Competitive Adsorption Ability of Organoclay to Heavy Metals Pb and Cd

[1,]Shu-Lung Kuo, [2*,]Edward Ming-Yang Wu

[1.] *Department of Technology Management, the Open University of Kaohsiung, Taiwan*
[2.] *Doctoral Program of College of Maritime, National Kaohsiung University of Science and Technology, Taiwan*

ABSTRACT: Due to isomorphic substitution in its structure, the surface of a clay mineral carries a negative charge. To achieve a balance in electrical properties, this permanent negative charge will attract exchangeable cations, such as Ca^{2+}, Mg^{2+}, K^+ and Na^+. As most normal soils carry a negative charge, they can be used to absorb metal cations; this property of said soils can also be used to absorb or replace heavy metal pollutants in soils. Organoclay is modified using an expansion-type clay mineral with cations from quaternary ammonium salt. The hydrophilic properties of the modified clay mineral will turn into hydrophobic ones, which can effectively absorb non-ionic organic pollutants and remove them. This study first used quaternary ammonium cations from carboxydecyltriethylammonium chloride (CDTEA) to modify the smectite. Tests on the basic properties of the modified smectite-CDTEA organoclay were conducted, including mineral identification using x-ray diffraction (XRD) and functional group identification using Fourier-transform infrared spectroscopy (FT-IR) to determine the modifying effects of quaternary ammonium cations on the smectite.

This study also conducted an experiment on the absorption of cadmium and lead by the modified smectite-CDTEA organoclay, respectively. The results show that more lead than cadmium was absorbed by the smectite-CDTEA organoclay. Furthermore, the results of a dual-solute absorption test show that the amounts of cadmium and lead absorbed by the smectite-CDTEA organoclay were reduced due to the existence of another type of heavy metal. The addition of lead had a greater impact on the amount of cadmium being absorbed. Thus, it is evident that competitive absorption occurs if the two metal ions exist in the modified smectite-CDTEA organoclay.

KEYWORDS: competitive adsorption, organoclay, CDTEA, isothermal adsorption

I. INTRODUCTION

Organoclay materials are defined as hybrid materials resulting from the association of clay minerals (swelling ones such as montmorillonite, vermiculite, and saponite) with surfactants and/or other various organic compounds (He et al., 2014; de Paiva et al., 2008). With the incorporation of the surfactants in their internal structure through different chemical and physical processes, the obtained materials combine a large specific surface and a hydrophobic behavior, enhancing the applications of clay minerals in various fields. A large volume of the research work focused on and pointed out the use of organoclays as reinforcers in polymer nanocomposites, starting materials for photophysical films, rheological agents, and as adsorbents for organic pollutants in soil and aquatic environments (Ugochukwu and Fialips, 2017; Shah et al., 2018). Despite previous research efforts (Li et al., 2003; Sander and Pignatello, 2005; Yang et al., 2006), the actual adsorption process is extremely complex and is not fully understood. This is particularly the case for adsorbents being applied to polluted water samples, due to their complexity. One traditional method to characterize adsorption is to use model compounds instead of actual polluted water samples (Pelekani and Snoeyink, 2001). Yang et al. (2010) used 2,4-dichlorophenol (DCP), naphthalene (NAP), and 4-chloroaniline (PCAN) as simple models for lower molecular weight aromatic pollutants (<200 g/mol) in water that contribute to direct competition. In an affecting atrazine (215.7 g/mol) adsorption competition study, compounds with molecular weights between 200 to 700 g/mol were found to be mostly responsible for pore constriction adsorption (and Pignatello, 2005). Similarly, Newcombe et al. (2002) evaluated the competitive effect of organic pollutant fractions and found that their smallest fraction, with molecular weight (MWw) of 949 g/mol, respectively, was the most detrimental to 2-methylisoborneol (168 g/mol) adsorption capacity and removal rates.This study aims to use quaternary ammonium cations with functional group to modify the smectite. An experiment on the absorption of cadmium and lead by the resulting organoclay was conducted to explore the organoclay's capacity to absorb said two types of heavy metal. The pollutants chosen were cadmium and lead involved in environmental pollution events. These two types of heavy metal are raw materials commonly used in the industrial sector, agriculture, and chemical engineering and processes; they are therefore more representative.

II. MATERIALS AND METHODS:

Purification and preparation of sodium saturated smectite : Put 60 g commercially available smectite into a 2-liter beaker, and add 1.8 liters of deionized water to it. After stirring, soak it for days to fully expand it. After it is expanded, take 250 ml of the smectite suspension out of the beaker. Filter sand using the wet sieving method with a 300-mesh sieve. Transfer the filtrate to a 1-liter sedimentation cylinder, and add deionized water to make 1 liter. Leave it to naturally sediment after stirring it rigorously with a stirring rod. Siphon the suspension at the top of the sedimentation cylinder by 10 cm 8 hours later. Use an 18000 rpm high-speed centrifuge to have the suspension centrifuged. Perform sodium saturation of the smectite obtained after centrifugation with 1 M NaCl solution. Next, grind the saturated smectite into powder with an agate mortar after freeze drying it, and obtain the sodium saturated smectite.

