

การดูดซับลิเทียม ทองแดง สังกะสี และแมงกานีส ด้วยมอนต์มอริลโลไนต์

Li(I), Cu(II), Zn(II) and Mn(II) Adsorption by Montmorillonite

นิตินา เคารพพวงค์ (Nithima Khaorapong)¹

บทคัดย่อ

ทำการศึกษาการดูดซับลิเทียม ทองแดง สังกะสี และแมงกานีส ภายในช่องว่างระหว่างเลเยอร์ของมอนต์มอริลโลไนต์ โดยทำปฏิกิริยาแลกเปลี่ยนไอออนที่อุณหภูมิห้องระหว่างสารละลายคลอไรด์ของลิเทียม ทองแดง สังกะสี และแมงกานีส กับมอนต์มอริลโลไนต์ และทำการตรวจวิเคราะห์ผลิตภัณฑ์ที่ได้ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์แบบผง อินฟราเรดสเปกโทรสโกปี และการวิเคราะห์เชิงความร้อน ค่าระยะห่างระหว่างเลเยอร์ของลิเทียม ทองแดง สังกะสี และแมงกานีสมอนต์มอริลโลไนต์เป็น 1.46, 1.25, 1.52 และ 1.61 นาโนเมตร ตามลำดับ จากการวิเคราะห์เชิงความร้อนพบว่าการลดลงของน้ำหนักของลิเทียม ทองแดง สังกะสี และแมงกานีสมอนต์มอริลโลไนต์ในช่วงอุณหภูมิ 200–700°C, 200–650°C, 300–700°C และ 200–650°C ตามลำดับ แสดงว่ามีการสลายตัวของน้ำที่สร้างพันธะกับไอออนโลหะภายในช่องว่างระหว่างเลเยอร์ การสลายตัวของไอออนโลหะ และหมู่ไฮดรอกซิล (OH) ภายในโครงสร้างของมอนต์มอริลโลไนต์ ในช่วงอุณหภูมิดังกล่าว

Abstract

Homoionics, Li(I), Cu(II), Zn(II) and Mn(II), were adsorbed in the interlayer spaces of montmorillonite by conventional cation exchange reactions between the aqueous solution of Li(I), Cu(II), Zn(II) and Mn(II) chloride and montmorillonite at room temperature. The metal-adsorbed montmorillonites were characterized by powder X-ray diffraction, infrared spectroscopy and thermal analyses. The basal spacings were 1.46, 1.25, 1.52 and 1.61 nm for Li(I), Cu(II), Zn(II) and Mn(II) treated montmorillonites, respectively. The weight losses at the temperature ranges of 200–700°C, 200–650°C, 300–700°C and 200–650°C for Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites, respectively, corresponding to the endothermic peaks in the DTA curves, were ascribed to the dehydration of coordinated water molecules, metal evolution and dehydroxylation of montmorillonite.

คำสำคัญ: ลิเทียม ทองแดง สังกะสี แมงกานีส การดูดซับ มอนต์มอริลโลไนต์

Keywords: Lithium, Copper, Zinc, Manganese, Adsorption, Montmorillonite

¹ผู้ช่วยศาสตราจารย์ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยขอนแก่น, e-mail: nithima.kku.ac.th

Introduction

Studies and application of layered inorganic solids, which can accommodate various types of organic and inorganic species, are an important topic from the viewpoints of technological interests as well as industrial processes (Whittingham, 1982; Yariv and Cross, 2002). The layered inorganic materials such as smectite group of layered clay minerals are extensively studied due to their swelling behavior, ion exchange property, adsorptive property and large surface area (Van Olphen, 1977). These properties suggest potential practical applications as ion exchangers, adsorbents, catalysts and molecular sieves (Barrer, 1978, 1989; Theng, 1974; Ogawa and Kuroda, 1995, 1997). The ion exchange and adsorption methods of using layered materials are the most favorite techniques for immobilizing organic and inorganic substances because of the ease of operation and the ability to adsorb many different species from solutions, and so on. The ion exchange and adsorption processes of cationic, anionic and nonionic species into layered clay minerals (Angioi et al., 2005; Carrado et al., 1993; Khaorapong et al., 2002; Khaorapong and Ogawa, 2006; Lagaly, 1986; Lagaly and Beneke, 1991; Parfitt and Mortland, 1968; Yamanaka et al., 1974; Sanchez-Martin, 2006), layered double hydroxides (Beaudot et al., 2004; Carrado et al., 1993), and layered polysilicates (Ogawa and Takizawa, 1999; Peng et al., 2006) have been proposed so far.

