Síntesis y caracterización de partículas de hematita (α-Fe$_2$O$_3$) obtenidas por tratamiento térmico de FeSO$_4$ con azúcar

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Resumen

Las partículas de hematita fueron sintetizadas mediante tratamiento térmico de FeSO$_4$ con diferentes concentraciones de azúcar. Para la síntesis utilizamos una mezcla de sulfato ferroso (FeSO$_4$) y azúcar simple en polvo, esta mezcla se mantuvo en un horno a 600^0 C durante 14 horas. Se trabajó con proporciones de 1 g y 3 g de FeSO$_4$ con 0.1 g, 0.2 g y 0.3 g de azúcar respectivamente. El análisis de las propiedades magnéticas macroscópicas de las muestras se realizó con un magnetómetro de campo alternante. Para la caracterización estructural de las muestras se utilizó las técnicas de difractometría de rayos X (DRX) y espectroscopia Mössbauer por transmisión (EMT). Se observó la sola presencia de la fase de hematita, cuando se utilizó la proporción de 1 g FeSO$_4$ con 0.1 g, 0.2 g y 0.3 g de azúcar. No llegó a formarse hematita para las proporciones de 3 g FeSO$_4$ con 0.1 g, 0.2 g y 0.3 g de azúcar; en estos casos se obtuvo la fase cristalina de butlerita (Fe(SO$_4$)(OH)(H$_2$O)$_2$). De los parámetros hiperfinos Mössbauer, se determinó la fase mineralógica de hematita por la presencia del sexteto magnético de hematita para el caso de 1 g FeSO$_4$; y en el caso de 3 g FeSO$_4$ se observó sólo la presencia de dos sitios paramagnéticos atribuidos a cationes de hierro en estados de oxidación 3$^+$. Estos resultados nos permitió correlacionarlos con los obtenidos por DRX.

Palabras clave: método de reacción en estado sólido, difracción de rayos X, espectroscopia Mössbauer por transmisión, magnetometría.

Synthesis and characterization of hematite particles (α-Fe$_2$O$_3$) obtained by thermal treatment of FeSO$_4$ with sugar

Abstract

Hematite particles were synthesized by thermal treatment of FeSO$_4$ with different concentrations of sugar. The powder mix of FeSO$_4$ and simple sugar was held at 600 ^{0}C for 14 h in a furnace. Using ratios of 1 g and 3 g of FeSO$_4$, to 0.1 g, 0.2 g and 0.3 g of simple sugar respectively. The analysis of the macroscopic magnetic properties of the samples was made with an alternating field magnetometer.To characterize the structure of the samples, X-ray diffractometry (XRD) and transmission Mössbauer spectroscopy (TMS) were used. Depending on the concentrations of sugar used, the presence of hematite or butlerite was observed by XRD. The sole presence of the hematite phase was observed when the ratios of 1 g of FeSO$_4$ to 0.1 g, 0.2 g and 0.3 g of sugar were used. The hematite phase was not observed for the ratios of 3 g FeSO$_4$ to 0.1 g, 0.2 g and 0.3 g of sugar; in these cases the crystalline phase of butlerita (Fe(SO$_4$)(OH)(H$_2$O)$_2$) was obtained. Through the Mössbauer hyperfine parameters measured by TMS, the mineralogical phase was determined by the presence of the magnetic sextet of hematite for the mixtures with 1 g of FeSO$_4$; and in the cases of 3 g FeSO$_4$ by the presence of two paramagnetic doublets assigned to iron cations having 3$^+$ oxidation state. These results allowed us to correlate them with those obtained by XRD.

Keywords: solid-state reaction method, X ray diffractometry, transmission Mössbauer spectroscopy, magnetometry.

