Hyperfine Interact (2016) 237:56
DOI 10.1007/s10751-016-1257-x

Comparative study of biogenic and abiotic iron-containing materials

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Abstract Series of iron-based biogenic materials prepared by cultivation of *Leptothrix* group of bacteria in different feeding media (*Sphaerotilus-Leptothrix* group of bacteria isolation medium, Adler, Lieske and silicon-iron-glucose-peptone) were studied. Control samples were obtained in the same conditions and procedures but the nutrition media were not infected with bacteria, i.e. they were sterile. Room and low temperature Mössbauer spectroscopy, powder X-ray diffraction (XRD), and infrared spectroscopy (IRS) were used to reveal the composition and physicochemical properties of biomass and respective control samples. Comparative analysis showed differences in their composition and dispersity of present phases. Sample composition included different ratio of nanodimensional iron oxyhydroxide and oxide phases. Relaxation phenomena such as superparamagnetism or collective magnetic excitation behaviour were registered for some of them. The experimental data showed that the biogenic materials were enriched in oxyhydroxides of high dispersion. Catalytic behaviour of a selected biomass and abiotic material were studied in the reaction of CO oxidation. In situ diffuse-reflectance (DR) IRS was used to monitor the phase transformations in the biomass and CO conversion.

Keywords Biogenic nanosized iron oxides · *Leptothrix* genus of bacteria · Mössbauer spectroscopy · X-ray diffraction · IR spectroscopy

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2015), Hamburg, Germany, 13–18 September 2015*

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Published online: 22 February 2016

1 Introduction

Nowadays, considerable attention has been focused on the study of nanodimensional iron-containing materials due to their unique physical characteristics and the wide spectrum of their possible applications. Most of the technologies for their synthesis are based on the use of different chemical methods. Another totally different possibility is preparation of such materials in the cells of animals as well as a result of the vital activity of plants and microorganisms. Biogenic synthesis of nanocrystals can results in specific or unique characteristics. The obtained substances are nanosized, amorphous or poorly crystalline, and have porous structure, high surface area/volume ratio, active sites with unusual coordination, low toxicity, biocompatibility, etc. This combination of physicochemical properties is valuable for practical application in the environmentally friendly processes like catalysis and in other areas too. But the laboratory synthesis of such a specific structure is not easy or even impossible [1–3].

Iron bacteria of *Sphaerotilus-Leptothrix* group participate in iron rotation in the nature. As a result Fe^{2+} ions in aqueous medium are oxidized and transformed in insoluble Fe^{3+}-containing compounds in the form of oxides, hydroxides and salts [1–5]. So the oxidation of FeII is followed by hydrolysis process of the FeIII-hexa aquo cation $Fe^{3+}(OH_2)_6^{3+}$ [5]. However, it is well known, that in laboratory conditions the key factor, which governs the oxide that forms, its crystallinity and dispersity is the rate at which these species, mainly monomers and dimers, are supplied to the growing crystal. Other very important factors in this polymerization/crystallization process are temperature, media pH, concentrations, as well as the precursor materials (sulphates, nitrates, chlorides, etc.).

Nowadays natural inoculums from the *Sphaerotilus-Leptothrix* group of bacteria can be cultivated in laboratory conditions [1–5]. Different growth media are proposed for their laboratory cultivation. They can grow not only in mineral media but on such ones containing organic substances, too [1–7]. Investigations of this process have found that the bacteria of the *Leptothrix* genus developed intensively in the *Sphaerotilus-Leptothrix* group of bacteria isolation medium (SLGBIM) [7] and the feeding media of Lieske [6]. The obtained populations were enough in number to be isolated pure bacterial cultures in Adler media. It was found that in laboratory conditions in silicon-iron-glucose-peptone (SIGP) media the bacteria form nanotubes [2, 3]. These four nutrition media are quite different in their composition. The medium of Lieske is purely inorganic, but Adler and SIGP media are predominantly organic [2, 3, 6, 7]. SLGBIM has complex character and contains organic and inorganic ingredients [7].

Generally, the microorganisms of *Sphaerotilus-Leptothrix* genera do not tolerate high salt concentrations [1–7]. The biogenic elements C, H, O, N, S, Fe, P and Mg participate in the formation of 96 % of the microorganisms. The bacteria can use the energy obtained by transformation of the six basic elements - C, H, N, S, Fe and U by processes of chemolitotrophic and/or heterotrophic metabolism. Significance of one or another element is not determined as a requirement for given mineral availability in relation to the bacterial metabolism. The microelements K, Ca, B, Cu and Zn in very low concentrations are factors for the different enzymes functionality but they are toxic at increased levels. Carbonates and/or great variety of organic compounds can be utilized as carbon source but the glucose is the most often used as carbon and energy source. The *Leptothrix* genera of bacteria can use organic (amino acids, peptones) and inorganic compounds ($(NO_3)^-$ and $(NH_4)^+$ salts) as nitrogen sources. The bacteria of both genera require vitamin B12 as an essential growth factor. A number of *Leptothrix* strains have been found to require additionally vitamin B1 as growth factor [7].