Here, the ion exchange reactions of Li(I), Cu(II), Zn(II) and Mn(II) cations into montmorillonite are reported. Clays including layered clay minerals and their modified forms have believed to be important in affecting the organic and inorganic contaminates because of their adsorption and ion exchange properties.

The adsorptions of Cr(III), Ni(II), Cu(II), Pb(II), Hg(II), Cd(II) and La(II) by clays and clay minerals such as bentonite, kaolinite, montmorillonite and so on have been reported (Alba et al., 1997; Brigatti et al., 2005; Clementz, 1973; Gupta and Bhattacharyya, 2006; Labhsetwar and Shrivastava, 1992; Velghe et al., 1977). The surfactant-modified montmorillonite was used for the removal of heavy metal (Lin and Juang, 2002) and pesticides (Sanchez-Martin et al., 2005) from water. In this present work, the feasibility of using montmorillonite for the removal of metal ions from aqueous solution by cation exchange reactions between the aqueous solutions of metal chlorides and montmorillonite was studied.

Material and methods

1. Material

Na(I)-montmorillonite (a reference sample from the Clay Science Society of Japan, JCSS-3101, Kunipia F, obtained from Kunimine, Japan) was used as the host material. The cation exchange capacity (CEC) of Na(I)-montmorillonite was 119 meq/100 g of clay (Sugahara et al., 1984). Lithium(I) chloride, copper(II) chloride, zinc(II) chloride and manganese(II) chloride (Analytical Grade) were purchased from May & Baker Ltd. and Carro Erba Regenti. The chemicals were used without further purification.

2. Sample preparation

Homoionic (Li(I), Cu(II), Zn(II) and Mn(II)) montmorillonites were prepared by a conventional ion exchange method. Powders of Na (I)-montmorillonite were mixed with fresh aqueous solutions of lithium(I) chloride, copper(II) chloride, zinc(II) chloride or manganese(II) chloride and the mixtures were stirred

at room temperature for 24 h. The total Li(I)-, Cu(II)-, Zn(II)- and Mn (II)-contents were ten times of the cation exchange capacity of the Na(I)-montmorillonite. After the ion exchange reactions, the resulting solids were collected by centrifugation and washed with deionized water repeatedly until a negative chloride ion test with AgNO_3 was obtained. The amounts of homoionic cations determined by atomic absorption spectroscopy (AAS), were 106, 112, 105 and 109 meq/ 100 g of clay for Li(I)-, Cu(II)-, Zn (II)- and Mn(II)-montmorillonites, respectively.

3. Characterization

The purity and crystallinity were checked by powder X-ray diffraction measurements (Philips PW 3710 powder diffractometer using monochromatic CuK α radiation). The infrared spectra of the samples were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. The samples were prepared using the standard KBr method. TG-DTA curve measurements were performed on a Perkin Elmer Pyris Diamond TG-DTA instrument at a heating rate of 10°C/ min under a dry air atmosphere using α -alumina (α - Al_2O_3) as a standard material.

Results and discussion

The amounts of adsorbed homoionic cations determined by atomic absorption spectroscopy (AAS), were 106, 112, 105 and 109 meq/ 100 g of clay for Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites, respectively, confirming the high adsorption affinity of montmorillonite. The Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-contents were close to the CEC value for Na(I)-montmorillonite (119 meq/ 100 g of clay), indicating a complete ion exchange reaction.

