkable Ecotoxicological Impact,” *ACS Sustainable Chemistry & Engineering* 2 (2014): 1674–1680, <https://doi.org/10.1021/sc5001435>.
 30. G. Dorcioman, A. Hudiță, B. Gălățeanu, et al., “Magnetite-Based Nanostructured Coatings Functionalized With Nigella Sativa and Dicloxacillin for Improved Wound Dressings,” *Antibiotics* 12 (2022): 59, <https://doi.org/10.3390/antibiotics12010059>.
 31. T. Dippong, O. Cadar, M. H. Kovacs, M. Dan, and L. Senila, “Chemical Analysis of Various Tea Samples Concerning Volatile Compounds, Fatty Acids, Minerals and Assessment of Their Thermal Behavior,” *Foods* 12 (2023): 3063, <https://doi.org/10.3390/foods12163063>.
 32. A. N. Stephen, T. Mercer, W. Stockburn, S. R. Dennison, J. E. Readman, and S. M. Reddy, “Simple Size Tuning of Magnetic Nanoparticles Using a Microwave Solvothermal Method and Their Application in Facilitating the Solid-phase Synthesis of Molecularly Imprinted Polymers,” *Materials Advances* 6 (2025): 2016–2028, <https://doi.org/10.1039/D4MA01115E>.
 33. T. Girardet, P. Venturini, H. Martinez, J. C. Dupin, F. Cleymand, and S. Fleutot, “Spinel Magnetic Iron Oxide Nanoparticles: Properties, Synthesis and Washing Methods,” *Applied Sciences* 12 (2022): 8127, <https://doi.org/10.3390/app12168127>.
 34. C. Pucci, A. Degl’Innocenti, M. Belenli Gümüş, and G. Ciofani, “Superparamagnetic Iron Oxide Nanoparticles for Magnetic Hyperthermia: Recent Advancements, Molecular Effects, and Future Directions in the Omics Era,” *Biomaterials Science* 10 (2022): 2103–2121, <https://doi.org/10.1039/D1BM01963E>.
 35. C. Martins, C. Rolo, V. R. G. Cacho, et al., “Enhancing the Magnetic Properties of Superparamagnetic Iron Oxide Nanoparticles Using Hydrothermal Treatment for Magnetic Hyperthermia Application,” *Materials Advances* 6 (2025): 1726–1743, <https://doi.org/10.1039/D4MA01120A>.
 36. S. Bedanta and W. Kleemann, “Supermagnetism,” *Journal of Physics D: Applied Physics* 42 (2009): 013001, <https://doi.org/10.1088/0022-3727/42/1/013001>.
 37. Ò. Iglesias and A. Labarta, “Finite-size and surface effects in maghemite nanoparticles: Monte Carlo simulations,” *Physical Review B* 63 (2001): 184416, <https://doi.org/10.1103/PhysRevB.63.184416>.
 38. E. Burzo and R. Tetea, “New Insights on the Spin Glass Behavior in Ferrites Nanoparticles,” *Nanomaterials* 12 (2022): 1782, <https://doi.org/10.3390/nano12101782>.
 39. P. G. Acevedo, M. A. González Gómez, J. S. Garitaonandia, Y. Piñeiro, and J. Rivas, “Significant Surface Spin Effects and Exchange Bias in Iron Oxide-Based Hollow Magnetic Nanoparticles,” *Nanomaterials* 12 (2022): 456, <https://doi.org/10.3390/nano12030456>.
 40. A. Hajalilou, M. Tavakoli, and E. Parvini, *Magnetic nanoparticles: Synthesis, characterization, and applications*. (John Wiley & Sons, 2022), <https://doi.org/10.1002/9783527840762>.
 41. A. Nair, R. Chandrashekar, C. M. Day, et al., “Polymeric Functionalization of Mesoporous Silica Nanoparticles: Biomedical Insights,” *International Journal of Pharmaceutics* 660 (2024): 124314, <https://doi.org/10.1016/j.ijpharm.2024.124314>.

42. K. Enpuku, A. L. Elrefai, T. Yoshida, et al., “Estimation of the Effective Magnetic Anisotropy Constant of Multi-core Based Magnetic Nanoparticles From the Temperature Dependence of the Coercive Field,” *Journal of Applied Physics* 127 (2020): 133903, <https://doi.org/10.1063/1.5144713>.
43. Y. V. Alca-Ramos, N. R. C. Huaman, R. Rueda Vellasmin, E. C. Passamani, and J. A. R. Guivar, “Biosynthesis Scale-Up Process for Magnetic Iron-Oxide Nanoparticles Using Eucalyptus Globulus Extract and Their Separation Properties in Lubricant–Water Emulsions,” *Nanomaterials* 15 (2025): 382, <https://doi.org/10.3390/nano15050382>.
44. M. Abdolrahimi, M. Vasilakaki, S. Slimani, et al., “Magnetism of Nanoparticles: Effect of the Organic Coating,” *Nanomaterials* 11 (2021): 1787, <https://doi.org/10.3390/nano11071787>.
45. A. Lu, E. L. Salabas, and F. Schüth, “Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application,” *Angewandte Chemie International Edition* 46 (2007): 1222–1244, <https://doi.org/10.1002/anie.200602866>.
46. J. Drbohlavova, R. Hrdy, V. Adam, R. Kizek, O. Schneeweiss, and J. Hubalek, “Preparation and Properties of Various Magnetic Nanoparticles,” *Sensors* 9 (2009): 2352–2362, <https://doi.org/10.3390/s90402352>.

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