

# Sorption kinetics and chemical forms of Cd(II) sorbed by thiol-functionalized 2:1 clay minerals

D. Malferrari, M.F. Brigatti\*, A. Laurora, S. Pini, L. Medici<sup>1</sup>

*Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, I-41100 Modena, Italy*

Received 21 June 2006; received in revised form 29 August 2006; accepted 29 August 2006

Available online 1 September 2006

## Abstract

The interaction between Cd(II) in aqueous solution and two 2:1 expandable clay minerals (i.e., montmorillonite and vermiculite), showing different layer charge, was addressed via batch sorption experiments on powdered clay minerals both untreated and amino acid (cysteine) treated. Reaction products were characterized via X-ray powder diffraction (XRDP), chemical analysis (elemental analysis and atomic absorption spectrophotometry), thermal analysis combined with evolved gasses mass spectrometry (TGA-MSEGA) and synchrotron-based X-ray absorption spectroscopy via extended X-ray absorption fine structure (EXAFS) characterization. Sorption isotherms for Cd(II) in presence of different substrates, shows that Cd(II) uptake depends both on Cd(II) starting concentration and the nature of the substrate. Thermal decomposition of Cd–cysteine treated clay minerals evidences the evolution of H<sub>2</sub>O, H<sub>2</sub>S, NO<sub>2</sub>, SO<sub>2</sub>, and N<sub>2</sub>O<sub>3</sub>. These results are well consistent with XRDP data collected both at room and at increasing temperature and further stress the influence of the substrate, in particular cysteine, on the interlayer. EXAFS studies suggest that Cd(II) coordinates with oxygen atoms, to give monomer complexes or CdO molecules, either on the mineral surface and/or in the interlayer. For Cd–cysteine complexes EXAFS data agree with the existence of Cd–S clusters, thus suggesting a predominant role of the thiol group in the bonding of Cd with the amino acid.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Montmorillonite; Vermiculite; Cd(II); Cysteine; Adsorption

## 1. Introduction

Literature so far available on cadmium remarks its very high toxicity to animals and humans, thus accounting for the great environmental concern related to this element [1,2]. Cadmium may enter into natural environments following different paths, such as: (i) industrial, especially mining and metallurgy, runoffs; (ii) high-Cd phosphate fertilizers; (iii) nickel–cadmium batteries; (iv) chemical stabilizers [3–5]. Unlike many transition metals, which precipitate as hydroxides at pH values common in soils and surface waters, cadmium hydroxide is very soluble and its concentration in aqueous solutions is not appreciably limited at pH values lower than pH 10 [6]. Recent studies on Cd(II) [7–13] addressed its sorption on soil minerals, also when enhanced by the introduction of different functional groups on

the mineral surface, such as clay minerals with metal complexing groups [14–16].

Several studies, devoted to metal and metal–organic interactions with 2:1 clay minerals, demonstrated that metal adsorption and desorption depend on the magnitude of the 2:1 layer charge and on its location [17,18]. In smectites, the negative charge per half-unit cell ranges from –0.6 to –0.2, whereas in vermiculites this value is between –0.9 and –0.6. In both clay minerals, the layer charge is balanced by interlayer cations located between two adjacent layers. The location of isomorphous substitution in the layer (i.e., whether the layer charge derives from substitution in the tetrahedral or octahedral sheet) is an important factor affecting both hydration and cation speciation in the interlayer. In electrically neutral layers, the basal oxygen atoms act as a weak Lewis base (electron donor), forming weak hydrogen bonds with water molecules. When isomorphous substitution occurs, the basal oxygen atoms show an excess in negative charge, and their electron-donating capacity increases. Sposito [19] demonstrated that H-bonding between water molecules and basal oxygens atoms is enhanced by tetrahedral rather than by octahedral sheet

\* Corresponding author. Tel.: +39 059 2055805; fax: +39 059 2055887.

E-mail address: [brigatti@unimore.it](mailto:brigatti@unimore.it) (M.F. Brigatti).

<sup>1</sup> Present address: IMAA-CNR, Area della Ricerca di Potenza, C. da S. Loja, I-85050 Tito Scalo, PZ, Italy.

substitution. According to the HSAB theory of Pearson [20,21], the silicate 2:1 layers and the hydrated interlayer cations can be considered as Lewis bases and acids, respectively [22]. The location of the layer charge determines the strength of the Lewis base: montmorillonite behaves as a soft base because the layer charge derives from octahedral substitutions and thus the charge of tetrahedral basal oxygen atoms reflects the charge imbalance of the whole layer. On the contrary, vermiculite behaves as a hard base because the layer charge derives from tetrahedral substitutions, thus closely affecting the charge of coordinating oxygen atoms. In this way, the 2:1 layer charge location affects the layer hydration as well as the cation sorption process [18], since hard bases preferentially complex hard acids (cations) and soft bases preferentially complex soft acids. It is well known that clay minerals with high charge located in the tetrahedral sheet, such as in vermiculite, hydrate more strongly than those with lower charge located mainly in octahedral sheet, such as in montmorillonite. Organic cations are thus adsorbed less strongly on vermiculite surface because of the energy demand in displacing water from the adsorption site. Moreover residual negative charges can also develop along the edges of clay mineral particles where Si–O–Si and Al–O–Al bonds are ‘broken’ and converted into Si–OH and Al–OH groups [23].

Several studies described the interaction of metals on clays and modified clays such as pillared clays and grafted clays [16,24–27]. For example, the interaction between Cu and 2:1 expandable clays can follow different paths, such as the formation of dimmers, or a combination of monomers and dimmers, at the edge sites of clay mineral particles or also the formation of outer-sphere complexes on the permanently charged sites, where the metal is surrounded by a shell of at least one layer of water molecules. The environment of Cu(II) is completely different when the 2:1 clay mineral is functionalized by grafting organic groups, such as thiol or amine functions. The metal shows an octahedral coordination defined by four oxygen (related to the layer clay mineral) and two nitrogen atoms (related to amino acid) [18,28].

The focus of this study is thus the characterization of the uptake behavior of Cd(II) by montmorillonite and vermiculite in presence or absence of cysteine ( $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$ ). This amino acid is frequent in natural environments and presents –COOH, –NH<sub>2</sub> and –SH functional groups. Thus, starting from the background previously outlined, this work will describe the modification on the structure of clay minerals associated to the uptake process, the Cd(II) sorption behavior including kinetics, and the local configuration of Cd(II) and Cd(II)–cysteine complexes, as determined by extended X-ray absorption fine structure (EXAFS).

