

Article



# Synthesis of CoFe<sub>2</sub>O<sub>4</sub> through Wet Ferritization Method Using an Aqueous Extract of Eucalyptus Leaves

Dana Gingasu <sup>1,\*</sup><sup>(b)</sup>, Daniela C. Culita <sup>1</sup><sup>(b)</sup>, Jose Maria Calderon Moreno <sup>1</sup>, Gabriela Marinescu <sup>1</sup>, Cristina Bartha <sup>2,\*</sup><sup>(b)</sup>, Ovidiu Oprea <sup>3</sup><sup>(b)</sup>, Silviu Preda <sup>1</sup><sup>(b)</sup>, Mariana Carmen Chifiriuc <sup>4,5,6</sup><sup>(b)</sup> and Marcela Popa <sup>5</sup><sup>(b)</sup>

- <sup>1</sup> Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 060021 Bucharest, Romania; dculita@icf.ro (D.C.C.); calderon@icf.ro (J.M.C.M.); gmarinescu@icf.ro (G.M.); predas01@yahoo.co.uk (S.P.)
- <sup>2</sup> National Institute of Materials Physics, 405A Atomistilor Street, P.O. Box Mg-7, 077125 Magurele, Romania
- <sup>3</sup> Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Polizu Street, 011061 Bucharest, Romania; ovidiu73@yahoo.com
- <sup>4</sup> Microbiology Department, Faculty of Biology, University of Bucharest, 91-95 Splaiul Independentei, 050095 Bucharest, Romania; carmen\_balotescu@yahoo.com or carmen.chifiriuc@unibuc.ro
- <sup>5</sup> Research Institute of the University of Bucharest—ICUB, University of Bucharest, 91-95 Splaiul Independentei, 050095 Bucharest, Romania; bmarcelica@yahoo.com or marcela.popa@bio.unibuc.ro
- <sup>6</sup> Romanian Academy, 125 Calea Victoriei, 010071 Bucharest, Romania
- \* Correspondence: d\_gingasu@yahoo.com or dgingasu@icf.ro (D.G.); cristina.bartha@infim.ro (C.B.)

**Abstract:** This study explored a new green approach of the wet ferritization method to obtain magnetic cobalt ferrite ( $CoFe_2O_4$ ) by using eucalyptus leaves aqueous extract as a reducing/chelating/ capping agent. The spinel single cubic phases of prepared samples were proved by powder X-ray diffraction (XRD), Fourier-Transform Infrared (FTIR) and Raman spectroscopy. The average crystallite size is in the range between 3 and 20 nm. The presence of the functional groups coating the obtained material is confirmed from FTIR and thermal analysis. The scanning electron microscopy (SEM) analysis showed a morphology consisting of nanoparticle aggregates. Raman spectroscopy detects the characteristic bands of spinel-type  $CoFe_2O_4$ . Magnetic investigations reveal the formation of ferromagnetic compounds with cubic magnetic anisotropy and a blocking temperature around 140 K, specific for this type of material. The biosynthesized  $CoFe_2O_4$  could be an attractive candidate for biomedical applications, exhibiting promising antimicrobial and antibiofilm activity, particularly against Gram-negative bacteria and fungal strains.

Keywords: spinel ferrite; green synthesis; plant extract; magnetic properties; biomedical applications

# 1. Introduction

In recent years, there has been an increasing interest in the synthesis of nano-sized magnetic ferrites due to their diverse potential applications as permanent magnets, storage devices, magnetic recording devices, ferrofluids, magnetic drug delivery, catalysts, etc. [1–3].

Among them, cobalt ferrite ( $CoFe_2O_4$ ) has a special place, being a hard magnetic material with good chemical stability, high coercivity (Hc), and moderate magnetization (Ms) [4]. Cobalt ferrite has received a renewed research focus due to its multiple biomedical applications in magnetic refrigeration, magnetic resonance imaging, hyperthermia treatment, and in the field of nano-biosensors [5–7].

Nano-sized cobalt ferrite can be obtained by using a wide range of chemical and physical methods [3,8,9]. Some of these methods present a series of impediments such as the use of toxic solvents, prolonged high temperature heat treatments, and high energy consumption with risks for the environment. To reduce the negative impact on the environment, cleaner/greener synthesis methods are required. Green synthesis methods are guided by the twelve principles of green chemistry [10]. A green approach of chemistry



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). synthesis methods assume, among other things, the use of natural raw materials, simple equipment, and reduced synthesis times. All of these things lead to a lower cost of obtaining nanomaterials compared to other methods [11,12].