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Introduction

Hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) are the two most important iron oxides in nature [1, 2]. However, the former is the most abundant oxide and is localized not only in soils and sediments in regions having warm weather, but also in the Earth's crust. Above Curie temperature (965 K), hematite is paramagnetic and at room temperature hematite mineral is antiferromagnetic with a corundum structure [1]. This one is a hexagonal close-packed (HCP) array of oxygen ions piled up along the [001] direction. At 256 K, pure and well crystallized hematite undergoes a phase transformation from the antiferromagnetic to the weak ferromagnetic phase; this is known as the Morin transition [1]. Likewise, hematite has several important applications such as radiation shielding using a hematite-containing concrete [3]. Recently, hematite nanostructures have found applications in thermal conductivity, catalysis, antibacterial activity, humidity sensor, electrochemical capacitor electrodes, and arsenic removal from water through adsorption [4,5]. In the Soil Analysis Laboratory of the Faculty of Physical Sciences at the Universidad Nacional Mayor de San Marcos, lately we have synthesized hematite by applying an economical and reproducible method, Specifically, the synthesis of hematite was performed via a thermal decomposition of ferrous sulfate with different concentrations of simple sugar [6] (named sucrose by some authors). The synthesis of hematite, using this method, could have potential applications as remediation agent for wastewater having heavy metals. Afterwards, characterization of hematite and its possible physical modifications were studied with the following physical techniques: X-ray diffractometry (XRD), transmission Mössbauer spectroscopy (TMS) at room temperature, and magnetometry with an alternating field magnetometer.

Experimental setup

Physical characterization of the samples with XRD and MS measurements were performed in the Faculty of Physical Sciences at the Universidad Nacional Mayor de San Marcos. The magnetization measurements were carried out in the Center for Research and Advanced Studies of the National Polytechnic Institute located in Saltillo, Mexico (CINVESTAV).

Synthesis of hematite

For the synthesis of hematite particles (α-Fe$_2$O$_3$) the solid-state reaction method was used [6]. This one is known for being a practical, fast and economical method. Through it, several powder samples were obtained after the direct reaction of the initial mixing of solid materials under thermal treatment. Specifically, the samples were

synthesized via the thermal reaction of ferrous sulphate (FeSO$_4$) with traces of simple sugar at 600 ^{0}C for 14 h. Thus, in order to understand the influence of sugar content on the synthesis of hematite, we used 1 g and 3 g of FeSO$_4$ and 0.1 g, 0.2 g and 0.3 g of previously pulverized simple sugar. We have named Hematite 0 (only 1 g of FeSO$_4$), Hematite 0.1(1 g of FeSO$_4$ with 0.1 g of sugar) and Hematite 0.2 (1 g of FeSO$_4$ with 0.2 of sugar).
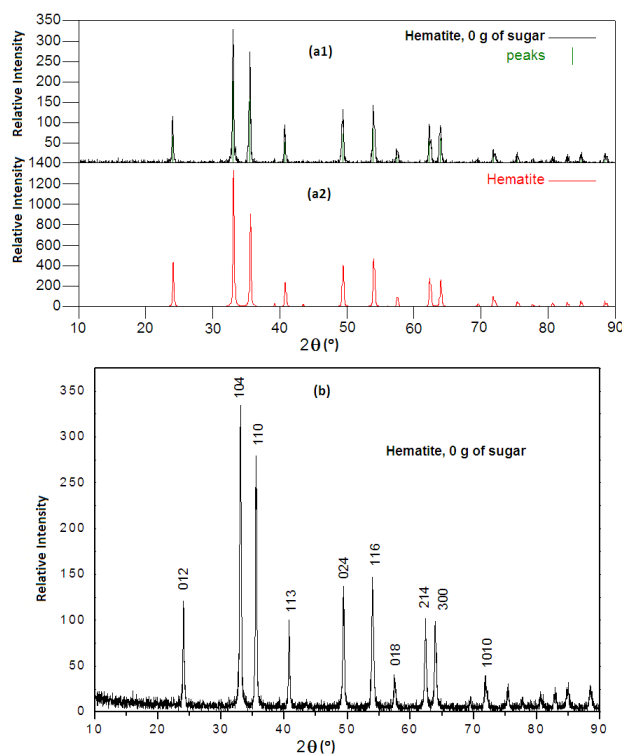
Characterization

Figure 1: (a1) and (b) X-ray pattern of thermal treatment of FeSO$_4$ with no sugar (was identified pure phase of hematite), (a2) hematite diffraction patterns of the Powder Diffraction File (PDF) Number 72-469.

