A preliminary study of oxides of Fe doped with Ba, Co, Cu and synthetized by the citrate sol–gel combustion route

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Abstract. In the present work we report the synthesis of mixed ferrites doped with Co²⁺, Cu²⁺ and Ba²⁺ cations, using citrate sol–gel combustion route in air atmosphere, at 950 °C for 3 hours, produced substituted M-type barium ferrites powders particles with crystallite sizes varying between 145 and 155 nm. The percentages of yield obtained were on average 42%. The synthesized ferrites were characterized by techniques such as powder X-ray diffraction, evidencing the formation of M-type barium hexaferrite and copper and cobalt substituted M-type barium ferrite with hematite in smaller proportion. The possible growth of M-type barium ferrite with copper and cobalt may be due to a larger size of the cobalt atom with respect to copper and that a higher proportion of cobalt salt was used in the synthesis route. Increase in the metal ion substituted content leads to a decrease in the lattice strain and may be responsible for an increase in the crystallite size because greater tensile strain leads to elongation of the particles. The particle size of the synthesized ferrites differs significantly when they are doped, with Ferrite doped with copper having the smallest particle size compared to Ferrite doped with cobalt. We also performed spectroscopic analyses, RAMAN that showed, the substitution of cooper or cobalt in the M-type barium ferrite powders particle leads to a minor intensity of resonance band when compared with the parent compound and the differences between Fe³⁺, Cu²⁺ and Co²⁺ ions in a tetrahedral coordination is their ionic radii. The increase in the ionic radii causes a local distortion and vibrational bands of distorted polyhedra in substituted M-type barium ferrites. The chemical composition of this sample was determined as Ba₁.0Fe₁₁.83O₁₉.2₂, Ba₁.₀Co₁.₀₂Fe₁₁.₀₁O₁₈.₃₅ and Ba₁.₀₂Cu₁.₅₆Fe₁₁.₃₅O₁₈.₂₆ using an AAS device. Both are very close to the theoretical formula. The influence of the synthesized ferrite samples was explored in the ozonation of a dye of unknown chemical structure. The results obtained show that the ink could be decolorized by applying oxidation by ozonation, however, when substituted M-type barium ferrite is added, the discoloration increases when this is doped with copper and cobalt, being higher using this last ferrite. The degradation process by ozonation presented in this work, carried out in the presence of copper and cobalt substituted M-type barium ferrites, would constitute an example of technology for the environment.
1. Introduction

M-type barium ferrite in general have a molecular formula BaFe$_{12}$O$_{19}$, it has a crystalline structure of magnetoplumbite [1]. They have been used as permanent magnets because of their excellent properties, such as coercivity, magnetic anisotropy [1]. The traditional process for obtaining M-type barium ferrites powders particles is the reaction in the solid state. However, other synthesis methods such as Sol-gel [2,3], coprecipitation [4], pyrolysis [5], hydrothermal [6], glass crystallization [7], ammonium nitrate melt [8,9] and oxidation in nitric acid techniques [10,11]. A widely used method the combustion [12-16] is a reliable, fast and efficient method that, using transition metal salts and metals from the second group, allows obtaining ferrites with a good particle size, [17] in this method, citric acid forms complexes with the metals where there are five coordination structures with equal probability of formation; the kinetics of the reaction will depend on the degree of dissociation of the citric acid and the pH. [18] Among the most used fuels reported in the literature are: triazine tetraformate, maleic hydrazide, urea and citric acid. [19]

Another factor to take into account, which influences the formation of ferrites, is the addition of a coadjuvant, which forms a polymeric network of coordination complexes, in order to provide stability to the system in the combustion and calcination stages.

The literature mentions the use of polyalcohols such as propylene glycol and glycerin, which facilitates esterification with the free carboxylate groups of citric acid. [18]

With the development of human societies, massive urbanization has led to the evolution of extensive industrialization, as a result large amounts of industrial pollutants arise from the use of natural resources, including organic compound volatiles (VOCs), chlorinated solvents, fertilizers, dyes, phenols. Among these, the presence of toxic dyes in wastewater is of great concern since these are biologically and chemically stable; Therefore, it is difficult to eliminate them by natural processes of degradation.