Among the biological agents, plants seem to be the best candidates, being easily accessible, widely distributed, and providing a vast reserve [13]. Moreover, every part of a plant could be useful in the synthesis of nanomaterials. Plant extracts contain phytochemicals (polysaccharides, phenolic acids, flavonoids, etc.) that have multiple functions (reducing, capping, chelating, and even stabilizing) in the synthesis of nanomaterials. The variation of these active biocomponents concentrations, their compositions, as well as their interactions with metal ions are among the main factors that feature the diversity of sizes and shapes of the obtained nanoparticles [14]. The biomolecules from the plant extracts are immobilized on the surface of nanoparticles during the synthesis process, leading to modified/functionalized/coating of nanoparticle surfaces that results in an increased stability of the biosynthesized nanoparticles. These processes also improve material properties and thus expand their ranges of applications.

In the last decade, a special focus was given to cobalt ferrite synthesized by green chemistry methods using different types of plant extracts. Routray et al. [15] reported the use of Aloe vera in the sol–gel auto-combustion process, to obtain  $CoFe_2O_4$  for high frequency application, magneto recording devices. Mahajan et al. [16] revealed tulsi seed and garlic extract-based synthesis of  $CoFe_2O_4$  with good antibacterial activity. A green synthesis method of cobalt ferrite using extracts of *Artemisia annua* L. "hairy" roots was demonstrated by Kobylinska et al. [17] and the effect and role of green synthesis parameters were evaluated. In our previous papers, we described the synthesis of  $CoFe_2O_4$  nanoparticles employing aqueous extracts of sesame seed extract, ginger root, cardamom seeds, tamarind fruit as fuel or reducing/chelating/capping agents [18–20]. The obtained  $CoFe_2O_4$  nanoparticles exhibited very good antimicrobial properties, demonstrated by the low minimal inhibitory concentration values against a wide range of microbial strains, suggesting their potential for the development of novel antimicrobial agents [18].

The *Eucalyptus* genus from the *Myrtaceae* family contains about 600 species native to Australia. The eucalyptus plant leaves extracts have various effects such as antibacterial, antihyperglycemic, antioxidant etc. [21].

The phytochemical studies of eucalyptus leaves highlighted the presence of alkaloids, aminoacids, carbohydrates, flavonoids, glycosides, tannins, phenols, terpenoids, steroids, and saponins [22,23]. The leaves extracts contain phenolcarboxylic acids (gallic and ellagic acids), hydroxycinnamic acids (caffeic, ferulic, chlorogenic, p-coumaric acids), flavonoids (lutelin, myricetin, quercetin, kaempferol), coumarin (coumarin, skinnin, scopolin), etc. [22], one of the major constituents being 1,8-cineole (between 73 and 85%) [21]. These components have an important role in the green synthesis process. The hydroxyl and carboxyl groups from the active biomolecules facilitate the interaction with the metal ions and have a high involvement in the metal ion reduction [24]. A high content of polyphenols leads to the formation of a protective coating around the synthesized nanoparticle, thus harboring functional groups (charged groups) that create repulsive forces preventing nanoparticle agglomeration and instability [25]. Generally, the green synthesis of nanoparticles has three phases [26]: (i) the activation phase consisting in the reduction of metal ions to zero-valent metal and nucleation; (ii) the growth phase, in which the combination of several nanoparticles leads to the formation of larger ones, with increased thermodynamic stability; (iii) the termination phase is essential for defining the size and shape of the resulted nanoparticle.

Previous studies revealed the use of eucalyptus extract, which is easy to obtain and sustainable, in the synthesis of metal nanoparticles such as Ag, Zn, Fe [25,27,28] and metal oxide TiO<sub>2</sub>, ZnO, La<sub>2</sub>O<sub>3</sub> [29–31]. These nanoparticles could be good candidates for biomedical, ecological, and agricultural applications. However, the use of this extract in the synthesis of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles has not yet been reported.

