Raman and IR spectroscopic investigation of As adsorbed on Mn_3O_4 magnetic composites

Gabriela C. Silva [a,c], Fabiana S. Almeida [b,c], Maria Sylvia S. Dantas [a,c], Angela M. Ferreira [b,c], Virginia S.T. Ciminelli [a,c,*]

[a] Department of Metallurgical and Materials Engineering - Universidade Federal de Minas Gerais (UFMG), 31270-901 - Belo Horizonte, Brazil
[b] Department of Chemistry - Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), 30421-169 - Belo Horizonte, Brazil
[c] National Institute of Science and Technology on Mineral Resources, Water and Biodiversity (INCT-Acqua), Brazil

ARTICLE INFO

ABSTRACT

Raman and IR spectra were recorded of the As-loaded Mn_3O_4 magnetic composites obtained from the adsorption studies performed with As(III). XANES results for the composite after As(III) removal tests show that the As adsorbed is at the oxidized arsenic form, As(V). Monodentate and bidentate surface complexes are suggested for arsenic adsorption onto the composite (5–16 mg/g). Precipitation of manganese arsenate is observed for high As loading (35 mg/g).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Arsenite and arsenate adsorption in metal oxides is one of the processes that control arsenic distribution in the environment. Manganese oxides are effective oxidants in the transformation of As(III) to As(V) and allow a stronger fixation and removal of greater amounts of arsenic at pH below 7. In particular, manganese dioxides are the most reported manganese oxides in literature used in water treatment [1–3]. Some researchers suggest that the oxidation of As(III) to As(V) by manganese dioxides involves the reduction of Mn(IV) to Mn(III) and, further, of Mn(III) to Mn(II) [4–8]. Many works on the complexation of arsenite and arsenate by manganese dioxides using XAFS show that As(III) is oxidized to As(V) and only arsenate is found as the adsorbed species on MnO_2 [7,9,10]. The majority of these works shows that arsenate is adsorbed in the edge of MnO_2, binding to the Mn(IV) octahedra in bidentate binuclear form [7,9]. A more recent work [10] has shown that arsenate can bind to the Mn(IV) octahedra in a monodentate mononuclear form and to the Mn(III) octahedra in a bidentate mononuclear form. Dias et al. [8] have shown that during As(III) sorption in a

manganese dioxide (Na-birnessita, $Na_{0.55}Mn_2O_4\cdot1.5H_2O$), haus-mannite ($Mn_3O_4$), a manganese oxide very common in soils, is the intermediate product of reductive dissolution of manganese dioxide and arsenate is adsorbed in Mn_3O_4 surface. Moreover, it has been demonstrated that precipitation of a Mn(II) arsenate, $Mn_3(AsO_4)_2$, occurs for high arsenic concentrations (above 160 mg/L). Hausmannite [Mn_3O_4 or $(Mn^{2+})(Mn^{3+})_2O_4$] is a spinel manganese oxide with structural distortions caused by Jahn–Teller effect, having Mn(II) ions in tetrahedral coordination and Mn(III) ions in distorced octahedral coordination. Mn_3O_4 magnetic composites combine the oxidative property of Mn_3O_4 with the magnetic property of ferromagnetic iron oxides, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), which will help the solid-liquid separation process that follows arsenic sorption. In a previous work [11], we have synthesized Mn_3O_4 magnetic composites to remove As(III) from solutions and have shown that the magnetic composite presents high affinity for arsenic. However, no detailed study has been carried out to show how arsenic is complexed on the surface of hausmannite. Raman and IR spectroscopy are techniques that measure the vibrational modes of molecules and present the benefits of the identification of less crystalline and amorphous phases, and small amounts of material. Many works have used both vibrational spectroscopic techniques to elucidate the molecular structure of many systems, such as natural and synthetic organic and inorganic materials to be applied in biotechnology, catalysis, magnetism, electronics and optics [12–15]. Our group has applied

---

vibrational spectroscopy in environmental area for the investigation of surface-bound complexes on a variety of materials, such as oxi-hidroxides, soil constituents, modified clays and biomass. The techniques contributed to define the speciation of the chemical element, the identification of molecules and the types of bonds involved, which allow inferring about the mobility of the contaminants in environmental systems [8,16–20]. The present work aims to understand the arsenic complexation by a magnetic Mn_3O_4 composite using Raman and IR spectroscopy.

