

Sorption of chromium (VI) by Mg/Fe hydrotalcite type compounds

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Abstract The synthesis by co-precipitation and characterization by X-ray diffraction, Raman and Mössbauer spectroscopies of Mg-Fe-hydrotalcite compounds, and their sorption capacities for Cr(VI) in aqueous media were carried out. The average sorption capacity of Cr(VI) for the non-thermal treated samples was of 6.2 mg/g. The ferrihydrite was

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omnipresent in all prepared hydrotalcite samples. A brief discussion is made on the role of both the hydrotalcite and ferrihydrite for removing such amount of Cr(VI).

Keywords Hydrotalcites · Cr(VI) · Environment

1 Introduction

Hexavalent chromium, Cr(VI), is used in a great variety of industrial processes including metal plating, leather tanning, chromium beneficiation, fertilizer, textile production and several other industries [1–4]. The residuals of these industries are the primary sources of Cr(VI) in the atmosphere, rivers and soil, representing a high risk for the human health.

Cr(VI) exists in solution as hydrochromate (HCrO_4^-), chromate (CrO_4^{2-}), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ionic species. The proportion of each one of these ions in solution is pH dependent and in basic and neutral pH, the chromate form predominates. The hydrochromate concentration increases as the pH is lowered from 6.2 to 6.0 and the dichromate species predominate at $\text{pH} < 6$ [5].

The Environmental Protection Agency (EPA) has stipulated the permissible limits of 0.1 mg/L or 100 ppb for total chromium in drinking water, including all the afore mentioned forms of Cr(VI). According to the Mexican regulations the permissible limit of Cr (VI) to be discharged on surface water for industrial effluents is 0.05 mg/L monthly [6].

Removing Cr(VI) from the environment is then of paramount importance, and in this work Cr(VI) is removed from aqueous solutions using a Mg-Fe hydrotalcite (Mg-Fe-HT) type compound as sorbent.

Sorption is one of the most common methods for the removal of hexavalent chromium from wastewaters and in recent reports layered double hydroxides (LDHs) or hydrotalcites have been used for the removal of several contaminants [7–13]. Some years ago Kok-Hui et al. [14] and the KWR Watercycle Research Institute [15] published review articles where methods for chromium removal from water using LDHs were included.

The general chemical formula of the LDHs is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{Al}^{n-}]_{x/n}\cdot n\text{H}_2\text{O}$ where M^{2+} could be Mg(II) with ionic radius of 0.65 Å, and M^{3+} could be Al (III) with ionic radius of 0.50 Å, or Fe(III) with 0.64 Å [16]. The partial or total substitution of Al by Fe in LDHs is an attractive line of research and of increasing interest for their use as catalyst precursors [17, 18] and for removal of colorants [19]. J. Das [12] has published a paper on the removal of chromium by using Mg-Fe-HT. In this line the present paper investigates the sorption characteristics of Cr(VI) in a Mg-Fe-HT compound in aqueous medium and the factors affecting it such as pH and Cr(VI) concentration, with the objective to provide an effective mean for the removal of Cr(VI) from wastewater streams. Furthermore, we present the synthesis, characterization and the adsorption isotherms of Cr(VI) in the synthesized Mg-Fe HT compound.

2 Experimental

2.1 Sample preparation

All chemical reagents used were of analytical reagent grade without further purification. The hydrotalcite compound of Mg-Fe, was prepared from the co-precipitation method [5].

The nitrates salts of iron and magnesium were the metal sources and the nominal metal molar ratio of Mg to Fe was 3. The solution reaction at 45 °C (± 1 °C) was kept under magnetic stirring and solutions of Na₂CO₃ and NaOH were used to keep a solution pH = 9.0. The obtained product (HTFeMO9A) was divided into two parts. One of them was re-crystallized at 65 °C for a time period ranging between 18 h (HTFeMO9B). The final solids were separated and dried at 80 °C for 48 hours. Two products were used and identified as: the non-re-crystallized (HTFeMO9A) and re-crystallized (HTFeMO9B) samples.

Each sample was used for obtaining sorption isotherms by batch test where 100 mg of HTFeMO9B or HTFeMO9A samples without calcinations were put in contact with the following solutions:

- a) Different concentrations of potassium dichromate (K₂Cr₂O₇) were prepared using distilled water: 5, 10, 15, 20, 25, 30, 50, 60, 75, 100 mg dichromate/L. Aliquots of 10 mL of these solution without pH adjustment were used, where the pH solution was approximately 5.
- b) The same as above but adjusting the pH solution to 3.