Considering the above aspects, in the present study we show for the first time in the literature the synthesis of cobalt ferrite ( $CoFe_2O_4$ ) through the wet ferritization method using an aqueous extract of eucalyptus leaves. The physico-chemical characterization of the obtained cobalt ferrite nanoparticles (XRD, SEM, thermal analysis, FTIR, Raman, and magnetic measurements) has been carried out. The antimicrobial activity of the obtained cobalt ferrite nanoparticles has also been investigated to formulate possible practical applications of the obtained materials.

#### 2. Materials and Methods

# 2.1. Materials

The iron (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and the cobalt (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) nitrates were of reagent quality (Merck, Darmstadt, Germany). Eucalyptus leaves (Fares brand, Eucalyptus globulus, contain volatile oil in which the main component is 1,8-cineole) were purchased from the local health food store and the ammonia solution 25% from Chimreactiv, Bucharest, Romania.

# 2.2. Preparation of the Plant Extract

The eucalyptus aqueous extract was prepared according to the following protocol: 2.5 g eucalyptus dry leaves were mixed with 100 mL of distilled water and heated up to 80 °C for 30 min under magnetic stirring. After cooling and filtering, a dark orange extract (pH = 5) was obtained.

# 2.3. Synthesis of Cobalt Ferrites

The metal nitrates ( $2Fe^{3+}:1Co^{2+}$ ) were added slowly into the 100 mL eucalyptus aqueous extract and the pH was raised to 10 by adding NH<sub>4</sub>OH 25%. During this time, under stirring, a dark brown precipitate was formed. The obtained suspension was maintained under continuously stirring at ~80 °C for 3 h. After this time, the weak magnetic dark precipitate was separated and washed until the washing water had a pH of 7. It was dried on P<sub>4</sub>O<sub>10</sub> until a black powder was obtained (N sample). To improve the crystallinity of the N sample, an additional thermal treatment at 800 °C/1 h was applied (N-800).

# 2.4. Characterization Techniques

The X-ray diffraction patterns were recorded using a Rigaku Ultima IV diffractometer (Tokyo, Japan). The equipment was set up in parallel beam geometry, using Cu K $\alpha$  radiation ( $\lambda = 1.5406$ ), CBO optics, a graphite monochromator, and 40 kV and 30 mA operating outputs. The measurements were carried out in the  $\theta$ -2 $\theta$  mode, with a step size of 0.02° and a scan speed of 1°/min. The phase identification was done using the Search/Match method, coupled with the ICDD PDF-2. The lattice constant was refined using the diffraction line position, adjusted by the external standard method. The crystallite size (d) was calculated from the diffraction line width (integral width) using the Scherrer equation:

## $d = 0.9\lambda/\beta \cos\theta$ ,

where d is the crystallite size,  $\lambda$  is the wavelength of the X-ray used,  $\theta$  is the angle of reflection, and  $\beta$  is the full width at half maximum or the broadening of the diffraction line in radians. X-ray fluorescence (XRF) was used for elemental analysis. The measurements were performed using a Rigaku ZSX Primus II spectrometer (Rigaku Corp., Tokyo, Japan), equipped with 4.0 kW X-ray Rh tube. EZ–scan combined with Rigaku SQX fundamental parameters module of ZSX v5.18 software (standard less) was used for data analysis. The microstructure of the obtained powders was investigated by scanning electron microscopy (SEM) in a FEI Quanta 3D FEG apparatus (Hillsboro, OR, USA) operating at accelerating voltages in 2–5 kV range, using secondary electron images. IR spectra were recorded on JASCO FTIR 4100 spectrophotometer (Tokyo, Japan) in the 4000–400 cm<sup>-1</sup> range, with solid samples prepared as KBr pellet. Unpolarized Raman spectra were achieved in a Horiba Jobin–Yvon LabRam HR spectrometer (Kyoto, Japan) with a He-Cd laser, using

