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Reactions of Cu^{2+} and Pb^{2+} with Mg/Al layered double hydroxide

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Abstract

The adsorption mechanisms of metal cations on the surfaces of clay minerals and other minerals are important for understanding their fate in contaminated soils and in waste water treatment. The reactions of Cu^{2+} and Pb^{2+} heavy metal cations with layered double hydroxide (LDH), has been investigated in aqueous solutions to elucidate their removal behaviors by LDH. The reaction of aqueous $CuCl_2$ solution with Mg/Al-LDH resulted in precipitation of Cu hydroxide chloride ($Cu_7Cl_4(OH)_{10}\cdot H_2O$) along with slight decomposition of Mg/AI-LDH. On the other hand, the reaction of aqueous $PbCl_2$ solution led to steady decomposition of Mg/Al-LDH structure along with the formation of various Pb precipitates such as carbonate chloride ($PbCO_3PbCl_2$) and hydroxide chloride (Pb(OH)Cl). Experimental techniques such as X-ray diffraction, X-ray photoelectron spectroscopy and cation removal isotherms were used to decipher the mechanism of uptake. This study indicates that LDH removes Cu^{2+} and Pb^{2+} transition metal cations from aqueous solution mainly by surface adsorption and precipitation.

Keywords: Layered double hydroxide (LDH); Transition metal cation; Adsorption; Precipitation

1. Introduction

Adsorption reactions at solid–water interfaces decrease solute mobility and often control the fate, bioavailability, and transport of heavy metal ions such as Zn^{2+}, Cu^{+2}, Pb^{+2} and Ni^{2+} in the environment (Alloway, 1995; Bailey et al., 1999). The adsorption mechanisms of metal ions on the surfaces of clay minerals and other minerals are important for understanding their fate in the environment. Although there are numerous studies on metal ion adsorption by clay minerals, metal oxides and hydroxides, and metal carbonates and phosphates for various purposes (Bailey et al., 1999; Babel and Kurniawan, 2003; Chrysochoou and Dermatas, 2006; Vespa et al., 2006), there are only a few studies on the interaction of metal ions with layered double hydroxides (Kameda et al., 2005; Pérez et al., 2006). The family of LDHs, the so-called anionic clays, are a large class of inorganic materials, which have been extensively studied for many uses such as catalysts, precursors and supports for catalysts, anionic exchangers, sorbent additives etc. (Carlino, 1997; Rives, 2002; Olanrewaju et al., 2003; Park et al., 2004; Mousty, 2004; Radha et al., 2005). In general, LDHs are constructed with a stacking of brucite structure of Mg $(OH)_2$ in which $Mg(OH)_6$ octahedra are connected through edge sharing into 2-dimensional sheets with a

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layer thickness of 4.8 Å. Some of the divalent cations in the brucite layer are isomorphically substituted by trivalent cations such as Al^{3+}, which leads to permanent positive layer charge. Various exchangeable anions could be inserted between the metal hydroxide sheets to compensate the positive layer charge. Hence, a general formula of synthetic LDHs is often written as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}{}_{x/n}]^{x-}\cdot m$S, where M(II) may be Mg, Zn, Co, Ni, Mn, etc.; M(III) may be Al, Cr, Fe, V, Co, etc.; A^{n-} is the interlayer anion (CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, organic anions, etc.); m the number of moles of co-intercalated solvent (S), generally water, per formula weight.

LDHs could adsorb metal cations from aqueous solution in spite of positive layer charge. A major reaction could be surface-induced precipitation that occurs due to localized high pH values and the released carbonate ions available to metal cations. Positive layer charge attracts hydroxide ions around the surfaces of LDH crystals in aqueous solution to induce formation of metal hydroxides. Meanwhile, charge-compensating carbonate ion attached on the surface and edge could also contact with metal cations to form insoluble metal carbonates. There is also another possibility to adsorb metal cations via diodachy, as suggested by Komarneni et al. (Komarneni et al., 1998). These imply that LDHs could be utilized as an adsorbent for heavy metal cations. However, there are only a few studies on the interaction between LDH and heavy metal cations in solution. Therefore, detailed mechanisms of reaction of metal cations in an aqueous solution with LDH is required to exploit these materials in remediation applications. In this study, the reactions of Cu^{2+} and Pb^{2+} heavy metal cations with Mg/Al-LDH was investigated in aqueous and ethanol solutions to elucidate the metal ion removal mechanisms by LDHs.