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.

Preparation of organoclay : Take 0.5 g sodium saturated smectite and add 30 ml of the CDTEA solution with a value equivalent to 0.75 times the CEC value. Continuously heat it up and oscillate it in a water bath at 80ºC for 24 h. Separate a solid from the liquid using a high-speed centrifuge at 20,000 rpm. Inspect whether the supernatant has white sediment after centrifugation using $AgNO_3$, to ensure that the chloride ions have been completely removed. After freeze-drying the modified smectite-CDTEA organoclay, grind it using an agate mortar and then store it. Conduct the subsequent characteristic analysis and absorption test.

Analysis of the properties of the smectite-CDTEA organoclay :
Verification of the function group of fourier-transform infrared spectroscopy (FT-IR) : The principle of FT-IR is using rotations or vibrations of molecules to absorb radiation at the same frequency. The fingerprint and Eigen areas in FT-IR can help to determine the existence of isomorphous replacement structure or organic molecules in the organoclay. Put the organoclay and KBr powders in an oven. After heating them up and drying them for 48 hours, mix them evenly in a 1:10 ratio, and then grind the mixture with an agate mortar. Use a hydraulic press to press the mixture at 10 tons/hour, making it into a transparent foil. Put the foil in a spectrometer and perform an analysis with a scan range of 4,000 cm^{-1} to 400 cm^{-1}.

X-ray Diffraction Analysis (XRD Analysis) : The XRD analysis is conducted using an x-ray diffractometer (Rigaku RINT-2000). With CuK_a as the light source, an analysis on the crystal patterns of the organoclay is performed to learn the spacing of layers of materials. The x-ray wavelength produced is 1.5418 $\overset{o}{A}$; the operating current during testing is 10 mA; the voltage is 20 kV; the scanning speed is 5 deg/min; and the scanning angle is 2θ=2~40º.

Absorption test on the organoclay
Dynamic absorption test: Take precisely 0.02 g smectite-CDTEA organoclay and 30 ml (250 mg/L) of the $Cd(NO_3)_2$ solution with a pH value of 7, mix them and oscillate them. Also, take precisely 0.02 g smectite-CDTEA organoclay and 30 ml (250 mg/L) of the $Pb(NO_3)_2$ solution with a pH value of 7, mix them and oscillate them. The oscillation times are 5, 10, 20, 30, 60, 120, 240, 480, 720 and 1440 min, respectively. Once the oscillation times are reached, test the residual concentrations using an atomic absorption spectrometer after filtering the mixtures with Whatman 47 mm filter papers. After changes in the residual concentrations stabilize, the equilibrium time can be obtained.

Isothermal absorption test: Formulate 10~250 mg/L of $Cd(NO_3)_2$ solutions. Take precisely 0.02 g smectite-CDTEA organoclay and mix it with different concentrations of 30 ml of $Cd(NO_3)_2$, and oscillate the mixtures for 12 h. Test the residual concentrations using an atomic absorption spectrometer after filtering the mixtures with Whatman 47 mm filter papers.

Dual-solute absorption test: Take precisely 0.02 g smectite-CDTEA organoclay and add 15 ml of 54.6 mg/L of the Cd solution and 18.75~312.5 mg/L of the Pb solutions to the centrifuge tube, respectively. Conduct a mixed absorption test at pH=7. Moreover, take precisely 0.02 g smectite-CDTEA organoclay and add 15 ml of 93.75 mg/L of the Pb solution and 10~182 mg/L of the Cd solutions to the centrifuge tube, respectively. Conduct a mixed absorption test at pH=7. Test the concentrations of the Cd and Pb solutions using AA and

observe the absorption effects when both co-exist.