The structural characterization was performed by X-ray diffraction, XRD patterns were obtained in a Brucker diffractometer in the Bragg-Brentano geometry using Cu-Kα radiation (λ = 1.54056 Å) [7, 8]. 2 theta-scan was performed from 10^0 to 90^0, using steps of 0.03^0 per 4 s. The XRD patterns were indexed using the Crystallography Search match program with the International Centre for Diffraction Data's PDF databases. The Mössbauer characterization was performed at room temperature (RT) with conventional Mössbauer equipment in the transmission mode with a ^{57}Co radioactive source embedded in a rhodium matrix [9, 10]. Specifically, we used samples of 25 mg, 100 mg and 196 mg contained,

respectively, in a sample holder of 1.0 cm diameter. Likewise, the Normos program was used to fit the Mössbauer spectra [11]. Furthermore, the magnetic properties of each samples were measured at RT with an alternating gradient magnetometer (AGM Micromag 2900) manufactured by Princeton Measurements applying a maximum field of 12 kOe.
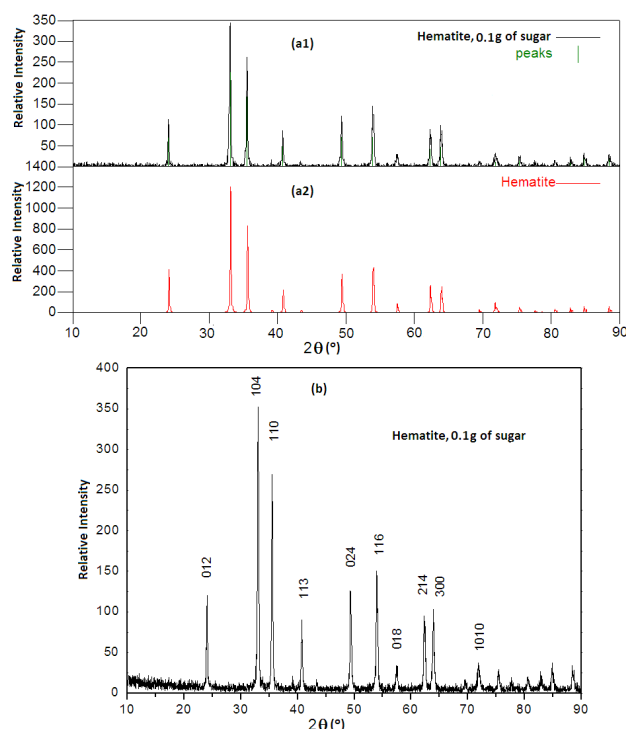
Results and discussion

Figure 2: (a1) and (b) X-ray pattern of thermal treatment of 1 g of FeSO$_4$ with 0.1 g of sugar (was identified pure phase of hematite), (a2) hematite diffraction patterns of the Powder Diffraction File (PDF) Number 72-469.

The following results were obtained: Figures 1, 2 and 3 show the XRD patterns of the samples synthesized in the proportion of 1 g of FeSO4 with no sugar, and with 0.1 g and 0.2 g of sugar respectively. Figure 4 shows an additional XRD pattern, but this time for a sample in the proportion of 3 g of FeSO$_4$ with 0.1 g of sugar. In this case, we do not show the results of 3 g of FeSO$_4$ with 0.2 g y 0.3 g of sugar. Figure 5 shows the deconvolution of the characteristic peak of the (104) plane by using a Lorentzian function. Figures 6 shows transmission Mössbauer spectra, at room temperature, of 1 g of FeSO$_4$, with no sugar and with 0.1 g and 0.2 g of sugar. Figures 7 also show transmission Mössbauer spectra, at room temperature, of 3 g of FeSO$_4$ with 0.1 g and 0.2