2. Experimental

All chemicals were of analytical grade and used without further purification. All solutions were prepared with deionized water with a conductivity of $18.2 \, \mu S/cm$ obtained with a Milli-Q water purification system (Millipore).

2.1. Synthesis of the Mn_3O_4 magnetic composite

For the preparation of the composite, 1000 mL of deionized water was placed in contact with 1.0 g of previously synthesized magnetite nanoparticles and 45 mL of 1 M $MnCl_2 \cdot 4H_2O$ (Sigma–Aldrich) solution at pH 12 (1 M KOH – Sigma–Aldrich) in a 2000 mL Pyrex beaker under stirring (mechanical stirrer, Fisatom 713 D) and constant air input (aquarium pump Power 500) during 30 min. A brown colored solid was separated from solution by a neodymium magnet (180 mm × 100 mm × 35 mm, Imatec *Produtos Magnéticos Ltda*), washed with deionized water solution and dried in a dessicator at room temperature. Magnetite particles were prepared by a chemical precipitation route. An aqueous solution prepared with 400 mL of deionized water, 9.61 g of $Fe_2(SO_4)_3 \cdot 5H_2O$ (97%, Aldrich), 7.13 g of $FeSO_4 \cdot 7H_2O$ (RegentPlus™, ≥99.0% – Aldrich) and 100 mL of a 5 M KOH (Sigma–Aldrich) solution was stirred under N_2 atmosphere at 70 °C for 2 h. The black suspension was filtered, washed with water several times, and finally dried in an oven at 45 °C.

2.2. Adsorption experiments

The adsorption studies were performed batchwise. The As solutions were prepared by dissolving sodium (meta)arsenite ($NaAsO_2$, purity >99%, Fluka) in Milli-Q water. The adsorption studies were carried out in 250 mL Pyrex vessels sealed with laboratory parafilm (Pechiney plastic packaging, USA). In the experiments 0.2 g of the adsorbent were added to the Erlenmeyer flasks, filled with 100 mL arsenic solution containing different amounts of arsenic. The Mn_3O_4 magnetic composite samples were exposed to As concentrations from 1 mg/L to 50 mg/L and also 1000 mg/L. Agitation at 200 rpm was provided by a thermostatic shaker, manufactured by New Brunswick Scientific Edison, USA. Agitation rate, pH and temperature were controlled in all sorption experiments; temperature and pH were maintained at (25 ± 5 °C) and 5, respectively. In order to produce an adequate reference material for the spectroscopic measurements, blank samples were prepared in Milli-Q water under the same pH conditions as the experiments with As. After 24 h, the pH of the solutions was measured and the solids of each flask were separated by a magnet and the supernatant solution vacuum-filtered through a 0.22 μm membrane filter (Fisher Scientific). Subsequently, the solids were rinsed with Milli-Q water. The filtrate was assayed for total arsenic directly by inductively coupled plasma optical emission spectrometry, ICP-OES (Perkin-Elmer Optima 7300 DV).

2.3. Spectroscopic analysis

Raman spectra were obtained on a Horiba Jobin Yvon LABRAM-HR 800 spectrograph, equipped with a 633 nm helium–neon laser, 20 mW of power, attached to an Olympus BHX microscope equipped with 10×, 50×, and 100× lenses. Raman-scattered radiation was collected with 600 g/mm grating, in a 180° backscattering configuration. The spectra were collected in a frequency range of 100 to at least 1100 cm^{-1} with a step size of 1.1 cm^{-1}. In order to suppress extra noise and to obtain sufficiently accurate results, a N_2 cooled charge couple device (CCD) detector was used as the detecting device. To reduce noise ratio, spectra were acquired at acquisition time of three minutes twenty times. Raman spectra were recorded of all freshly prepared samples, as well as of As-loaded samples. A small amount of the grounded sample was put on a glass and softly pressed with another one.