By the ion exchange reactions of Na(I)-montmorillonite with the aqueous solutions of Li(I)-, Cu(II)-, Zn(II)- and Mn(II) chlorides at the molar ratio of 1:10, the basal spacings (d) of the products changed as shown in Fig. 1. The powder X-ray diffraction patterns of Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites (Fig. 1b-e) showed peaks with basal spacings of 1.46, 1.25, 1.52 and 1.61 nm, respectively. The gallery heights of the interlayer spaces were determined to be ca. 0.46, 0.25, 0.52 and 0.61 nm by subtracting the thickness of the silicate layer (ca. 1.0 nm) from the observed basal spacings. Since the basal spacing of Cu(II)-montmorillonite is similar to that observed for Na(I)-montmorillonite (Fig. 1a), the coordinated water molecules are thought to take a monolayer arrangement in the interlayer spaces of Cu(II)-montmorillonite. For the basal spacings of Li(I)-, Zn(II)- and Mn(II)-montmorillonites (ca. 1.46, 1.52 and 1.61 nm), the intercalated water molecules are thought to form a bilayer arrangement in the interlayer spaces of the montmorillonites. It has been reported that the basal spacings of the monolayer and bilayer Cu(II)-hectorite are 1.24 and 1.60 nm (Clementz et al, 1973), being approximately consistent with the present results.

The TG-DTA curves of Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites prepared by the reactions with the metal ions are shown in Fig. 2. The endothermic reactions of the products starting from room temperature, which accompanied the weight losses, were ascribed to desorption of adsorbed and coordinated water. Because the starting materials were stirred in aqueous solution at room temperature under ambient conditions, an amount of adsorbed H_2O should reside on the surfaces and in the interlayer spaces. We have reported that the gas evolved at

57 C was proved to be water by TG-MS analysis (He flow) of Alq_3 -montmorillonite (Khaorapapong et al., 2002). It has been reported that weight losses at temperatures below 100 C are due to surface-adsorbed water (Guggenheim and Van Gross, 2001). In the TG curves (Fig. 2e-h), second weight losses were observed at the temperature ranges of 200-600 C, 200-650 C, 300-700 C and 200-650 C for Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites, respectively. In the corresponding DTA curves, the endothermic peaks, which were observed in these temperature ranges, were interpreted to the dehydration of coordinated waters, metal evolution of exchangeable cations and dehydroxylation of the silicate layer. The dehydration, metal evolution and dehydroxylation for the metal-exchanged montmorillonites appeared at around 200-780 C (Brigatti et al., 2005; Labhsetwar and Shrivastava, 1992).

In order to examine the adsorbed states of metal ions, the infrared spectra of Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites were recorded. The absorption bands characteristic of Na(I)-montmorillonite (abbreviated as Na-mont) (Labhsetwar and Shrivastava, 1992) and Li(I)-, Cu(II)-, Zn(II)- and Mn(II)-montmorillonites (abbreviated as Li-mont, Cu-mont, Zn-mont and Mn-mont, respectively) are given in Table 1. The infrared spectra of the products can be divided into two regions. The first region covers the frequency range 4000-1600 cm^{-1} where stretching and bending vibrations of the water molecules appear. The second region (below 1300 cm^{-1}) includes the vibrations due to the silicate layer. The bands in the region were slightly shifted when compared with those of the Na(I)-montmorillonite. It should thus be possible to prove the coordination between water molecules and Li(I), Cu(II), Zn(II) or Mn(II)

cations in the interlayer spaces of montmorillonites. Compared with the characteristic absorption bands ascribable to Na(I)-montmorillonite (Table 1), the slight shifts of the bands observed for metal-exchanged montmorillonites strongly suggest the formation of coordinated water with the Li(I), Cu(II), Zn(II) and Mn(II) interlayer cations.

The preparation of metal-exchanged montmorillonites may lead to novel microstructures and physicochemical properties. The adsorption and ion exchange reaction in the interlayer spaces of layered solids is an effective way to prepare metal-exchanged layered silicate and layered silicate nanohybrid materials. Further studies on the preparation and application of metal-exchanged layered materials using variable metal cations and layered solids with different cation exchange capacities are now under way in order to construct organic-layered silicate nanohybrid materials with controlled microstructures and functions.

