Adsorption of cadmium and aniline of organoclay by HDTMA and CDTEA intercalating

Shu-Lung Kuo[a] and Edward Ming-Yang Wu*[b]

[a]Engineering Consultant, Kelee Environmental Consultant Corporation, 6F.-2, No. 288-8, Sinya Road, Kaohsiung City 806, Taiwan

E-mail : singsuey@ms28.hinet.net   *Fax* : 886-7-8150816

[b]Department of Civil and Ecological Engineering, I-Shou University, No. 1, Sec. 1, Syecheng Rd., Daishu District, Kaohsiung City 840, Taiwan

E-mail : edmywu@isu.edu.tw

Abstract : Organic cations such as quaternary ammonium cations (QACs) can be used to replace inorganic cations to form an organic-inorganic complex termed organoclay and to modify the clay surface from hydrophilic to hydrophobic. Organoclay can largely improve the sorption of organic contaminants. This study uses carboxydecyltriethylammonium cations (CDTEA) and general QACs, hexadecyltrimethylammonium cations (HDTMA) to modify clays, including Wyoming bentonite and the clay of Ton-Wei series soil and Chang-Bin series soil in Taiwan. The CDTEA cations were synthesized in laboratory scale, and the FTIR spectrum shows the presence of a carboxylic functional group and quaternary ammonium in the product. X-Ray diffraction detected that the clay layer spacing expanded and polymer cations were arranged as overlapping long chain hydrocarbons. Modified clays are observed for sorption of both cadmium and aniline. The adsorption of the cadmium in clay decreased after HDTMA was intercalated due to the occupation of exchange sites. The CDTEA modified clays can provide ligands to increase the adsorption of cadmium; this could be observed on the titration curve of electric potential with two end points. Both HDTMA and CDTEA modified clays are effective in regard to the sorption of aniline. The sorption of aniline in CDTEA clays was lower than that of HDTMA clays due to the polarity of the carboxylic functional group and the modification efficiency and purity of CDTEA. The dual sorption of cadmium and aniline by CDTEA clays showed noncompetitive adsorption, proving that the sorption mechanisms of the two solutes are ion exchange and partition, respectively.

Keywords : Organoclay, nanocomposite, hexadecyltrimethylammonium (HDTMA), carboxydecyltriethylammonium (CDTEA).

Introduction

Clay minerals in soil have great ability in adsorbing exchangeable cations and often form an impermeable liner in municipal solid waste landfill, preventing the spread of heavy metals and contaminants leaching[1–6]. Modification of the surface of clay to exchange inorganic to organic cations forms organic-inorganic nanocomposite material as organoclay or polymer-clay[7,8].

Organoclays have been studied for soil remediation, groundwater purification, industrial waste water treatment, and oil spill remediation using batch systems[9–12]. Studies have shown good adsorption capacity of organoclays for chlorinated compounds such as trichloroethylene and polychlorophenols[13,10,14]. However, there are no studies available that demonstrate the affinity of PCBs for organoclays or the capacity of this sorbent material. Furthermore, high concentrations of dissolved organic carbon in sediment pore water (up to 0.6 to 7.5 g=L according to Burgie[15]) indicate the need to understand the effect of dissolved organic acids on sorption by organoclays. The two main objectives of this study were to determine the sorption affinity of PCBs for commercially available organoclays, and to determine the effect of humic acid on the sorption affinity of organoclays, in order to evaluate their applicability in contaminated sediment remediation[16].

To enhance the physical properties of polymeric materials, various fillers can be used; for example, calcium carbonate, talc, glass fiber and wood flour are used as fillers for preparing reinforced synthetic organic polymers, as their anisotropy can help to reinforce the matrix[17,18]. However, strong interparticle interactions between fillers limit their application. Recently, to overcome this problem, organoclay has been added to or blended with polymeric materials. Wyoming bentonite clay, which is found in a layered silicate structure with a high surface area, has frequently been used for this purpose. Exchanging the cations present between the silicate layers with bulkier and more-organophilic cations can alter the clay structure to allow easier exfoliation or intercalation into the organic polymer structure. Nanocomposites can be obtained by exfoliation or intercalation of the organoclay layers into polymers. This nanocomposite structure makes it possible to change the physical properties of the organic polymers for deriving their beneficial use[19].