A Perkin Elmer, Paragon 1000 spectrometer was used for IR spectra collection. The sample scans ranged from 400 to 4000 cm^{-1} with 4 cm^{-1} resolution and were obtained as 128 scans. IR spectra were obtained as dry samples mixed with KBr corresponding to 8 mg of sample in approximately 40 mg of spectral grade KBr. In IR spectroscopy it is of importance to work with dried samples, since minor amounts of humidity disturbs the IR signal. Thus, before sample preparation, KBr was kept in an oven (130 ± 2 °C) for at least 24 h. The samples were stored at room temperature (25 ± 2 °C) in a desiccator, filled with silica gel. The KBr was grained along with each sample manually by using a mortar and pestle. Subsequently, the mixture was filled into the sample cup with attention to homogeneity and leveled surface, and absence of clusters.

The collected Raman and IR data were baseline-corrected and curve-fitted to obtain quantitative band parameters, such as peak maxima, widths, intensities and areas, by using the software Peakfit 4.0.

X-ray absorption near-edge structure (XANES) spectra of the arsenic K edge (11,868 eV) were obtained to determine arsenic oxidation states at As-loaded solids using the synchrotron facilities at the Brazilian Synchrotron Light Laboratory (LNLS), in Campinas, Brazil, at the XAFS2 workstation in the transmission mode under operation conditions of 1.37 GeV and beam currents of approximately 250 mA. The spectra were collected at room temperature using a Si (1 1 1) double crystal monochromator with an upstream vertical aperture of 0.3 mm and calibrated with Au L_1-edge (11,918 eV). The samples were fixed onto acrylic holders, sealed with Kapton tape film, placed at a specific angle to the incident beam. Energy calibration was monitored during data collection by acquiring reference Au foil spectra simultaneously.

3. Results and discussion

The Raman spectrum of Mn_3O_4 magnetic composite shows the main bands reported in literature for Mn_3O_4: a very sharp peak at 661 cm^{-1}; two smaller peaks located at 293, 323 and 378 cm^{-1}; and a weak signal at 485 cm^{-1} (Fig. 1) [21].