In the last two decades the synthesis of ferrites has been a subject of study, due to the variety of applications [20] of these materials such as in the manufacture of permanent magnets, data storage, magnetic fluids and microwave devices. [21] In addition to having application in biomedicine due to its biocompatibility. [22] It is also important to highlight its catalytic applications in oxidation reactions, in order to selectively reduce some contaminant. [23-30]

The advanced oxidative processes (AOP) can be used efficiently for the degradation of organic contaminating molecules. These processes are based on the generation of hydroxyl radicals, which are highly reactive and can degrade many organic compounds.

Among the various existing methodologies of AOPs, is the ozonation process has been highly efficient in the degradation of several recalcitrant organic pollutants. [31] Chemical oxidation with ozone has a high oxidative character, which is a fundamental property for the treatment of effluents containing recalcitrant compounds, achieving satisfactory efficiencies in the decomposition of organic pollutants. The use of solid materials in the ozonation process promotes significant improvements in the degradation of organic matter. In addition, the solid material can produce more potent and non-selective oxidative radicals, allowing a high rate of degradation through ozonation.

On this basis, copper and cobalt substituted M-type barium ferrite powders particles with Fe/Ba molar ratio 4, could be used to catalyze ozonation processes. In addition, the utility magnetic properties substituted M-type barium ferrites could help recycle materials via the external magnetic field. The substituents of the ferrites are very important since they determine the variation of the physical, magnetic and electrical transport properties. [19]

To the best of our knowledge, there are few reports presented in the literature for molar ratios Fe/Ba < 10, particularly for the sol–gel combustion route [32-33]. Furthermore, no results were reported from the preparation and application of copper and cobalt substituted M type barium ferrite powder particles with Fe/Ba ratio of four, in advanced oxidation processes with ozone for dye degradation.

Therefore, the present investigation addresses the synthesis of copper and cobalt substituted M type barium ferrite powder particles with Fe/Ba ratio of 4, for the sol–gel combustion route. In a
preliminary way, the influence of the ferrite samples has been tested in the ozonation of a toxic ink of unknown chemical structure. The effect was evidenced by visible ultraviolet spectroscopy technique.

2. Materials and Methods

2.1. Synthesis
Barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Cobalt chloride$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, Copper chloride $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, GR grade), Ferric chloride anhydrous, $\text{FeCl}_3$ (Sigma Aldrich, $> 98$ % purity), Citric acid, $\text{C}_6\text{H}_8\text{O}_7$ (Merck, GR grade), propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$) brand Merck and $\text{NH}_4\text{OH}$ (Merck, GR grade) were used as starting materials.

Copper and Cobalt substituted $M$-type barium ferrite powders particles were synthesized using the citrate sol-gel method [16]. In order to achieve the molar ratio of $\text{Fe}/\text{Ba}= 4.0$, appropriate amounts of iron chloride, barium chloride and cobalt chloride or copper chloride were dissolved in a minimum amount of deionized water with conductivity of 0.05 $\mu\text{scm}^{-1}$. [34] Citric acid in the molar ratio 1:1 to total moles of metal ions was dissolved in equal amount of deionized water separately. Ammonia was added to adjust the pH value to 7. Subsequently, it heated for half an hour at 50 °C and 10% of the volume of propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$) brand Merck added to the solution. It was evaporated at 70 °C and then carried to the muffle for two hours at 250 °C, then it was macerated for 10 minutes and calcined for three hours at 950 °C. Thus substituted $M$-type barium hexaferrite powders particles were obtained. Powders having $\text{Fe}/\text{Ba} = 4.0$ were washed with diluted HCl [35]. Finally, powders were washed with deionized water several times and dried at 100 °C in a furnace.