Smectite or vermiculite in moist environments hydrate with metal ions prior to achieving hydrophobic neutral organic compound (NOCs). Inorganic cations on the clay surface are replaced by organic cations such as quaternary ammonia cations from organic clay which can increase the adsorption efficiency of NOCs. This study uses CDTEA and general QACs, HDTMA to modify clays, including Wyoming bentonite and the clay of Ton-Wei series soil and Chang-Bin series soil in Taiwan. The CDTEA cations were synthesized in laboratory scale, and the FTIR spectrum shows the presence of a carboxylic functional group and quaternary ammonium in the product.

Materials and methods :

Different QACs were prepared for modified clay to measure the adsorption ability for metal ions or nonionic organic compound (NOCs) separately and simultaneously. The QACs include HDTMA and CDTEA prepared in laboratory scale to modify Wyoming bentonite or the clay of Ton-Wei series and Chang-Bin series in Taiwan. Cadmium and aniline were chosen as the contaminants for the adsorption experiment as these are generally used in industrial processes.

Clay preparation and character analysis :

All clay samples were prepared and underwent character analysis following the reference literature[20,21].

Preparation processes include removing carbonate and soluble salt, organic matter and metal oxides by sequentially wet chemical digestion. After dispersion and separation for clay, the clay samples were saturated with NaCl and had subsequent testing for CEC value, organic carbon content, functional group identification by FTIR and mineral speciation identification by XRD.

Synthesis and identification of CDTEA :

Have appropriate 11-bromoundecanoic acid dissolved in sodium carbonate solution, add in triethylamine with equivalent mole concentration, and heat reflux with stirring until the solution becomes clear. After acidifying the product solution by hydrochloric acid to pH 2–3, let it sit to crystallize overnight. Recrystallize with acetone and dry to complete the procedure.

Identify and compare the differences in the functional group of reaction product CDTEA and raw material of 11-bromoundecanoic acid, triethylamine by FTIR.

Organoclay preparation and character analysis :

Modify Chang-Bin series clay by HDTMA with equivalent 75% CEC content as HDTMA-CP. Then modify Wyoming bentonite, Chang-Bin series clay and Ton-Wei series clay with equivalent 75% CEC content as CDTEA-Smectite, CDTEA-CP and CDTEA-TW. All types of organoclay underwent the following testing to understand the property variation against sodium saturated clay : functional group identification by FTIR, mineral speciation identification by XRD and electric potential measurement titration that observe variations from pH 3 to 11.

Adsorption comparison of modified clay :

Isotherm adsorption :

Weigh 0.05 g of each type of clay and add different concentration of $Cd(NO_3)_2 \cdot 4H_2O$ solutions and adjust to pH 7. After 12 h of biaxial shaking, filter by Whatman GF/C 47 mm filter paper. Analyze the solution concentration to measure the adsorption efficiency of modified clay for cadmium.

For organic contaminants, weigh 0.05 g of each type of clay, mix with different concentration aniline solutions and engage in biaxial shaking for 12 h. During the ad-

sorption procedure, samples should be sheltered to prevent degrading by light. A high speed centrifuge will separate the solid and upper solution; the solution aniline concentration is analyzed by UV/Vis spectrum.

Dual solute adsorption :

Weigh 0.05 g of each organoclay sample. The concentration of aniline increases while cadmium remains constant in solution. During 12 h of biaxial shaking, the sample should be sheltered to prevent degrading by light. After being subjected to a high speed centrifuge to separate the solid and upper solution, the solution is analyzed for aniline and cadmium by UV/Vis spectrum and Flame AA.