The arsenic sorption isotherm (initial As concentrations from 1 mg/L to 50 mg/L) for the Mn_3O_4 magnetic composite is shown in Fig. 2. The maximum sorption capacity and affinity of arsenic ions were evaluated from the isotherms by combined Langmuir and Freundlich model (Fig. 2), where q is the amount of arsenic adsorbed per unit surface area of adsorbent (mg/m^2), C_e is the equilibrium concentration of arsenic (mg/L), b is the constant related to the free energy of adsorption (L/mg), q_m is the maximum adsorption capacity (mg/m^2), and ($1/n$) is the adsorption intensity. The sample shows high affinity, as indicated by the slope ($b = 2$ and $n = 1.5$), for As with maximum sorption capacity of $0.42 \, mg/m^2$ (14 mg/g or 0.0048 $mmol/m^2$). Raman spectra were obtained for As
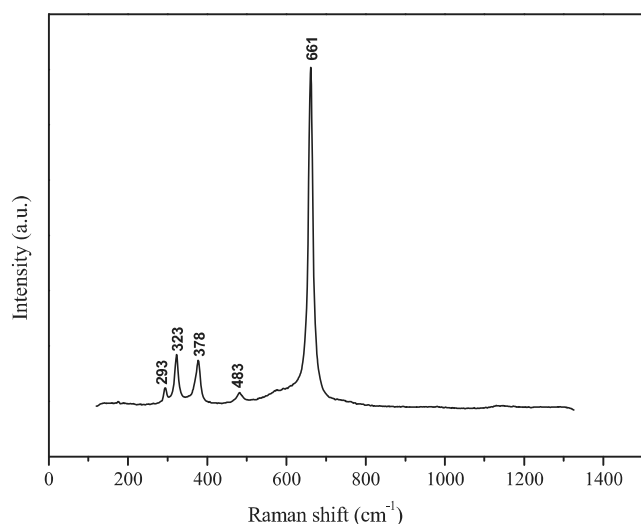
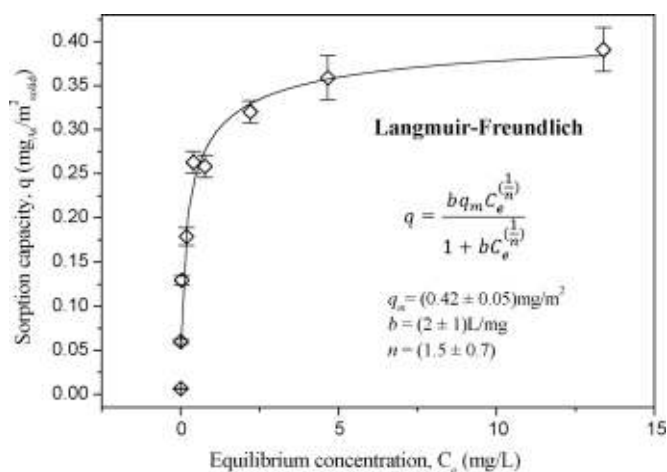**Fig. 1.** Raman spectra of the Mn_3O_4 magnetic composite.

Fig. 4. Derivative of As K-edge room temperature XANES spectra of the As-loaded Mn_3O_4 magnetic composite and As(III) and As(V) standards (AsNaO$_2$ and AsHNa$_2$O$_4 \cdot$7H$_2$O, respectively).

Fig. 2. Isotherm for As(III) sorption on the Mn_3O_4 magnetic composite. Experimental conditions: pH 5, 200 rpm, 24 h (25 ± 0.5)°C.

adsorbed onto the synthesized Mn_3O_4 magnetic composite sample. As a result of the adsorption process the obtained spectra present distinct differences in the region from 750 to 950 cm^{-1}. The results are compiled in Fig. 3 and the peak fittings of the spectra are shown in Fig. S1. All reacted samples with As loading varying from 5 to 16 mg/g (Fig. 3a, Fig. S1 and Table S1) exhibit, in their Raman spectra, bands centering at $\sim$830 cm^{-1} and $\sim$900 cm^{-1}, which are related to arsenic adsorption, since they do not appear in the spectrum of blank sample (Fig. S1 and Table S1). XANES results show that the As adsorbed in the samples from 5 to 35 mg/g of arsenic loading is at the oxidized arsenic form, As(V) (Fig. 4). Therefore, arsenate not arsenite species are complexed to the Mn_3O_4 surface in the composite.