2.2. Characterization
To obtain the powder X-ray diffraction patterns (DRX), a Panalytical Empyrean device used in a flush beam configuration with a scintillation detector and a parallel plate collimator. The measurements were made from 10 to 90 ° at an angle of 2θ with a sampling time of 0.02 seconds and a step size of 0.0040 °/step using Co radiation with a wavelength of $K_{\alpha 1} = 1.7890$. The data taken at the Universidad Militar de Nueva Granada. The FTIR-ATR spectra measured in a JASCO FT / IR-4100 device with Fourier transform, with a resolution of 4 cm$^{-1}$ and ATR source (PRO450-S), a scan of 650 - 4100 cm$^{-1}$ with 512 scans. The data were taken in the teaching and research laboratory of the chemical engineering school of the Universidad del Valle. The RAMAN spectra were measured with a DXR Smart Raman device, with a range of 50 to 3370 cm$^{-1}$, containing a refrigerated CCD detector (-51 °C), with a diode laser of (785 nm). The data taken at the INCITEMA (Institute for Research and Innovation in Materials Science and Technology) at the Universidad Pedagógica y Tecnológica de Colombia (UPTC) in Tunja. The thermo gravimetric analysis and differential scanning calorimetry (TGA-DSC) performed with a Discovery SDT650 TA instrument with a temperature ramp of 10 °C/min, up to 1300 °C. Concentrations of the barium and iron were determined using AA9100 Shimadzu. The data taken in the organic and inorganic chemical synthesis laboratory of the Universidad Santiago de Cali (USC).

The tests were carried out in a cylindrical reactor 35 cm high and 10 cm in diameter with a capacity of 500mL, which contains a porous diffuser that allows the ozone to be distributed evenly in the effluent. Figure 1 shows a photograph of the equipment used for ozonation, the hose located at the top enters the ozone and the side hose corresponds to the ozone outlet after reacting with the contaminant, the ozone received in a water trap.
3. Results and discussion

Figure 2 shows an X-ray diffraction pattern of M-type barium ferrites after being sintered at 950 °C for 3 hours. XRD pattern of the samples, is a modification of M-type barium ferrite system by the addition of Co and Cu element into Fe respectively. Phase identification of raw data was carried out by using software of XRD Match! 3, Version 3.7.0.124, that refer to COD based on the information of peak position and intensity as shown in Figure 2.

From the matching peak using software for further identification, the phase of M-type barium ferrite, Copper and Cobalt substituted M-type barium ferrite powders particles and α–hematite were obtained, which respectively refer to the research findings of Obradors et al. [36], Wangchang et al. [15], Vadivelan et al. [3], Finger et al. [37] and Sözeri et al. [33].

![Figure 1](image1.png)

**Figure 1.** (a) Ozonation reactor. (b) In the reactor the ferrite is deposited with the dye to be treated dissolved in water $t = 0$ min. (c) Advance of the reaction of process, $t = 10$ min. Input flow at 50% 1L min$^{-1}$, $V = 200$ ml

![Figure 2](image2.png)

**Figure 2.** DRX of (a) M-type barium ferrite (b) Copper M-type barium ferrite (c) Cobalt M-type barium ferrite
Figure 2-(a) shows the XRD pattern of the sample after heat treatment. The sample shows very thin peaks, indicating the fine nature and small crystallite size of the particles. The result agrees with a M-type barium ferrite BaFe$_{12}$O$_{19}$ phase refer to the research findings of Obradors et al. [36], and the weak peaks observed at d-values of 2.94 (D$_{110}$), 2.78 (D$_{107}$), 2.62 (D$_{114}$), 2.42 (D$_{203}$), 2.23 (D$_{206}$), 2.12 (D$_{208}$), 1.66(D$_{217}$), 1.62 (D$_{201}$) and 1.47 (D$_{220}$)Å (peaks marked as ‘F’), with preferred orientation along (D$_{107}$) and (D$_{114}$) planes, correspond to (major phase hexagonal structure) [15, 21, 33, 36].

Figure 2-(b) and 2-(c) in addition to the barium ferrite signals, other signals that corresponded to α–hematite Fe$_2$O$_3$ phase refer to the research findings of Finger et al. [37], with weak peaks observed at d-values of 2.69 (D$_{104}$), 2.51 (D$_{110}$), 1.69 (D$_{116}$) Å (peaks marked as ‘H’), correspond to minor phase [33]. Formation of impurities like hematite (α–Fe$_2$O$_3$) is lower compared to that of copper (b) and cobalt (c) substituted M-type barium ferrite. It confirms that the reaction was not complete and that the dilute HCl wash was not sufficient.

At low temperatures BaFe$_2$O$_4$ is formed and an increase in temperature around 950 °C allows the formation of M-type barium ferrite. At temperatures below 950 °C, hematite and barium oxide will form barium monoxide which will then diffuse into hematite at 950 °C to form M-type barium ferrite. When sintering the sample at 950 °C, the fraction of M-type barium ferrite will rise while the amount of hematite still remains [38-40]. That is the reason by which we could see that the hematite phase still occurs figure 2 (b-c).