The resulting mixtures were mechanically stirred at 30 °C for 24 hours, then the reaction products were decanted by centrifugation during 10 minutes at 5000 rpm and these products were washed twice using distilled water; the residual levels of chromium not adsorbed by the Mg-Fe-HT samples were determined from the mother liquid by atomic absorption in a Perkin Elmer Analyst 200 unit using a chromium lamp at 428.9 nm. All experiments were carried out twice for consistency.

After processing the samples with chromium, they were identified as HTFeMO1003A and HTFeMO1003B for measurements for pH = 3, and HTFeMO1005A and HTFeMO1005B for pH = 5, respectively.

2.2 Sample characterization

2.2.1 Sorption isotherms

Langmuir model This model considers that the maximum sorption corresponds to a monolayer saturated with adsorbate molecules on the sorbent surface. The Langmuir isotherm is represented by the following equation:

$$q_e = \frac{q_o b C_e}{1 + b C_e} \quad (1)$$

where q_o is the amount of chromium adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g), q_e is the amount of chromium adsorbed at equilibrium (mg/g), calculated by the following expression:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

C_i is the initial concentration and C_e is the remaining concentration of the chromium in the solution at equilibrium (mg/L), m (g) was the amount of sorbent used, V (L) the volume of the solution and b is the constant related to the energy or net enthalpy of the sorption.

Freundlich model The Freundlich model has been applied to adsorbents with heterogeneous surfaces and considers multilayer sorption, which is given as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

where q_e is the amount of chromium adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of chromium in solution (mg/L), K_f is the equilibrium constant indicative of adsorption capacity, and n is the adsorption equilibrium constant whose reciprocal is indicative of the heterogeneity of surface sorbent. If the ratio $1/n < 1$, implies a heterogeneous surface with minimum interaction between adsorbed atoms is present [20]. The heterogeneity concept refers to different chemical species not to different textures in the same material.

2.2.2 Specific surface area and pore size

The specific surface area (m^2g^{-1}) and pore size was determined for the studied samples using the multipoint N_2 adsorption/desorption Brunauer-Emmett-Teller (BET) method in a BEL Instrument. The samples submitted to this analysis were heated previously to $200\text{ }^\circ\text{C}$ for 2 hours.

2.2.3 X-ray diffraction (XRD)

The samples, before and after sorption of chromium, were characterized by X-ray diffraction (XRD) by using a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ radiation and a diffracted beam mono-chromator. The X-ray tube was operated at 35 kV and 20 mA. The crystalline compounds were conventionally identified by using the Joint Committee of the Powder Diffraction Standard (JPDFS) cards.

2.2.4 Raman spectroscopy (RS)

Raman scattering spectra were acquired by using a Jobin Yvon Horiba LabRam HR 800 spectrometer equipped with an Olympus BX41 microscope and at 532.12 nm. The spectra were recorded from 250 to 3800 cm^{-1} .

2.2.5 Mössbauer spectroscopy (MS)

The Mössbauer characterization of the samples was performed by using a Wissel equipment in the conventional transmission mode and operating with the constant acceleration option. A $^{57}\text{Co}/\text{Rh}$ source was used and the isomer shifts are referred to that of metallic iron.

3 Results and discussion

3.1 Sorption isotherms

The maximum sorption of chromium in these experiments was of about 6 mg of Cr(VI) per gram of hydrotalcite adsorber, as shown in Fig. 1. There was a slight difference in sorption characteristics between the non-re-crystallized and re-crystallized samples. The data of the isotherms were analyzed by using the Langmuir and Freundlich equations to investigate the sorption characteristics. The best fit to this data was made by using the Freundlich equation suggesting a multilayer adsorption process in a heterogeneous surface. Figure 1 shows the fitting data of the obtained isotherms at $\text{pH} = 3$, (a) and at $\text{pH} = 5$, the sorption of Cr (VI) for $\text{pH} = 5$ was a little higher than at $\text{pH} = 3$.