III. RESULTS AND DISCUSSION

Results of FT-IR analysis

Results of the FT-IR analysis on CDTEA functional groups: Figure 1 shows the infrared spectroscopy analysis results of CDTEA. As shown in the figure, CDTEA obtained following the synthesis has a C-N absorption peak around 1068 cm^{-1} and C-H absorption peaks around 2908 cm^{-1} and 2845 cm^{-1}. A strong absorption peak still exists in -COOH around 1710 cm^{-1}, which proves the existence of quaternary ammonium salt within the synthesis.
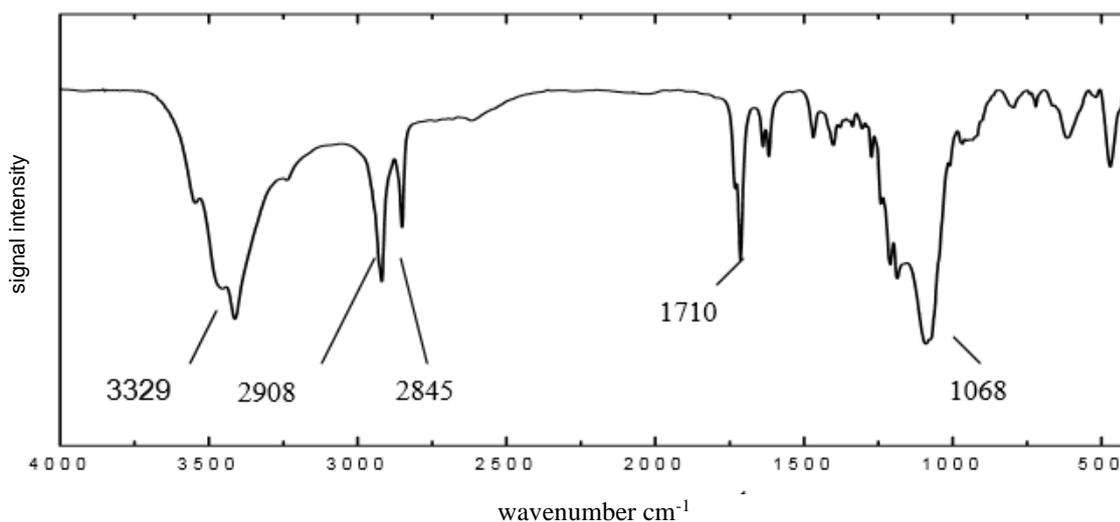
Figure 1. FT-IR spectrum of the CDTEA

Results of smectite-CDTEA organoclay FT-IR analysis: Figure 2 shows the infrared spectroscopy analysis results of the smectite-CDTEA organoclay. As shown in the figure, there is an increase in the C-H bonds around 2900 cm^{-1} and 2850 cm^{-1} and the COOH bond around 1750 cm^{-1} for the organoclay modified by CDTEA when compared with that unmodified by CDTEA. This means that the optimal effects can be obtained when CDTEA intercalates with the smectite. Furthermore, factors such as temperature control when CDTEA synthesizes and the rate of adding triethylamine can affect the purity of the synthesized CDTEA. In this study, the intercalation effects of CDTEA are optimal due to ideal temperature control when synthesizing as well as the rate of adding triethylamine.
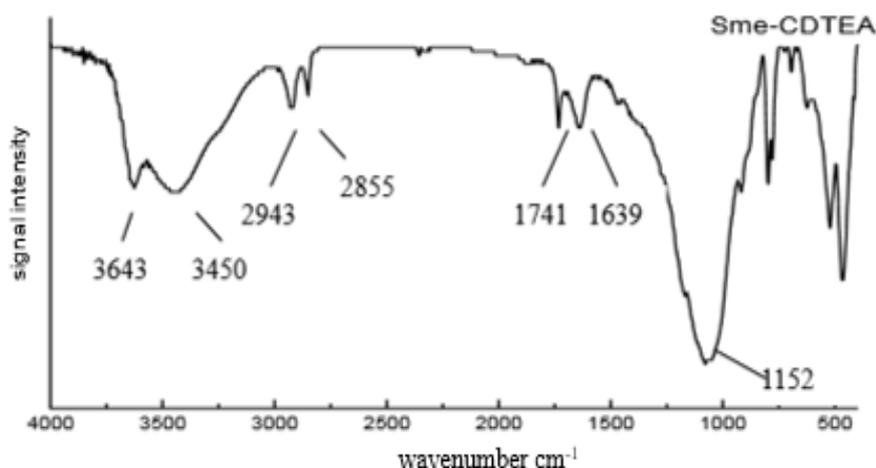