Results and discussion

Property of sample clay :

Modified clay from natural Taiwan soil and purchased Wyoming bentonite are compared in Table 1. Wyoming bentonite has 94.20 cmole/kg, which is the highest CEC value. The CEC value of Chang-Pin clay increased rapidly from 28.62 cmole/kg to 91.30 cmole/kg after being

Table 1. Characteristics of sample clay

Sample clay	Wyoming bentonite	Chang-Pin clay	Ton-Wei clay
CEC (cmole/kg)	94.20	91.30	86.96
Organic matter (%)	N.D	N.D	N.D

separated from soil by removing organic matter and metal oxide on the surface of the clay. Even though the proportion of clay is not very high in natural soil, the high density of the charge of clay is exposed after pretreatment[5,18]. And Ton-Wei clay has a similar condition.

Characteristics of carboxydecyltriethyl ammonium :

The results of examining the functional group for the reactant of 11-bromoundecanoic acid, triethylammonium and product carboxydecyltriethylammonium, CDTEA by FTIR spectrum are shown in Fig. 1. The spectrum of triethylammonium has strong bands around 2969 cm^{-1} and 2794 cm^{-1}, which represent the C-H bonding of ethyl molecules. And 1068 cm^{-1} of C-N bonding also represent the tertiary ammonium; 11-bromoundecanoic acid show bands on 2913 cm^{-1} and 2846 cm^{-1} for C-H bonding and
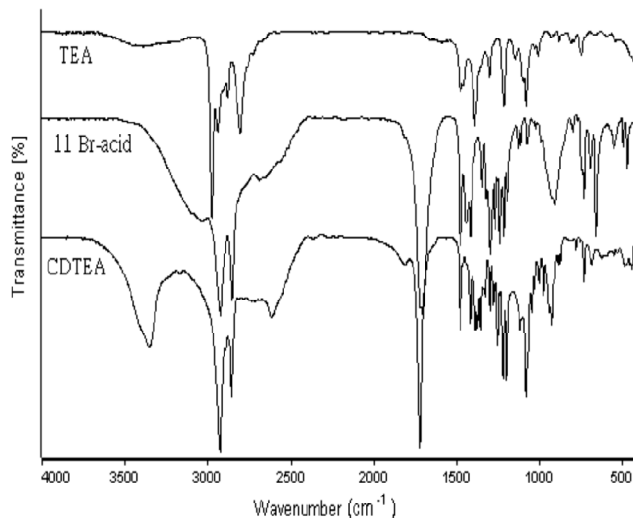

Fig. 1. FTIR spectrum of CDTEA synthesis.

1689 cm^{-1} for carboxyl functional group. The spectrum of the product CDTEA has bands on 2915 cm^{-1}, 2850 cm^{-1} for C-H bonding, 1068 cm^{-1} for C-N bonding, and on 1710 cm^{-1} for carboxyl structure, demonstrating a quaternary ammonium cation formation with a carboxyl functional group.

Characteristics of organoclay :

XRD analysis :

This study analyzed Chang-Pin clay with modified HDTMA (HDTMA-CP) and sodium saturated (Na-CP) by XRD for comparing layer spacing. D-spacing of Na-CP measured 1.00 nm and expanded to 2.16 nm after HDTMA was modified. HDTMA cation line in d-spacing of Chang-Pin clay might form a pseudotrimolecular layer or paraffin complex. Three types of clay were modified by CDTEA cations and measured layer spacing by XRD. The layer spacing of Wyoming bentonite, Chang-Pin and Ton-Wei clay are 1.16, 1.19 and 1.00 nm, respectively; they expanded to 1.42, 1.40 and 1.46 nm after CDTEA cations were inserted into the clay layer which was not raised as HDTMA intercalation. The arrangement of CDTEA in the clay layer could be a monolayer or product of bi-layer adsorption.