## 2. Materials and methods

### 2.1. Clay mineral samples

Vermiculite sample (label Mg-V) under investigation is from Bikita (Zimbabwe). Chemical composition, determined on several selected crystals, was found not to change within the given crystal, but to differ from crystal to crys-

tal. The mean chemical formula is:  $^{[\text{iv}]}\text{(Si}_{3.041}\text{Al}_{0.959})_{4.000}^{[\text{vi}]}\text{(Ti}_{0.023}\text{Al}_{0.049}\text{Fe}_{0.403}^{3+}\text{Mg}_{2.518}\text{Mn}_{0.007})_{3.000}(\text{Mg}_{0.228}\text{Na}_{0.005})_{0.233}\text{O}_{10}(\text{F}_{0.152}\text{OH}_{1.848})$  and nominal cation exchange capacity is 0.461 epfu (i.e., electron per formula unit). The cation exchange capacity (CEC), experimentally determined on 60 mg of ground vermiculite crystals by the method introduced by Emmerich et al. [29], is 116 meq/100 g. The unit cell parameters are:  $a = 5.320(7)$ ;  $b = 9.28(1)$ ;  $c = 14.500(7)$  Å;  $\beta = 96.4(1)^\circ$  (space group  $C2/m$ ).

Montmorillonite STx-1 (label Ca-M) is from Gonzales County Texas and was provided by the Clay Minerals Society. The chemical composition is:  $^{[\text{iv}]}\text{Si}_{4.0}^{[\text{vi}]}\text{(Al}_{1.59}\text{Fe}_{0.035}^{3+}\text{Fe}_{0.01}^{2+}\text{Mg}_{0.14}^{2+}\text{Ti}_{0.01})^{[\text{XIII}]}\text{(Ca}_{0.12}\text{Na}_{0.035}\text{K}_{0.005})\text{O}_{10}(\text{OH})_{22}$ . Cation exchange capacities is 84.4 meq/100 g. Further mineralogical and chemical details can be found in the report of the Clay Minerals Society [30].

Montmorillonite derives its layer charge mostly from lower charge cations substituting for Al<sup>3+</sup> (Fe<sup>2+</sup> and Mg<sup>2+</sup>) in octahedral sites, whereas the layer charge of vermiculite is mostly related to Al<sup>3+</sup> for Si<sup>4+</sup> substitutions in tetrahedral sites. Thus montmorillonite can be classified as a soft base and vermiculite as a hard base [22].

### 2.2. Chemicals and solutions

Cadmium acetate dihydrate, sodium acetate, and all the other chemicals are analytical-grade reagents and were not treated for further purification.

Cd(II) solutions  $10^{-3}$  M were prepared by dissolving cadmium acetate dihydrate in deionized water. Cysteine  $10^{-2}$  M solutions were prepared by using a commercial reagent with no impurity declared above 0.1%. The choice of solution concentration both for Cd(II) solution and cysteine solution was driven by the theoretical calculation performed via the MINTEQA2 program [31]. MINTEQA2 program was also applied to derive experimental conditions aimed at excluding the formation of precipitated Cd-phases. This theoretical calculation suggests that no precipitated phases occur over a large pH range, i.e., at pH < 8.5, as also confirmed by X-ray diffraction studies on treated clay minerals.

### 2.3. Preparation of cysteine-treated clay minerals

A fixed amount of montmorillonite and vermiculite (50 g) was subject to ultrasonic treatment, and the <2 μm size fraction was separated by sedimentation [32]. Each clay mineral sample was pre-treated with 1 L of 1 M sodium acetate solution [33]. The suspensions were continuously shaken for 24 h at 50 °C. After this time, the solution was siphoned off from the bottom sediment and treated several time with a 1 M sodium acetate solution. The procedure was repeated until X-ray diffraction results confirmed Na-saturated interlayers (montmorillonite  $d_{001} = 13.1$  Å; vermiculite  $d_{001} = 12.3$  Å). After sedimentation and filtration of the suspensions, both clay minerals were air-dried.

Afterwards, 25 g both of Na-exchanged vermiculite (Na-V) and montmorillonite (Na-M) were dispersed in 0.5 L of  $10^{-2}$  M

cysteine solution. The initial pH of each dispersion was adjusted to 5.0, using acetic acid. During the experiments, pH was monitored continuously via a pH-meter (Jenway 3310) equipped with a glass electrode. The pH variation did not exceed  $\pm 0.1$  pH units. The cysteine was differently adsorbed by montmorillonite and vermiculite. Thus the contact time between cysteine solution and the two clay mineral layers was not equal and the treatment was extended until elemental, thermogravimetric and X-ray diffraction analyses confirmed the presence of cysteine into the layer. After filtration, the solutions were analyzed and the solid characterized. At the end of this procedure two samples were obtained, i.e., vermiculite treated with cysteine (Cys-V) and montmorillonite treated with cysteine (Cys-M).

#### 2.4. Cd adsorption experiments

Different experimental procedures using Cd(II) solution at  $10^{-3}$  M were carried out for evaluating the Cd(II) sorption kinetics by the two clay mineral layers in presence or not of the amino acid. Four different clay mineral-Cd(II) solution systems were prepared using Na-M, Na-V, Cys-M, and Cys-V samples. Each system was characterized by 22 sealed tubes, containing 150 mg of clay mineral and 50 mL of Cd(II) solution, to allow subsequent samplings, with a frequency ranging from few seconds up to some hours. Each sealed tube thus gives a single data-point in the kinetic adsorption curves. This method was preferred to the widely used batch experiment approach (with subsequent samplings from a unique suspension) to prevent that the progressive reduction of mass may influence the adsorption processes. No constraints were imposed on pH during the course of these reactions. Constant temperature at 25 °C was maintained. Each system was continuously shaken on an orbital stirrer at 420 rpm for periods ranging from few seconds up to a maximum of 5 days. At the end of the scheduled time solution was separated from solid by centrifugation at 8000 rpm for 10 min. Three replicates were made for each sample to determine the reproducibility and relative deviation of the experiments reported in figures. Kinetic curves, each consisting of 22 data points, were built by analyzing the decrease of Cd(II) in solution, due to the adsorption from different substrates (differently treated and untreated clay minerals), from each sealed tube after centrifugation.

Characterization of solid phases by X-ray diffraction, thermal and EXAFS studies was obtained by exchanging 1 g of Na-M, Na-V, Cys-M, and Cys-V with the Cd(II) solution for 5 days (labels Cd(II)-M = Cd(II) exchanged Na-M; Cd(II)-V = Cd(II) exchanged Na-V; Cd(II)-M-Cys = Cd(II) exchanged (or complexed) Cys-M; Cd(II)-V-Cys = Cd(II) exchanged (or complexed) Cys-V. Cd and cysteine concentration values in all the above mentioned samples are reported in Table 1.

#### 2.5. Apparatus

Elemental analysis (Elemental Analyzer, Carlo Erba 1106) was performed in order to check the amount of amino acid sorbed. An atomic absorption spectrophotometer (Perkin-Elmer

Table 1

Chemical quantification of adsorbed/exchanged Cd and cysteine in vermiculite and montmorillonite samples; for calculation of the ratios between adsorbed/exchanged species and cation exchanged capacity (CEC), Cd and cysteine are expressed in meq/100 g and mmol/100 g, respectively

	Cd (wt%)	Cd(II)/CEC	Cysteine (wt%)	Cysteine/CEC
Cd(II)-V	2.45	0.38		
Cys-V			1.30	0.09
Cd(II)-V-Cys	2.51	0.38	0.61	0.04
Cd(II)-M	2.13	0.45		
Cys-M			1.20	0.12
Cd(II)-M-Cys	2.06	0.44	0.56	0.06

Analyst 100) was used to analyze the amount of metal both on the clay mineral after acid digestion [34] and in the solution. Metal content measured via solid analysis was checked against the residual Cd(II) content determined in solutions.