2. Experiment

A carbonate form of LDH with a Mg:Al ratio of 3:1 (referred to as Mg/Al-LDH) was prepared by the method of Gardner et al. (Gardner et al., 1998). Elemental analysis of this synthetic LDH gave a Mg/Al ratio of 3.35. Reactions of the metal cation solutions with Mg/Al-LDH was conducted in both aqueous and ethanol solutions with a total concentration of 5 mM of metal chlorides in the presence of 0.05 M NaCl at room temperature. Ethanol was employed to minimize the formation of metal hydroxides and/or carbonates. The 5 mM concentration was chosen to be less than solubility of metal hydroxides. The metal solutions were acidified to pH 3.0 with HCl in order to maintain an equilibrium pH of less than 5.0 in the presence of LDH, which could minimize simple precipitation of metal species. Typically, 100 mg of Mg/Al-LDH was mixed with 300 ml solution to result in an equilibrium pH of 4.8 for the water solution and of 3.5 for the ethanol solution during the first 30 min. Concentrations of metal cations in the solutions were analyzed with the reaction times by AAS after removing the solid phase by a filter paper with 0.22 μm of pore size. The removal amount of metal cation from solution was calculated from the decrease of metal concentration in the solution phase. All chemicals with a purity of greater than 99.9% were purchased from Aldrich Co. Also, deionized water and ethanol of HPLC grade were used.

The solid phases reacted for 2 days and 2 weeks were dried at room temperature for further characterization. X-ray diffraction (XRD) patterns were obtained by powder method using Ni-filtered CuKα radiation at 40 KV and 100 mA with scanning speed of 5°/min (Rigaku D/Max 2500). The HRTEM images were examined with a Philips CM200 at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were collected on ESCALAB250 (VG Scientific) with an energy resolution of 0.45 eV and Mg *K*a (1253.6 eV) X-ray gun operating at 20 mA and 15 kV.

3. Results and discussion

Reaction of metal solutions with Mg/Al-LDH led to significant precipitation of metal hydroxide species along with reduced intensity of XRD peaks of Mg/Al-LDH as indicated in Figs. 1 and 2. With the aqueous $CuCl_2$ solution, Mg/Al-LDH resulted in precipitation of Cu hydroxide–chloride ($Cu_7Cl_4(OH)_{10}\cdot H_2O$) along with slight decomposition of Mg/AI-LDH. Structural

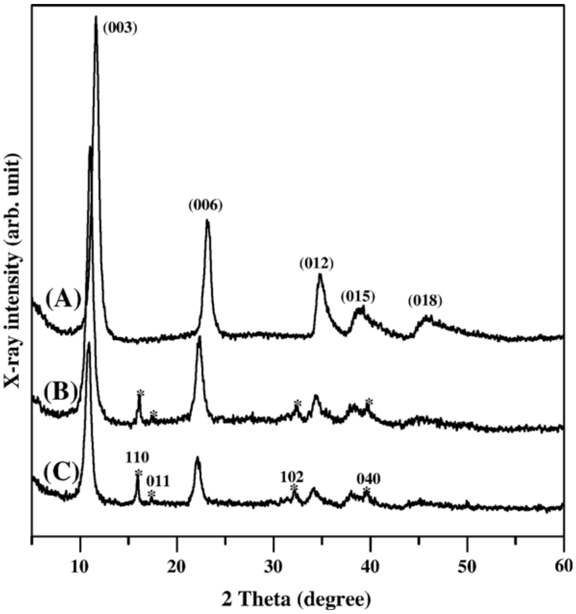

Fig. 1. XRD patterns of the pristine LDH and the LDH treated with aqueous 5 mM $CuCl_2$ solution. (A): Untreated LDH; (B): LDH treated for 2 days; (C): LDH treated for 2 weeks; *: $Cu_7Cl_4(OH)_{10}\cdot H_2O$.