Table 1 Composition and pH of used feeding media

Cultivation medium	Start pH	Final pH	Medium composition
Adler	7.02	7.81	$(NH_4)_2[Fe(SO_4)_2].6H_2O$, $MgSO_4.7H_2O$, sodium lactate, yeast extract, ascorbic acid, K_2HPO_4, distilled water
Lieske	7.22	7.71	$Mg(HCO_3)_2$ saturated solution 1:10, K_2HPO_4 traces, $MgSO_4.7H_2O$ traces, distilled water, iron grits, $FeSO_4$
Sphaerotilus-Leptothrix group bacteria isolation medium (SLGBIM)	7.09	7.2	Glucose, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, K_2HPO_4, $MgSO_4$, KCl, $CaCO_3$, Vitamin B12, Vitamin B1, distilled water, iron grits, $FeCO_3$ and $FeCl_2$
Silicon-iron-glucose-peptone (SIGP)	7.03	7.41	Glucose, Bacto peptone, $MgSO_4.7H_2O$, $KH_2PO_4.2H_2O$, $Na_2HPO_4.12H_2O$, $Na_2SiO_3.9H_2O$, $CaCl_2$, $FeSO_4$, HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid)

However, there are still opened questions about the influence of different feeding media on the iron oxide products formation. One of them is how the process of iron phases formation in laboratory conditions proceeds? Is the chemical (physico-chemical) route predominant or iron oxidising bacteria plays a key role on phase composition and crystallinity? The main experimental difficulty in proving autotrophy by these iron bacteria is that the organisms grow and thrive well between the pH of about 5 to 9 (7.5 for *Leptrothrix*).

The aim of the present study was to determine the composition of biomass samples obtained after cultivation of laboratory isolated *Leptothrix* genus of bacteria in different nutrient media, to clear up the reasons that define the differences between the compositions of the laboratory obtained biomasses in relation to iron compounds in sterile feeding media and to check/examine their catalytic behaviour in reaction of CO oxidation.

2 Experimental

2.1 Materials

Series of iron-based biogenic materials are obtained by cultivation of laboratory isolated *Leptothrix* genus of bacteria in nutrition media of SLGBIM, Lieske, Adler, and SIGP. Biomasses for the present study were supplied by V. Groudeva, M. Iliev, and R. Angelova from the Faculty of Biology of St. Kliment Ohridski University of Sofia. The compositions of the used media are listed in Table 1. The cultivation was carried out using Ferenbach flasks in static conditions at room temperature for 36 days except in the case of SIGP medium, where cultivation was carried out in dynamic conditions (70 rpm). The obtained biomass was separated by decantation of the limpid solution and filtration. It was washed several times with distilled water and dried at 40°C. Control samples were obtained in the same conditions and procedures but the nutrition media were not infected with bacteria, i.e. they were sterile.

2.2 Methods of investigation

Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation

and LynxEye detector. Phase identification was performed with the Diffrac*plus* EVA using ICDD-PDF2 Database. Mean crystallite size were determined with the Topas-4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry.

Mössbauer spectra were recorded using Wissenschaftliche Elektronik GmbH electromechanical apparatus (Germany), operating at a constant acceleration mode. ^{57}Co/Rh source and α-Fe standard were used. The spectra were collected at room temperature and at the liquid nitrogen temperature. The parameters of hyperfine interactions of the Mössbauer spectral components (isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field (H_{eff}), line width (FWHM) and component relative weight (G)) were determined by computer fitting with CONFIT program. The used calculations are based on the method of the least squares.

IR spectroscopy – FTIR spectra of the material in KBr pellets were recorded with a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) in the middle-IR region. Also, the materials were studied using high-temperature/vacuum chamber accessory (Thermo Spectra-Tech, USA) in diffuse-reflectance mode (DRIRS). Spectra were collected in the range 1111-4000 cm^{-1} determined by the transparency of CaF_2 windows that were used in the measuring cell.

3 Results and discussion

X-ray diffraction patterns of control and biogenic samples obtained by cultivation in the four different media are shown in Fig. 1. They demonstrate the presence of significant X-ray amorphous component as well as low intensity patterns of crystalline phases. Depending on the feeding media used these crystal phases are different. Their positions match with the characteristic ones for an iron oxide phase with spinel structure (magnetite Fe_3O_4 or maghemite γ-Fe_2O_3) in all studied cases. For Adler feeding media only spinel iron oxide phase was registered (Fig. 1a). In another cases (SLGBIM and Lieske) different polymorphous modifications of iron oxyhydroxide phases (goethite α-FeOOH, lepidocrocite γ-FeOOH, ferrihydrite) were also presented in X-ray diffractograms (Fig. 1, b–c). 2-line ferrihydrite and magnetite were obtained in SIGP sample (Fig. 1d). The mean crystallite size, unite cell parameters, and relative weights of registered crystal phases were determined (Table 2). It can be seen that the mean crystallite size increases for biogenically prepared materials in comparison to controls. The data for SIGP samples are not representative due to the small ratio signal/noise in diffractograms (Fig. 1d). They are not presented in Table 2.