FTIR spectrum analysis :

The FTIR spectrum of sodium saturated (Na-CP), CDTEA (CDTEA-CP) or HDTMA (HDTMA-CP) modified Chang-Pin clay is shown as Fig. 2. The band of
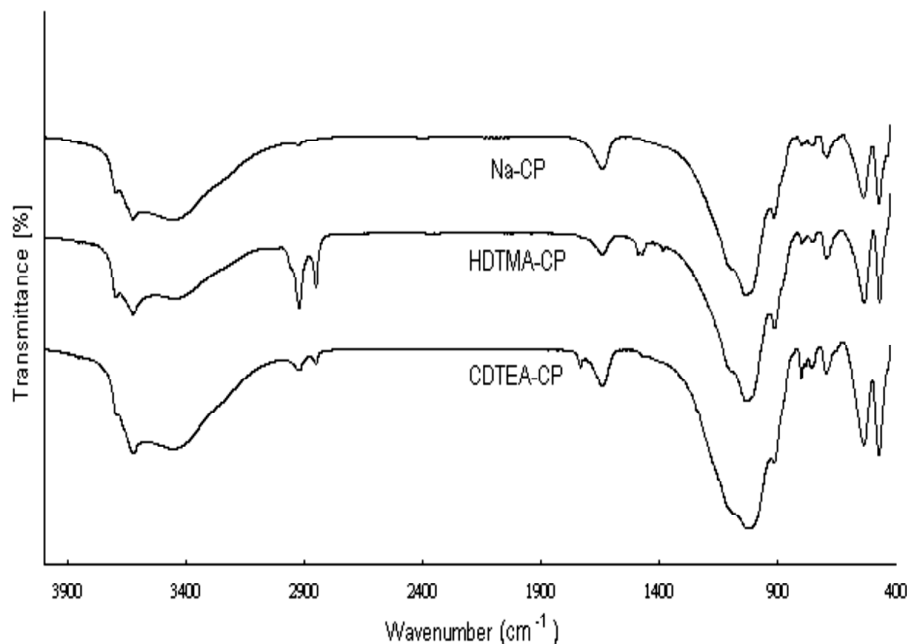
Fig. 2. FTIR spectrum of three type modified Chang-Pin clay.

octahedral hydroxyl on 3400–3700 cm^{-1} was shown on Na-CP, and the band of 2915, 2846 and 1461 cm^{-1} for methyl or alkyl molecule bonding were added on HDTMA-CP, which demonstrated HDTMA intercalation; however C-N bonding of HDTMA on 960 cm^{-1} was hidden by strong Si-O bonding. Modification of CDTEA caused the bonding of 2915 and 2846 cm^{-1} of hydrocarbon molecules, and also brought the carboxyl functional group on 1730 cm^{-1}. The intensity of the band however was not as strong as the intercalation of HDTMA. Three ethyl groups in CDTEA could not provide enough sites for intercalation; this may be the possible reason for the slight modification efficiency, and the purity of CDTEA synthesis also needs to be considered as a factor.

Measurement of electric potential titration :

Fig. 3 shows the titration curve of the electric potential of HDTMA-CP and CDTEA-CP. We can observe the curve of HDTMA-CP sharply rising to meet the titration end point; however, the end point of CDTEA-CP is hard to determine and the titration curve gently rises two stages. We calculate the amount of titrated NaOH as the CEC content of Wyoming bentonite, HDTMA-CP, takes less than 0.5 times that of CEC to the end point and CDTEA-CP takes 0.8 times that of CEC to the end point.
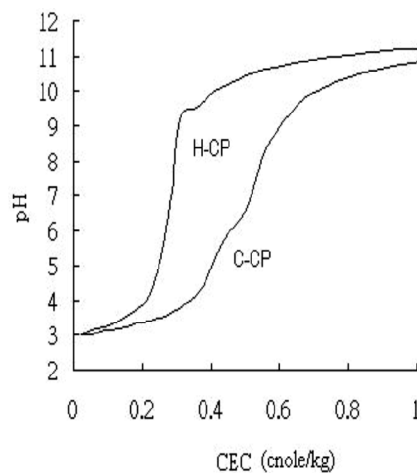

Fig. 3. Titration curve of HDTMA-CP and CDTEA-CP.