g of sugar. Likewise, Figure 8 shows the magnetization measurements of the respective samples.
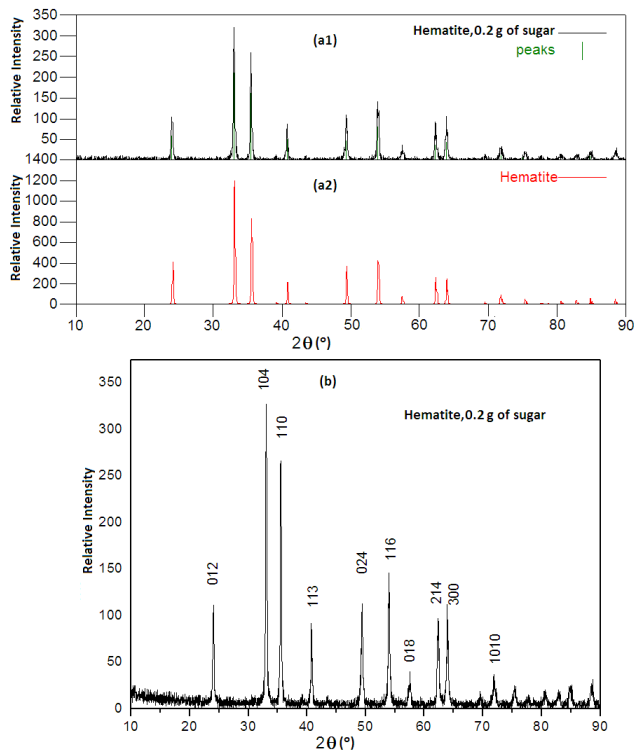

Figure 3: (a1) and (b) X-ray pattern of thermal treatment of 1 g of FeSO$_4$ with 0.2 g of sugar (was identified pure phase of hematite), (a2) hematite diffraction patterns of the Powder Diffraction File (PDF) Number 72-469.

Concerning the XRD pattern, (Figures 1, 2 and 3) were identified the presence of the pure mineralogical phase of hematite (α-Fe$_2$O$_3$). In the XRD pattern (Figure 4), only have identified the crystalline phase of butlerite (Fe(SO$_4$)(OH)(H$_2$O)$_2$) [12,13]; the presence of the hematite phase was not observed. This could indicate that the formation of hematite could be affected also by the concentrations of the FeSO$_4$ precursor material and the sugar.

Furthermore, for each sample, the interplanar distances were calculated by using the angular positions of the peaks given by XRD; specifically, using the Bragg's law [14]. The results are given in Table 1 as well as the interplanar distances from the diffraction patterns of the Powder Diffraction File (PDF) 72-469. The lattice constants for the samples hematite 0 (only 1 g of FeSO$_4$), hematite 0.1 (1 g of FeSO$_4$ with 0.1 g of sugar) and hematite 0.2 (1 g of FeSO$_4$ with 0.2 g of sugar) were calculated using the interplanar distance of the planes (104) and (110), via Eq. 1. It is worthy to mention that the PDF 72-469 corresponds to a rhombohedral system, but the description of this system is more appropriate if
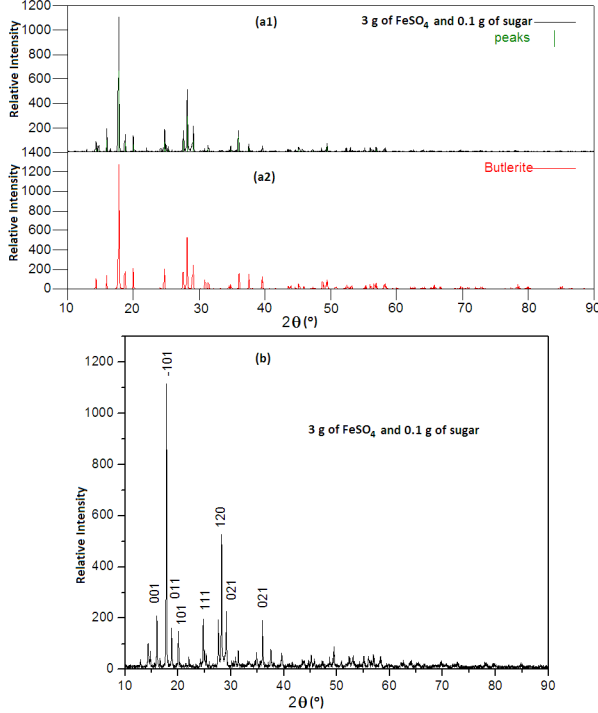
the hexagonal system is used.