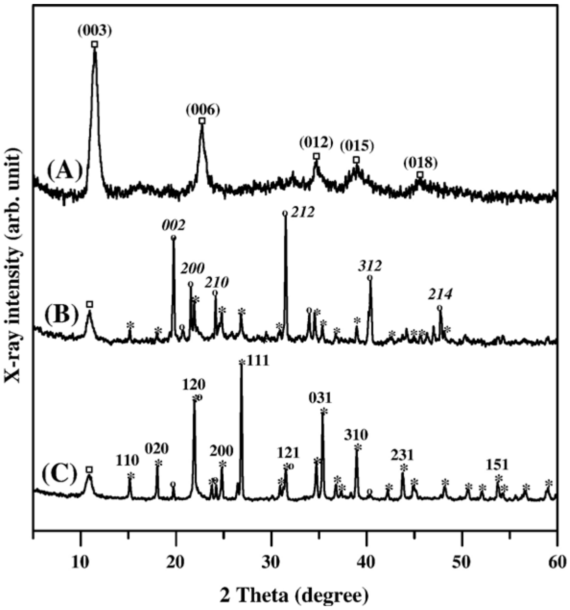

Fig. 2. XRD patterns of the LDHs treated with ethanol solution containing Cu, Cd, Ni, Zn, Co metal chlorides of each 1 mM concentration for 2 days (A) and aqueous 5 mM $PbCl_2$ solution for 2 days (B) and 2 weeks (C). □: LDH; ○: $PbCO_3PbCl_2$; *: Pb(OH)Cl.

decomposition resulted mainly from initial high acidity of the solution, as indicated by insignificant decomposition with extended treatment times. When the suspension was treated at 80 °C for overnight, the same result was obtained. These results indicated that Cu^{2+} cations were removed mainly by the precipitation of hydroxides, specifically $Cu_7Cl_4(OH)_{10}{\cdot}H_2O$ in this experiment. On the other hand, the aqueous $PbCl_2$ solution led to steady decomposition of Mg/Al-LDH structure along with the formation of various Pb precipitates such as carbonate chloride ($PbCO_3PbCl_2$) and hydroxide chloride (Pb(OH)Cl). The XRD patterns showed that the initial precipitates were Pb carbonate and hydroxide. This result indicates that Pb cations in solution react initially with both surface hydroxide and carbonate ions to destroy interlayer structure. Subsequently, the interlayer carbonate could be also available to Pb cations. However, Pb hydroxide prevailed over Pb carbonate as the reaction proceeded. This occurred probably because of the relative stability of Pb carbonate ($K_{sp}=1.5\times10^{-13}$) to Pb hydroxide ($K_{sp}=2.8\times10^{-16}$). Cu carbonates were not detected because of much higher stability of $Cu(OH)_2$ ($K_{sp}=1.6\times10^{-19}$) compared to $CuCO_3$ ($K_{sp}=2.5\times10^{-10}$) (Lide and Frederikse, 1992).

Slight increase in the interlayer space was also observed in both XRD patterns. However, it was not clear whether anion exchange reaction took place or not in this study, because the interlayer carbonate in LDHs is well known to be hardly exchangeable due to its high affinity to the interlayer space of LDHs (Radha et al., 2005). In addition, Mg/AI-LDH in the ethanol solutions did not lead to any removal of metal cations such as Co^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} etc. However, Cu^{2+} cations were removed from ethanol solutions (results not shown). The analysis of XRD patterns indicated that Cu^{2+} removal was accompanied by the formation of Cu hydroxides (about 90 meq/100 g of LDH), which needs further study for explanation.