Draw the electric potential variation per volume unit as the function of the CEC value; the maximum of this function is the end point of titration[12]. Fig. 4 shows the electric potential variation and end point of HDTMA-CP and CDTEA-CP. The end point of HDTMA-CP occurred at 0.29 times that of CEC; CDTEA-CP has two on 0.40 and 0.53 times that of CEC which proves that the hydrogen oxide on the clay surface and the carboxyl group of CDTEA both exist.
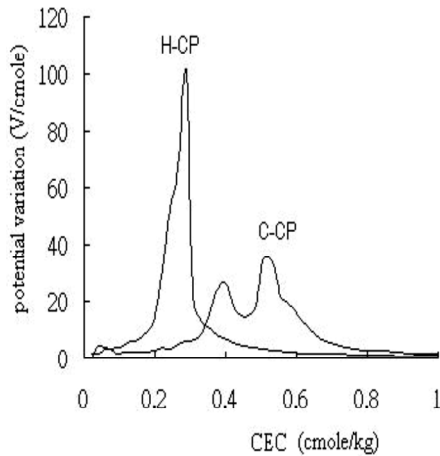
Fig. 4. Differential curves of HDTMA-CP and CDTEA-CP titration.

Adsorption experiment of clay :

Isotherm adsorption of cadmium :

The adsorption capacity versus the concentration of cadmium in different clay is shown in Fig. 5. CDTEA-bentonite (C-Sme) has the greatest adsorption capacity for cadmium, and following are CDTEA-TW, CDTEA-CP and Na-CP HDTMA-CP, the lowest one.

For the Chang-Pin clay, CDTEA modified clay adsorbs more than the Na saturated clay does for Cd; HDTMA-
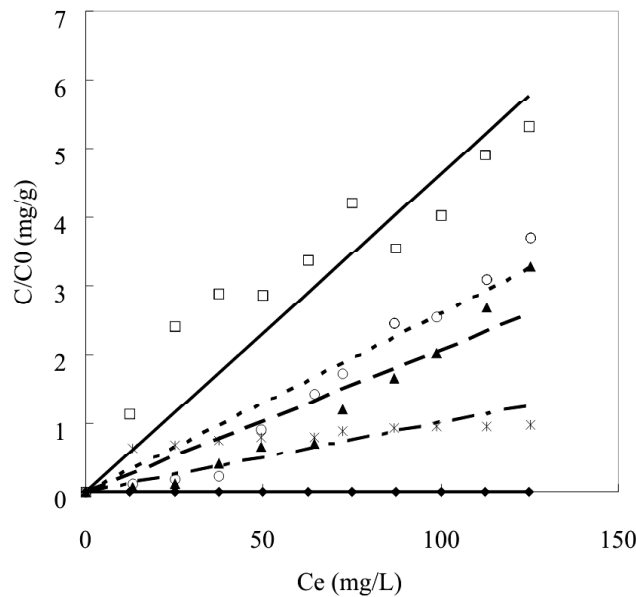
CP has lowest capacity. This phenomenon may reveal that HDTMA cations fill the exchange site on the surface of clay sheltering the adsorption ability; the carboxyl group can provide coordinate bonds for more cations, and even more than Na saturated clay[16]. Wyoming bentonite has higher CEC content than Chang-Pin and Ton-wei clay, which is most expandable and exchange site. Silicate layers combined by van der Waals force were easy to pull up, allowing more CDTEA cations to be coordinated. However the three types of modified clay have similar adsorption capacity for Cd, which determines that Taiwan clays may include bentonite and have similar characteristics[22,23].