Figure 4: (a1) and (b) X-ray pattern of thermal treatment of 3 g of FeSO$_4$ with 0.1 g of sugar; only was identified phase of butlerite (Fe(SO4)(OH)(H2O)2), (a2) butlerite diffraction patterns of the Powder Diffraction File (PDF) Number 71-2397.

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \qquad (1)$$

Hematite 0			
Plane	$2\theta(^0)$	d (nm)	d_{PDF} (nm)
104	33.06	0.2707	0.2703
110	35.50	0.2527	0.2519
Hematite 0.1			
Plane	$2\theta(^0)$	d (nm)	d_{PDF} (nm)
104	33.05	0.2709	0.2703
110	35.48	0.2528	0.2519
Hematite 0.2			
Plane	$2\theta(^0)$	d (nm)	d_{PDF} (nm)
104	33.05	0.2709	0.2703
110	35.48	0.2528	0.2519

Table 1: Interplanar distances (d) for the crystallographic planes (104), (110) and the angular positions (2θ) of the XRD of the samples. Hematite 0, Hematite 0.1 and Hematite 0.2

Besides, Table 2 shows the positions of the diffraction peaks obtained for each sample and the calculated lattice constants a and c, which agree with the structural patterns of the mentioned PDF, where $a = 0.5038$ nm and $c = 1.377$ nm. The crystallite sizes for the samples hematite 0, hematite 0.1 and hematite 0.2 were calculated from the full-width at half-maximum corresponding to the most intense reflection of the (104) plane of hematite

Sample	$2\theta(^0)$	τ (nm)	a (nm)	c (nm)
Hematite 0	33.06	64.85	0.5053	1.378
Hematite 0.1	33.05	63.34	0.5056	1.335
Hematite 0.2	33.05	73.96	0.5056	1.335

Table 2: Angular positions (2θ), cystallite sizes (τ) for each sample as well as the corresponding lattice constants a and c. Hematite 0, Hematite 0.1 and Hematite 0.2

Specifically, the crystallite sizes were calculated using the Scherrer equation [15]:

$$\tau_{104} = \frac{K\lambda}{\beta\cos(\theta)} \qquad (2)$$

where $\lambda = 1.54056$ Å is the wavelength, β is the full-width at half-maximum, θ the angular position, K is the scattering factor equal to 1. Parameters θ and β were obtained by using a Lorentzian function corresponding to the characteristic peak of the (104) plane, as shown in Figure 5.
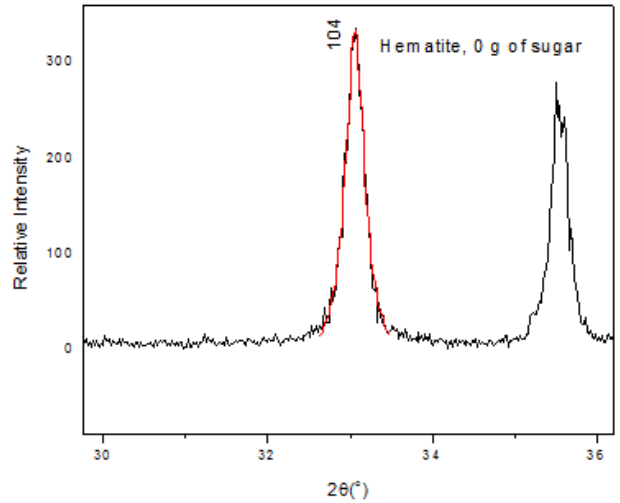

Figure 5: Deconvolution of the characteristic hematite (104) profile by using a Lorentzian function.