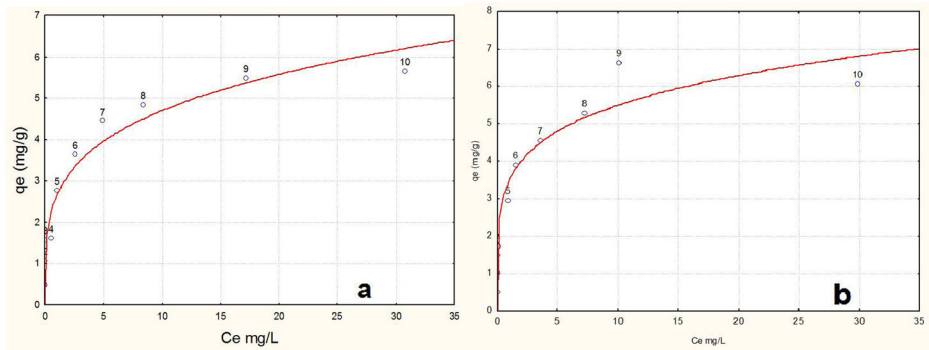


Fig. 1 Experimental and fitted data of the resulting sorption isotherms according to the used pH solution: **a** HTFeMO1003A, pH = 3 and **b** HTFeMO1005A, pH = 5

Table 1 Sorption data of Cr(VI) in Mg-Fe-HT at different pHs using the Langmuir and Freundlich models

Langmuir model	HTFeMO1005A	HTFeMO1005B	HTFeMO1003A	HTFeMO1003B
pH	5	5	3	3
q_o (mg/g)	6.35	6.20	5.79	6.82
b	1.039	2.61	0.74	0.416
R^2	0.924	0.85	0.938	0.9508
Freundlich Model				
K_F	3.51	3.54	2.66	2.63
n	5.15	4.54	4.04	4.04
$1/n$	0.19	0.22*	0.25	0.25
R^2	0.959	0.881	0.921	0.943

If $1/n < 1$ means that the sorption is favorable and a heterogeneous surface is present

The numerical sorption data for Cr(VI) in the studied Mg-Fe-HT samples applying the Langmuir and Freundlich models are given in Table 1 where an average value of 6.2 mg/g were removed from the initial aqueous solutions. Present results can be compared with those reported by Das et al. [12], where potassium dichromate was also used as the Cr source. These authors reported 2.53 mg/g using a pH = 6 and the sorbed chemical specie was suggested to be the hydrochromate ion (HTCrO_4^-) which interacts with the hydroxide surface strongly the studied pH [12].

3.2 Specific surface area and pore characteristics

The specific surface area before and after the sorption process have about the same value with an average value of 76.6 m^2/g . Once the Chromium was incorporated to both the non-re-crystallized (HTFeMO9A) and re-crystallized (HTeFeMO9B) samples, this value decreased as shown in Table 2, being this decrease for the non-re-crystallized sample higher than for the re-crystallized sample. Whereas the *MDP* (mean pore diameter) of both samples increased after the sorption experiments, the *TPV* (total pore volume) remained basically the

Table 2 Specific surface area (*S*), pore characteristics and Crystal size (*D*)

Sample	<i>S</i> (<i>m</i> ² / <i>g</i>)	MPD (<i>nm</i>)	TPV (<i>cm</i> ³ / <i>g</i>)	<i>D</i> (Å)
HTFeMO9A	77.29	13.07	0.25	1.53
HTFeMO1003A	54.47	17.05	0.23	1.78
HTFeMO1005A	58.13	16.24	0.24	1.84
HTFeMO9B	75.90	14.14	0.27	1.52
HTFeMO1003B	66.82	17.63	0.29	1.85
HTFeMO1005B	64.50	17.03	0.27	1.85

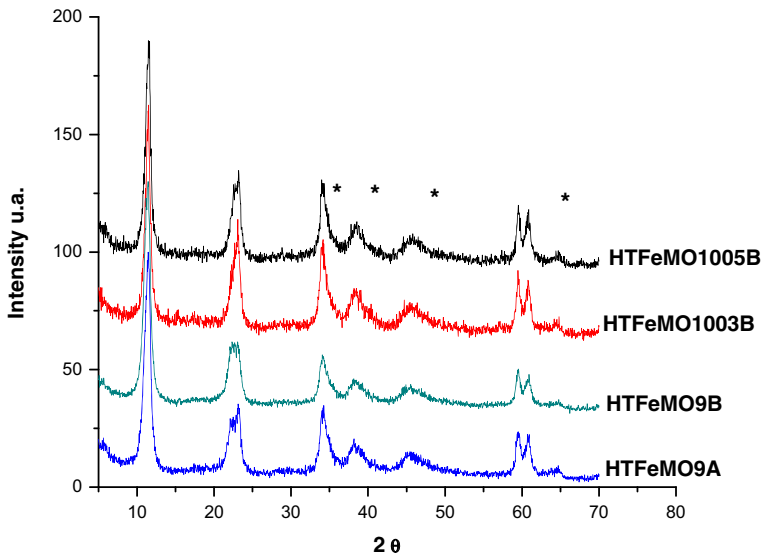


Fig. 2 Typical powder XRD patterns of the different studied products. The asterisks indicate the broad lines of the six line ferrihydrite, the fourth line with Miller numbers 114 at around 53° does not appear because of its low intensity