Isomorphic substitution in crystalline materials typically results in the change of XRD patterns (Karthik et al., 2004; Balitsky et al., 2005; Suárez and García-Romero, 2006). In particular, isomorphic substitution of layered clays leads to the change in the *d*-spacings and relative intensities of 0*kl* peaks that reflect lattice parameters of layer framework. Thus, XRD patterns of Mg/Al-LDH could be affected by substitution of Mg^{2+} by Cu^{2+} because of the difference in ion size (66 pm for Mg^{2+} and 72 pm for Cu^{2+}) and scattering power between the two cations. However, any apparent changes were not observed either in the basal spacings or in relative intensities of the XRD peaks characteristic of the layers of Mg/AI-LDH, as was previously observed by Komarneni et al. (Komarneni et al., 1998). They also reported the precipitation of Cu in the presence of LDHs but not other cations such as Co, Ni and Zn. Although it was not clear in this study whether isomorphic substitution occurred or not, the above results suggest that removal of Cu^{2+} and Pb^{2+} metal cations by Mg/AI-LDH took place mainly though precipitation reaction.

The removal isotherms of Cu^{2+} and Pb^{2+} cations shown in Figs. 3 and 4 indicated that Mg/Al-LDH apparently removed a considerable amount of metals from the aqueous solutions. While Cu^{2+} removal attained equilibrium within 30 min of reaction time, a logarithmic isotherm resulted from Pb^{2+} removal. This significant difference in the removal isotherms with reaction time between these two metal cations are partially explained by stability of the precipitates. As indicated in the XRD patterns, the adsorbed Cu^{2+} were stabilized in the form of copper hydroxide on the external surfaces of LDH crystals, which could protect LDH framework from being attacked by further reaction. Eventually, rapid equilibrium could be established between Cu^{2+} in solution and copper hydroxide precipitated on the LDH surfaces. On the other hand, Pb^{2+} results in the formation of two species of the precipitates which exhibit comparable stability. In addition, lead carbonates originated from the carbonate anions of the interlayer space. Lead ions could react with the

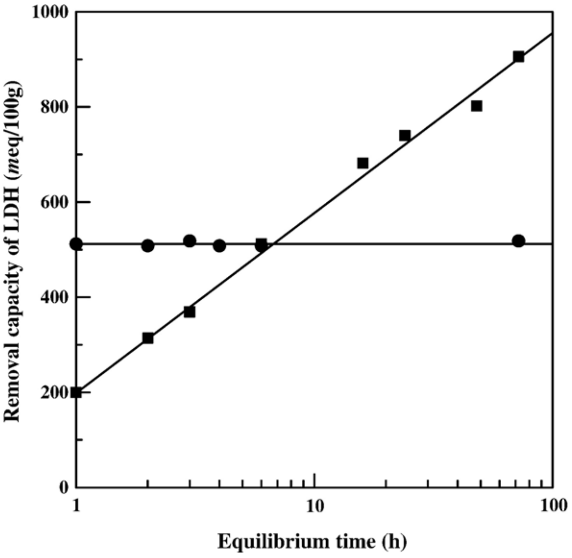

Fig. 3. Removal isotherms of Cu (filled circles) and Pb (filled squares) cations with equilibrium times in aqueous solution.

framework hydroxide to slowly decompose LDH structure. Thus, steady formation of Pb carbonate and hydroxide results in the logarithmic removal isotherm. It is suggested that Pb^{2+} could be precipitated until complete disintegration of LDH structure occurs.

The removal isotherms with initial metal cation concentrations exhibited no difference in the patterns between Cu^{2+} and Pb^{2+}. Their removal amounts were linearly proportional to the initial metal concentrations. However, complete removal of metal cations was not observed for both Cu^{2+} and Pb^{2+} at any concentration. Because the highest concentration used in this experiment was less than water solubility of the metal chlorides and the equilibrium pH was maintained below the value of 5.0, simple precipitation from the solution could be prevented. Precipitation of the metal cations would be caused by their interaction with Mg/Al-LDH. Consequently, the equilibration between solid and solution phases depended on their initial concentrations to result in the linear isotherms and the incomplete removal. These results also indicate that removal of Cu^{2+}

