Technical Note

LOWLAND TECHNOLOGY INTERNATIONAL Vol. 7, No. 2, 69-73, December 2005
International Association of Lowland Technology (IALT), ISSN 1344-9656

SORPTION CHARACTERISTICS OF THE SOFT BANGKOK CLAY

L. Sthapit[1], C. S. P. Ojha[2] and U. Glawe[3]

ABSTRACT: Asian countries are in a need for identification of suitable sites for disposal of municipal solid wastes. The travel of pollutants is significantly influenced by the properties of the porous medium through which these travel. In Thailand, existing land disposal sites, which were initially selected in view of the low lying areas or the water bodies, are likely to last not for many years. In the light of this, it is essential that soils available in the region are tested and evaluated for their specific characteristics relevant to the safe disposal of solid wastes and planning of future landfill sites. Sorption characteristics are of special significance in the design of landfills. In this paper, the Bangkok clay has been evaluated for its sorption characteristics. Various adsorption isotherm models are tested and it has been observed that the Langmuir model performs best. The study indicates that the process of sorption is non-linear in nature and is sensitive to the type of influent characteristics.

Keywords: Isotherm, batch equilibrium, heavy metals and soft Bangkok Clay

INTRODUCTION

Thailand is now practicing to use natural clay and compacted clay liner or clay barriers combined with geomembrane as a barrier material in waste disposal landfill. Evaluation of the mechanism of contaminant migration and the ability to reduce contaminant migration through barrier material is important to prevent the contamination of soil and groundwater under landfills (Jang and Hong 2003). For clay liners, which have a high cation exchange capacity (CEC) and large specific surface area is the most suitable for clay barriers (Yong et al. 1992). In addition, the transport of contaminant should also be considered which mainly depends on the sorption characteristics of clay.

Sorption is a term used to include all the processes responsible for the mass transfer-absorption, adsorption, and ion exchange. The parameters governing sorption are contaminant and pore fluid characteristics which may include pH of the pore fluid, water solubility of the contaminant and polar nature of the contaminant. In addition, solids and porous media characteristics may also govern sorption (Reddy and Inyang, 2000). Studies on sorption through clayey soils have been performed by many researchers, e.g., (Crooks and Quigley 1984; Rowe et al. 1988; Shackelford and Daniel 1991; Rowe and Badv 1996). Sorption of ions can play a very significant role in describing their movement through clayey soils. Studies of sorption characteristics of soft Bangkok clay are relatively few. It is found that the leachate samples collected at 8 disposal sites in Thailand were contaminated with heavy metals particularly nickel, lead, mercury, zinc and manganese. Due to certain constraints, the heavy metals Zn and Mn have been considered in the present investigation. To study the sorption characteristics of the clay, commonly used laboratory method batch-equilibrium test is performed.

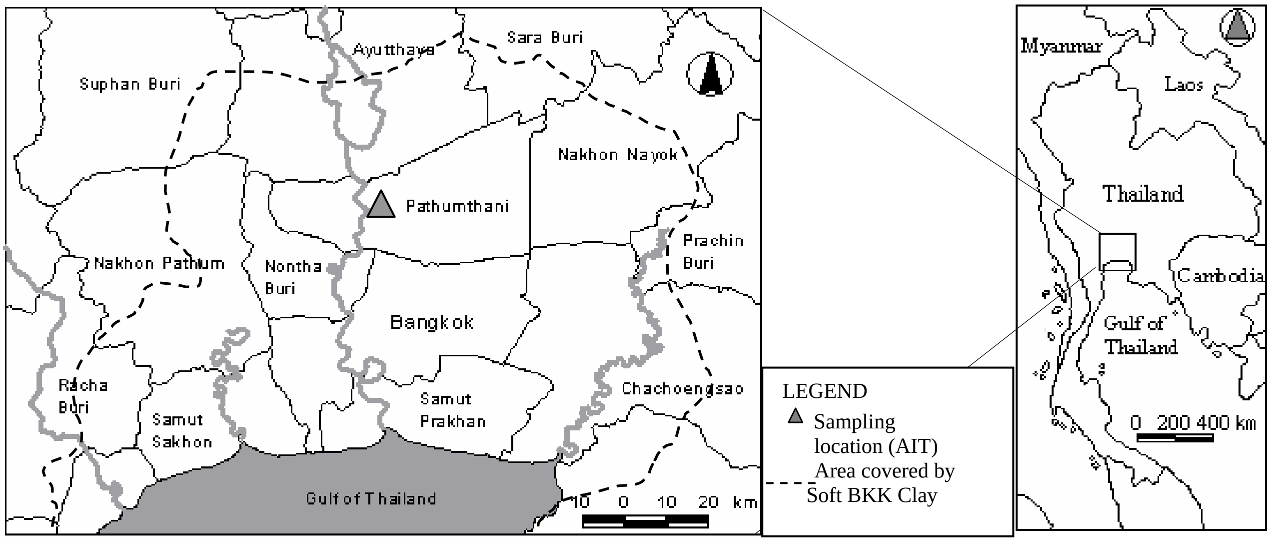
In this paper, the objective is to study the sorption characteristics of the soft Bangkok clay using three popularly used models, i.e. Linear, Freundlich and Langmuir isotherm (Reddi and Inyang 2000) and to assess the suitability of the appropriate models. As the model parameters have a direct influence on the resultant quality coming out of a liner, the study can be useful in the design of landfill sites in Bangkok region.