The vibrational spectra of bound As compounds seem to be more complex to interpret than those of protonated aqueous As species. Arsenic complexes may exhibit shifts in As–OM (M = Metal) symmetric vibrations, according to the type of interactions, such as ion-pair, monodentate complex, bidentate complex or polymer formation. Furthermore, these vibration shifts are specific to the type
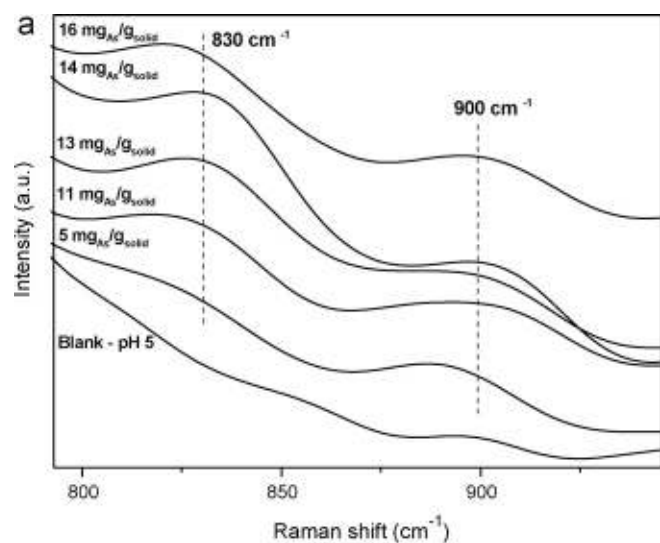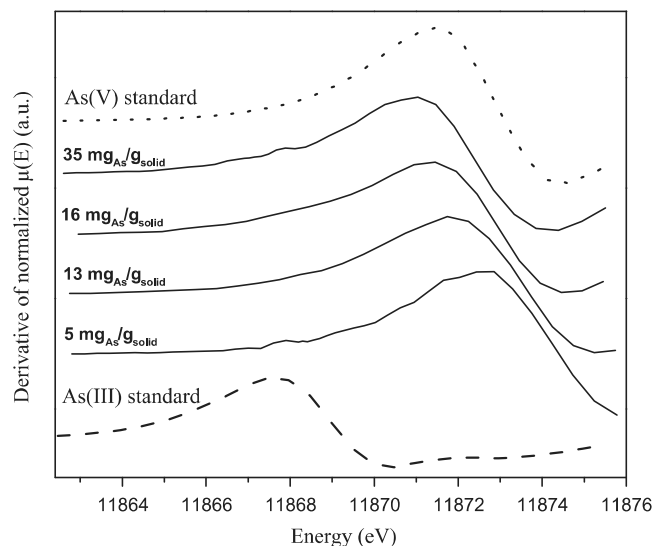

Fig. 3. Raman spectra of the Mn_3O_4 magnetic composite after As(III) sorption tests: (a) blank sample (solid in contact with a pH 5 solution) and As-loaded samples from 5 mg$_{As}$/g$_{solid}$ until 16 mg$_{As}$/g$_{solid}$; (b) 35 mg$_{As}$/g$_{solid}$ loaded sample; inset showing a Raman microscope image of the sample.

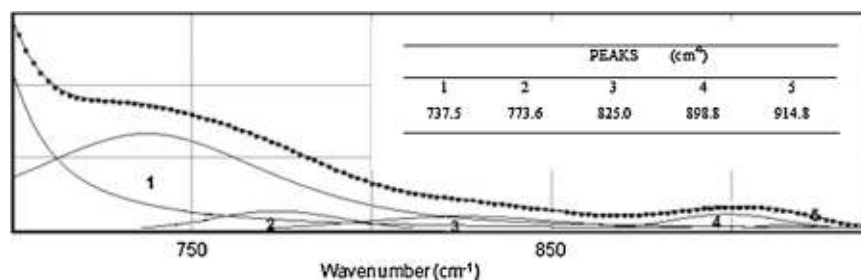|	PEAKS	(cm)		
1	2	3	4	5
737.5	773.6	825.0	898.8	914.8

Fig. 5. Peak fitting of the IR spectra of the 14 mg_{As}/g_{solid} loaded Mn_3O_4 magnetic composite.