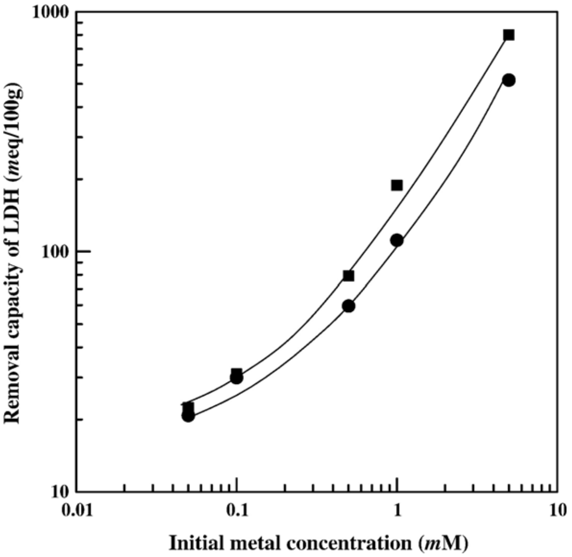

Fig. 4. Removal isotherms of Cu (filled circles) and Pb (filled squares) cations with metal concentrations in aqueous solution (equilibrium time: 2 days).

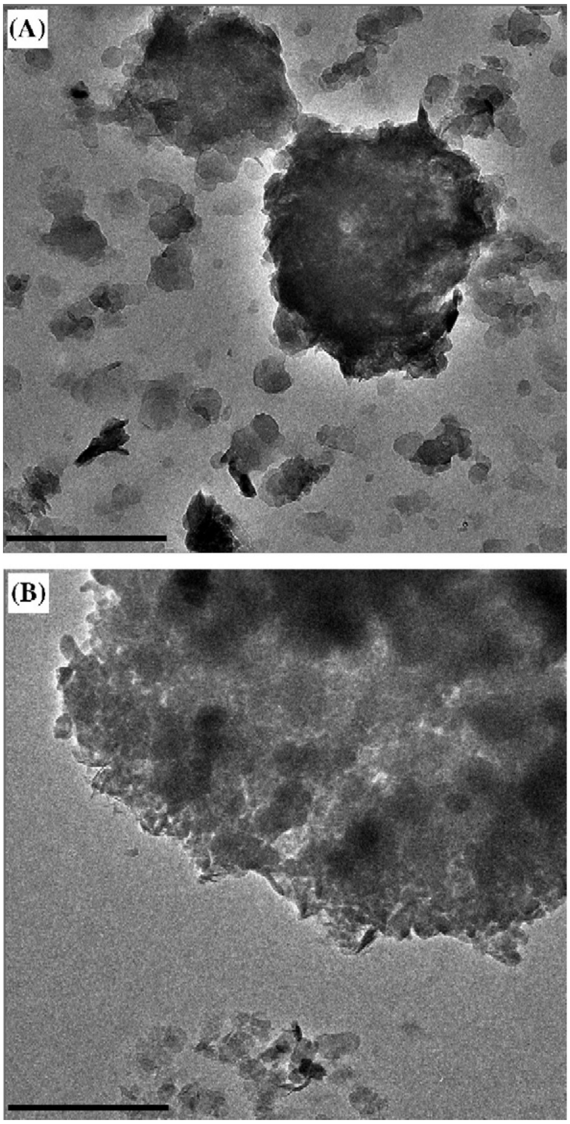

Fig. 5. TEM images of the LDH crystals treated with aqueous 5 mM $CuCl_2$ (A) and $PbCl_2$ (B) solutions for 2 days. A scale bar indicates a length of 500 nm.