Mössbauer spectroscopy was used in order to investigate in details the iron-containing phases including even the X-ray amorphous ones. Figures 2 a-d show the room temperature Mössbauer spectra of biogenic and control samples after their mathematical fitting. All Mössbauer spectra consist of paramagnetic doublet component (quadrupole doublet - Dbl), but different quantity of non-resolved magnetically split sextet pattern (six line component - Sx) can be seen in some spectra. This component is not very well presented and it can be seen mainly in sample Lieske-control. On the base of XRD analysis a complex phase composition of our materials is registered. Partial or complete separation of SPM phases and paramagnetic components will be given by low temperature Mössbauer spectra. The calculated Mössbauer parameters are listed in Table 3 for each spectrum. The slightly asymmetrical central doublet in the spectrum of materials (see Fig. 2) indicates the presence of at least two nonequivalent iron positions in the structure. The best fit spectra confirmed this

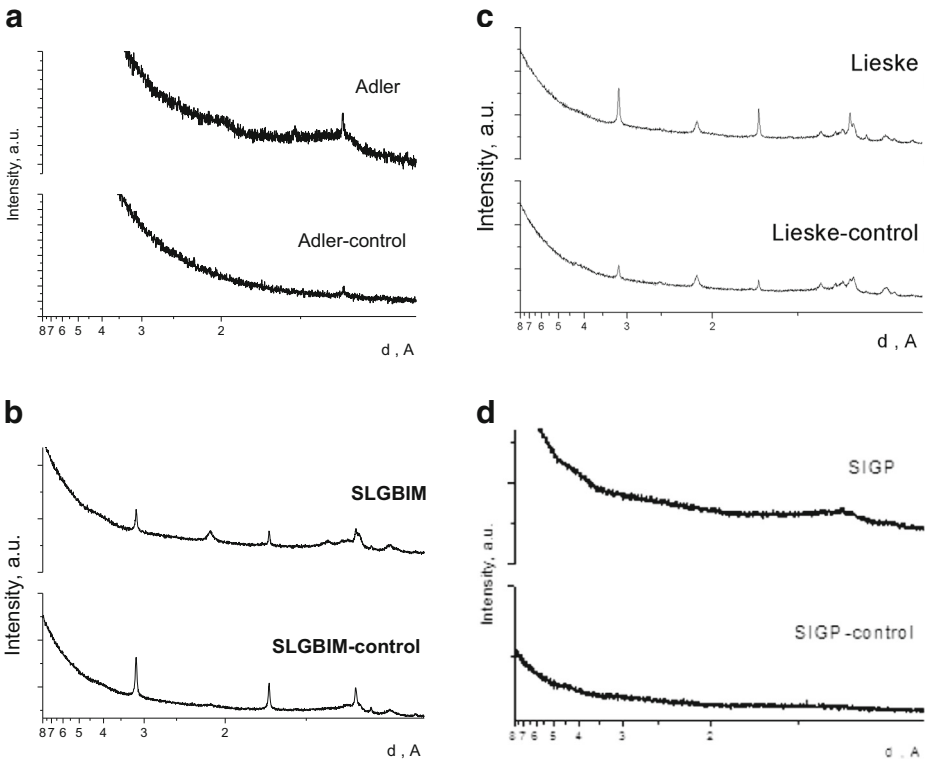

Fig. 1 X-ray diffraction patterns of biogenic and control samples obtained in different growth media

observation. This spectrum is hence fitted by using two quadrupole spectral components named as Db1 and Db2. Each of these components summarized the presence of paramagnetic γ-FeOOH or Ferrihydrite (having two very close doublet components at RT), as well as relaxation in the system of superparamagnetic particles of iron oxides (see Table 3). The estimated isomer shift values of the doublet components (0.33-0.35mm/s) indicated that the valence states of iron ions were mainly trivalent in all samples. The quadrupole splittings of the spectral components are QS1 = 0.51-0.61 mm/s and QS2 = 0.84-1.04mm/s. The control samples displayed a larger averaged quadruple splitting (QS) than that of biogenic ones. Because the QS values reflect the electric field gradient at Fe nuclei, which is affected by an asymmetric electronic charge distribution or ligand arrangements, the increasing QS values mean the formation of highly distorted FeO_6 coordination polyhedra and the contraction of the Fe-O bond. Such an impact of feeding media composition is lower in biogenic materials, probably due to the elimination of physisorbed and structural groups (sulphates, nitrates, chlorides, organics, etc.). This observation is very well seen in XRD where patterns of biogenic materials have sharper and more intensive diffraction lines than those of controls.