X-ray powder diffraction (XRD) analysis was carried out in a temperature range  $25 < T$  (°C)  $< 400$  (heating rate 2 °C/min) on randomly oriented mounts of clay minerals, using a Philips X'Pert PRO diffractometer equipped with X'Celerator detector (Cu K $\alpha$  radiation 40 kV and 40 mA;  $2\theta$  range: 4–75°; quartz as standard) and HTK16 Anton Paar heating apparatus.

Thermal analyses were performed with a Seiko SSC 5200 thermal analyzer equipped with a quadrupole mass spectrometer (ESS, GeneSys Quadstar 422) to analyze gases evolved during thermal reactions. Gas sampling by the spectrometer was via an inert, fused silicon capillary system, heated to prevent gases condensing. Gas analyses were carried out in multiple ion detection mode (MID) which allows the qualitative determination of evolved masses *versus* temperature or time. Background subtraction was performed to obtain the point zero conditions before starting MID analysis.

A synchrotron-based X-ray absorption spectroscopy (EXAFS) technique was used to obtain information on the local environments of Cd-sorbed species. Cd K-edge X-ray absorption experiments were performed at the European Synchrotron Radiation Facility (ESRF) at GILDA beamline. Spectra were collected in transmission mode at room temperature conditions on powder-pressed disks obtained by mixing an appropriate amount of the clay mineral sample with cellulose. This procedure was the one that provided better noise–signal ratio. Energy calibration was performed using a Cd metal foil with the first inflection point of the K-absorption edge at 26,711 eV. Sample were analyzed at liquid nitrogen temperature using an evacuated cryostat. Measurement at room temperature showed that the freezing procedure improved the spectral quality without altering samples.

The experimental Fourier filtered EXAFS spectrum was compared with theoretical EXAFS spectra, calculated from the FEFF-8 program [35] using Cd(OH) $_2$ , CdO, and CdS as reference compounds. A Fourier transform of the experimental spectrum provides the approximate radial distribution function around the central absorbing atom; the peaks represent shells of atoms surrounding the central atom.

### 3. Results and discussion

#### 3.1. Adsorption experiments

Fig. 1 describe the variation of Cd in solution as a function of time in presence of montmorillonite exchanged with Na (sample Na-M, Fig. 1.1a) and cysteine (sample Cys-M, Fig. 1.2a), and in presence of vermiculite exchanged with Na (sample Na-V, Fig. 1.3a) and cysteine (sample Cys-V, Fig. 1.4a). The initial Cd concentration is  $10^{-3}$  M.

Sample Na-M is characterised by an initial sharp decrease of Cd in solution [ $\text{Cd(II)} = 49 \text{ mg/L}$ ;  $t = 150 \text{ s}$ ]. After this period of time the system seems to show an instable behaviour, and in the range  $3 < t \text{ (min)} < 180$  adsorption and desorption steps of Cd(II) take place, with a maximum content of Cd in solution of approximately  $71 \text{ mg/L}$  (i.e., approximately 63% of the starting concentration). After this peak, occurring approximately after 120 min, the system evolves to an asymptotic value [ $\text{Cd(II)} = 47 \text{ mg/L}$ ], which is close to the value reached after 150 s. In the interval

$30 < t \text{ (s)} < 150$ , the kinetics for the system can be assumed as second order ( $1/C - 1/C_0 = 2 \times 10^{-5}t - 4 \times 10^{-4}$ ;  $R^2 = 0.95$ ), with a reaction rate of  $5.6 \times 10^{-2} \text{ mg L}^{-1} \text{ s}^{-1}$  (Fig. 1.1b).

The treatment with cysteine does not affect significantly the early adsorption of Cd(II) by the clay mineral occurring in the first 120 s of the treatment (Fig. 1.2a). However, the following adsorption and desorption reactions are much less pronounced than in montmorillonite treated with Na only. The reaction kinetics (Fig. 1.2b) occurring between  $30 < t \text{ (s)} < 120$  is better fitted by a zero order kinetics ( $C_0 - C = 5.2 \times 10^{-2}t - 2.06$ ;  $R^2 = 0.92$ ).

With respect to montmorillonite, vermiculite is able to adsorb a greater amount of Cd(II). The system Na-V and Cd(II)  $10^{-3}$  M, after the first 120 s of treatment shows a Cd content in solution of  $37 \text{ mg/L}$ . The second order reaction kinetics (Fig. 1.3b) is  $1/C - 1/C_0 = 5 \times 10^{-5}t - 1.3 \times 10^{-3}$  ( $R^2 = 0.99$ ), with a reaction rate of  $1.2 \times 10^{-1} \text{ mg L}^{-1} \text{ s}^{-1}$ . After this first uptake, an unstable behaviour with subsequent Cd(II) adsorption and desorption steps takes place, even if these reactions are much less