Conclusions

Montmorillonite is capable of removal of Li(I), Cu(II), Zn(II) and Mn(II) cations from aqueous solutions. The amount of the absorbed metal ions into montmorillonite is very close to the ion exchange capacity of Na(I)-montmorillonite. The gallery heights of the products varied slightly as compared to the neat Na(I)-montmorillonite, indicating the different arrangements of the coordinated water in the interlayer spaces. The thermal stabilities of the metal-exchanged montmorillonites were slightly changed by the adsorption of metal ions and water coordination in montmorillonite.

Acknowledgements

The author is deeply grateful for the financial support from the Research and Development Institute (RDI), Khon Kaen University through the new researcher fund and the research assistants, Ms. Kanda Saosong, Mr. Utit Yaovarit, Ms. Sawanya Laumlum, Ms. Pathayarat Srisangwan and Ms. Kanjana Kodsuree.

References

- Alba, M., Alvero, R., Becerro, A.I., Castro, M.A., Mu oz-Paez, A. and Trillo, J.M. 1997. Study of the reversibility on the local La³⁺ environment after thermal and drying treatments in lanthanum-exchanged smectites. **Nucl. Instr. Meth. Phys. Res. B.** 133: 34–38.
- Angioi, S., Polati, S., Roz. M., Rinaudo, C., Gianotti, V. and Gennaro, M.C. 2005. Sorption studies of chloroanilines on kaolinite and montmorillonite. **Environ. Pollut.** 134: 35–43.
- Barrer, R.M. 1978. **Zeolites and Clay Minerals as Sorbents and Molecular Sieves.** London: Academic Press.
- Barrer, R.M. 1989. Shape-selective sorbents based on clay mineral: a review. **Clays Clay Miner.** 37: 385–395.
- Beaudot, P., De Roy, M.E. and Besse, J.P. 2004. Intercalation of noble metal complexes in LDH compounds. **J. Solid State Chem.** 177: 2691–2698.
- Brigatti, M.F., Colonna, S., Malferrari, D., Medici, L. and Poppi, L. 2005. Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study. **Appl. Clay Sci.** 28: 1–8.
- Carrado, K.A., Forman, J.E., Botto, R.E. and Winans, R.E. 1993. Incorporation of Phthalocyanines by cationic and anionic clays via ion exchange and direct synthesis. **Chem. Mater.** 5: 472–478.
- Clementz, D.M., Pinnavaia, T.J. and Mortland, M.M. 1973. Stereochemistry of hydrated copper(II) ions on the interlamellar surfaces of layer silicates. an electron spin resonance study. **J. Phys. Chem.** 77: 196–200.
- Guggen, S. and Van Gross, K. 2001. Baseline studies of the clay minerals society source clays: thermal analysis. **Clays Clay Miner.** 49: 433–443.
- Gupta, S.S. and Bhattacharyya, K.G. 2006. Adsorption of Ni(II) on clays. **J. Colloid Inter. Sci.** 295: 21–32.
- Gupta, S.S. and Bhattacharyya, K.G. 2006. Interaction of metal ions with clays: a case study with Pb(II). **Appl. Clay Sci.** 30: 199–208.
- Khaorapong, N., Kuroda, K. and Ogawa, M. 2002. Intercalation of 8-hydroxyquinoline into Al-smectites by solid-solid reactions. **Clays Clay Miner.** 50: 428–434.
- Khaorapong, N. and Ogawa, M. 2006. Solid-state intercalation of 8-hydroxyquinoline into Li(I)-, Zn(II)- and Mn(II)-montmorillonites. **Appl. Clay Sci.** in press.
- Labhsetwar, N.K. and Shrivastava, O.P. 1992. Thermally stable coordination compounds intercalated in montmorillonite clay mineral. **Can. J. Chem.** 70: 1927–1931.
- Lagaly, G. 1986. Interaction of alkylamines with different types of layered compounds. **Solid State Ionics.** 22: 43–51.