excitation of 325 nm wavelength. In order to avoid sample damage by irradiation, the power on the sample was kept below 0.5 mW. The UV Raman spectra were collected on a  $40 \times$  objective, in a UV-enhanced CCD camera and corrected by subtracting the background spectrum. The Raman shift was recorded from 300 to 900 cm<sup>-1</sup> and the integration time of the measurements 60 s. The thermal analysis TG-DSC was performed with a STA 449C F3 system, TG-DSC (thermogravimetry—differential scanning calorimetry) from Netzsch (NETZSCH-Gerätebau GmbH, Selb, Germany), from room temperature up to 900 °C, in a constant air flow of 50 mL/min. A Bruker Tensor 27 (Bruker Co., Ettlingen, Germany) with thermostatic gas cell was used to record the FTIR spectra of the evolved gases. Magnetic properties were investigated with a MMPS SQUID magnetometer from Quantum Design (San Diego, CA, USA). Hysteresis curves have been acquired at four different temperatures (10 K, 100 K, 200 K, and 300 K, respectively) under an applied magnetic field of -50,000 Oe and +50,000 Oe. The evolution of magnetization under field cooling (FC) and zero field cooling (ZFC) conditions as a function of temperature was analyzed under a magnetic field of 500 Oe.

# 2.5. Antimicrobial Activity Assays

The antimicrobial activity of the obtained cobalt ferrite nanoparticles has been assessed against four bacterial and one fungal standard strain, i.e., *Staphylococcus aureus* ATCC 25923, *Enterococcus faecalis* ATCC 29212, *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853, and *Candida albicans* ATCC 10231, at a density of 0.5 McFarland. The selected strains have been tested both in planktonic and biofilm growth states, by using qualitative (adapted disk diffusion method allowing the quantification of growth inhibition zones diameters on solid agar) and quantitative (broth microdilution method and violet crystal microtiter allowing to establish the minimal inhibitory concentration–MIC and minimal biofilm inhibitory concentration-MBIC) assays [32,33].

The tested concentration in the qualitative assay was 10 mg/mL, while in the quantitative assays, two-fold serial dilutions ranging from 10 to 0.0195 mg/mL have been obtained in the liquid culture medium. In the quantitative assays, the MIC and MBIC have been established by inspecting the turbidity and respectively the color intensity of the well contents, in comparison with the aspect of the negative and positive controls. The lowest concentrations inhibiting the microbial growth revealed by the absence of turbidity for the planktonic growth and the absence of the blue color for the biofilm growth have been noted as MIC and respectively, MBIC. The assays were performed in duplicate [32,33].

#### 3. Results and Discussion

The cobalt ferrite nanoparticles were obtained through the wet ferritization green approach, using eucalyptus leaves aqueous extract. The phytochemical basis of the plant extract is adequate, containing the bioactive molecules involved in the reduction (enol groups) and capping (methoxy/phenyl groups) action [34]. The biomolecules present in the eucalyptus leaves extract form coordinated metal complexes with the  $Co^{2+}$  and  $Fe^{3+}$ ions. The ferritization process takes place through the degradation of complex precursors (metals/active biomolecules) directly in the reaction medium, by varying the pH and the temperature of the reaction medium [18]. A possible mechanism of  $CoFe_2O_4$  formation using the eucalyptus extract is presented in Scheme 1.



**Scheme 1.** A possible CoFe<sub>2</sub>O<sub>4</sub> formation mechanism by a green approach of the wet ferritization method, using eucalyptus leaves aqueous extract.

#### 3.1. X-ray Fluorescence and X-ray Diffraction

X-ray fluorescence (XRF) spectrometry was used to determine the elemental composition of both samples, N and N-800. The ratio between Co and Fe was 32.51:67.49 by mass percentage for the N sample and 33.21:66.79 for the N-800 sample, respectively. These ratios are close to the theoretical composition of  $CoFe_2O_4$ .

The crystal structure, phases, and purity of the as-synthesized sample (N sample) and the thermally-treated sample (N-800 sample) were investigated by X-ray diffraction (XRD). Figure 1 shows the XRD patterns of both powder samples. It was found that all diffraction lines in Figure 1b, corresponding to the crystal planes (111), (220), (311), (222), (400), (331), (422), (511), (440), (531), (620), (533), (622), and (444) could be indexed to a cubic inverse spinel structure. No additional diffraction lines corresponding to other phases or an amorphous halo were observed. Based on the XRD pattern of the sample N-800, coupled with XRF results, the spinel phase could be indexed to CoFe<sub>2</sub>O<sub>4</sub>, which matches well against ICDD file no. 22-1086. Figure 1a shows the XRD patterns of the sample N, the as-prepared sample. The diffraction lines are broad, but the positions of the lines are specific to a spinel structure. As for the thermally treated sample, the lack of an amorphous phase (amorphous halo), combined with the mass ratio between Co and Fe, indicates the presence of a spinel structure, with a composition of CoFe<sub>2</sub>O<sub>4</sub>.