LITERATURE REVIEW

The soil properties which influence the transport of contaminants through porous medium are its diffusion/dispersion characteristics along with sorption and reactivity. The generalized one dimensional advection dispersion equation is popularly written as (Reddy and Inyang 2000).

[1] Senior Research Associate, Asian Institute of Technology, P.O. Box 4, Klong Luang, Pathumthani 12120, THAILAND
[2] Professor, Department of Civil Engineering, IIT Roorkee, INDIA
[3] Associate Professor, Asian Institute of Technology, P.O. Box 4, Klong Luang, Pathumthani 12120, THAILAND

Note: Discussion on this paper is open until June 30, 2006



Key map

Fig. 1 Area covered by the Soft Bangkok Clay and sampling location.

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} \pm \frac{r}{n} = \frac{\partial C}{\partial t} \qquad (1)$$

where D_x includes the two components of the molecular diffusion and mechanical dispersion, V_x is the pore velocity in the *x* direction, *r* is the rate of mass production/consumption given by the kinetic model of reaction, *n* is the porosity, and *C* is the solute concentration expressed as mass of solute per unit volume of solution. *x* and *t* refer to space and time variables. The role of sorption characteristics is included in the term r.

One of the dominant mass transfer mechanisms occurring during mass transport is sorption. The simplest way of incorporating sorption is to use the linear isotherm

$$q = K_d C \qquad (2)$$

where *q* is the quantity of mass sorbed on the surface of solids and K_d is the distribution coefficient. The rate expression *r* is equal to the product of time derivative of *q* and dry mass density, ρ_b. Thus,

$$r = \rho_b \frac{\partial q}{\partial t} = K_d \rho_b \frac{\partial C}{\partial t} \qquad (3)$$

Substituting Eq. (3) in Eq. (1) leads to

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} K_d \frac{\partial C}{\partial t} = \frac{\partial C}{\partial t} \qquad (4)$$

Rearrangement of terms in Eq. (4) yields

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial x}\left(1 + \frac{\rho_b K_d}{n}\right) \qquad (5)$$

or, in its familiar form,

$$\frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{V_x}{R} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (6)$$

where $R = (1 + \rho_b K_d / n)$ is known as the retardation factor since it has the effect of retarding the transport of adsorbed species relative to the advection front. Given the initial and boundary conditions,

$$\begin{aligned} C(x,t) &= 0 \quad for\ t = 0\ and\ x > 0 \\ C(x,t) &= C_0 \quad for\ x = 0 \\ C(x,t) &= 0 \quad for\ x = \infty \end{aligned} \qquad (7)$$

the solution of Eq. (6) is (Ogata and Bank 1961; Ogata 1970)

$$C(x,t) = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{Rx - V_x t}{2\sqrt{RD_x t}}\right) + \exp\left(\frac{V_x x}{D_x}\right)\operatorname{erfc}\left(\frac{Rx + V_x t}{2\sqrt{RD_x t}}\right)\right] \qquad (8)$$

The role of K_d is apparent from Eq. 8. Unfortunately, a linear isotherm model is not suitable and thus, one needs to linearize non-linear isotherms in order to use analytical expressions, such as Eq. (8).

SOIL PROPERTIES

The map of study area is shown in Fig.1. Undisturbed soft Bangkok clay specimens from a depth of 3 to 4m

Table 1 Physico-chemical properties of the soil tested (Asavadorndeja and Glawe 2004)

Soil Type	
Natural water content, w_n (%)	90±2
Liquid limit, L.L. (%)	100
Plastic limit, P.L. (%)	40
Specific gravity	2.67
Clay mineralogy (%)	
Kaolinite	58±5
Smectite	28±5
Illite	14±5
CEC	20.2 meq/100g

beneath the weathered crust layer were used in this study. It is strongly believed that the soft Bangkok clay has a potential for use as geological barriers for landfill sites. The properties of the soil, as determined by standard methods, are presented in Table 1.

Sample Preparation

To perform the test, the soft Bangkok clay was oven-dried for 24 hours at the temperature of 110^o C. After the sample had oven-dried, it was crushed into powder and sieved through a 2-mm screen sieve.