On the other hand, concerning the transmission Mössbauer spectra at room temperature (Figures 6 and 7); they provided structural information about the samples. Thus, in Figure 6, the Mössbauer spectra of the

samples hematite 0, hematite 0.1 and hematite 0.2 corresponding to only a mineral phase (hematite) [1]. This one was assigned to a unique magnetic phase whose hyperfine parameters are shown in Table 3; for each Mössbauer spectrum, the area of the respective sextet corresponds to approximately 100% of the total area, because only one phase was identified.

Hiperfine parameters		
Hermatite 0 ($FeSO_4$)		
Sites	$B_{hf}(T)$	δ Fe (mm/s)	2ϵ (mm/s)
Fe^{3+}	51.457	0.302	-0.247
	Hermatite 0.1 ($FeSO_4$ 0.1 g of sugar)		
	$B_{hf}(T)$	δ Fe (mm/s)	2ϵ (mm/s)
Fe^{3+}	52.008	0.285	-0.219
	Hermatite 0.2 ($FeSO_4$ 0.2 g of sugar)		
	$B_{hf}(T)$	δ Fe (mm/s)	2ϵ (mm/s)
Fe^{3+}	52.008	0.285	-0.219

Table 3: Hyperfine parameters of thermal treatment of 1 g of $FeSO_4$ with no sugar, and with 0.1 g and 0.2 g of sugar. Hyperfine magnetic field (B_{hf}), isomeric shift (δ) and quadrupolar shift (2ϵ).

Hyperfine Mössbauer parameters of the samples provided information about the presence of a single mineralogical phase corresponding to hematite (α-Fe_2O_3) as a single crystalline phase in the samples with no sugar, and with 0.1 and 0.2 g of sugar. The values of the obtained hyperfine parameters are similar to hyperfine parameters of the hematite reported in the literature [1]. Thus, the synthesized samples having 1 g of $FeSO_4$ with no sugar and with 0.1 and 0.2 g of sugar were fitted with a magnetic component, which was assigned to hematite (Figure 6).

Figure 7 shows the Mössbauer spectra at RT of the samples of 3 g of $FeSO_4$ with 0.1 and 0.2 g of sugar, their Mössbauer spectra were fitted with two paramagnetic components assigned to the Fe^{3+} sites, and Table 4 shows the hyperfine parameters obtained from each spectra.

Hiperfine parameters		
0.1 g of sugar and mass of 100 mg		
Sites	δ Fe (mm/s)	ΔE_Q (mm/s)	A (mm/s)
Fe^{3+}	0.208	0.946	0.219
Fe^{3+}	0.206	0.455	0.042
	0.2 g of sugar and mass of 196 mg		
	δ Fe (mm/s)	ΔE_Q (mm/s)	A (mm/s)
Fe^{3+}	0.209	0.957	0.299
Fe^{3+}	0.201	0.435	0.054