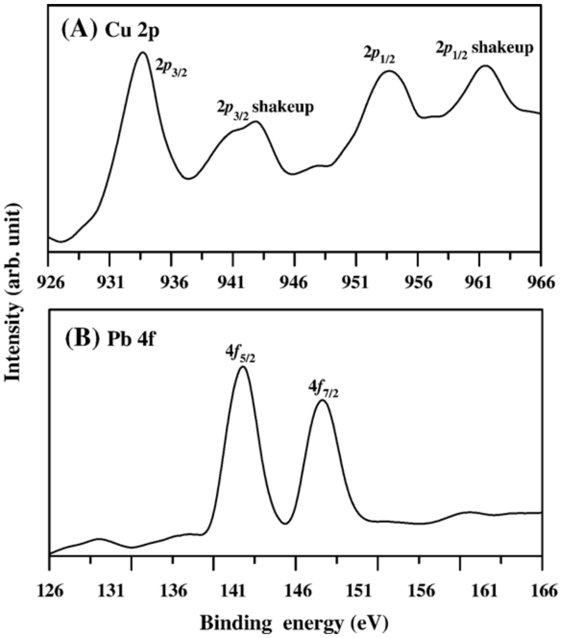

Fig. 6. X-ray photoelectron spectra of the precipitates from Cu (A) and Pb (B) cation solutions in the presence of LDH.

and Pb^{2+} metal cations by Mg/Al-LDH is facilitated mainly by surface precipitation.

A clear difference in the reaction mode between Cu^{2+} and Pb^{2+} was observed by the morphological change of LDH crystals through the reaction. As shown in Fig. 5, the Cu-treated crystals maintained the original shape of pristine LDH, plates in a size of 2–3 μm (Gardner et al., 1998), although their size decreased significantly. They show smooth surfaces and rounded edges. A decrease in size together with rounded edge resulted from partial dissolution of the pristine crystals. Smooth surface supports the surface-mediated formation and stabilization of copper hydroxide. Meanwhile, the Pb-treated ones were split into fine laths (see bottom of Fig. 5B). In addition, many dark spots can be seen spread over their surface. The framework fracture could be induced by the reaction of Pb^{2+} with interlayered carbonate ions and formation of Pb hydroxides, which also explains the dark spots over the surface. This result strongly supports the different reaction modes; Cu^{2+} reacts with surface OH, whereas Pb^{2+} with interlayered carbonate as well as surface OH.

Identification of metal species in the precipitates was attempted by XPS, shown in Fig. 6. The LDH treated in the aqueous $CuCl_2$ solution led to a XPS spectrum typically obtained from copper hydroxides, showing the characteristic Cu 2p peaks at 934, 954, and 962 eV (Farquhar et al., 1996). On the other hand, the LDH treated in the aqueous $PbCl_2$ solution exhibited two XPS peaks at 138 and 143 eV which resulted from Pb 4f absorption. In general, Pb carbonates show the $4f_{7/2}$ peak around 138.7 eV, whereas Pb hydroxides around 137.3 eV (Chada et al., 2005). The $4f_{7/2}$ peak in this study was observed around 138 eV, an intermediate position between two species. This result suggests the presence of both Pb species in the precipitates. The XPS results are consistent with the above XRD results to indicate the formation of hydroxides for Cu^{2+} cations and of both hydroxides and carbonates for Pb^{2+} cations. This result also suggests surface adsorption and precipitation as the main reactions in the removal of Cu^{2+} and Pb^{2+} metal cations by Mg/Al-LDH.

Plausible reactions of metal cations to LDH comprise precipitation of metal hydroxides, adsorption of metal cations on surface hydroxyl groups of LDH, precipitation of metal carbonates by anion exchange and/or structure decomposition, and presumably diodachy. The reaction mechanisms depend also on the nature of cations, for example, their electronegativity. LDH surfaces are covered with hydroxyl groups bonded to octahedral metal atoms and surrounded by excess hydroxide ions due to its high buffering capacity. Therefore, the preferred reaction between LDH and Cu^{2+} and Pb^{2+} metal cations are surface adsorption and precipitation. Komarneni et al., also reported precipitation with Cu^{2+} ions confirming the present results (Komarneni et al., 1998). There is also a chance for interlayer carbonate anions to be replaced by chloride anions at the edges, although LDH exhibits high selectivity to carbonate anions. Therefore, it is apparent form this study that LDH removes Cu^{2+} and Pb^{2+} transition metal cations from aqueous solution mainly by surface adsorption and precipitation.

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References

Alloway, B.J., 1995. Heavy Metals in Soils. Blackie, Glasgow.

Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater. 97, 219–243.

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Res. 33, 2469–2479.

Balitsky, V.S., Balitsky, D.V., Nekrasov, A.N., Balitskaya, L.V., 2005. Growth and characterization of $Si_xGe_{1-x}O$ solid solution single crystals with quartz structure. J. Cryst. Growth 275, e807–e811.

Carlino, S., 1997. The intercalation of carboxylic acids into layered double hydroxides: a critical evaluation and review of the different methods. Solid State Ionics 98, 73–84.

Chada, V.G.R., Hausner, D.B., Strongin, D.R., Rouff, A.A., Reeder, R.J., 2005. Divalent Cd and Pb uptake on calcite cleavage faces: an XPS and AFM study. J. Colloid Interface Sci. 288, 350.

Chrysochoou, M., Dermatas, D., 2006. Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: literature review and experimental study. J. Hazard. Mater. 136, 20–33.

Farquhar, M.L., Charnock, J.M., England, K.E.R., Vaughan, D.J., 1996. Adsorption of Cu(II) on the (0001) plane of mica: a REFLEXAFS and XPS Study. J. Colloid Interface Sci. 177, 561–567.

Gardner, E.A., Yun, S.K., Kwon, T., Pinnavaia, T.J., 1998. Layered double hydroxides pillared by macropolyoxometalates. Appl. Clay Sci. 13, 479–494.

Kameda, T., Saito, S., Umetsu, Y., 2005. Mg–Al layered double hydroxide intercalated with ethylene-diaminetetraacetate anion: synthesis and application to the uptake of heavy metal ions from an aqueous solution. Sep. Purif. Technol. 47, 20–26.

Karthik, M., Vinu, A., Tripathi, A.K., Gupta, N.M., Palanichamy, M., Murugesan, V., 2004. Synthesis, characterization and catalytic performance of Mg and Co substituted mesoporous aluminophosphates. Microporous Mesoporous Mater. 70, 15–25.

Komarneni, S., Kozai, N., Roy, R., 1998. Novel function for anionic clays: selective transition metal cation uptake by diadochy. J. Mater. Chem. 8, 1329–1331.

Lide, D.R., Frederikse, H.P.R., 1992. 74th ed. CRC Handbook of Chemistry and Physics (Eds.), CRC Press, London, p. 8–49.

Mousty, C., 2004. Sensors and biosensors based on clay-modified electrodes—new trends. Appl. Clay Sci. 27, 159–177.

Olanrewaju, J., Newalkar, B.L., Mancino, C., Komarneni, S., 2003. Simplified synthesis of nitrate form of layered double hydroxide. Mater. Lett. 45, 307–310.

Park, M., Lee, C.-I., Lee, E.-J., Choy, J.-H., Kim, J.-E., Choi, J., 2004. Layered double hydroxides as potential solid base for beneficial remediation of endosulfan-contaminated soils. J. Phys. Chem. Solids 65, 513–516.

Pérez, M.R., Pavlovic, I., Barriga, C., Cornejo, J., Hermosín, M.C., Ulibarri, M.A., 2006. Uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} on Zn–Al layered double hydroxide intercalated with EDTA. Appl. Clay Sci. 32, 245–251.

Radha, A.V., Kamath, P.V., Shivakumara, C., 2005. Mechanism of the anion exchange reactions of the layered double hydroxides (LDHs) of Ca and Mg with Al. Solid State Sci. 7, 1180–1187.

Rives, V., 2002. Characterisation of layered double hydroxides and their decomposition products. Mater. Chem. Phys. 75, 19–25.

Suárez, M., García-Romero, E., 2006. FTIR spectroscopic study of palygorskite: influence of the composition of the octahedral sheet. Appl. Clay Sci. 31, 154–163.

Vespa, M., Dähn, R., Grolimund, D., Harfouche, M., Wieland, E., Scheidegger, A.M., 2006. Speciation of heavy metals in cement-stabilized waste forms: a micro-spectroscopic study. J. Geochem. Explor. 88, 77–80.