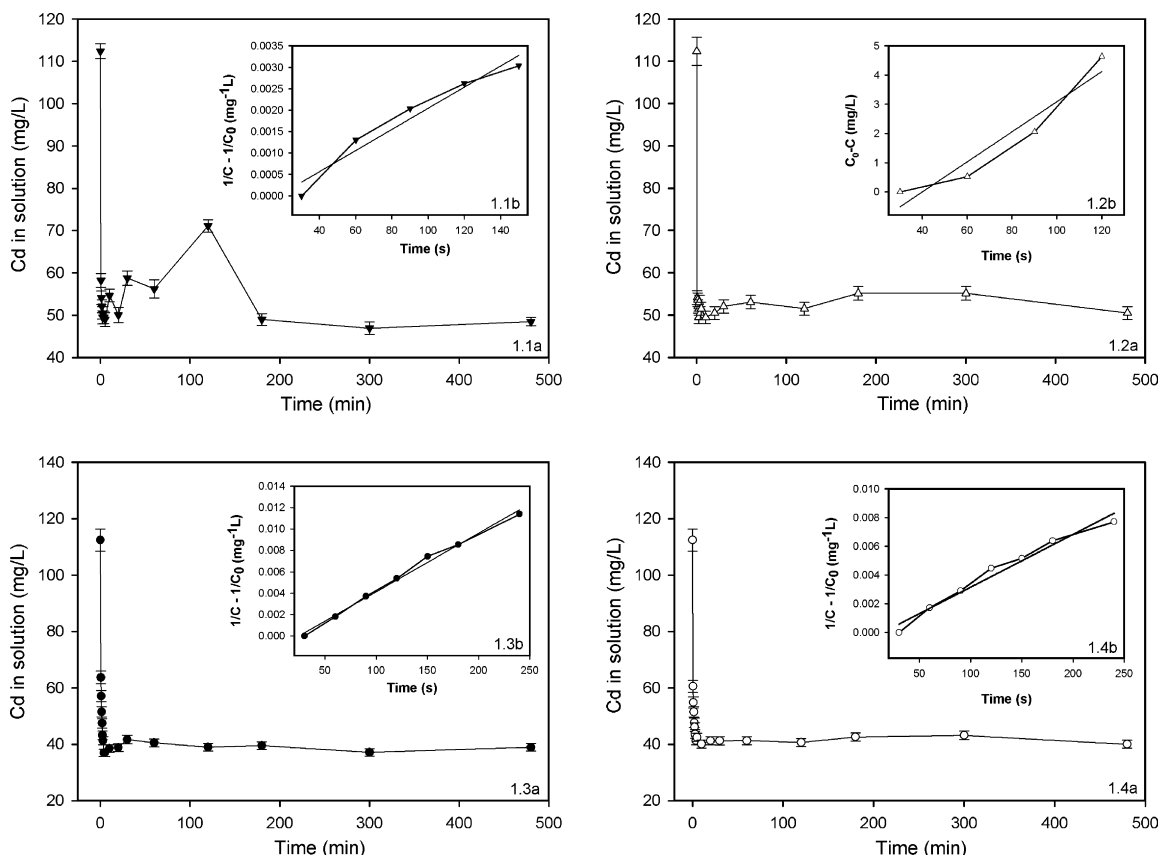


Fig. 1. (1.1) Cd adsorption by Na-montmorillonite (sample Na-M) vs. time; (1.1a) Cd in solution (mg/L) during the experiment starting from a Cd(II) concentration of  $10^{-3}$  M (112.4 mg/L); (1.1b) calculation of the sorption kinetics for the interval  $30 < t \text{ (s)} < 150$ ;  $C$  and  $C_0$  represent the Cd concentration (mg/L) at the time  $t$  and at the starting time ( $t = 30 \text{ s}$ ), respectively. (1.2) Cd adsorption by Na montmorillonite pre-treated with cysteine (sample Cys-M) vs. time; (1.2a) Cd in solution (mg/L) during the experiment starting from a Cd(II) concentration of  $10^{-3}$  M (112.4 mg/L); (1.2b) calculation of the sorption kinetics for the interval  $30 < t \text{ (s)} < 120$ ;  $C$  and  $C_0$  represent the Cd concentration (mg/L) at the time  $t$  and at the starting time ( $t = 30 \text{ s}$ ), respectively. (1.3) Cd adsorption by Na vermiculite (sample Na-V) vs. time; (1.3a) Cd in solution (mg/L) during the experiment starting from a Cd(II) concentration of  $10^{-3}$  M (112.4 mg/L); (1.3b) calculation of the sorption kinetics for the interval  $30 < t \text{ (s)} < 240$ ;  $C$  and  $C_0$  represent the Cd concentration (mg/L) at the time  $t$  and at the starting time ( $t = 30 \text{ s}$ ), respectively. (1.4) Cd adsorption by Na vermiculite pre-treated with cysteine (sample Cys-V) vs. time; (1.4a) Cd in solution (mg/L) during the experiment starting from a Cd(II) concentration of  $10^{-3}$  M (112.4 mg/L); (1.4b) calculation of the sorption kinetics for the interval  $30 < t \text{ (s)} < 240$ ;  $C$  and  $C_0$  represent the Cd concentration (mg/L) at the time  $t$  and at the starting time ( $t = 30 \text{ s}$ ), respectively.

pronounced than in montmorillonite, with a maximum Cd(II) concentration in solution of 42 mg/L.

When vermiculite is treated with cysteine, the initial uptake of Cd(II) is not significantly affected and the following adsorption/desorption processes seem to disappear (Fig. 1.4a). The effect of cysteine thus seems to be similar for both montmorillonite and vermiculite. The kinetics of the reaction (Fig. 1.4b) is  $1/C - 1/C_0 = 4 \times 10^{-5}t - 5 \times 10^{-4}$  ( $R^2 = 0.97$ ), with a reaction rate of  $9.7 \times 10^{-2} \text{ mg L}^{-1} \text{ s}^{-1}$ .

In clay mineral-aqueous systems, the adsorption of cadmium on 2:1 expandable layers occurs by exchange with the cations occupying the interlayer position as well as by adsorption on the deprotonated octahedral sites at the edges of clay mineral. With respect to the edge site, sorption in the interlayer reduces the cation mobility as a consequence of the formation of  $\text{H}_2\text{O}$ –metal complex embedded between two tetrahedral sheets. Normally, this latter kind of adsorption is less dependent on external variables such as temperature, pH fluctuation and clay mineral/Cd(II) concentration ratio [8]. In all the systems studied, pH and temperature were kept constant at the beginning of each experiment and verified not to have changed appreciably at the end time. This last assertion does not mean that pH was maintained constant for all the time of the batch experiment (pH fluctuations could be a consequence of the desorption and subsequent adsorption of Na cations that shows a greater affinity for the interlayer than cadmium). Thus the metastability of the system can be related to variations in physical–chemical parameters of both components (i.e., clay mineral and solution). The unstable behaviour of Na–V with Cd(II)  $10^{-3} \text{ M}$  and Na–M with Cd(II)  $10^{-3} \text{ M}$  systems cannot be related to the formation of unstable precipitated phases. In fact the expected range of variation of pH range prevents the formation of precipitated phases, given the high solubility of Cd(II).

### 3.2. X-ray diffraction characterization

The powder X-ray diffraction pattern of Cd(II)-M and Cd(II)-V samples show that  $d_{001}$  values at room temperature are 15.42 and 14.80 Å, respectively. Reflections are consistent with a 2:1 expandable layer silicate structure characterized by an interlayer cation solvated by two  $\text{H}_2\text{O}$  layer molecules. The position of  $d_{001}$  reflection reaches the closest 2:1 packing (Fig. 2) as the temperature is increased to 225 °C for Cd(II)-M ( $d_{001} = 9.95 \text{ Å}$ ) whereas Cd(II)-V sample maintains a periodicity of  $d_{001} = 10.3 \text{ Å}$  until 300 °C. The decrease of layer periodicity can be related to the progressive loss of  $\text{H}_2\text{O}$  molecules in the interlayer region. The  $d_{001}$  value of Cd(II)-V can be related to residual molecules in the interlayer region, probably  $\text{Mg}_3(\text{OH})_6$  octahedral domains which were found also in the untreated sample.