The corresponding Mössbauer spectra were measured at the temperature of the liquid nitrogen in order to resolve the presented SPM phases (presented in Fig. 3). The Mössbauer

Table 2 Calculated values of mean crystallite size (D), unite cell parameters (a, b, c) and relative weight (G) of crystal phases obtained from X-ray powder diffraction data

Sample	Crystal phases	a, Å	b, Å	c, Å	D,nm	G, %
Adler	Fe_3O_4	8.372			3	100
Adler- control	Fe_3O_4	8.380			3	100
SLGBIM	Fe_3O_4	8.367			3	39
	Ferrihydrite	2.584		8.235	10	13
	$\alpha-$FeOOH	4.617	9.988	3.021	11	38
	$\gamma-$FeOOH	3.875	12.527	3.068	51	10
SLGBIM -control	Fe_3O_4	8.389			3	50
	Ferrihydrite	2.587		8.213	9	13
	$\alpha-$FeOOH	4.624	10.050	3.027	8	16
	$\gamma-$FeOOH	3.874	12.522	3.069	47	21
Lieske	Fe_3O_4	8.359			3	46
	Ferrihydrite	2.583		8.245	13	11
	$\alpha-$FeOOH	4.614	9.963	3.019	22	25
	$\gamma-$FeOOH	3.872	12.523	3.069	59	18
Lieske-control	Fe_3O_4	8.359			4	49
	Ferrihydrite	2.584		8.234	12	14
	$\alpha-$FeOOH	4.610	9.960	3.019	20	30
	$\gamma-$FeOOH	3.872	12.514	3.067	51	7

parameters obtained after mathematical treatment of the experimentally registered spectra are given in Table 3 also. It can be seen that LNT spectra are also complex revealing composition of several phases. The isomer shift calculated values show the presence of iron ions in third oxidation degree and octahedrally coordinated, mainly. Sextet component Sx1 has the characteristic hyperfine parameters of α-FeOOH. Sx2 and Sx3 or Sx4 can be associated with the presence of nonstoichiometric/partially oxidized magnetite (or maghemite) phase. It is well known that both phases with small particles produce Mössbauer spectra with strongly broadened non-Lorenz type curve at room temperature as well as at the liquid nitrogen temperature [5, 9, 10]. Their hyperfine field values (H_{eff}) are lower than the characteristic ones of bulk well-crystallized phases, i.e. highly dispersed character of the particles is registered. During computation three-sextet model was used because of the non-Lorentz character of the spectral lines as was mentioned above. The registered two doublet components show the presence of paramagnetic and/or superparamagnetic phases. Probably these are magnetite or goethite particles with nanometric size bellow 10 nm, as well as lepidocrocite phase (γ-FeOOH).

The obtained Mössbauer results are in very good agreement with powder XRD analysis showing significantly smaller size of magnetite particles ($Fe_{3-x}O_4$) in comparison with presented iron oxyhydroxide particles (α-FeOOH and γ-FeOOH).

Additional information about chemical composition, chemical linkages and functional groups besides those for the iron oxide structure was obtained by IR spectroscopy. The method is useful for phase identification in iron oxides providing information about crystal morphology, the nature of surface hydroxyl groups and adsorbed species. The IR spectra of studied biogenic and control samples are presented on Fig. 4a-f.

Table 3 Mössbauer hyperfine parameters of spectra components of the studied samples measured at room temperature (RT) and at liquid nitrogen temperature (LNT)