Figure 2 shows the XRD spectrum for the powder samples obtained by the sol-gel citric combustion method. Data were obtained using Co radiation with a wavelength of Kα1 = 1.78900. However, these peaks correlate very well with data reported in literature for M-type ferrites substituted with cobalt [16] and copper [3]. The characteristics peaks confirm the crystal structure is hexagonal according to [16]. The XRD patterns of the ferrite samples show characteristic diffraction peaks corresponding to the M-type barium ferrite structure, having point group P63/mmc, indicating that the crystal structure does not transform and remains hexagonal magnetoplumbite after substitution with copper or cobalt ions.

Table 1 shows the particle size of the synthesized M-type barium ferrite sample (a) differ significantly when they are doped with copper and cobalt. This is due to the size of the copper atom (157 pm) and the cobalt atom (167 pm). It is also observed with barium ferrites whose atomic radius is 268 pm [57] being sample (b) the one with the smallest particle size compared to sample (c). Furthermore, with an increase in the concentration of cobalt. The intensities of the highest signals depend on the number and type of atomic centers of reflection that exist in each group of planes and the relative concentrations of the different planes, in other words, depend on the nature of each ferrite synthesized. The intensity of the peak is greater for the ferrite that contains the larger bundles such as barium (268 pm) and cobalt.

**Table 1.** Crystallite size, D (nm); Lattice parameter (a, c); Elastic strain ε and Crystalline size of the copper and cobalt substituted M-type barium ferrites powders particles synthetized at 950°C.

| Sample | Crystalline size (nm) | a (Å)       | c (Å)       | Elastic strain ε (10$^{-3}$) |
|--------|-----------------------|-------------|-------------|-----------------------------|
|        |                      | W–H method |             |                             |
| (a)    | 146.7                 | 5.885       | 23.122      | 1.11                        |
| (b)    | 152.4                 | 5.873       | 23.131      | 1.09                        |
| (c)    | 161.8                 | 5.881       | 23.119      | 1.12                        |

Lattice parameters (a and c), were calculated by using equations (1) respectively and reported in Table 1 [3, 44]

\[
\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 +hk + l^2}{a^2} \right] + \frac{l^2}{c^2} \tag{1}
\]
“d” denotes the d spacing of the XRD pattern and h, k and l are the Miller indices. It is clear, from table 1, that the lattice parameters are almost unchanged with either Cu²⁺ and Co²⁺ addition or 950 °C calcination temperature. This indicates that Cu²⁺ and Co²⁺ occupies only interstitial places in M-type barium ferrite powder particle without entering the structure and that the calcination temperature has no effect in changing the crystal structure of the phase.

Using the Williamson and Hall method, the crystalline size of the powder samples is found [3, 41]. This method considers that the widening of the diffraction profiles was caused by the grain size and the strain tension, treating them as additive phenomena: \( \text{size} + \text{strain} \). It is a method that allows to obtain the apparent size \( D \) of the particle by means of the equation (2)

\[
\beta_{hkl} \cos \theta_{hkl} = 4 \varepsilon \sin \theta_{hkl}
\]

\( K \) is known as the constant (0.9), \( \lambda \) is the wavelength of the X-ray source (1.78901 Å), \( D \) is the crystalline size, \( \beta \) be the full width half maximum of the specified diffracted peak, \( h, k, \) and \( l \) is the miller indices and \( \varepsilon \) is the micro strain. The elastic strains of the samples also calculated by the given expression (3) [3, 42]

\[
\varepsilon = \frac{\beta}{2 \cot \theta}
\]

Plot between \( \beta \cos \theta \) and \( 4 \sin \theta \) known as W-H plot gives the information of strain [43]. The sign of the slope gives the nature of strain. Positive slope corresponds to tensile strain whereas negative corresponds to compressive strain and the cut with the axis y "provides the particle size \( D \). The values of induced strain can be calculated by using (2).