Isotherm adsorption for aniline :

The result of modified clays adsorption of aniline is shown in Fig. 6. Ranking of adsorption capacity for aniline is as follows : HDTMA-CP > CDTEA-CP > Na-CP. The sorption mechanism of NOCs in natural soil with moisture is mainly by partition, with residue no longer remaining after the removal of organic matter. A typical example for the above characteristic is Na-CP.

HDTMA-CP has organic medium on the clay surface which was formed by connecting alkyl chains adsorbing aniline by partition. CDTEA-CP has a long chain hydrocarbon group for the same function; there are several
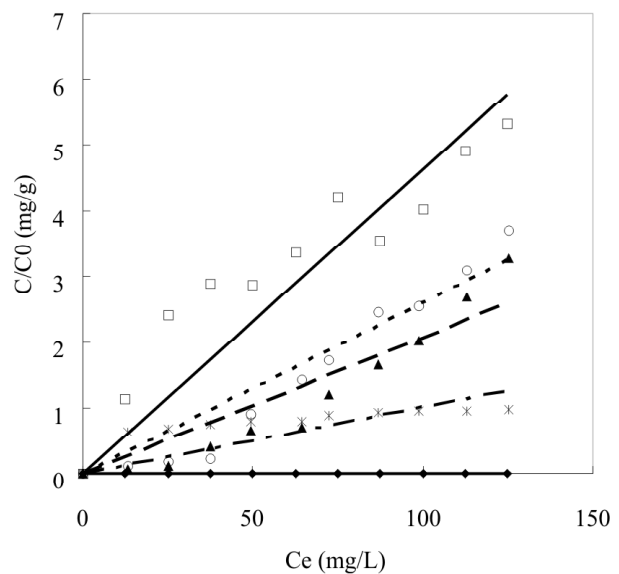

Fig. 5. Isotherm adsorption curves of different modified clays for cadmium : (◆) Na-CP, (□) HDTMA-CP, (▲) C-sme, (∗) C-TW, (○) C-CP.

Fig. 6. Isotherm adsorption curves of different modified clays for aniline : (◆) Na-CP, (■) CDTEA-Sme, (▲) CDTEA-TW, (○) CDTEA-CP, (∗) HDTMA-CP.
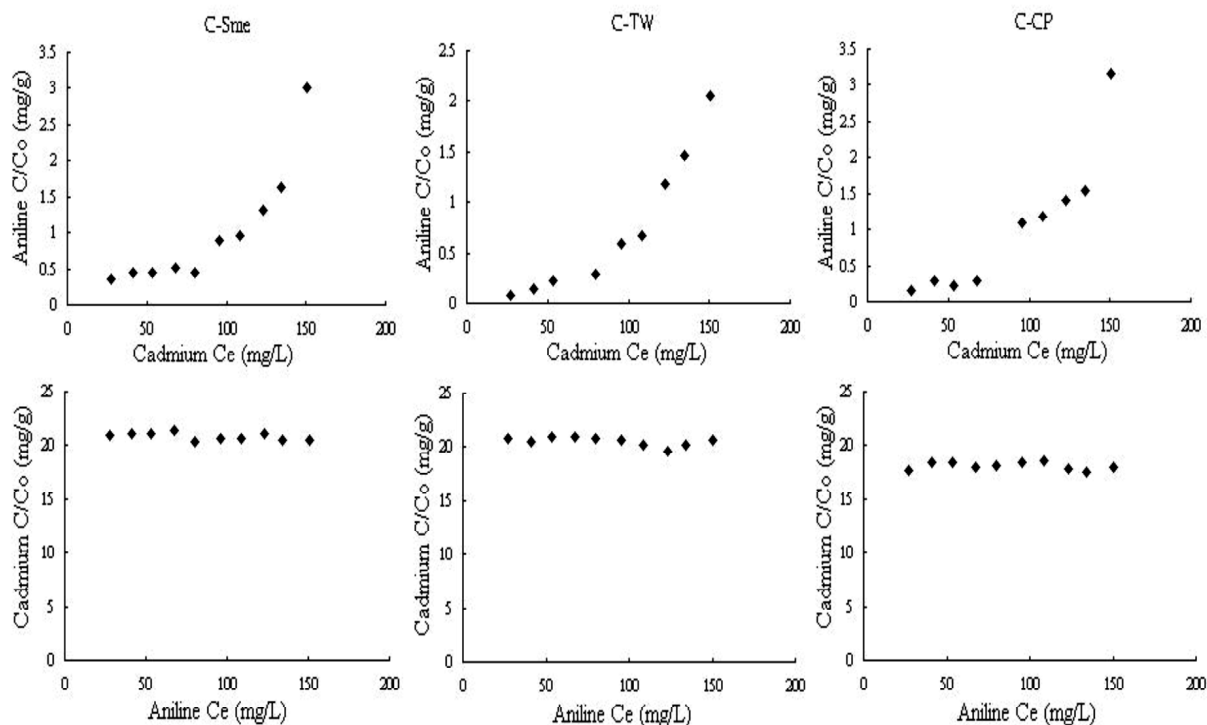
Fig. 7. Adsorption of CDTEA modified clays for dual absorption.