Table 4: Hyperfine parameters of thermal treatment of 3 g of $FeSO_4$ with 0.1g and 0.2 g of sugar, isomeric shift (δ), quadrupolar splitting (ΔE_Q), and relative area A.
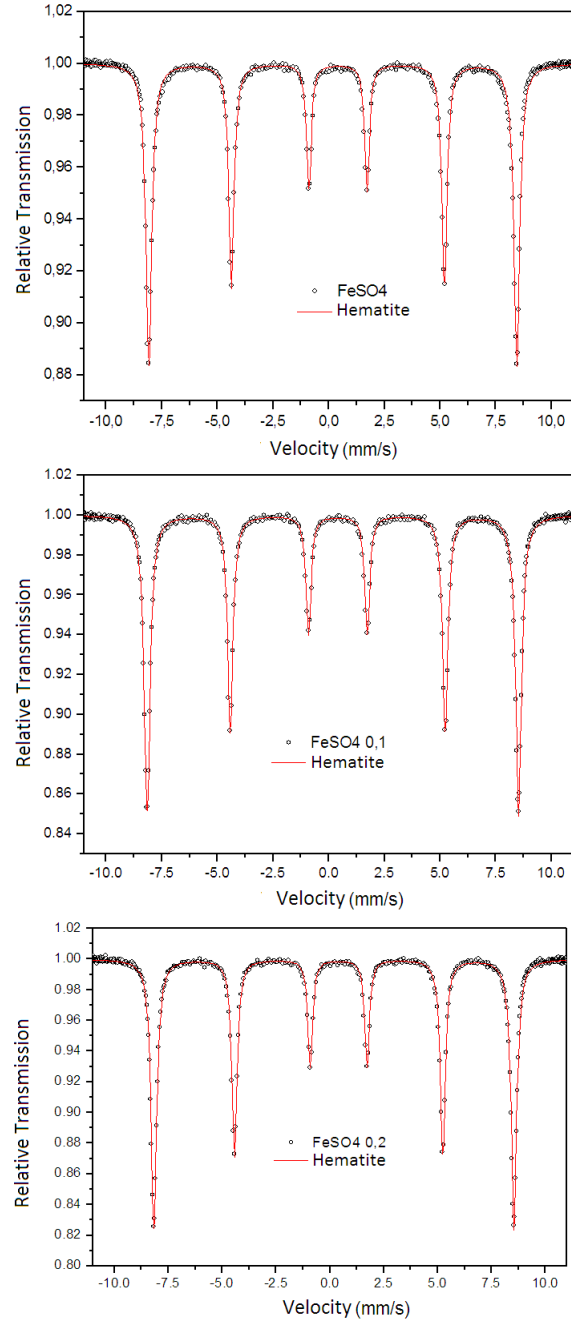

Figure 6: At room temperature, Mössbauer spectra of the samples Hematite 0 ($FeSO_4$), Hematite 0,1 ($FeSO_4$ 0.1), and Hematite 0,2 ($FeSO_4$ 0.2); pure phase of hematite is observed.

The magnetization measurements of the samples are shown in Figure 8. From the hysteresis loops, important magnetic properties can be determined, such as the coercive field (Hc), saturation magnetization (Ms), these properties are listed in Table 5. The values of the coer-

cive field (Hc) of the samples decrease with the increase in the sugar concentration. The obtained Ms value of 1 g of $FeSO_4$ with no sugar is relative lower than 1 g of $FeSO_4$ with 0.1. It is important to note that the samples of 1 g of $FeSO_4$ with 0.1 and 0.2 g of sugar, lower values of Hc and higher values of Ms are observed, when compared to the samples of 3 g of $FeSO_4$ with 0.1 and 0.2 g of sugar. The hysteresis loops show that the synthesized samples have a ferromagnetic behavior [16, 17].

Sugar (g)	1 g of FeSO		3 g of FeSO	
	Hc (Oe)	Ms (emu/g)	Hc (Oe)	Ms (emu/g)
0	350	0.45	350	0.45
0.1	185	3.50	440	1.01
0.2	280	1.62	320	0.89
0.3	—	—	265	1.16

Table 5: Values of magnetization of thermal treatment of 1 g and 3 g of $FeSO_4$ with 0.1 g and 0.2 g of sugar, respectively. Coercive field (Hc) and saturation magnetization (Ms).
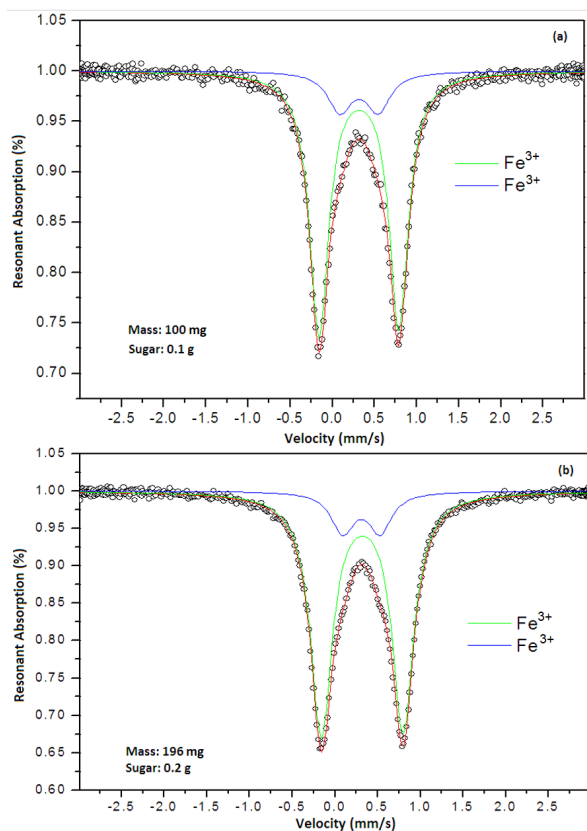