Sample / measurement temperature	Spectral components / compounds	IS, mm/s	QS, mm/s	H_{eff}, T	FWHM, mm/s	G,%
LIESKE, RT	Sx1 - Fe^{3+}, α-FeOOH	0.31	−0.12	26.2	1.30	26
	Db1 - Fe^{3+}	0.35	0.54	–	0.35	41
	Db2 - Fe^{3+}	0.33	0.91	–	0.52	33
LIESKE - control,	Sx1 - Fe^{3+}, α-FeOOH	0.30	−0.14	28.4	1.75	40
RT	Db1 - Fe^{3+}	0.35	0.55	–	0.34	30
	Db2 - Fe^{3+}	0.34	0.92	–	0.36	30
LIESKE, LNT	Sx1 - Fe^{3+}, α-FeOOH	0.48	−0.15	47.8	0.85	24
	Sx2 - $Fe_{3-x}O_4$	0.52	0.00	44.1	0.72	19
	Sx3 -$Fe_{3-x}O_4$	0.32	0.04	40.6	1.72	31
	Sx4 - $Fe_{3-x}O_4$ - CME	0.47	0.00	39.3	0.51	9
	Db1 - Fe^{3+}	0.46	0.59	–	0.35	17
SLGBIM, RT	Db1-Fe^{3+}	0.35	0.51	–	0.32	28
	Db2-Fe^{3+}	0.34	0.84	–	0.56	72
SLGBIM	Db1-Fe^{3+}	0.35	0.53	–	0.34	43
-control, RT	Db2-Fe^{3+}	0.34	0.89	–	0.50	54
SLGBIM, LNT	Sx1 - Fe^{3+}, α-FeOOH	0.44	−0.15	47.9	0.42	10
	Sx2 - $Fe_{3-x}O_4$	0.52	0.03	47.2	0.68	14
	Sx3 - $Fe_{3-x}O_4$	0.32	0.04	42.5	0.91	33
	Sx4 - $Fe_{3-x}O_4$-CME	0.47	0.00	41.6	0.31	31
	Db1 - Fe^{3+}	0.46	0.58	–	0.38	12
SIGP, RT	Db1-Fe^{3+}	0.34	0.55	–	0.34	27
	Db2-Fe^{3+}	0.33	0.93	–	0.54	73
SIGP-control, RT	Db1-Fe^{3+}	0.34	0.60	–	0.34	47
	Db2-Fe^{3+}	0.34	1.03	–	0.54	53
SIGP, LNT	Sx1 - Fe^{3+}, α-FeOOH	0.58	−0.15	40.1	0.35	11
	Sx2 - Fe^{3+}, $Fe_{3-x}O_4$-CME	0.40	0.04	46.1	1.3	5
	Db1 - Fe^{3+}	0.44	0.62			39
	Db2 - Fe^{3+}	0.43	1.09	–	0.52	45
ADLER, RT	Db1-Fe^{3+}	0.35	0.62	–	0.30	9
	Db2-Fe^{3+}	0.33	0.90	–	0.55	91
ADLER-control, RT	Db1-Fe^{3+}	0.35	0.61	–	0.38	44
	Db2-Fe^{3+}	0.35	1.04	–	0.51	56
ADLER, LNT	Sx1 - Fe^{3+}, α-FeOOH	0.51	−0.12	47.2	1.01	18
	Sx2 - Fe^{3+}, $Fe_{3-x}O_4$-CME	0.54	0.03	51.4	0.43	7
	Sx3 - Fe^{3+}, $Fe_{3-x}O_4$-CME	0.34	−0.06	50.9	0.42	10
	Db1 - Fe^{3+}	0.47	0.52	–	0.31	36
	Db2 - Fe^{3+}	0.47	0.78		0.44	29

IR spectra of biomass and control samples obtained in SLGBIM are shown on Fig. 4a. Spectral analysis showed that the biomass contains α-FeOOH (670, 744, 786, 890, 1127,

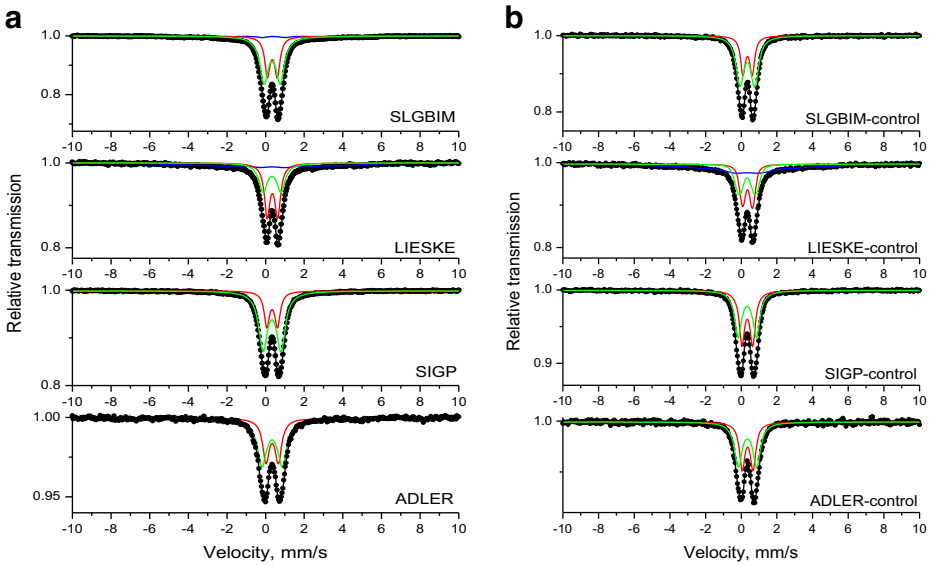

Fig. 2 Room temperature Mössbauer spectra of biogenic **(a)** and control **(b)** samples after mathematical fitting

and 3228 cm^{-1}) and γ-FeOOH (457, 486, 563, 744, 890, 1023, and 1127 cm^{-1}) and that control sample contains γ-FeOOH [11–14]. Comparison between biomass and control sample using subtraction of spectra (subtraction between biomass spectrum and spectrum of the control sample is shown on Fig. 4b), reveals higher amount of iron oxyhydroxides in the biomass. Other bands characteristic of hydrocarbons C-H_i (1384, 2853, 2925 cm^{-1}) and CO_3 (1402, 1527, 1641, 1659 cm^{-1}) are registered in the spectra, too [15]. Some rests of PO_4 in the samples can be proposed because of increased absorbance in the range around 1000 cm^{-1} [15]. Although all sets of characteristic bands are not distinguished the presence of hydrocarbons, carbonates and phosphates should not be excluded taking into account the isolation medium composition.