The sharp and narrow diffraction lines of the cobalt ferrite calcined at 800 °C for 1 h (N-800) indicate the better crystallinity of the sample. The lattice parameters for the N and N-800 samples were 8.3114(10) Å and 8.38364(2) Å, respectively, being in good agreement with the literature data [18]. The crystallite sizes, calculated using the Scherrer equation, were 3 nm (N sample) and 20 nm (N-800 sample). The calculated values are lower than the values of  $CoFe_2O_4$  samples (~26 nm) obtained by the sol–gel method using olive leaves aqueous extracts [35].



Figure 1. XRD patterns of spinel ferrites: (a) N; (b) N-800 sample.

#### 3.2. Scanning Electron Microscopy

The morphology of the CoFe<sub>2</sub>O<sub>4</sub> powders obtained by wet ferritization using eucalyptus extract was revealed by SEM images (Figure 2). Micro-sized aggregates are observed in the 10,000× micrograph in Figure 2a with aggregates size up to ten microns. The aggregates have a fluffy appearance, observed in the 200,000× micrograph (Figure 2b) and consist of loosely aggregated nanoparticles embedded in a disordered matrix. The nanoparticles have typical sizes below 10 nm, distinguishable in the 1,000,000× image in the inset in Figure 2b. The particle size distribution histogram is shown in Figure 2c. After thermal treatment at 800 °C for 1 h there is a densification of the aggregates into micro-sized solid polycrystalline particles (Figure 2d) consisting of primary CoFe<sub>2</sub>O<sub>4</sub> nanocystallites sized about 20 nm (Figure 2e), as shown in the particle size distribution histogram (Figure 2f).

# 3.3. FTIR and Raman Spectroscopy

The IR spectra of the  $CoFe_2O_4$  samples were recorded in the 4000–400 cm<sup>-1</sup> range and were compared with the IR spectrum of eucalyptus leaf dry extract (Table 1 and Figure S1, see Supplementary Materials).

Literature data mention that the IR spectra recorded for different types of eucalyptus extract revealed the functional groups which could be the responsible candidates for the obtained nanoparticles [28–31].

The IR spectrum of sample N contains the intense bands characteristic of spinel ferrites, but also weak vibration bands characteristic of the carboxylate groups from the eucalyptus extract and traces of nitrate anion (Table 1). After the treatment at 800 °C/1 h (N-800 sample), these bands disappear and only the bands of cobalt ferrite in the 600–400 cm<sup>-1</sup> region, assigned to the stretching vibrations of the metal–oxygen bond [4,5], are observed (Table 1).

Eucalyptus Leaves Dry Extract	Ν	N-800	Assignement
3382 vs, br	3419 vs, br	-	vOH/H <sub>2</sub> O
2915 m, sh	-	-	$vCH_{2 asym}$
2850 w, sh	-	-	$\nu CH_{2 sym}$
-	1635 s	-	vOH in water
1616 vs	-	-	$\nu COO^{-}$ asym
1396 m	1384 m	-	$\nu COO^{-} sym / \nu NO_{3}^{-}$
1072 s	-	-	vC-O-C <sub>sym</sub>
-	1031 w	987 w	-
-	578 s	573 vs	vM-O spinel
	486 w	490 m	vM-O spinel

Table 1. The characteristic bands of eucalyptus leaves dry extract and synthesized CoFe<sub>2</sub>O<sub>4</sub> samples.

w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad.



**Figure 2.** SEM micrographs at different magnifications:  $10,000 \times (\mathbf{a},\mathbf{d})$ ;  $200,000 \times (\mathbf{b},\mathbf{e})$ ;  $1,000,000 \times (inset in \mathbf{b})$ ; and particle size distributions ( $\mathbf{c},\mathbf{f}$ ) of the CoFe<sub>2</sub>O<sub>4</sub> powders obtained by wet ferritization using eucalyptus extract, as prepared ( $\mathbf{a}-\mathbf{c}$ ), and calcined at 800 °C/1 h ( $\mathbf{d}-\mathbf{f}$ ).