Figure 2. FT-IR spectrum of the smectite-CDTEA organoclay

IV. RESULTS OF XRD ANALYSIS

Results of smectite XRD analysis: Figure 3 shows the XRD analysis results of the sodium saturated smectite. Smectite is itself a layered structure; its layers are tightly bonded by the van der waals force. There are exchangeable positive ions between these layers. As such, we can exchange various positive ions with the sodium ions between layers of the smectite to achieve the objective of absorption equilibrium. Before the smectite was modified, the diffraction angle is $2\theta=6.91^{\circ}$ for the crystallographic plane of the regularly arranged silicates layer (001). According to Bragg's law: $2d\sin\theta=n\lambda$; the first diffraction peak is n=1, and λ is the wavelength of copper-palladium materials (1.5405 $\overset{o}{A}$). This result shows that the spacing of layers of the sodium saturated smectite at room temperature is 1.2782 nm.
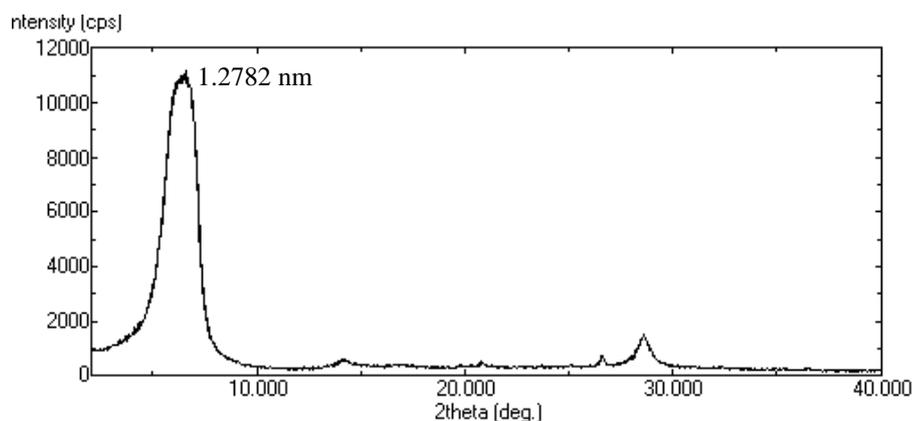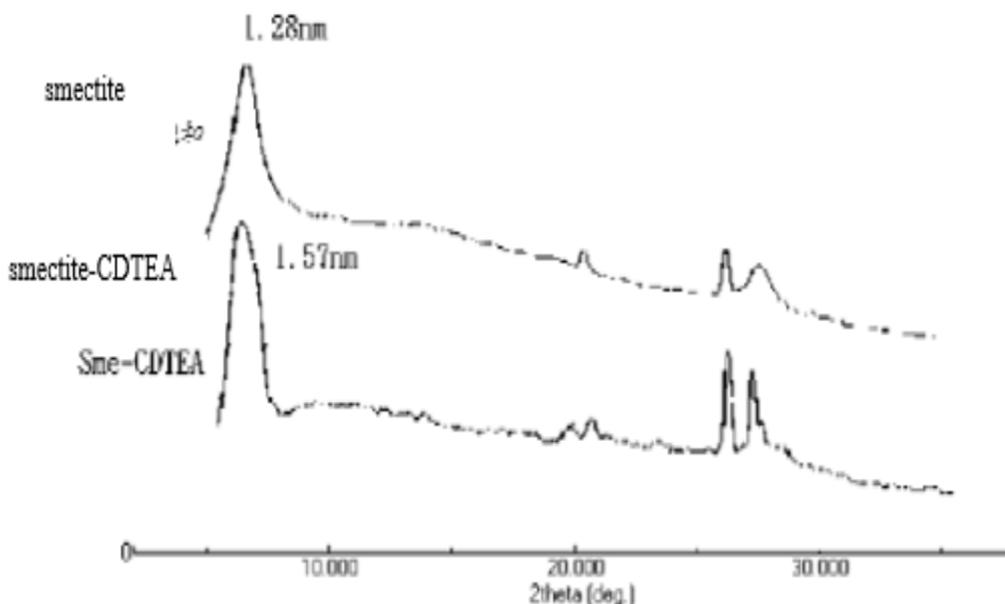

Figure 3. XRD analysis of the smectite

Figure 4. XRD analysis of smectite-CDTEA organoclay shows that the dynamic absorption of cadmium by the organoclay is relatively unstable between 8 and 12 h;

Results of smectite-CDTE A organoclay XRD analysis : Figure 4 shows the XRD analysis results of the smectite-CDTEA organoclay. As shown in the figure, the spacing of layers after the smectite is modified by CDTEA can be increased to 1.57 nm, an increase by 0.3 nm. This means that the way in which CDTEA is arranged between layers when it intercalates with the organoclay is based on single-layer absorption.

III. Absorption test on the smectite-CDTEA organoclay

Dynamic absorption test: Figures 5 and 6 show the dynamic absorption of cadmium and lead by the smectite-CDTEA organoclay at pH=7. Figure 5 shows that organoclay absorption response to lead reaches absorption saturation within 4 h; changes in the concentrations of lead stabilize within 24 h. As such, this study considers 4 h to be the duration required for reaction equilibrium when conducting a test on the absorption of lead. Figure 6 shows that the dynamic absorption of cadmium by the organoclay is relatively unstable between 8 and 12 h; it is presumed that the existence of quaternary ammonium salt has led to unstable and incomplete absorption response of cadmium ions (Shah et al., 2018). Thus, as shown in Figure 6, 24 h is considered to be the duration required for reaction equilibrium when conducting an absorption test.
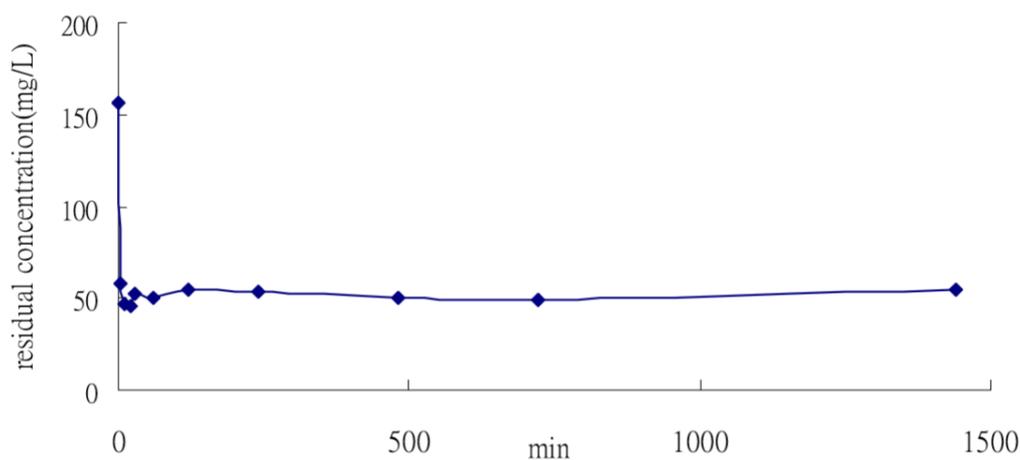
smectite