Bands/shoulders characteristic of γ-FeOOH (480, 575, 1040, 1150 cm^{-1}) are observed in the spectra of samples obtained in SIGP medium (Fig. 4c) [11–14]. Subtraction spectrum shows bigger quota of this phase in the biomass. Referring to the cultivation medium composition, especially that of the bacto peptone and the used HEPES buffer, the presence of medium rests could explain the bands in the region under 2000 cm^{-1} assigned to N-H and N-C vibrations (1248, 1270, 1320, 1340, 1551, 1641, and 1659 cm^{-1}) [15, 16]. The bands at 477/80 and 670 cm^{-1} are assigned to SO_4 [15] (one of the bacto peptone ingredients). The bands at 1383, 2857, 2873, 2925, 2959 cm^{-1} are assigned to the C-H_i vibrations in residues of medium ingredients HEPES and glucose [15]. The wide band at about 1000 cm^{-1} can be assigned to PO_4 (from the peptone) and Si-O. Despite all set of the bands corresponding to characteristic vibrations of these groups was not observed, their presence in the studied materials should not be excluded.

Characteristic bands of α-FeOOH (477, 669, 791, 886, 1126, and 3208 cm^{-1}) and γ-FeOOH (455, 562, 743, 886, 1024, and 1126 cm^{-1}) are registered in the spectra of biomass and control samples obtained in Lieske medium (Fig. 4e) [11–14]. Since the most intensive

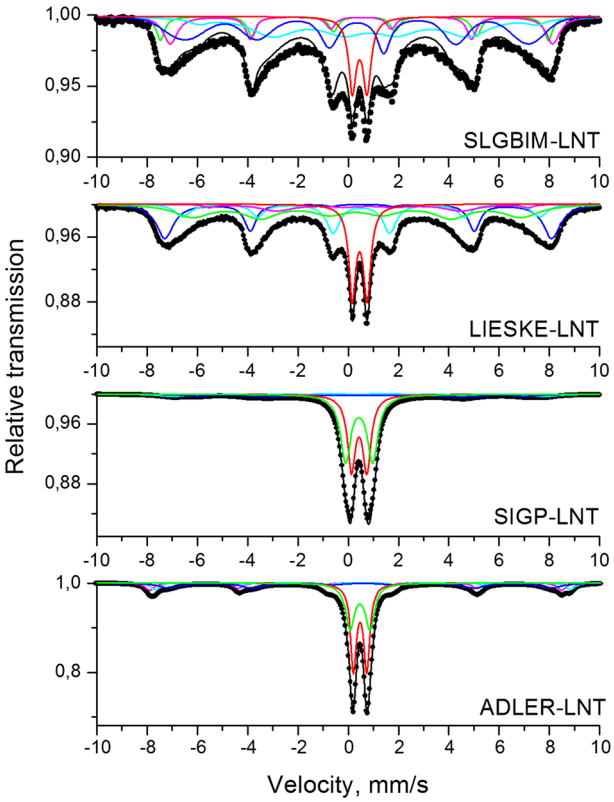

Fig. 3 Mössbauer spectra of biogenic materials measured at the temperature of *liquid* nitrogen

(normally) band in the spectrum of γ-FeOOH at 1024 cm^{-1} is very weak in the spectrum of control sample it is reasonable to suppose decreased rate of formation by chemical processes of this phase. Comparative analysis of the spectra together with the subtraction spectrum (Fig. 4f) support an enrichment in γ- and α-FeOOH of the biomass. Similarly to the samples obtained using SIGP and isolation media, the samples of Lieske medium demonstrate bands assigned to CO_3 (886, 1523, 1641, 1659 cm^{-1}), PO_4 (562, around 1000 (976) cm^{-1}) and SO_4 (455, 669, and 1126 cm^{-1}) groups, originating from residues of the cultivation medium in the end products [15]. Lieske medium has purely inorganic character and the low intensity bands at about 2900 and 1271 cm^{-1} confirm that the final material contains rests of bacterial origin – fatty acids components from the cell membrane and polysaccharides from the bacterial capsule [17].

The spectra of all studied samples demonstrate the presence of oxyanions (sulfate, phosphate and carbonate groups) which we explain with insufficient washing at the filtration step. Carbonization during the exposure of the samples to air is a possible reason of carbonates appearance. It is known that the surface of the ferric oxides is positively charged at neutral pH. Thus, these compounds are good adsorbents for negatively charged species like oxyanions [8]. It is known also that the phosphorus desorption from such materials is hampered [18, 19].