At room temperature, the  $d_{001}$  values of Cd(II)-M-Cys and Cd(II)-V-Cys are 15.39 and 14.25 Å, respectively. For montmorillonite the treatment with cysteine produces a slight  $d_{001}$  decrease, whereas for vermiculite a more evident reduction of  $d_{001}$  value is observed. The lower  $d_{001}$  value of Cd(II)-V-Cys could be related to the different layer charge location. The hard base (vermiculite) adsorbs less energetically organocations

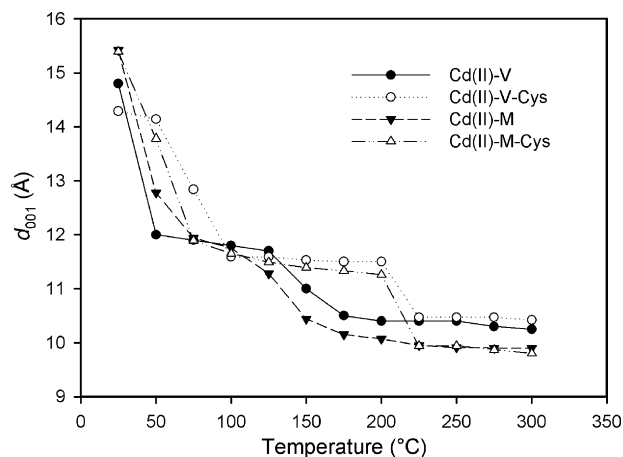


Fig. 2. Variation of  $d_{001}$  reflection as function of temperature observed for Cd(II)-V (filled circle), Cd(II)-M (filled triangle down), Cd(II)-V-Cys (open circle) and Cd(II)-M-Cys (open triangle up).

due to the greater energy cost in displacing water molecules. In addition the broadness of the reflection for both clays suggests an increasing in layer stacking disorder and/or randomly intercalated 2:1 layers (i.e., random distribution of water and organocations within the same interlayer or intercalation of organocations-rich layer and  $\text{H}_2\text{O}$ -rich layers). However, even if the discussion reported above appears to be convincing, the decrease in  $d_{001}$  produced by the treatment with cysteine can also be related to a lower hydration of organic cations, such as cysteine, when compared to inorganic cations, thus giving a lower basal spacing value. This mechanism also agrees with the reduced water-loss observed in cysteine-treated minerals, when compared to the untreated samples, as evidenced by thermal analysis.

The  $d_{001}$  variation as a function of temperature is qualitatively similar for Cd(II)-M-Cys and Cd(II)-V-Cys. The reaction for samples treated with the amino acid occurs in two steps. An initial sharp decrease also characterizing Cd(II)-M and Cd(II)-V occurs for temperatures below 100 °C. This reaction, which is usually associated to weakly bonded water molecules desorption from the interlayer, is followed by a constant  $d_{001}$  value in the temperature range  $100 < T (\text{°C}) < 200$ , thus suggesting the presence of molecules able to introduce an additional 2 Å spacing between two adjacent 2:1 layers. These molecules are then desorbed at temperature higher than 200 °C, which is consistent with the pyrolysis of the organo-clay. Afterwards the 2:1 layer periodicity reaches the closest packing.

Samples treated with cysteine present water molecules between the layers. This effect can be related either to the coexistence of Cd– $\text{H}_2\text{O}$  and Cd–cysteine clusters or to the establishment of hydrated Cd–cysteine complexes. Vermiculite and montmorillonite show a similar behaviour, thus suggesting a limited influence of the clay mineral substrate on these processes.

### 3.3. Thermal behaviour and evolved gas analysis

Thermal analyses for Cd(II)-M and Cd(II)-V samples in the temperature range  $25 < T (\text{°C}) < 200$  show two endothermic

reactions, the first is at 75 °C for both Cd(II)-M and Cd(II)-V samples and the second at 155 °C for Cd(II)-M and at 190 °C for Cd(II)-V, respectively. Both effects are related to H<sub>2</sub>O loss. The percentage of weight loss (wt%) is 12.2 and 7.3 wt% for Cd(II)-M and Cd(II)-V, respectively. This different weight loss between Cd(II)-M and Cd(II)-V agrees with the different hydration energy of the two clay minerals. In the temperature range 200 < *T* (°C) < 400 further endothermic reactions take place at 284 and 322 °C for Cd(II)-V only.

A broad but unique dehydroxylation effect was registered for Cd(II)-M at 670 °C, whereas two effects were found for Cd(II)-V at 627 and 837 °C. At 1000 °C the total weight loss is 16.8 and 15.3 wt% for Cd(II)-M and Cd(II)-V, respectively.

Thermal behaviour of Cd(II)-M-Cys and Cd(II)-V-Cys was obtained from TGA and MS-EGA analyses. Analyses thus performed show that in the temperature range 25 < *T* (°C) < 200 the decrease of clay mineral weight related to loss of H<sub>2</sub>O molecules (Cd(II)-M-Cys = 9.5 wt%; Cd(II)-V-Cys = 6.6 wt%) is different for each clay mineral and is reduced with respect to the sample untreated with cysteine. Furthermore the loss of H<sub>2</sub>O, like in samples untreated with cysteine, is related to two effects: the first at 75 °C for both Cd(II)-M and Cd(II)-V and the second at 155 °C for Cd(II)-M and at 190 °C for Cd(II)-V, respectively. This behaviour, together with X-ray diffraction results, seems to suggest the presence of Cd–H<sub>2</sub>O domains in Cd–cysteine treated samples.

In the temperature range 200 < *T* (°C) < 900 the weight loss is 10.6 wt% (sample Cd(II)-M-Cys) and 10.8 wt% (sample Cd(II)-V-Cys) and it is associated to several reactions which correspond to the emission of H<sub>2</sub>O, NO (or CH<sub>3</sub>CH<sub>3</sub>), H<sub>2</sub>S, CO<sub>2</sub>, SO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub>. Sample Cd(II)-M-Cys shows the emission of: (i) NO (or CH<sub>3</sub>CH<sub>3</sub>), H<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub>, SO<sub>2</sub>, and N<sub>2</sub>O<sub>3</sub> at 232 and 264 °C; (ii) NO (or CH<sub>3</sub>CH<sub>3</sub>), CO<sub>2</sub>, and SO<sub>2</sub> at 549 °C; (iii) H<sub>2</sub>O and SO<sub>2</sub> at 673 °C. Sample Cd(II)-V-Cys shows the emission of: (i) NO (or CH<sub>3</sub>CH<sub>3</sub>), H<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub> and SO<sub>2</sub> at 236 °C; (ii) H<sub>2</sub>O, NO (or CH<sub>3</sub>CH<sub>3</sub>), CO<sub>2</sub> and SO<sub>2</sub> at 494 °C; (iii) SO<sub>2</sub> at 669 °C; (iv) H<sub>2</sub>O at 840 °C. At 1000 °C the total weight loss is 20.6 and 18.0 wt% for montmorillonite and vermiculite, respectively. The thermal decomposition of the amino acids takes place in different steps; reactions at lower temperature (in the range 200 < *T* (°C) < 300) may produce the formation of residual molecules in the interlayer which are oxidised simultaneously with the dehydroxylation reaction. After thermal decomposition of cysteine occurring at temperatures below 300 °C the 2:1 closest packing values are reached. These results could suggest that residual molecules in the interlayer are hosted inside the cavity of two adjacent layers. Several hypotheses can thus be formulated to better explain the emission of H<sub>2</sub>S and, in particular, SO<sub>2</sub> at 600 °C, namely: (i) the formation of a strong bond between the dehydrated layer and S, which can thus be removed only at higher temperature; (ii) the breaking of the bonds between Cu and aminic and carboxylic groups, following the decomposition reaction at 200 °C, thus leading to the formation of Cd<sub>x</sub>S-like compounds. These latter are then subjected to decomposition reactions at higher temperatures with the consequent emission of SO<sub>2</sub> and formation of mostly CdO as residual phase most likely according to the reaction  $2\text{CdS} + 3\text{O}_2 \rightarrow 2\text{CdO} + 2\text{SO}_2$ .