Table 1 shows the elastic tension whose value decreased with the substitution of copper Figure 2-(b) and cobalt Figure 2-(c) respectively on the structure of M-type barium ferrite. It reveals that the possible growth of M-type barium ferrite with copper and cobalt may be due to a larger size of the cobalt atom with respect to copper and that a higher proportion of cobalt salt was used in the synthesis route. It is clearly seen that the particles experience a tensile strain [43]. Increase in the metal ion substituted content leads to a decrease in the lattice strain, Table 1. However, when concentration of cobalt increase, the lattice strain increases. This strain may be responsible for an increase in the crystallite size because greater tensile strain leads to elongation of the particles [45]. Figure 2 shows the diffraction peaks (D_{105}) and (D_{114}) and their displacement due to introduction of Cu and Co atoms in M-type barium ferrite matrix. In Figure 2-(b) and 2-(c) the peak related to Cu and Co sample is shifted to the left and has lower intensity that the corresponding peak for M-type barium ferrite pure.

To investigate the formation of ferrite phases, calcined sample spectra were recorded via infrared spectral analysis (FTIR) in the average IR range, 4000 cm⁻¹ to 500 cm⁻¹.

According to the results shown in Figure 3. The absorption bands between 544 and 468.57 cm⁻¹ assigned to the vibration of the bond between the oxygen atom and the metal ions (M–O), confirming the formation of hexaferrite [43]. In Figure 3-(b), the deep fascination bands Cu–O and Fe–O are present between the frequency ranges of 550–900 cm⁻¹ [3]. The peaks between 950 and 1070 cm⁻¹ are associated with vibrations of M–O–M (M = Ba²⁺ or Fe³⁺) in the orthorhombic crystalline structure of the ferrite and the peaks between 750 and 650 cm⁻¹ are related to stretching of the vibrations of Ba²⁺–O²⁻ and Fe³⁺–O²⁻ at the octahedral and tetrahedral sites for the three synthesized barium ferrites. [46-48], no signals due to vibration were observed in the 630–640 cm⁻¹ range of metal-oxygen bonds of Fe₂O₃ [49]. The peak at 1630.34 cm⁻¹ and the broadband absorption at 3434.51 cm⁻¹ are attributed to the vibration of bending and stretching of the O–H bond associated with the adsorbed water. There are two weak absorptions around 1400 and 1600 cm⁻¹ corresponding to the presence of a small amount of residual carbon in the samples as generally observed in the case of samples prepared by the citrate precursor method.
From figure 3, the peaks position of the pure sample M-type barium ferrite is not altered or shifted after copper or cobalt substituted. This reflects that the structure was not perturbed by the presence of copper or cobalt in its matrix, which is consistent with XRD results. Moreover, the influence of Co concentration on M-type barium ferrite structure is displayed in figure 3-(c). It is obvious, from figure 3-(c), that the peaks position of the sample is slightly affected by increasing the concentration and size atomic of copper or cobalt substituent. The results indicated that an increase in the amount of replacement ions caused a decrease in vibration frequencies of the Fe-O band at the tetrahedral site due to the replacement of Cu$^{2+}$> Co$^{2+}$ ion heavier than the Fe$^{3+}$ ion in the tetrahedral region. This was consistent with that reported for hexagonal phases of barium ferrites that coexist with hematite along with other metastable phases [50].

The RAMAN spectra presented in figure 4 show peaks of single phases of M-type barium ferrite, with no presence of any additional phase or an impurity.
The peaks at 713 and 684 cm\(^{-1}\) can be assigned to \(A_{1g}\) vibrations of Fe-O bonds at the tetrahedral \(4f_1\) and bipyramidal \(2b\) sites, respectively.\(^{[51-53]}\) Other peaks at 614, 512, 467, 453 cm\(^{-1}\) are due to \(A_{1g}\) vibrations of Fe-O bonds at the octahedral \(4f_2\), \(2a\), and \(12k\) sites, whereas peak at 409 cm\(^{-1}\) is due to \(A_{1g}\) vibration at the octahedral \(12k\) dominated site. The peaks at 527, 285 and 212 cm\(^{-1}\) were due to \(E_{1g}\) vibrations, while the peak at 335 cm\(^{-1}\) was due to \(E_{2g}\) vibration. Figure 4-(b) and 4-(c) show some characteristic peaks of M-type barium ferrite phase. Other peaks in different positions are found on the spectrum. The peaks of \(\alpha\)-Fe\(_2\)O\(_3\) appear in the spectral range 200-650 cm\(^{-1}\) where two main signals fall near 225, and 612 cm\(^{-1}\)\(^{[54-55]}\). From the result of Raman Spectrum, the substitution of cooper or cobalt in the M-type barium ferrite powders particle leads to a minor intensity of resonance band when compared with the parent compound and the differences between Fe\(^{3+}\) and Cu\(^{2+}\) and Co\(^{2+}\) ions in a tetrahedral coordination is their ionic radii. The increase in the ionic radii causes a local distortion and vibrational bands of distorted polyhedra in substituted M-type barium ferrites.