reasons for HDTMA-CP adsorbing aniline greater than CDTEA-CP : first, HDTMA-CP has larger d-spacing than CDTEA-CP judging from the XRD spectrum. The hydrocarbon arranges as paraffin in the former layer and as a monolayer in the latter one[6]; even though the efficiency of the CDTEA modification may not be as high as for the HDTMA, it can also cause partition. Second, two quaternary ammonium cations have different alkyl chain length and HDTMA has stronger non-static electricity force. Third, the carboxyl group of the CDTEA provides coordinate for metal ions; however the polarity of CDTEA-CP may act against the adsorption of aniline, which is similar to organic matter in natural soil[4,12].

Dual adsorption experiment :

Three CDTEA modified clays simultaneously and continually adsorb concentrations of cadmium, and sequentially adsorb concentrations of aniline; the measurements of both residual solutes are shown in Fig. 7. Adsorption of aniline in CDTEA-CP did not decrease the effect, nor adsorption, of cadmium. Two adsorbates in CDTEA-CP can retain the same adsorption amount as a single adsorbate.

The result of the dual adsorption experiment shows non-competitive adsorption, which proves that HDTMA cations adsorb aniline via the partition mechanism, and CDTEA cations adsorb Cd by ligand bond. The two mechanisms work respectively without no conflict[18,24].

Conclusion

Tertiary ammonium cations and carboxyl acid synthesize a compound with quaternary ammonium cations, alkyl chains and a carboxyl group; the structure is verified by FTIR spectrum. Electric potential titration demonstrates that the carboxyl group of CDTEA provides more ligands than the alkyl modified clay does.

Clays separated from natural Taiwan soil were modified by HDTMA and CDTEA cations, and organic cation arrangement in the silicate layer with Wyoming bentonite were compared. Referring to the FTIR spectrum, CDTEA modified clay shows bands of alkyl and carboxyl group, but the intensity of the bands weakens, perhaps due to the incomplete modification, synthesis efficiency or the polarity of CDTEA cations against intercalation.

Cadmium adsorption on different modified Chang-Pin

clay presents that CDTEA-CP provides not only a surface exchangeable site, but also ligands from the carboxyl group adsorbing Cd even more than the Na-CP. Most of the cations exchangeable sites on the HDTMA-CP were occupied by HDTMA cations and covered by Cd.

HDTMA-CP has the greatest adsorption capacity for aniline in all types of clay, followed by CDTEA-CP; Na-CP is the worst. HDTMA cations arrange in silicate layer as a high charge density condition, and the stronger hydrophobic bonds contribute the partition effect for aniline; however the polarity of the carboxyl group in the CDTEA cations provides a contrary effect. To improve the partition effect of CDTEA modified clays, it is necessary to optimize the parameters for CDTEA synthesis, and modification is the first priority.