Additionally, the cobalt ferrites obtained by wet ferritization were studied by Raman vibrational spectroscopy. The Raman spectra (Figure 3) of the N and N-800 powders present six vibrational modes at 683, 615, 562, 494, 460, and 325 cm<sup>-1</sup>. After calcination at 800 °C, N-800 shows very similar Raman spectra, including the same vibrational modes and relative intensities, indicating the same crystalline structures and types of bonds in N and N-800, so our discussion is valid for the Raman spectra of both materials. The measured spectra correspond to spinel-type structures. Broad Raman peaks indicate the presence of disorder and defects within the crystal structure. Group theory predicts five active Raman modes for spinel-type structures (A<sub>1g</sub> + E<sub>g</sub> + 3F<sub>2g</sub>) which are typically observed at Raman shifts from 200 to 800 cm<sup>-1</sup> [36–38]. The highest-frequency A<sub>1g</sub> mode at 683 cm<sup>-1</sup> is assigned to the symmetric stretching vibrations of the oxygen atoms with respect to the metal ion in the tetrahedral sites, a mode that can be also described as tetrahedral breath mode [36,39]. Spinel inversion is usually considered the cause for the appearance of an additional A<sub>1g</sub>

peak in the Raman spectra, observed as a weak feature at 615 cm<sup>-1</sup>, according to [39]. The  $F_{2g}$  mode at 562 cm<sup>-1</sup> is very weak. The strong  $F_{2g}$  band at 450–500 cm<sup>-1</sup>, that corresponds to the bending vibrations of oxygen atoms in the tetrahedral sites, shows two distinct peaks at 494 and 460 cm<sup>-1</sup>, indicating different local environments experienced by the Fe<sup>3+</sup> ions in the tetrahedral sites, leading to distinct vibrational frequencies. The  $E_g$  mode, associated with the stretching vibration of the octahedral units, is observed at 325 cm<sup>-1</sup>.



**Figure 3.** Raman spectra of  $CoFe_2O_4$  powders obtained by wet ferritization using eucalyptus extract, as prepared (N sample), and calcined at 800 °C/1 h (N-800 sample).

## 3.4. Thermal Analysis

The thermal behavior of the  $CoFe_2O_4$  obtained by wet ferritization (N sample) was followed to confirm the presence of the functional groups of eucalyptus extract on the particles' surface (Figure 4).





The degradative-oxidative process can be grouped in three temperature intervals. The first step between room temperature and 180 °C is associated with an endothermic effect on the DSC curve (weight loss ~20.5%). The gases evolved in this step indicate water as the main product together with traces of CO<sub>2</sub>, and, also, the less stable/volatile components (Figure 5) from eucalyptus extract [40]. The second mass loss step (~9%), between 180 and 320 °C, is accompanied by a strong exothermic effect on the DSC curve. This step corresponds to the total oxidation of the organic part to CO<sub>2</sub> and H<sub>2</sub>O. The carbonaceous residue from eucalyptus extract is eliminated in the third step between 320 and 700 °C (weight loss ~2.5%). The thermal decomposition is complete below 700 °C with the formation of CoFe<sub>2</sub>O<sub>4</sub> (ox%~68%). Corroboration of these results with the IR spectrum of the N sample suggests the presence of organic components from the plant extract on the prepared cobalt ferrite.



**Figure 5.** FTIR 3D diagram for the evolved gases from thermal analysis of N sample (**a**) and its projection in the wavenumber/temperature plane, indication of temperature intervals in which  $H_2O$ ,  $CO_2$ , and CO are identified (**b**); the absorbance increases from light blue to orange-yellow.

The participation of the eucalyptus extract to the cobalt ferrite synthesis is indicated by the difference observed in the thermal analysis of the N sample vs. eucalyptus extract powder (Figures S2 and S3). While in the case of the N sample the oxidation reactions of organic traces take place up to 350 °C, for the eucalyptus extract the thermal analysis indicates a strong oxidation process between 435–680 °C, when high quantities of CO<sub>2</sub>, H<sub>2</sub>O, and hydrocarbon fragments are eliminated (Figure S3). This different thermal behavior of the organic part can indicate a dramatic change in composition of eucalyptus extract due to its participation in the process of cobalt ferrite synthesis.