of complexed metal [22]. Müller et al. [16] recorded Raman spectra from As(V) aqueous solutions at various pH conditions and have shown that the AsO_4^{3-} species presents a strong line at 811 cm^{-1} and a small line at 785 cm^{-1}, which are assigned to the symmetric and asymmetric stretching vibrations of As–O, respectively. The results of Müller et al. [16] for As adsorbed onto iron oxides show only a band at ∼840 cm^{-1}, which was related to a shift of the As–O symmetric vibration of AsO_4^{3-}. Dias et al. [8] have shown that during As(III) sorption on a manganese dioxide (Na-birnessita, $Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$), Mn_3O_4 is the intermediate product of reductive dissolution of manganese dioxide and a band at 830 cm^{-1} in the Raman spectra is associated to the presence of arsenate adsorbed in Mn_3O_4 surface. Comparing the obtained Raman spectra of As adsorption (Fig. 3a, Fig. S1 and Table S1) with the results obtained by Müller et al. [16] and Dias et al. [8] (unique bands centered at 840 and 830 cm^{-1}, respectively), one can conclude that the bands found in this work, at ∼830 cm^{-1} and ∼900 cm^{-1}, which present similar intensities, are also due to the symmetric vibration of As–O. However, the presence of two bands instead of one is probably related to different type of interactions. Lafferty et al. [10] have shown that arsenate can bind to Mn(III) octahedra in both bidentate and monodentate mononuclear forms. Therefore, the band at ∼900 cm^{-1} could be associated to bidentate mononuclear forms, while the band at 830 cm^{-1} could be associated to monodentate mononuclear forms, since in bidentate mononuclear forms (As–Mn distance of 2.78 Å [10]) the As–O vibration is expected to occur in higher frequencies than in the monodentate mononuclear forms (As–Mn distance of 3.35 Å [10]) due to the smaller distances between Mn(III) and As(V). Raman spectroscopy mainly exhibits more intense bands resulting of symmetric vibrations, differently from IR spectroscopy, which provides primarily bands due to asymmetric vibrations. Both are important to characterize surface complexes. Hence, IR spectroscopy was applied to the 14 mg/g As loaded synthesized Mn_3O_4 magnetic composite. The recorded IR spectrum of arsenic adsorption onto the sample is compiled in Fig. 5. Fitting the spectral data suggests the presence of three bands at ∼737, 774 and 835 cm^{-1} and two bands at ∼899 and 915 cm^{-1}. The bands may result from splitting of asymmetric vibration related to symmetry reduction. The AsO_4^{3-} molecule with T_d symmetry presents one frequency for the symmetric stretching vibration and one for the asymmetric stretching vibrations. When the symmetry is reduced to C_{2v} (one oxygen of AsO_4^{3-} is bound – monodentate complexes), the frequency of the symmetric stretching vibration increases and the asymmetric stretching vibrations present two frequencies. Moreover, when the symmetry is reduced to C_{3v} (two oxygens of AsO_4^{3-} are bound – bidentate complexes), the frequency of the symmetric stretching vibration increases more and the asymmetric stretching vibrations present three frequencies [16]. Therefore, the presence of five bands related to asymmetric vibrations in IR spectra suggests the formations of both monodentate and bidentate complexes, confirming the Raman results.

Dias et al. [8] have shown that precipitation of a Mn(II) arsenate, $Mn_3(AsO_4)_2$, occurs at high arsenic loading, such as those occurring

close to saturation (i.e. maximum loading capacity of the sorbent). In our work, the only evidence of precipitation occurs for the sample with the highest As loading (35 mg/g) (Fig. 3b). As it can be seen in the Raman microscope image shown in the inset of Fig. 3b, the sample presents some translucent crystals. For this sample, only a band at ∼850 cm^{-1} appears, with much higher intensity than the bands at ∼830 cm^{-1} and ∼900 cm^{-1} that appear in the samples with lower As loadings (Fig. 3). The precipitate presents As–O symmetric vibration frequency between 830 and 900 cm^{-1} probably because each arsenate ion in $Mn_3(AsO_4)_2$ is bonded to two Mn(II) in both monodentate and bidentate mononuclear forms.

4. Conclusions

The sorption of As on the synthesized Mn_3O_4 magnetic composite samples was investigated using Raman and IR spectroscopy. XANES results have shown that the As adsorbed in the samples is at the oxidized arsenic form, As(V). Raman spectra of adsorbed As(V) species onto Mn_3O_4 occur at about 830 cm^{-1} and 900 cm^{-1}. IR spectral data suggests the presence of three bands at ∼737, 774 and 835 cm^{-1} and two bands at ∼899 and 915 cm^{-1}. The results are in agreement with monodentate and bidentate mononuclear complexation models. The obtained Raman spectral data for the highest As loading (35 mg/g) result in a distinct band at about 850 cm^{-1}. In the Raman microscope image of this sample, the presence of translucent crystals could be detected. These findings indicate the precipitation of manganese arsenate at high As loadings.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.04.061.