same. All these little changes in *S* (specific surface area) as well as *TPV* did not influence the sorption capacity of chromium.

3.3 DRX

Figure 2 shows the powder XRD patterns of the non-re-crystallized (HTFeMO9A) and re-crystallized (HTFeMO9B) samples. These patterns do not show significant differences, the line widths of the first peak at 11° 2θ, for example, are 0.91° 2θ, suggesting practically the same crystal for the HTFeMO9A and HTFeMO9B samples. The estimated crystal size from the Debye-Scherrer formula, using the line at 11° 2θ of the samples is given in the last column of Table 2, where a small increase is observed for the samples after the sorption of chromium.

One can also observe from the XRD patterns the asymmetry of some lines suggesting the presence of the six line ferrihydrite as impurity [22].

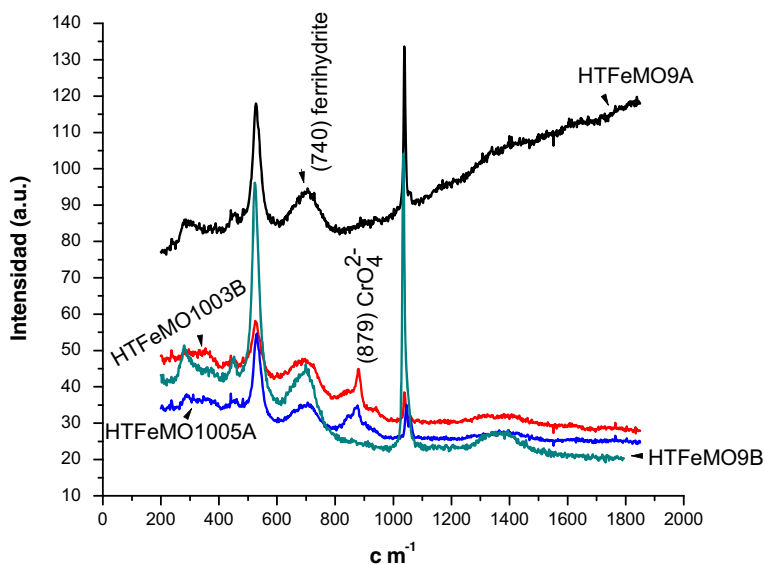


Fig. 3 Raman spectroscopy of the hydrotalcites before and after Cr(VI) sorption at pHs 3 and 5

3.4 Raman spectroscopy

Raman spectroscopy is suited to identify the nature of the layer and interlayer vibrations and to investigate the interactions of the whole structure, particularly the hydrogen-bond network. Raman bands (around 510 cm^{-1} , 1040 cm^{-1} , $1270 - 1500\text{ cm}^{-1}$) are typical for hydrotalcite structure [21]. According to Dias et al. [23], the bands at 440 and 510 cm^{-1} may arise from symmetrical vibrations of Fe-OH bonds. The broad bands at $600-800$ and $1260-1500$ can be associated with ferrihydrate [24]. On the other hand, the band appearing at around 880 cm^{-1} has been assigned to chromates ions [25] and finally according to Degen et al. [26] the sharp line at 1020 cm^{-1} can be assigned to carbonates ions. Again the ferrihydrate is always observed in the Raman spectra of all studied samples as by product that can not be avoid while preparing the Mg-Fe-HT compound. In addition to this, the Raman bands associated with the hydrotalcite structure may be shifted by the presence of this by product (Fig. 3).