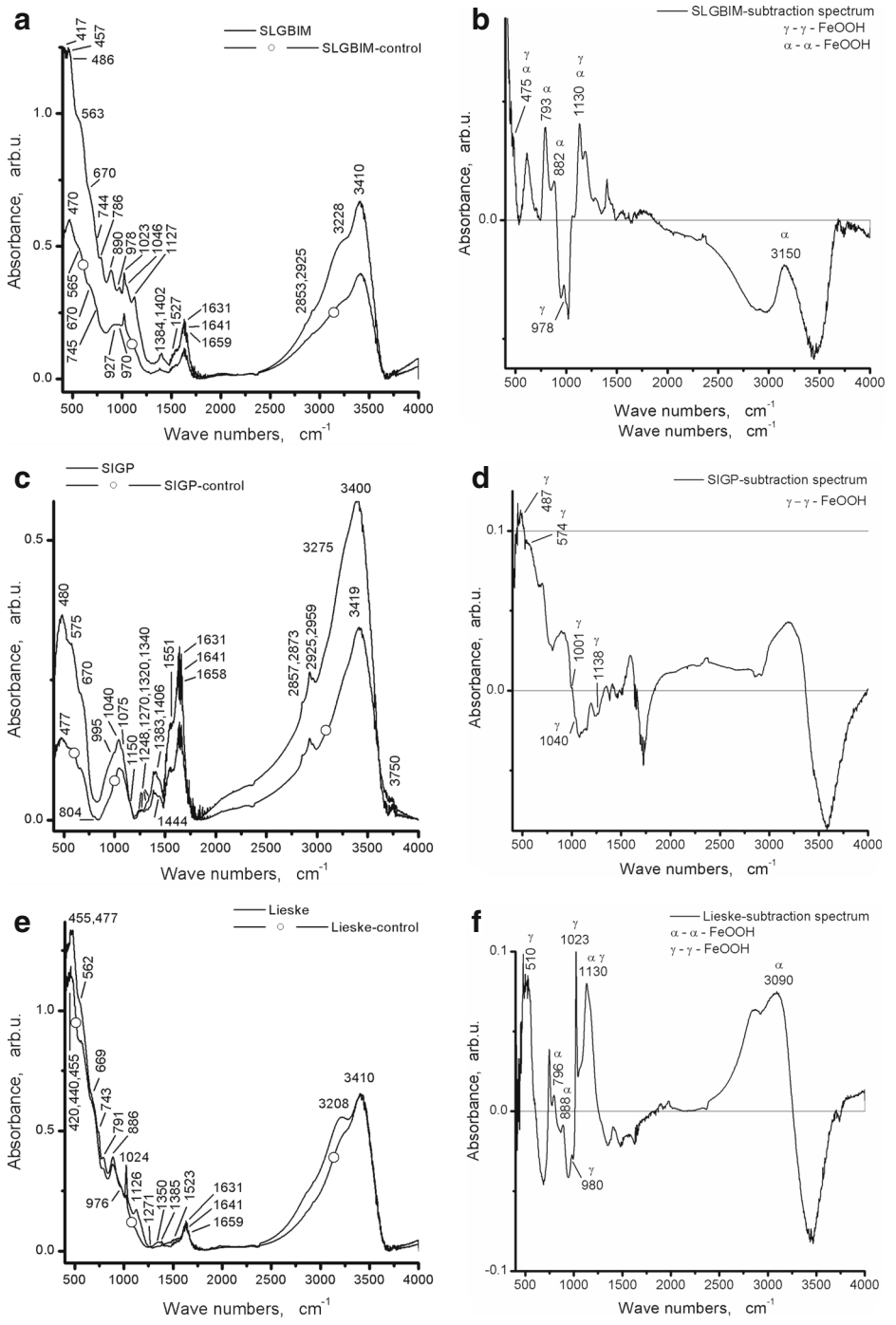

Fig. 4 Infrared spectra of biomasses **(a,c,e)** and subtraction spectra **(b,d,f)** obtained in the used media

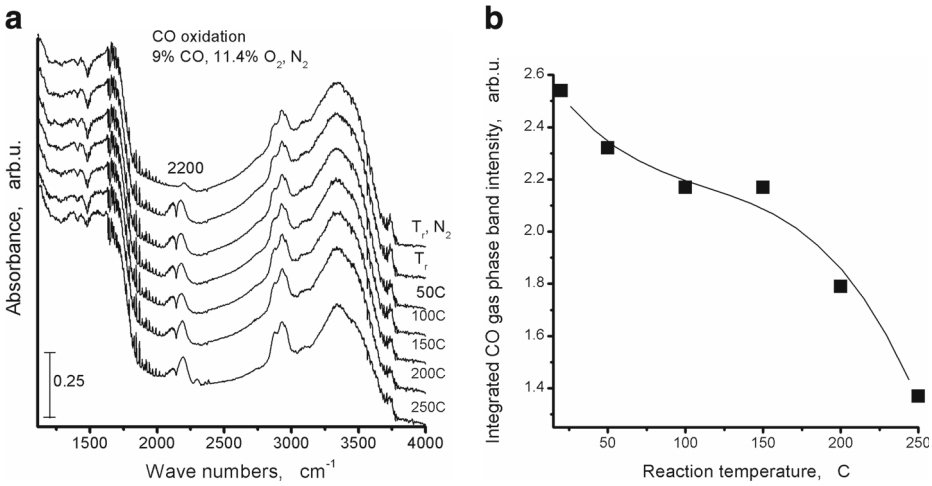

Fig. 5 Diffuse-reflectance infrared spectra collected in situ in the reaction of CO oxidation on SIGP biomass **(a)**. Change of integrated CO gas phase band intensity with the reaction temperature **(b)**