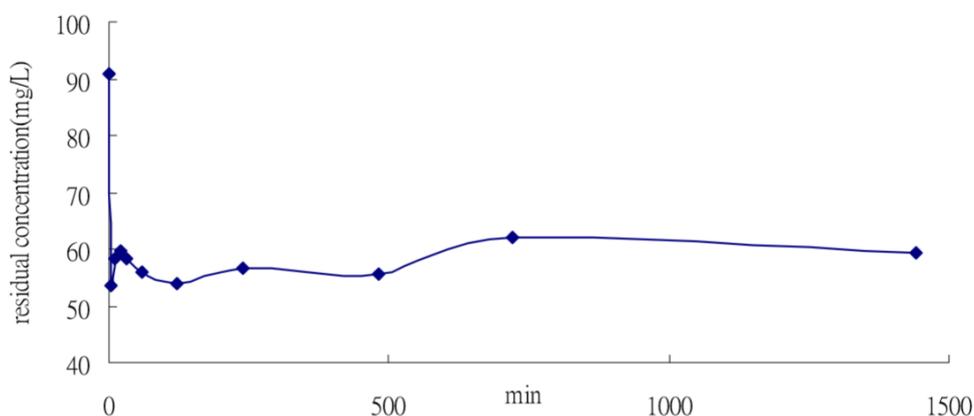Figure 5. Results of the test on dynamic absorption of Pb by the smectite-CDTEA organoclay

Figure 6. Results of the test on dynamic absorption of Cd by the smectite-CDTEA organoclay

Isothermal absorption test: Figures 7 and 8 show the isothermal absorption of heavy metals: Pb and Cd, by the smectite-CDTEA organoclay at pH=7, respectively. The figures were drawn based on the equilibrium concentrations of lead and cadmium absorbed by the smectite-CDTEA organoclay. The experiment results of Figure 7 show that the amount of Pb absorbed by the organoclay has linear growth as the concentration increases. Figure 8 shows an increase in the amount of Cd absorbed by the smectite-CDTEA organoclay as the equilibrium concentration increases. A steady increase in absorption capacity appears when the concentration of Cd is approximately 40 mg/L. However, the amount of Cd absorbed by the smectite-CDTEA organoclay is obviously less than that of Pb, an experiment result that is the same as Lin et al.'s (2015). This study conducted an isothermal absorption test on the smectite-CDTEA organoclay using the Freundlich isothermal absorption model to obtain its constant and maximum absorption capacity, as shown in Table 1. The equation of the Freundlich isothermal absorption model is as follows:

$$\frac{X}{m} = KC^n \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(1)$$

where,

C is the equilibrium concentration of the adsorbate. $\frac{X}{m}$ is the amount of adsorbate on the surface of the absorbent. K is generally considered the distribution coefficient. Both K and n are experience constants. Since the Freundlich absorption isotherm is linear, the constant of the Freundlich isothermal absorption model: n is considered 1, which can be simplified as follows (Lagaly, 1982):

$$\frac{X}{m} = KC \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

In Table 1, the constant of the Freundlich absorption model: K is generally considered the distribution coefficient, which means that the ratio of its existence in a two-phase octanol/water system is the level of an organic phase's absorption capacity. The experiment results suggest that the radius of Pb^{2+} is 119 pm, which is greater than that of Cd^{2+}: 95 pm. The smectite-CDTEA organoclay's spacing of layers has greater capacity for absorbing heavy metal ions with a larger radius than with a smaller radius; its capacity to absorb Pb^{2+} is therefore greater than that needed to absorb Cd^{2+} (Plus and Bohn, 1988; McBride, 1994). This can be verified with the K value in Table 1.
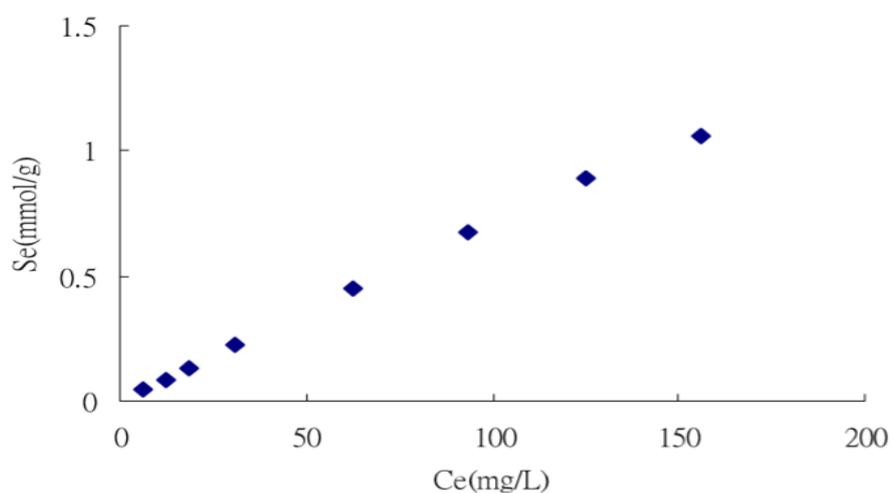