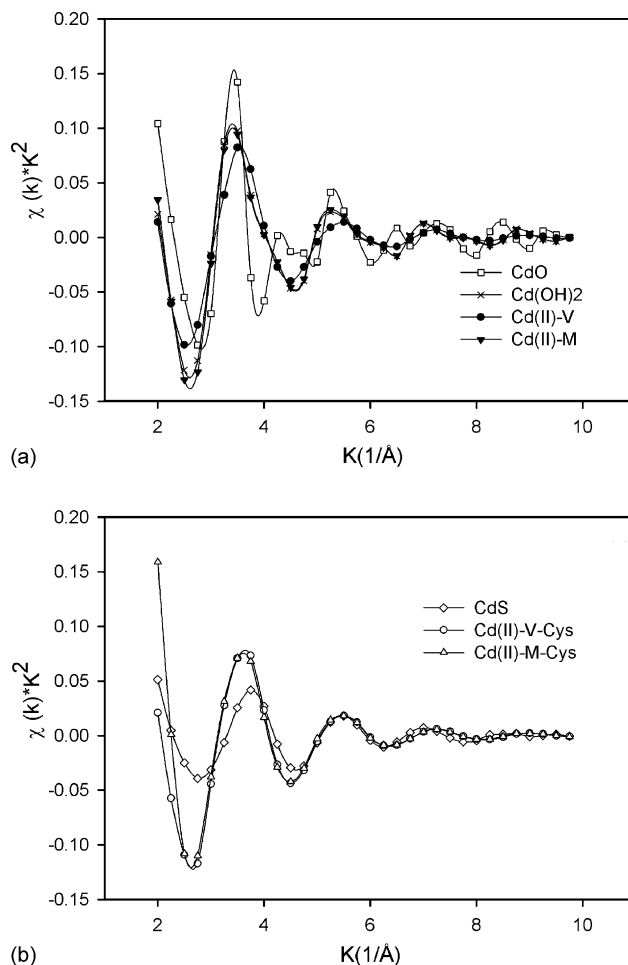


Fig. 3. (a) Normalized background-subtracted Cd-EXAFS spectra weighted by  $k^2$  for CdO (open square), Cd(OH)<sub>2</sub> (crosses), Cd(II)-V (filled circle) and Cd(II)-M (filled triangle down). (b) Normalized background-subtracted Cd-EXAFS spectra weighted by  $k^2$  for CdS (open diamond), Cd(II)-V-Cys (open circle) and Cd(II)-M-Cys (open triangle up).

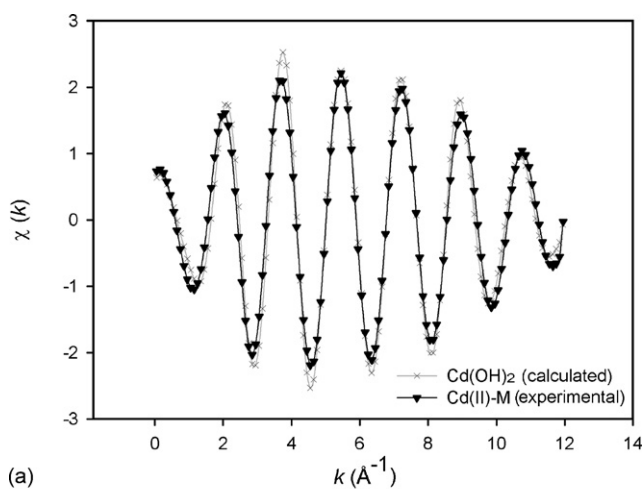
### 3.4. EXAFS spectroscopy

Cd-EXAFS spectra suggest that Cd is bonded by oxygen atoms in Cd treated samples (Fig. 3a) and by sulphur atoms in Cd and cysteine treated samples (Fig. 3b). In Table 2 are concisely reported the results of the refinement. Cd(II)-M spectra are matched not only via Cd(OH)<sub>2</sub> as reference compound (Fig. 4a) but also via CdO, even if with a lower agreement factor. In this latter system, Cd–O distances of 2.24 Å well agree with the possible formation of cadmium oxide molecules both in the interlayer position and/or on the clay mineral surface. This latter conclusion also agrees with Cd–Cd distances of 3.30 and 4.76 Å. The good match in position and intensity between experimental spectra of Cd(II)-V sample and Cd(OH)<sub>2</sub> model compound (Fig. 4b) suggests that interatomic Cd–O distances agree with a model in which Cd is tetrahedrally coordinated by four water molecules (Cd–O distances of 2.16 Å); the Cd–O distances of 2.28 Å should be attributed to a second layer of water molecules bound to the central atom. Cd–Cd distances of 2.90 Å suggest that Cd(II) is adsorbed in the interlayer of the vermiculite, which, consequently, forms a double inner sphere of coordination.

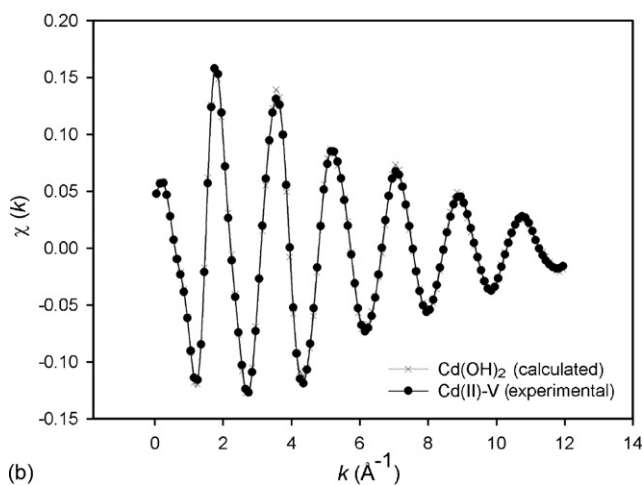
Table 2  
Result of EXAFS analyses

Aa–Sa	<i>N</i>	<i>R</i> (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$
<b>Cd(II)-V</b>				
Cd–O	3.7	2.16	0.005	–7.1
Cd–O	1.8	2.28	0.055	
Cd–Cd	1.9	2.90	0.044	
<b>Cd(II)-M</b>				
Cd–O	3.9	2.24	0.004	–7.5
Cd–Cd	1.1	3.30	0.007	
Cd–Cd	2.1	4.76	0.002	
<b>Cd(II)-V-Cys</b>				
Cd–S	3.9	2.49	0.0300	–9.7
<b>Cd(II)-M-Cys</b>				
Cd–S	3.8	2.43	0.020	–8.9

Aa–Sa, relationship between central absorber and scattering atom; *N*, coordination number; *R*, refined interatomic distance;  $\sigma^2$ , Debye–Waller factor;  $\Delta E_0$ , energy shift. Reference compounds for Cd and Cd–cysteine treated clay minerals are Cd(OH)<sub>2</sub> and greenockite, respectively.