3.5 Mössbauer spectroscopy

The Mössbauer spectrum of any of the studied samples, consisting of a broad asymmetrical doublet, can be analyzed by two quadrupole doublets as indicated in Table 3 and shown in Fig. 4a. A singlet of low relative intensity could also be included in the fitting analysis, improving a little the fitting criterion. The average parameters of this singlet were $\delta = 0.06\text{ mm/s/Fe}^0$, $W = 0.23\text{ mm/s}$ and a relative intensity of $I = 4.9\%$. One of the doublets is usually associated with structural Fe-OH bonds of the hydrotalcite and the other doublet to the presence of the ferrihydrate [27–29]. The hyperfine parameters of ferrihydrate are those of the lower isomer shift and having the higher relative intensity that ranges from 57.75 up to 71.05% , the lower relative intensity ranging from 28.95 up to 42.25% can be associated with the structural iron.

Table 3 Mössbauer data of the Mg-Fe-HT samples before and after the sorption of Cr(VI)

Sample	$\delta^{(*)}$,	Δ ,	W	I (%)
		(mm/s)		
HTFeMO9A	0.34	0.50	0.37	67.19
	0.38	0.80	0.46	32.81
HTFeMO1003A	0.35	0.50	0.35	65.70
	0.39	0.81	0.43	34.30
HTFeMO1005A	0.34	0.50	0.37	70.90
	0.40	0.79	0.41	29.10
HTFeMO9B	0.33	0.49	0.36	57.75
	0.38	0.72	0.45	42.25
HTFeMO1003B	0.33	0.49	0.37	71.05
	0.40	0.76	0.42	28.95
HTFeMO1005B	0.34	0.50	0.37	69.68
	0.39	0.79	0.43	30.32

(*) relative to metallic iron

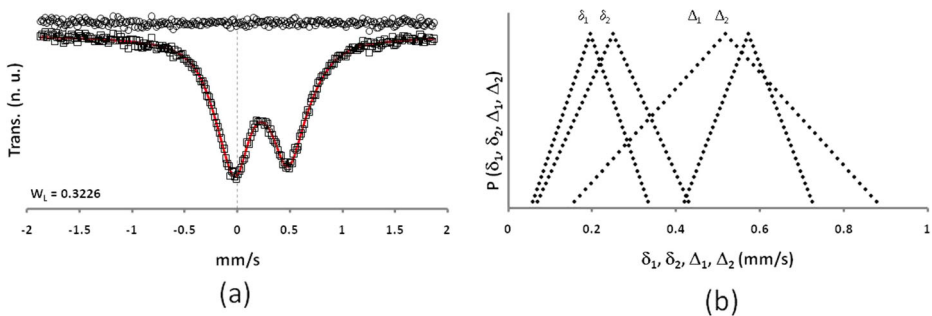


Fig. 4 Mössbauer spectrum of the Mg-Fe-HT sample. The isomer shifts (δ_1 , δ_2) in this figure are no referred to that of metallic iron

Under the present preparation condition of the hydrotalcite, the ferrihydrite is omnipresent [29] and its effect on the sorption must be studied further. The capacity sorption of our Mg-Fe-HT samples is higher than the hydrotalcites prepared by Das et al. [12]. A possible explanation for difference may be associated with the amount of ferrihydrite that is present in our samples with respect to those of Das et al. [12].

Figure 4 shows a fitting analysis of one of the Mössbauer spectra of our samples by using triangular distribution functions for each of the hyperfine parameters of the two quadrupole doublets. First, by doing this analysis the line asymmetry that presents the spectrum is solved. When a discrete fitting analysis is done by using quadrupole doublets of equal intensity such a line asymmetry is not solved. Ferreira et al. [28] have shown that this line asymmetry is not related to texture effects but due to a distribution of values on the hyperfine parameters of these quadrupole doublets. On the other hand, one can observe from Fig. 4b that the distribution of the quadrupole doublet associated with structural Fe in the hydrotalcite is wider than that due to the ferrihydrite. This would suggest that the surrounding of the

structural Fe of the hydrotalcite is more heterogeneous than those iron sites of the ferrihydrite. Alternatively this heterogeneity should contribute to the larger capacity of sorption of present samples.

4 Conclusions

The sorption characteristics of Mg-Fe-HT compounds were studied using pH's 3 and 5. The sorption capacity for samples treated at pH = 5 was slightly higher than those samples treated at pH = 3. An average value of 6.2 mg/g of Cr(VI) was removed from aqueous solutions using the Mg-Fe-HT samples without calcinations.

XRD, Raman and Mössbauer spectroscopies show the presence of nano-metric ferrihydrite, which may also be involved in the sorption process of chromium. From the Mössbauer analysis a heterogeneous surrounding for the structural Fe of the hydrotalcite is inferred which would suggest that these iron sites also contribute to the sorption process.