CDTEA modified clay shows noncompetitive adsorption for inorganic metal ions and NOCs can hold different contaminants at the same time. Improving the synthesis efficiency of CDTEA cations may help to increase the adsorption capacity. Also the modified parameter of clay requires more research.

References

1. S. Xu, G. Sheng and S. A. Boyd, *Adv. Agron.*, 1997, **59**, 25.
2. R. W. Gullick, PhD dissertation, The University of Michigan, 1998.
3. N. C. Brady and R. R. Weil, "The Nature and Properties of Soils", Prentice-Hall, Inc., USA, 1999.
4. I. M. C. Lo and X. Yang, *J. Environ. Eng.*, 2001, **3**, 154.
5. B. Sharma, K. H. Gardner, J. Melton, A. Hawkins and G. Tracey, *Env. Eng. Sci.*, 2009, **26**, 1279.
6. J. Y. Kim, C. Kim and I. S. Chang, *Env. Eng. Sci.,* 2012, **29**, 14.
7. K. A. Carrado, *Appl. Clay Sci.*, 2000, **17**, 1.
8. F. Bergaya and G. Lagaly, *Appl. Clay Sci.*, 2001, **19**, 1.
9. S. K. Dentel, A. I. Jamarah and D. L. Sparks, *Water Res.*, 1998, **32**, 3689.
10. M. C. Wiles, H. J. Huebner, T. J. McDonald, K. C. Donnelly and T. D. Phillips, *Chemosphere*, 2005, **59**, 1455.
11. O. Carmody, R. Frost, Y. Xi and S. Kokot, *J. Colloid Interface Sci.*, 2007, **305**, 17.
12. H. Gao and W. J. Blanford, *Env. Eng. Sci.,* 2012, **29**, 533.
13. C. L. Ake, M. C. Wiles, H. J. Huebner, T. J. McDonald, D. Cosgriff, M. B. Richardson, K. C. Donnelly and T. D. Phillips, *Chemosphere*, 2003, **51**, 835.
14. T. Pernyeszi, R. Kasteel, B. Witthuhn, P. Klahre, H. Vereecken and E. Klumpp, *Appl. Clay Sci.*, 2006, **32**, 179.
15. D. J. Burgie, *Organic Geochem.*, 2001, **32**, 487.
16. W. J. Blanford and H. Gao, *J. Env. Moni.*, 2012, **14**, 3024.
17. C. H. Hong, Y. B. Lee, J. W. Bae, J. Y. Jho, B. U. Nam and T. W. Hwang, *J. Appl. Polymer Sci.*, 2005a, **98**, 427.
18. D. Schumann, H. Hartman, D. D. Eberl, S. K. Sears, R. Hesse and H. Vali, *Astrobiology*, 2012, **12**, 549.
19. C. H. Hong, Y. B. Lee, J. W. Bae, J. Y. Jho, B. U. Nam, G. J. Nam and K. J. Lee, *J. Appl. Ploymer Sci.*, 2005b, **97**, 2375.
20. G. W. Kunze and J. B. Dixon, "Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods", Agronomy Monograph no. 9, 1986.
21. B. H. Sheldrick and C. Wang, "Soil Sampling and Methods of Analysis", Lewis Publishers, 1993.
22. S. Y. Lee, S. J. Kim, S. Y. Chung and C. H. Jeong, *Chemosphere*, 2005, **55**, 781.
23. S. Ray, P. S. Khillare, K. H. Kim and R. J. C. Brown, *Env. Eng. Sci.,* 2012, **29**, 1008.
24. J. W. Shi, J. T. Zheng and X. J. Ji, *Env. Eng. Sci.,* 2012, **27**, 923.