Figure 7: At room temperature, Mössbauer spectra of thermal treatment of 3 g of $FeSO_4$ with 0.1 g of sugar (a) and 3 g of $FeSO_4$ with 0.2 g of sugar (b).
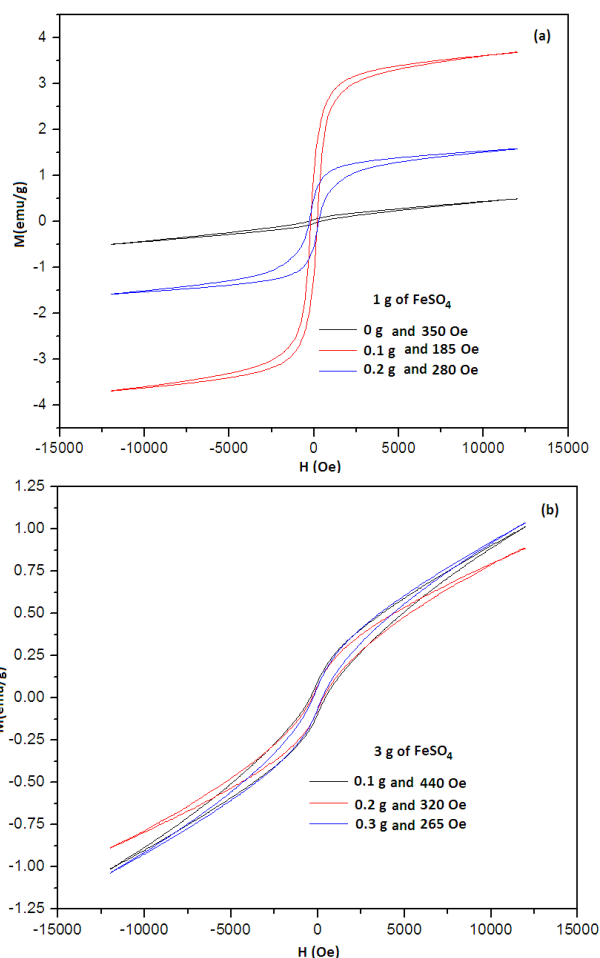

Figure 8: Magnetization measurements of thermal treatment of 1 g and 3 g of $FeSO_4$ with 0.1 g and 0.2 g and 0.3 g of sugar, respectively.

Conclusions

In the analysis of the X-ray pattern, depending on the concentrations of sugar, it was observed the presence of the mineral phases of either hematite or butlerite. Transmission Mössbauer spectroscopy results, in five samples, on one hand, in the first three ones, we found that the Mössbauer hyperfine parameters correspond to characteristic values of mineral hematite. On the other hand, in the other two samples, there was no evidence of the presence of hematite. However, these Mössbauer spectra were assigned to two paramagnetic sites, which were attributed to iron cations having oxidation state 3^+. The magnetometry technique allowed determining that the sugar concentration modified the values of both the coercive field and the saturation magnetization. Finally, the low-cost and short time for the synthesis of hematite,

using this method, could have potential applications as remediation agent for wastewater having heavy metals.

Acknowledgements

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