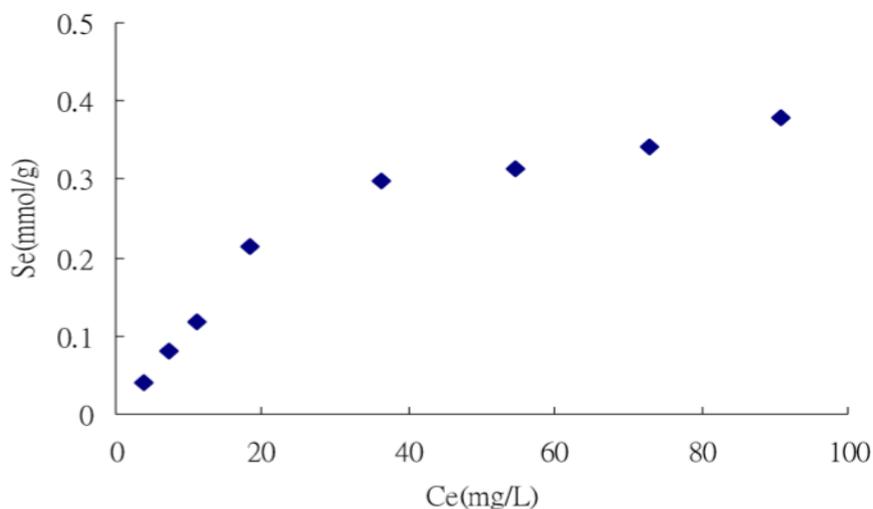Figure 7. Results of the isothermal absorption of Pb by the smectite-CDTEA organoclay

Figure 8. Results of the isothermal absorption of Cd by the smectite-CDTEA organoclay

Table 1. Comparison of Freundlich model isotherm parameters of sorption for Pb and Cd

Heavy metals	Freundich Equation	
	K(L/g)	R^2
Pb	2.801	0.9997
Cd	1.437	0.9387

Dual-solute absorption test on the smectite-CDTEA organoclay : Figure 9 shows the smectite-CDTEA organoclay's capacity to absorb lead and cadmium obtained by calculating the concentrations of both heavy metals within the residual solutions based on the absorption tests conducted simultaneously under different concentrations of Cd solution and fixed concentration of Pb solution. As shown in the figure, the smectite-CDTEA organoclay's capacity to absorb Pb ions slightly decreases as the concentration of Cd ions increases. Figure 10 shows the smectite-CDTEA organoclay's capacity to absorb lead and cadmium, obtained by calculating the concentrations of both heavy metals within the residual solutions based on the absorption tests conducted simultaneously under different concentrations of Pb solutions and fixed concentration of Cd solution. As shown in the figure, the smectite-CDTEA organoclay's capacity to absorb Cd ions decreases as the concentration of Pb ions increases. The results of this dual-solute absorption suggest that the smectite-CDTEA organoclay's capacity to selectively absorb Pb ions is greater than that needed to selectively absorb Cd ions. The selective absorption of Pb and Cd ions obtained from the above tests is due to the fact that the absorption of Pb^{2+} and Cd^{2+} by the organoclay depends on their exchange positions on the surface of a clay mineral (Yang et al., 2010); such exchange positions on the surface of the modified smectite-CDTEA organoclay have larger surface areas. With -COOH contained in CDTEA cations, which can provide coordinate covalent bonds for exchange, selective absorption is formed out of the following dual mechanism when Pb^{2+} and Cd^{2+} co-exist: Pb's dissociation constant is greater than Cd's, while Pb^{2+}'s radius is greater than Cd^{2+}. The organoclay's capacity to absorb Pb is greater than that needed to absorb Cd (McBride, 1994; Sciban et al., 2007).
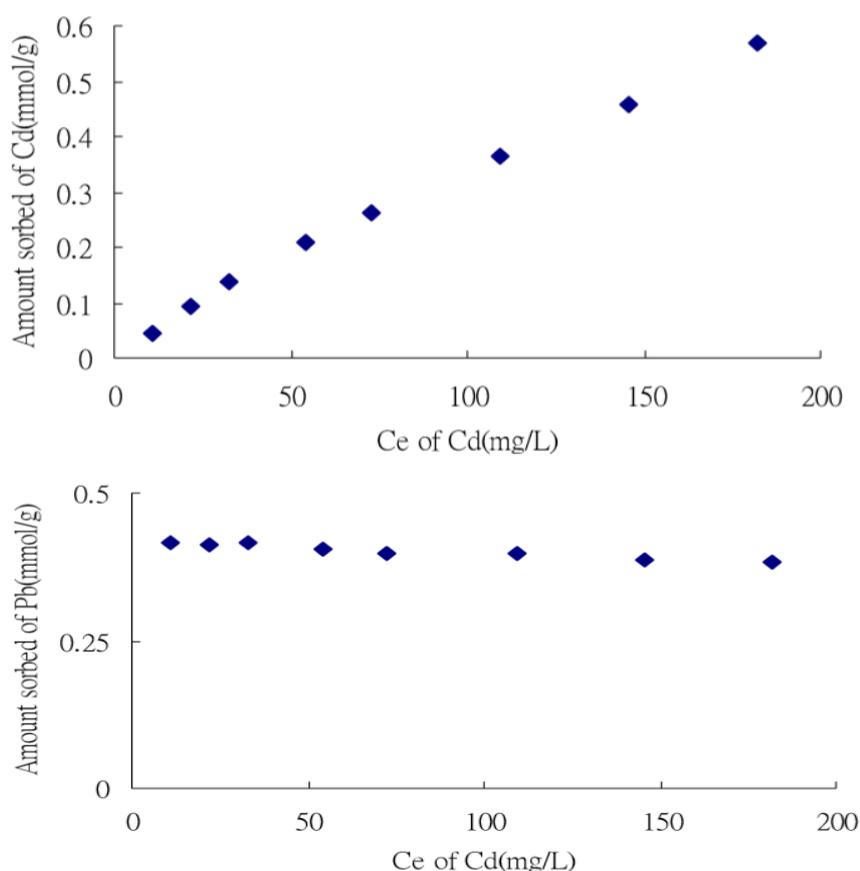