#### 3.5. Magnetic Measurements

The hysteresis curves corresponding to the two samples, N and N-800, respectively, are shown in Figure 6.

Both samples are magnetically ordered at both low and room temperatures and exhibit ferromagnetic behavior. The samples were measured starting from the demagnetized state (virgin curve visible especially for sample N-800, Figure 7b) at B = 0. At a low applied magnetic field, the magnetization process is reversible, magnetic moments being aligned along an axis of low magnetization. When the magnetic field increases, magnetization becomes irreversible, the magnetic moments aligning with the direction of the applied field. Magnetizations increase rapidly at low fields (0–10,000 Oe), tending to saturate as the magnetic field strength increases. The saturation magnetization values obtained at 10 K are 45.85 emu/g for sample N and 73.16 emu/g for the calcined sample N-800. These values are lower than the saturation magnetization of bulk cobalt ferrite, 93.9 emu/g when measured

at 5 K, and 80.8 emu/g at ambient temperature [41], but comparable to the values obtained on nanoparticles synthesized by wet chemistry [42,43]. The coercive magnetic fields (Hc) obtained at 10 K were 6566 Oe for the N sample and 13,372 Oe for the N-800 sample and much lower at room temperature, respectively 107 Oe for the N sample and 2223 Oe for the N-800 sample. These values can be correlated with the particle sizes, i.e., for the N sample we obtained the smallest crystallite size in XRD (~3 nm) and the smallest coercive field, while for the heat-treated sample, N-800, the highest value for both crystallite size (~20 nm) and coercive field was obtained. Another important aspect is the coercivity value at 300 K of the N sample; it is very small, but not zero. This means that a small fraction of the nanoparticles are not superparamagnetically relaxed even at this temperature. This behavior is similar to that reported by Palade et al. [42]. The ratio (R = Mr/Ms) between remanent magnetization (Mr) and magnetization at saturation (Ms) was also calculated. At 10 K, the obtained values for R were 0.49 for the N sample and 0.89 for the N-800 sample. According to the Stoner–Wohlfarth model [44], for an ensemble of non-interacting single magnetic domain nanoparticles with uniaxial symmetry, under the condition of a random distribution of easy magnetization axes, this factor should be 0.5. It has also been reported that, for spherical nanoparticles with cubic magneto-crystalline anisotropy, the value of R is 0.83 [45]. In our case, the corresponding R value for N-800 sample clearly shows the existence of a cubic magnetic anisotropy provided by the magnetocrystalline anisotropy of  $CoFe_2O_4$  that exceeds the shape anisotropy effect. The N sample, with R of 0.49, is characterized by a single non-interacting magnetic domain.

Figure 7 shows the magnetizations as a function of temperature of the two samples measured in two different modes: zero field cooling (ZFC) and field cooling (FC) under an applied magnetic field of 0.05 T.



**Figure 6.** Hysteresis curves at selected temperatures in the range of 10–300 K for samples: N (**a**) and N-800 (**b**).

In ZFC mode, the two samples were cooled in a zero magnetic field to 5 K. At this temperature, a magnetic field of 500 Oe was applied and the magnetic moments were measured as a function of temperature in the process of sample heating. In FC mode, samples were cooled in an applied external magnetic field (B = 0.05 T), measuring the evolution of magnetic moments as a function of temperature. It can be seen that the two curves coincide with each other at room temperature, but as the temperature decreases, they begin to separate. Both ZFC curves show a maximum at 140 K representing the blocking temperature ( $T_b$ ). It is known that  $T_b$  depends on several factors, such as: particle size, effective anisotropy constant, applied magnetic field, experimental measurement time, etc. If the measured sample has almost equal particle size (small particle distribution), then the blocking temperature will be almost the same for all particles. This is also the case of

our samples that have almost the same particle distribution ( $\geq$ 5 nm), hence the same T<sub>b</sub>. Differences may occur at large particle distributions ( $\geq$ 100 nm). Over this temperature, FC curves increase as the temperature decreases. At this temperature, the nanoparticles have enough thermal energy to overcome the magnetic energy barrier separating the two possible magnetic orientations of the magnetic moments.



**Figure 7.** Temperature dependences of magnetic moments (ZFC and FC measurements) for samples: N (a) and N-800 (b). Measurements were carried out in magnetic field B = 0.05 T.