References

1. U.S. Environmental Protection Agency Washington, www.epa.gov (1998)
2. Li, Y., Gao, B., Wu, T., Sun, D., Li, X., Wang, B., Lu, F.: *Water Res.* **43**, 3067 (2009)
3. Mor, S., Ravindra, K., Bishnoi, N.R.: *Bio. Tech.* **98**, 954 (2007)
4. Weckhuysen, B.M., Wachs, I.E., Schoonheydt, R.A.: *Chem. Rev.* **96**, 3327 (1996)
5. Grevatt, P.C.: U.S. environmental protection agency Washington. www.epa.gov (1998)
6. NOM-002-ECOL-1996
7. Goswamee, R.L., Sengupta, P., Bhattacharyya, K.G., Dutta, D.K.: *App. Clay Sci.* **13**, 21–34 (1998)
8. Lazaridis, N.K.: *Water Air Soil Pollut.* **146**, 127 (2003)
9. Terry, P.A.: *Chemosphere* **57**, 541 (2004)
10. Lazaridis, N.K., Pandi, T.A., Matis, K.A.: *Ind. Eng. Chem. Res.* **43**, 2209 (2004)
11. Gasser, M.S., Mohsen, H.T., Aly, H.F.: *Colloids Surf. A Physicochem. Eng. Asp.* **331**, 195–201 (2008)
12. Das, J., Das, D., P.Dash, G., Das, D.P., Parida, K.: *Intern. J. Environ. Studies* **61**(5), 605 (2004)
13. Triantafyllidis, K.S., Peleka, E.N., Komvokis, V.G., Mavros, P.P.: *J. Colloid Interface Sci.* **342**, 427–436 (2010)
14. Kok-Hui, G., Teik-Thye, L., Dong, Z.: *Water Res.* **42**, 1343 (2008)
15. KWR, Watercycle Research Institute BTO 2012.004. www.kwrwater.nl (2012)
16. Cavani, F., Trifiró, F., Vaccari, A.: *Catal. Today* **11**, 173 (1991)
17. Kumbhar, P.S., Sánchez-Valente, J., Millet, J.M.M., Figueras, F.: *J. Catal.* **191**, 467–473 (2000)
18. Kawabata, T., Fujisaki, N., Shishido, T., Nomura, K., Sano, T., Takehira, K.: *J. Mol. Cat. A: Chem.* **253**, 279 (2006)
19. Benselka-Hadj Abdelkader, N., Bentouami, A., Derriche, Z., Bettahar, N., de Menorvald, L.-C.: *Chem. Eng. J.* **169**, 231–238 (2011)
20. Jimenez-Becerril, J., Solache-Rios, M., García-Sosa, I.: *Water Air Soil Pollut.* doi:10.1007/s1-1270-011-0925-3
21. Rozov, K., Berner, U., Taviot-Gueho, C., Leroux, F., Renaudin, G., Kulik, D., Diamond, L.W.: *Cem. Concr. Res.* **40**, 1248–1254 (2010)
22. Drits, V.A., Sakharov, B.A., Salyn, A.L., Manceau, A.: *Clay Minerals* **28**, 185–207 (1993)
23. Días, A., Cunha, L., Vieira, A.C.: *Mat. Res. Bull.* **46**, 1346–1351 (2011)
24. Bellot-Gurlet, L., Neff, D., Règuer, S., Monnier, J., Saheb, M., Dillmann, P.: *J. Nano Res.* **8**, 147–156 (2009)
25. Nakamoto, K. *Infrared and raman spectra of inorganic and coordination compounds*, 4th edn. John Wiley & Sons (1986)
26. Degen, I.A., Newman, G.A.: *Spectrochim. Acta A: Molecular Spectroscopy* **49**(5/6), 859–887 (1993)
27. Schütz, M.R., Schedl, A.E., Wagner, F.E., Breu, J.: *Appl. Clay Sci.* **54**, 281–286 (2011)
28. Ferreira, O.P., Alves, O.L., Gouveia, D.X., Souza Filho, A.G., de Paiva, J.A.C., Mendes Filho, J.: *J. Sol. State Chemistry* **177**, 3058–3069 (2004)
29. Sanchez Valente, J., Millet, J.M.M., Figueras, F., Fournes, L.: *Hyperfine Interactions* **131**, 43–50 (2000)