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

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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_2O, H_2S, NO_2, SO_2, and N_2O_3. 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.

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

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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 ($H_2NCH(CH_2SH)CO_2H$). This amino acid is frequent in natural environments and presents –COOH, $-NH_2$ 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 crystal. The mean chemical formula is: $^{[iv]}(Si_{3.041}Al_{0.959})_{4.000}$ $^{[vi]}(Ti_{0.023}Al_{0.049}Fe_{0.403}{}^{3+}Mg_{2.518}Mn_{0.007})_{3.000}$ $(Mg_{0.228}Na_{0.005})_{0.233}$ O_{10} $(F_{0.152}OH_{1.848})$ 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: $^{[IV]}Si_{4.0}$ $^{[VI]}(Al_{1.59}Fe_{0.035}{}^{3+}\text{-}Fe_{0.01}{}^{2+}Mg_{0.14}{}^{2+}Ti_{0.01})$ $^{[XII]}(Ca_{0.12}Na_{0.035}K_{0.005})$ O_{10} $(OH)_{22}$. 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^{3+} (Fe^{2+} and Mg^{2+}) in octahedral sites, whereas the layer charge of vermiculite is mostly related to Al^{3+} for Si^{4+} 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