## 3.6. Antimicrobial Activity

The results of the qualitative assay indicated that the two  $CoFe_2O_4$  nanoparticles exhibited relatively similar antimicrobial activity against four of the tested strains, including two Gram-negative bacterial strains (*P. aeruginosa* and *E. coli*), one Gram-positive bacterial strain (*S. aureus*) and the fungal strain (*C. albicans*), the average diameters of the growth inhibition zones ranging between 9.5 and 7.25 mm, with the highest and respectively lowest efficiency recorded for N against *P. aeruginosa* and *S. aureus*, respectively. None of the tested nanoparticles inhibited the growth of *E. faecalis* on the solid medium (Figure 8).



**Figure 8.** The results of the qualitative assay of the antimicrobial activity quantified by the growth inhibition zone diameters (mm).

Taking into account the limitations of the qualitative assay consisting in the unknown diffusion patterns of novel compounds in the solid medium, making it impossible to have a glimpse into the concentration–activity relationship, we have further tested different binary concentrations of the obtained nanoparticles (from 5 to 0.0195 mg/mL) in liquid medium assays, in order to establish quantitative parameters of their antimicrobial and anti-biofilm activity, respectively the MIC and MBIC values.

The results of the quantitative assay revealed that in all cases the MIC and MBIC values ranged from 5 to 10 mg/mL (Figure 9), suggesting a good efficiency of these nanoparticles both against planktonic and sessile microorganisms, due probably to the good penetration of the obtained materials through the protective biofilm matrix. The *E. faecalis* strains were indeed the most resistant, both in planktonic and biofilm growth states, followed by *S. aureus*, particularly in the biofilm growth state. These results suggest that the Grampositive strains seem to be more resistant to the obtained nanoparticles, compared to the Gram-negative bacteria and fungal strain, probably due to differences in the structure of the bacterial wall. The obtained nanoparticles are probably better interacting with the outer membrane of the Gram-negative bacteria, than with the thick peptidoglycan cellular wall of the Gram-positive ones through the carboxylate groups. Once adhered to the Gram-negative bacteria outer membrane, they will destabilize it and favor the microbial cell lysis. The qualitative assay shows that N nanoparticles are more active than N-800 against planktonic and biofilm embedded *E. coli* as well as against planktonic *S. aureus* strain.



**Figure 9.** The results of the quantitative assay of the antimicrobial activity against planktonic and biofilm growing strains quantified by the MIC and MBIC (mg/mL) values.

#### 4. Conclusions

In this study, a facile and eco-friendly method of plant-based synthesis of  $CoFe_2O_4$ using eucalyptus leaves extract is reported for the first time in the literature. XRD patterns revealed  $CoFe_2O_4$  with a face-centered cubic spinel structure. SEM analysis shows that wet ferritization using eucalyptus extract results in disordered aggregates consisting of noncrystallites sized below 10 nm, in agreement with the average crystalline size measured from diffraction patterns. Vibrational Raman spectroscopy confirms the formation of a  $CoFe_2O_4$  spinel phase and evidences a high degree of spinel inversion. Thermogravimetric analysis also indicated three steps weight loss for the functional groups-coated  $CoFe_2O_4$ , confirming the presence of the organic components from the plant extract. The magnetic behavior of the two samples is strongly influenced by particle size and shows a rapid increase in magnetization at low fields with saturation at 5 T. The existence of a cubic magnetic anisotropy provided by the magnetocrystalline anisotropy of this material has been demonstrated. The blocking temperature is similar for both samples and coincides with that reported on nanoparticles of this type processed by other chemical methods. The results of the qualitative and quantitative bioassays confirm their potential for the development of novel antimicrobial agents, active both against planktonic and biofilm embedded microbial cells, being particularly efficient on the Gram-negative and fungal strains. Eucalyptus extract can be a valuable natural resource in the synthesis of cobalt ferrite. Plant-based synthesis methods are opening new ways to obtain various materials by cleaner pathways.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/coatings13071250/s1, Figure S1: FTIR spectra of the samples; Figure S2: Thermal analysis of dry eucalyptus extract; Figure S3: The FTIR 3D diagram for the evolved gases from thermal analysis of eucalyptus extract and its projection in the wavenumber/temperature plane.

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