Figure 9. Dual-solute absorption test on the smectite-CDTEA organoclay under different concentrations of Cd solutions and fixed concentration of Pb solution
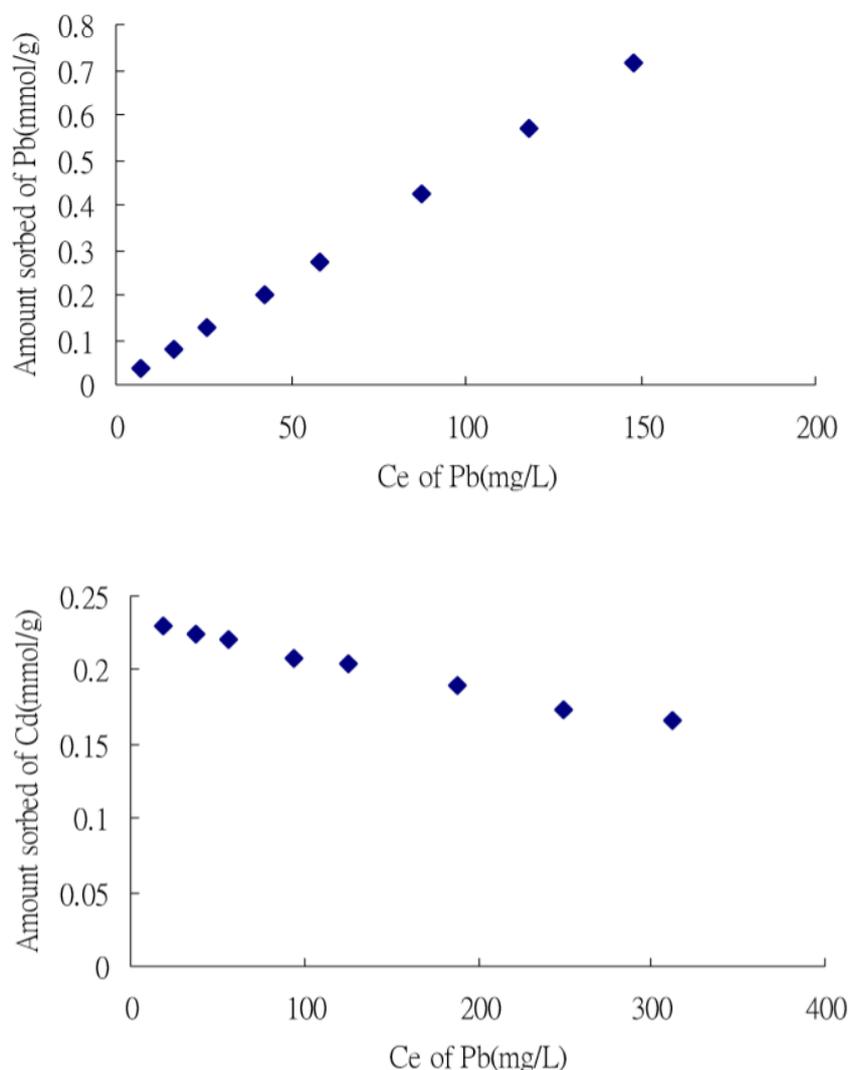
Figure 10. Dual-solute absorption test on the smectite-CDTEA organoclay under different concentrations of Pb solutions and fixed concentration of Cd solution