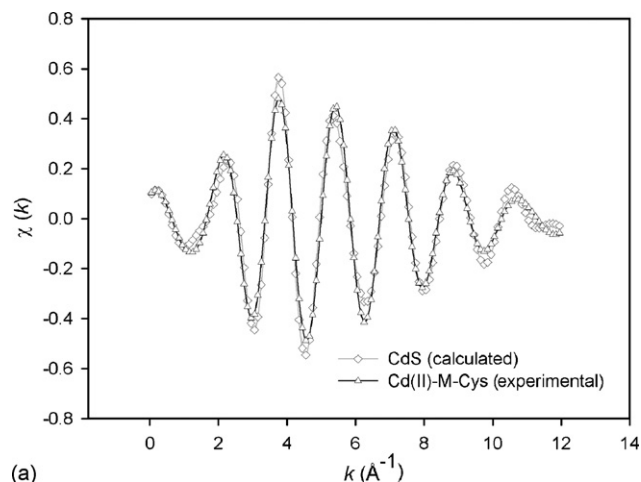


(a)

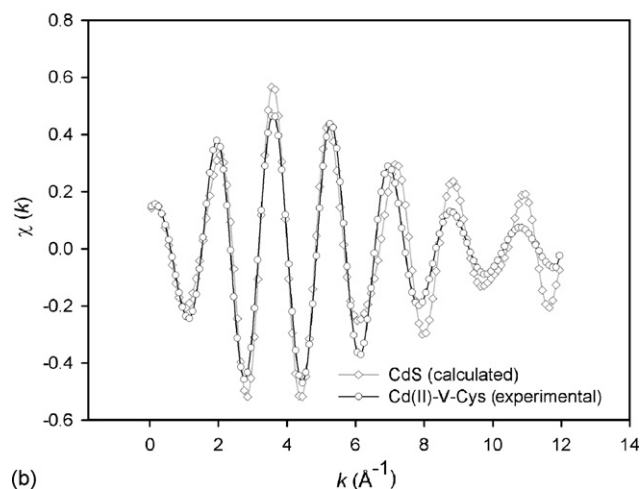


(b)

Fig. 4. Inverse Fourier-filtered scattering curves from Cd K-edge EXAFS data for: Cd(II)-M (a) and Cd(II)-V (b) samples. Filled triangles down on black lines indicate experimental data, crosses on grey line indicate the fit curve obtained using Cd(OH)<sub>2</sub> as reference compound.



(a)



(b)

Fig. 5. Inverse Fourier-filtered scattering curves from Cd K-edge EXAFS data for: Cd(II)-M-Cys (a) and Cd(II)-V-Cys (b) samples. Open triangles up on black lines indicate experimental data, open diamond on grey line indicate the fit curve obtained using CdS (greenockite structure) as reference compound.

For samples Cd(II)-M-Cys (Fig. 5a) and Cd(II)-V-Cys (Fig. 5b), the best fit was obtained by using CdS (greenockite structure) as reference compound. Only for vermiculite sample there was an evidence of agreement also using cadmium oxide as reference compound further evidencing that vermiculite favours the precipitation of cadmium oxide which could not be complexed by the amino acid. Because of high background in both samples it was possible to refine only up to the first shell and refinement suggests Cd–S bond distances of 2.43 and 2.49 Å for Cd(II)-M-Cys and Cd(II)-V-Cys, respectively, indicative of sulphide-type molecules and/or organo-metallic complexes in which metal bonds to the amino acid through the thiol group.

As shown in Table 2 the Cd–O and Cd–S distances refined by EXAFS analyses are different on the two substrates; unfortunately these differences are not significant within the uncertainty of the EXAFS technique applied to clay minerals. Thus the role of the layer charge in determining the bond distances for the same complexes into the two 2:1 layers could not be determined explicitly. Similarly the ratio between CdO and Cd–H<sub>2</sub>O (the inner sphere of coordination) could not be determined exactly

in vermiculite sample. Powder X-ray diffraction, which does not show any peak associable to CdO molecules, as well as the low intensity of the second shell of coordination associated to Cd–Cd and longer Cd–O bonds, evidenced by EXAFS analyses, suggests that CdO compound is not in crystalline form. Goodness of fit between cysteine and Cd(II) treated sample and CdS compound well agrees with Lewis acid–base theory as Cd(II) is soft Lewis acid and therefore should bind strongly with thiol which is a soft Lewis base. The formation of such bonds should strongly improve the stability of the pollutant metal inside the silicate layer.

#### 4. Concluding remarks

This investigation addressed the behaviour of Cd ion when adsorbed into vermiculite and montmorillonite clay minerals, both treated and untreated with cysteine. EXAFS investigation demonstrated, for samples treated with cysteine, the establishment of Cd–S bonding together with Cd–O bonding revealed in the amino acid untreated samples. Cd–S bonding is significantly stronger than Cd–O bonding and was not revealed for Cu–cysteine treated samples [18], thus also accounting for the different effect of similar treatment with different metal cations. These evidences well account for different adsorption kinetics of Cd from different substrates. The total amount of Cd adsorbed from vermiculite and montmorillonite is greater in the first, because of the different layer charge and its location. The treatment with cysteine does not appear to affect significantly the total amount of sorbed metal by the two clay minerals, even if the adsorption kinetics is completely different. This effect is more evident in montmorillonite. Moreover, in cysteine treated samples, S is released at temperature values around 670 °C, which is close to dehydroxylation temperature, thus further confirming the strong bonding of cysteine in the clay layer.

The significantly different behaviour, following from treatments of different clay minerals, with different cation and complexing amino acid, suggests, also considering potential industrial and environmental applications, the extension of this study to different cations, treatments and clay minerals.

#### Acknowledgements

We would like to acknowledge Dr. Harouna Drame and the associate Editor Mark Hodson for the useful comments on the manuscript. We are grateful to Dr. R. Fernandes who kindly provided vermiculite sample. This work was made possible by the financial support of Ministero dell'Università e della Ricerca Scientifica and by Consiglio Nazionale delle Ricerche of Italy and by the availability of beam time at European Synchrotron Radiation Facility (ESRF, Gilda Beamline, Grenoble, France).