- Lagaly G. and Beneke, K. 1991. Intercalation and exchange reactions of clay minerals and non-clay layer compounds. **Colloid Polym. Sci.** 269: 1198-1211.
- Lin, S.-H. and Juang, R.-S. 2002. Heavy metal removal from water by sorption using surfactant-modified montmorillonite. **J. Hazard. Mater. B** 92: 315-326.
- Ogawa, M. and Kuroda, K. 1995. Photofunctions of intercalation compounds. **Chem. Rev.** 95: 399-438.
- Ogawa, M. and Kuroda, K. 1997. Preparation of inorganic-organic nanocomposites through intercalation of organoammonium ions into layered silicates. **Bull. Chem. Soc. Jpn.** 70: 2593-2618.
- Ogawa, M. and Takizawa, Y. 1999. Intercalation of tris(2,2'-bipyridine) ruthenium(II) into a layered silicate, magadiite, with the aid of a crown ether. **J. Phys. Chem. B** 103: 5005-5009.
- Parfitt, R.L. and Mortland, M.M. 1968. Ketone adsorption on Montmorillonite. **Soil Sci. Amer. Proc.** 32: 355-363.
- Peng, S., Gao, Q., Du, Z. and Shi, J. 2006. Precursors of TAA-magadiite nanocomposites. **Appl. Clay Sci.** 31: 229-237.
- Sanchez-Martin, M.J., Rodriguez-Cruz, M.S., Andrades, M.S. and Sanchez-Camazano, M. 2006. Efficiency of different clay minerals modified with a cationic surfactant in adsorption of pesticides: influence of clay type and pesticide hydrophobicity. **Appl. Clay Sci.** 31: 216-228.
- Sugahara, Y., Kuroda, K. and Kato, C. 1984. Synthesis of β -sialon from a montmorillonite-polyacrylonitrile intercalation compound by carbothermal reduction. **J. Am. Ceram. Soc.** 67: C-247-C-248.
- Theng, B.K.G. 1974. **The Chemistry of Clay-Organic Reactions.** London: Adam Hilger.
- Van Olphen, H. 1977. **An Introduction to Clay Colloid Chemistry.** 2nd ed., New York: Wiley-Interscience.
- Velghe, F., Schoonheydt, R.A. and Uytterhoeven, J.B. 1977. The co-ordination of hydrated Cu(II)- and Ni(II)-ions on montmorillonite surface. **Clays Clay Miner.** 25: 375-380.
- Whittingham M.S. 1982. **Intercalation Chemistry.** (M.S. Whittingham and A.J. Jacobson, editors). New York: Academic Press.
- Yamanaka, S., Kanamaru, F. and Koizumi, M. 1974. Studies on the orientation of acrylonitrile adsorbed on interlamellar surfaces of montmorillonites. **J. Phys. Chem.** 79: 1285-1288.
- Yariv, S. and Cross, H. 2002. **Organo-Clay Complexes and Interactions.** New York: Marcel Dekker.