IV.   CONCLUSION

This study used quaternary ammonium cations from CDTEA to modify the smectite. Tests on the basic properties of the modified smectite-CDTEA organoclay were conducted, including mineral identification using x-ray diffraction (XRD) and functional group identification using Fourier-transform infrared spectroscopy (FT-IR), to determine the modifying effects of quaternary ammonium cations on the smectite. The FT-IR analysis results show an increase in the C-H bonds around 2900 cm^{-1} and 2850 cm^{-1} and the COOH bond around 1750 cm^{-1} for the organoclay modified by CDTEA when compared with that unmodified by CDTEA. This means that the optimal effects can be obtained when CDTEA intercalates with the smectite. In terms of the XRD analysis, the spacing of layers after the smectite is modified by CDTEA can be increased to 1.57 nm, an increase by 0.3 nm. This signifies that the way in which CDTEA is arranged between layers when it intercalates with the organoclay is based on single-layer absorption. This study conducted an isothermal absorption test on heavy metals: Pb and Cd, using the modified smectite-CDTEA organoclay. The experiment results show that since the radius of Pb^{2+} is greater than that of Cd^{2+}, the smectite-CDTEA organoclay's spacing of layers has greater capacity in absorbing heavy metal ions with a larger radius than with a smaller radius; its capacity to absorb Pb^{2+} is therefore greater than that needed to absorb Cd^{2+}. Lastly, in terms of the dual-solute absorption test, the exchange positions on the surface of the modified smectite-CDTEA organoclay have larger surface areas. With -COOH contained in CDTEA cations, which can provide coordinate covalent bonds for exchange, selective

absorption results from the following dual mechanism when Pb^{2+} and Cd^{2+} co-exist: Pb's dissociation constant is greater than Cd's, while Pb^{2+}'s radius is greater than Cd^{2+}'s. The organoclay's capacity to absorb Pb is greater than that needed to absorb Cd.

REFERENCES

1. He, H., Ma, L., Zhu, J., Frost, R.L., Theng, B.K.G., Bergaya, F.O., 2014. Synthesis of organoclays: A critical review and some unresolved issues. Appl. Clay Sci. 100, 22-28.
2. Lagaly, G., 1982. Layer charge heterogeneity in vermiculites. Clays clay miner. 30: 215-222.
3. Li, Q.L., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: The roles of PAC pore size distribution and NOM molecular weight. Water Res. 37, 4863-4872.
4. Li, Q.L., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: The roles of PAC pore size distribution and NOM molecular weight. Water Res. 37, 4863-4872.
5. Lin, D.R., Hu, L.J., Xing, B.S., You, H., Loy D.A., 2015. Mechanisms of competitive aAdsorption organic pollutants on hexylene-bridged polysilsesquioxane. Materials 8, 5806-5817.
6. McBride, M.B., 1994. Environmental chemistry of soil. Oxford, New York, 24, 63-121.
7. Newcombe, G., Morrison, J., Hepplewhite, C., Knappe, D.R.U., 2002. Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitiveeffects. Carbon 40, 2147-2156.
8. de Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R., 2008. Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. Appl. Clay Sci. 42, 8-24.
9. Pelekani, C., Snoeyink, V.L., 2001. A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: The importance of pore size distribution. Carbon 39, 25-37.
10. Plus, R.W., Bohn, H. L., 1988. Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. Soil Sci. Soc. Am. J. 52, 1289-1292.
11. Sander, M.; Pignatello, J.J., 2005. Characterization of charcoal adsorption sites for aromatic compounds: Insights drawn from single-solute and bi-solute competitive experiments. Environ. Sci. Technol. 39, 1606-1615.
12. Sciban, M., Radetic, B., Kevresan, Z., 2007. Adsorption of heavy metals from electroplating wastewater by wood sawdust. Bioresource Technology 98, 402-409.
13. Shah, K.J., Pan, S.Y., Shukla, A.D., Shah, D.O., Chiang, P.C., 2018. Mechanism of organic pollutants sorption from aqueous solution by cationic tunable organoclays. Journal of Colloid Interface Science 529, 90-99.
14. Ugochukwu, U.C., Fialips, C.I., 2017. Removal of crude oil polycyclic aromatic hydrocarbons via organoclay-microbe-oil interactions. Chemosphere 174, 28-38.
15. Yang, K., Zhu, L.Z., Xing, B.S., 2006. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. Environ. Sci. Technol. 40, 1855-1861.
16. Yang, K., Wu, W.H., Jing, Q.F., Jiang, W., Xing, B.S., 2010. Competitive adsorption of naphthalene with 2,4-dichlorophenol and 4-chloroaniline on multiwalled carbon nanotubes. Environ. Sci. Technol. 44, 3021-3027.