In situ IR spectra during the catalytic test of CO oxidation on SIGP biomass are shown on Fig. 5a. The increase in reaction temperature gave rise to an increase in intensity of the bands at about 2900, in the region of 2142-2255, and under 1800 cm^{-1} but a decrease in intensity of the bands between 2051-2142, and at 2848 cm^{-1} and of the wide envelope in the region 3200-3700 cm^{-1}. It was calculated that the intensity of the wide band at about 3340/3400 cm^{-1} decreased gradually by ~5 % in the interval T_{room}-200 °C. The next increase of the reaction temperature to 250 °C leads to an additional decrease by 6 %. Reverse dependence was registered in the region under 1600 cm^{-1} where the absorbance increased. Obviously, the decrease in OH coverage is accompanied by an increase in surface species which are formed during the reaction (formates, carbonates, products of organic destruction/oxidation, etc). CO concentration in the reaction mixture was monitored by the characteristic doublet in the spectra with minimum at 2142 cm^{-1} representing the two wings of bands in CO gas phase spectrum. The spectra revealed that increasing the reaction temperature the integrated intensity of wings changed to a different extent. The wing between 2051 and 2142 cm^{-1} (P-bands) decreased in intensity while the other one between 2142 and 2255 cm^{-1} (Q-bands), grew up. A band at 2200 cm^{-1}, characteristic for the sample itself, was registered. This band is overlapped by the Q-wing of CO spectrum. The changes in the spectrum are in accordance with an increase in intensity of this band with the temperature because of changes into the sample surface and/or composition. The lower wave numbers CO wing was not affected by other bands and its intensity was considered as a measure of CO content in the reaction mixture. Collected in situ spectra, during the reaction, showed that temperature increase resulted in CO band decrease, i.e. sample activity increased. The change of CO band integral intensity with the reaction temperatures is shown on Fig. 5b. The activity at temperatures up to 150 °C increased slowly. Bands of very low intensity, characteristic for CO_2, were registered at 2301 cm^{-1} in the spectrum at 200 °C. They were well visible in the spectrum recorded at 250 °C and certifies for a noticeably higher catalytic activity of the sample at this temperature.

4 Discussion and conclusions

Comparison was done between series of iron-based biogenic materials prepared by cultivation of *Leptothrix* group bacteria in different type feeding media (*Sphaerotilus-Leptothrix* group of bacteria isolation medium, Adler, Lieske, and silicon-iron-glucose-peptone), and control samples obtained in the same conditions and procedures but in the sterile nutrition media. The used characterization methods reveal the role of bacteria and the impact of media composition on the type and physicochemical properties of prepared materials. Comparative analysis showed differences in the phase composition and dispersity of iron compounds. The obtained materials included different ratio of nanodimentional iron oxyhydroxide and oxide phases. Relaxation phenomena were registered as superparamagnetism or collective magnetic excitation behaviour. The biogenic materials were enriched in oxyhydroxides of high dispersion. The composition of cultivation medium, the concentration of substrates, the conditions during the incubation period, and the presence of nucleation sites influence the mechanism of biotic and abiotic Fe^{2+} oxidation resulting in formation of a variety of iron compounds. The role of a given factor can be predominant in one or another case but the join effect cannot be excluded. The *Leptothrix* genus of bacteria could be used for selective production of highly dispersed iron oxyhydroxide but the process of separation of the biomass should be improved and the conditions that diminish the chemical oxidation rate of Fe^{2+} ions should be adjusted. The study clearly shows formation of different materials in used feeding media, i.e. in feeding media with different chemical composition. One can speculate, the reasons for this are different ions (sulphates, nitrates, chlorides, organics, etc.) which are included in the feeding media used for bacteria cultivation. Variation of the medium composition gives rise to formation of different precursors containing FeO_6 coordination polyhedra. The cultivation of the *Leptothrix* genus of bacteria in the growth media of Adler, SIGP, Lieske, and SLGBIM results in the formation of biomass that contains nanosized iron oxyhydroxides (α-, γ-, and/or β-FeOOH) and Fe_3O_4 in different ratios. The comparison of the biogenic and abiotic (control samples) leads to a conclusion that the produced nanosized iron oxide materials are relatively close as phase composition, but the choice of feeding media determinates in great extent the properties of prepared biogenic materials.

Catalytic behaviour of a selected biomass (SIGP) in the reaction of catalytic oxidation of CO with oxygen studied by in situ DRIRS revealed that the phase transformations in the biomass determine the catalytic properties.

Acknowledgments The authors are grateful to the Bulgarian Science Fund for the financial support through project T02-17/2014.

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