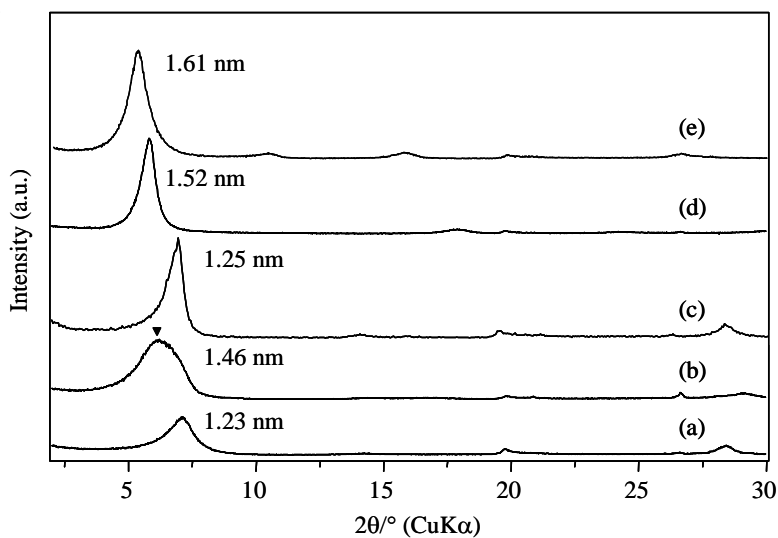


Fig. 1 XRD patterns of Na(I)- (a), Li(I)- (b), Cu(II)- (c), Zn(II)- (d) and Mn(II)-montmorillonites (e).

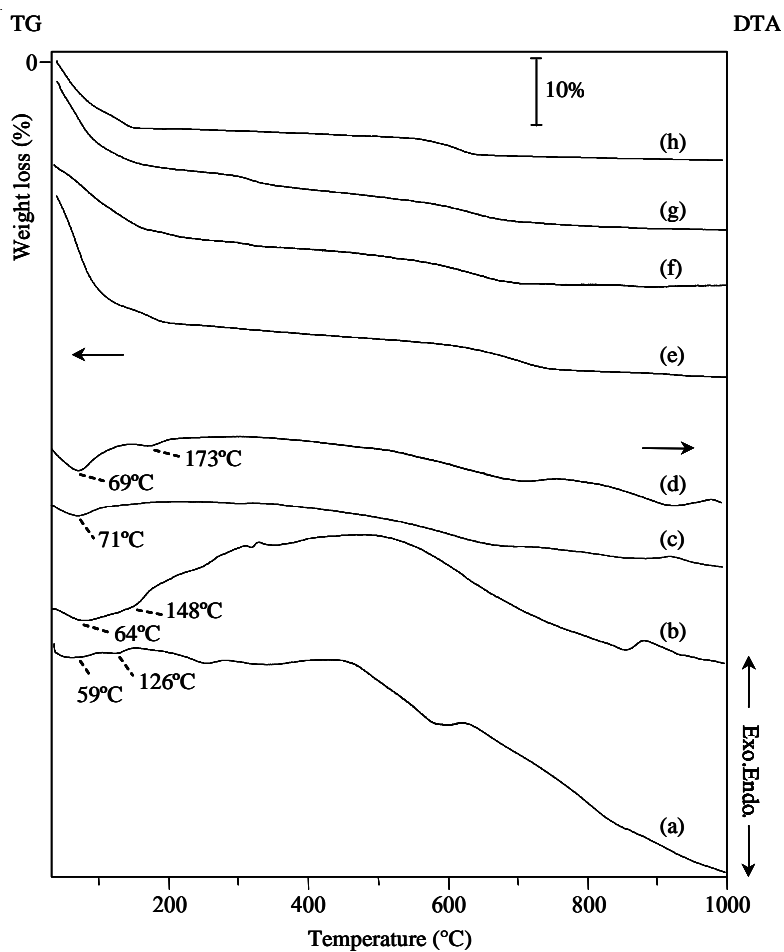


Fig. 2 TGA and DTA curves of Li(I)- (a, e), Cu(II)- (b, f), Zn(II)- (c, g) and Mn(II)- montmorillonites (d, h).

Table 1. Wavenumbers (cm^{-1}) of infrared bands of the products and their assignments.

Assignments	Na-mont	Cu-mont	Li-mont	Zn-mont	Mn-mont
Al-Al-OH stretching	3632	3632	3628	3630	3628
-OH stretching	3450	3446	3445	3461	3410
-OH bending	-	1647	1646	1639	1638
Si-O-Si stretching	1039	1041	1043	1038	1041
Al-Al-OH bending	914	913	915	914	912
Mg-Al-OH bending	846	845	847	843	835
Si-O-Al stretching	794	799	799	800	-
	-	779	779	-	749
Si-O-Al bending	522	522	522	520	522
Si-O-Si bending	467	467	467	466	467