#### References

- [1] F.W. Oehme, Toxicity of Heavy Metals in the Environment, Part 1, Marcel Dekker, Inc., New York and Basel, Switzerland, 1979.
- [2] J.W. Moore, S. Ramamoorthy, Cadmium, in: J.W. Moore (Ed.), Heavy Metals in Natural Waters–Applied Monitoring and Impact Assessment, Springer-Verlag, Germany, 1984, pp. 28–57.
- [3] A.L. Page, M.M. El-Amamy, A.C. Chang, Cadmium in the environment and its entry into terrestrial food chain crops, in: E.C. Foulkes (Ed.), Handbook of Experimental Pharmacology, Springer-Verlag, Germany, 1986, pp. 33–74.
- [4] R.J. Larison, G.E. Likens, J.W. Fitzpatrick, J.G. Crock, Cadmium toxicity among wildlife in the Colorado Rocky Mountains, *Nature* 406 (2000) 181–183.
- [5] B. Subramanian, G. Gupta, Adsorption of trace elements from poultry litter by montmorillonite clay, *J. Hazard. Mater.* 128 (2006) 80–83.
- [6] B.C. Bostick, S. Fendorf, M. Fendorf, Disulfide disproportionation and CdS formation upon cadmium sorption on FeS, *Geochim. Cosmochim. Ac.* 64 (2000) 247–255.
- [7] B. Lothenbach, R. Krebs, R. Furrer, S.K. Gupta, R. Schulin, Immobilization of cadmium and zinc in soil by Al-montmorillonite and gravel sludge, *Eur. J. Soil Sci.* 49 (1998) 141–148.
- [8] T. Undabeytia, S. Nir, G. Rytwo, E. Morillo, C. Maqueda, Modeling adsorption–desorption processes of Cd on montmorillonite, *Clay. Clay Miner.* 46 (1998) 423–428.
- [9] R.H. Parkman, J.M. Charnock, N.D. Bryan, F.R. Livens, D.J. Vaughan, Reactions of copper and cadmium ions in aqueous solution with goethite, lepidocrocite, mackinawite, and pyrite, *Am. Mineral.* 84 (1999) 407–419.
- [10] F. Barbier, G. Duc, M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite–water interface, *Colloid. Surface. A* 166 (2000) 153–159.
- [11] S. Pivovarov, Adsorption of cadmium onto hematite: temperature dependence, *J. Colloid. Interf. Sci.* 234 (2001) 1–8.
- [12] B. Bayat, Combined removal of Zn(II) and Cd(II) from aqueous solutions by adsorption onto high-calcium Turkish fly ash, *Water Air Soil Poll.* 136 (2002) 69–92.
- [13] E. Benincasa, M.F. Brigatti, D. Malferrari, L. Medici, L. Poppi, Sorption of Cd–cysteine complexes by kaolinite, *Appl. Clay Sci.* 21 (2002) 191–201.
- [14] M. Arias, M.T. Barral, J.C. Mejuto, Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids, *Chemosphere* 48 (2002) 1081–1088.
- [15] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite, effect of pH and organic substances, *Water Res.* 37 (2003) 1619–1627.
- [16] L. Mercier, C. Detellier, Preparation, characterization, and applications as heavy metal sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite, *Environ. Sci. Technol.* 29 (1995) 1318–1323.
- [17] S.A. Boyd, W.F. Jaynes, Role of layer charge in organic contaminant sorption by organo-clays, CMS Workshop Lectures, Clay Minerals Society (1994) 48–77.
- [18] M.F. Brigatti, S. Colonna, D. Malferrari, L. Medici, Characterization of Cu-complexes in smectite with different layer charge location: chemical, thermal and EXAFS studies, *Geochim. Cosmochim. Ac.* 68 (2004) 781–788.
- [19] G. Sposito, The Surface Chemistry of Soils, Oxford University Press, New York, 1984.
- [20] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533–3539.
- [21] R.G. Pearson, Hard and soft acids and bases HSAB, part 1: fundamental principles, *J. Chem. Educ.* 45 (1968) 581–587.
- [22] S. Xu, J.B. Harsh, Alkali cation selectivity and surface charge of 2:1 clay minerals, *Clay. Clay Miner.* 40 (1992) 567–574.
- [23] N. Güven, Molecular aspects of clay–water interactions, in: N. Güven, R.M. Pollastro (Eds.), Clay–Water Interface and its Rheological Implications, CMS Workshop Lectures, vol. 4, The Clay Minerals Society, Boulder, CO, 1992, pp. 1–80.
- [24] S.-H. Lin, R.-S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, *J. Hazard. Mater.* 92 (2002) 315–326.
- [25] D. Sahah, G. Fytas, D. Vlassopoulos, J. Di, D. Sogah, E.P. Giannelis, Structure and dynamics of polymer-grafted clay suspensions, *Langmuir* 21 (1) (2005) 19–25.
- [26] M. Cruz-Guzman, R. Celis, M.C. Hermosin, W.C. Koskinen, E.A. Nater, J. Cornejo, Heavy metal adsorption by montmorillonites modified with natural organic cations, *Soil Sci. Soc. Am. J.* 70 (1) (2006) 215–221.



- [27] A. Sampieri, G. Fetter, P. Bosch, S. Bulbulian, Cobalt sorption in silica-pillared clays, *Langmuir* 22 (1) (2006) 385–388.
- [28] M. Jaber, J. Mische-Brendle, L. Michelin, L. Delmotte, Heavy metal retention by organoclays: synthesis, applications, and retention mechanism, *Chem. Mater.* 17 (21) (2005) 5275–5281.
- [29] K. Emmerich, F.T. Madsen, G. Kahr, Dehydroxylation behavior of heat-treated and steam-treated homoionic cis-vacant montmorillonites, *Clay. Clay Miner.* 47 (1999) 591–604.
- [30] P.M. Costanzo, S. Guggenheim, Clay Minerals Society source, *Clay. Clay Miner.* 49 (2001) 371–453.
- [31] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQA2/PRODEFA2, in: A Geochemical Assessment Model For Environmental System: Version 3.0, United States Environmental Protection Agency, Athens, USA, 1991.
- [32] M.L. Jackson, *Soil Chemical Analysis*, in: *Advanced Course*, 2nd ed., Madison-Wisconsin, University of Wisconsin, USA, 1975 (published by the author).
- [33] J. Singh, P.M. Huang, U.T. Hammer, W.W. Liaw, Influence of citric acid and glycine on the adsorption of mercury(II) by kaolinite under various pH conditions, *Clay. Clay Miner.* 44 (1996) 41–48.
- [34] M. Bettinelli, C. Baffi, G.M. Beone, S. Spezia, Soil and sediment analysis by spectroscopic technique. Part I: determination of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, *Atom. Spectrosc.* 21 (2000) 50–59.
- [35] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Real space multiple scattering calculation and interpretation of X-ray absorption near edge structure, *Phys. Rev. B* 58 (1998) 7565.