References

[1] E. Deschamps, V.S.T. Ciminelli, W.H. Höll, Water Research 39 (2005) 5212–5220.
[2] G.R. Bochkarev, G.I. Pushkareva, K.A. Kovalenko, Journal of Mining Science 46 (2010) 197–202.
[3] H. Yin, X. Feng, G. Qiu, W. Tan, F. Liu, Journal of Hazardous Materials 188 (2011) 341–349.
[4] W. Driehaus, R. Seith, M. Jekel, Water Research 29 (1994) 297–305.
[5] M.J. Scott, J.J. Morgan, Environmental Science and Technology 29 (1995) 1898–1905.
[6] H.W. Nesbitt, G.W. Canning, G.M. Bancroft, Geochimica et Cosmochimica Acta 62 (1998) 2097–2110.

[7] B.A. Manning, S.E. Fendorf, B. Bostick, D.L. Suarez, Environmental Science and Technology 36 (2002) 976–981.

[8] A. Dias, R.G. Sá, M.C. Spitale, M. Athayde, V.S.T. Ciminelli, Materials Research Bulletin 43 (2008) 1528–1538.

[9] A.L. Foster, G.E. Brown Jr., G.A. Parks, Geochimica et Cosmochimica Acta 67 (2003) 1937–1953.

[10] B.J. Lafferty, M. Ginder-Vogel, M. Zhu, K.J. Livi, D.L. Sparks, Environmental Science and Technology 44 (2010) 8467–8472.

[11] G.C. Silva, V.S.T. Ciminelli, F. Almeida, A.M. Ferreira, Materials Research 15 (2012) 1–6.

[12] M. Ibrahim, A.A. El-Barbary, M.M. El-Nahass, M.A. Kamel, M.A.M. El-Mansy, A.M. Asiri, Spectrochimica Acta Part A 87 (2012) 202–208.

[13] E.H.A. Nashy, O. Osman, A.A. Mahmoud, M. Ibrahim, Spectrochimica Acta Part A 88 (2012) 171–176.

[14] M. Ibrahim, A.A. Mahmoud, O. Osman, A. Refaat, E.-S.M. El-Sayed, Spectrochimica Acta Part A 77 (2010) 802–806.

[15] I.K. Battisha, H.H. Afify, M. Ibrahim, Journal of Magnetism and Magnetic Materials 306 (2006) 211–217.

[16] K. Müller, V.S.T. Ciminelli, M.S.S. Dantas, S. Willscher, Water Research 44 (2010) 5660–5672.

[17] M. Teixeira, V.S.T. Ciminelli, M. Dantas, S. Diniz, H. Duarte, Journal of Colloid and Interface Science 315 (2007) 128–134.

[18] A.M.F. Guimarães, V. Ciminelli, W. Vasconcelos, Applied Clay Science 42 (2009) 410–414.

[19] C.L. Caldeira, V.S.T. Ciminelli, K. Osseo-Asare, Geochimica et Cosmochimica Acta 74 (2010) 1777–1789.

[20] G. Duarte, V.S.T. Ciminelli, M.S.S. Dantas, H.A. Duarte, I.F. Vasconcelos, A.F. Oliveira, K. Osseo-Asare, Geochimica et Cosmochimica Acta 83 (2012) 205–216.

[21] C.M. Julien, M. Massot, C. Poinsignon, Spectrochimica Acta Part A 60 (3) (2004) 689–700.

[22] S.C.B. Myneni, S.J. Traina, G.A. Waychunas, T.J. Logan, Geochimica et Cosmochimica Acta 62 (1998) 3285–3300.