The synthesized ferrites were analyzed by TGA-DSC, a weight loss of approximately 3 to 4\% in 900 °C was evidenced due to a phase transition, since it is close to the calcination temperature results not showed. These transitions can be attributed to the weight loss corresponding to an oxygen molecule released.\(^{[56]}\) It is also possible to observe the thermal stability of synthesized ferrites up to about 800 °C, relevant data for the different applications of ferrites.

For the study of the influence of ferrites by ozonation substituted M-type barium ferrite (a), (b) and (c) respectively were used, an unknown toxic ink was used as catalyst in the degradation. The ozonation process was carried out in a cylindrical reactor where the percentage and the inlet flow of ozone were controlled variables, the time was specified according to the appreciable color change at 10 minutes, corresponding to the smallest amount of time in which a change is observed, was carried out at room temperature since at temperatures higher or lower than the mentioned one a lot of foam is generated on the surface of the catalyst. By introducing the magnetic catalyst to the ozonation process the generation of hydroxyl radicals accelerates, inducing the rapid reaction of molecular ozone with aromatic and unsaturated compounds, achieving reductions in only 10 minutes of treatment.

Figure 5 shows FESEM micrographs of nanostructured particles with average particle size 160 nm, and irregular hexagonal. Structured particles in the form of agglomerated platelets in the samples of barium ferrite doped with copper figure 5-(a) and cobalt figure 5-(b).

Figure 5. FESEM images of barium ferrite doped with (a) copper and (b) cobalt, prepared at 3 hours of calcination at 950 °C. UV spectra: (a) water + color, (b) water + color + ozone, (c) [(b) + CuBa ferrite], (d) [(b) + CoBa ferrite]. Insert shows decrease in absorption signal near 254 nm
In Figure 5, the absorption signal of the pilot test of degradation of an unknown ink was shown by ozonation using previously synthesized ferrites [58]. Both doped ferrites showed catalytic power during the ozonation experiment. However, it was observed that ferrite doped with Cobalt has a greater effect on the ink. The decrease of the absorption band near 254 nm can be associated with the rupture of aromatic rings that would reveal a degradation of the ink of unknown origin.

4. Conclusion
The characterization of mixed ferrites performed by DRX, RAMAN, FTIR-ATR, TGA-DSC and FESEM techniques, showed that the synthesis of ferrites by the combustion method, using metal chloride salts as precursors, generated the proposed ferrites, in addition to the presence of hematite. The particle sizes of the synthesized ferrites described in Table 1 are in nanometric levels and are between 145 nm and 160 nm. Thus, to the best of our knowledge, it has been shown for the first time that high quality copper and cobalt substituted M-type barium ferrite powders particle can be prepared by Fe/Ba = 4 molar ratio in the sol–gel method. The chemical composition of this sample was determined as Ba$_{1.0}$Fe$_{11.83}$O$_{19.22}$, Ba$_{1.0}$Co$_{1.02}$Fe$_{11.01}$O$_{18.35}$ and Ba$_{1.02}$Cu$_{0.56}$Fe$_{11.35}$O$_{18.26}$ using AAS device, that is very close to the nominal composition. Although the chemical composition of the ink studied in this work is not available, it cannot be ignored that the chemical structure of any substance constitutes a determining factor in relation to the degradation process and the affinity of each molecule to adsorption on the surface of the ferrite when this process is present. The results obtained show that the ink could be discolored by applying oxidation by ozonation, however, when barium ferrite is added the discoloration increases when it is doped with copper and cobalt, being greater using the latter ferrite. The degradation process through ozonation presented in this work, carried out in the presence of barium ferrites doped with copper and cobalt, would constitute an example of technology for the environment.

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