Contaminant Leachate

Two kinds of heavy metal solutions ($ZnCl_2$ and $MnCl_2$ solutions) with different initial concentrations e.g. 50, 100, 250, 500, 1000, 1500, 2000 ppm were used. The replaceability of the some cations is shown in Table 2. (Reddy and Inyang 2000) also list the adsorption selectivity of heavy metals in different soils. For example, the selectivity of Zn is more than Mg in case of Kaolinite clay while it is reversed in case of Illite clay. Thus, depending on the composition of a soil, the sorption characteristics may vary. In other words, it is difficult to precisely mention that out of Zn and Mn, which are the focus of present work, which one will be more sorbed.

Table 2 Replaceability of certain cations (Triegel 1980 and Mehlich 1981, cited in Du et al. 2000)

Soil Type	Replaceability
Montmorillonite	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > H^+ > K^+ > Na^+$
Illite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > H^+ > K^+ > Na^+$
Kaolinite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > H^+ > K^+ > Na^+$

BATCH EQUILIBRIUM TEST

The batch equilibrium tests were performed to determine the adsorption characteristics of the soft Bangkok clay with respect to the specified ions. A 1: 4 soil**:** solution ratio (w/w ratio), which is the highest recommended ratio (U.S. Environmental Protection Agency 1987, cited in Shackelford and Daniel 1991) was used in the batch equilibrium tests. 1:4 ratio was maintained by adding 5 g (oven-dried basis) of prepared soil sample with 20 ml of solution in Erlenmeyer flasks of 125-ml. All the flasks were sealed and placed in an end-over-end rotary mixer, and shake at 120 rpm for 24 hours at a temperature of 25^o C ± 2^o C. At the end of the mixing period, the soil-solution slurry was poured into 50-ml centrifuge tubes, sealed properly and centrifuged. The tubes were centrifuged for 30 minutes at 3000 rpm. The obtained supernatant from each tube was then analyzed for equilibrium concentrations using spectrophotometer. Dilutions of the solution were required to bring the concentrations into range of spectrophotometer. The procedure was repeated until each soil sample was completed. The adsorption mass ratio, q, was determined using the following equation:

$$q = \frac{(C_0 - C)}{M_s} V_{sol} \qquad (9)$$

where, C_0 is the initial concentration of the specified ion in the flask, C is the equilibrium concentration, V_{sol} is the volume of the solution (20-ml) and M_s is the soil mass (5 g). The results of the tests were plotted in the form of adsorption isotherm. Fig. 2 shows that the variation of q

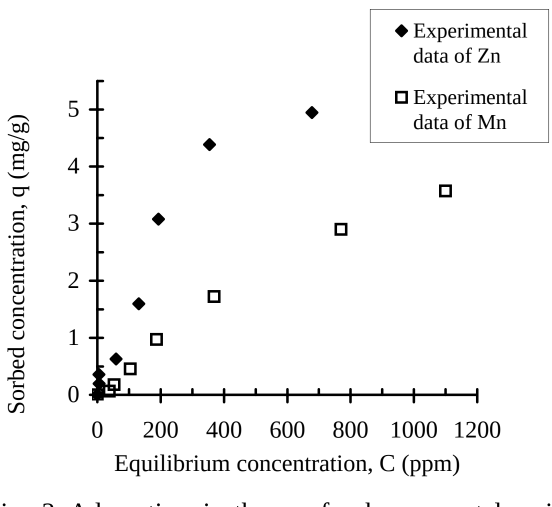


Fig. 2 Adsorption isotherms for heavy metals with Soft Bangkok Clay

Table 3a Analysis for $ZnCl_2$

Model	α	β	MSE	R^2
Linear	0.00894	1	0.6959	0.8577
Freundlich	0.11113	0.59521	0.2283	0.9327
Langmuir	0.00255	8.23186	0.1316	0.9605

Table 3b Analysis for $MnCl_2$

Model	α	β	MSE	R^2
Linear	0.00354	1	0.0596	0.9721
Freundlich	0.01464	0.7897	0.0192	0.9901
Langmuir	0.00064	8.7367	0.0065	0.9976

with C is non-linear. The sorbed concentration, *q*, were plotted as a function of the equilibrium concentration, *C*.

RESULTS AND DISCUSSIONS

The adsorption isotherms for the Zn^{++} and Mn^{++} cations are presented in Fig. 2. The isotherms obtained are non-linear. Zn^{++} is absorbed more than Mn^{++} in soft Bangkok clay. Zn^{++} is adsorbed more in case of Bangkok clay when compared to Kaolinite and Lufkin clay (Shackelford and Daniel 1991). Using the experimental data, attempts were made to fit a variety of models. Basically, three models are attempted.

Linear isotherm model: $$q = \alpha.C \quad (10)$$

Freundlich isotherm model: $$q = \alpha.C^{\beta} \quad (11)$$

Langmuir isotherm model: $$q = \frac{\alpha.\beta.C}{1+\alpha.C} \quad (12)$$

where *q* is the quantity of mass sorbed on the surface (mg/g), *C* is the equlibrium concentration of the solution.

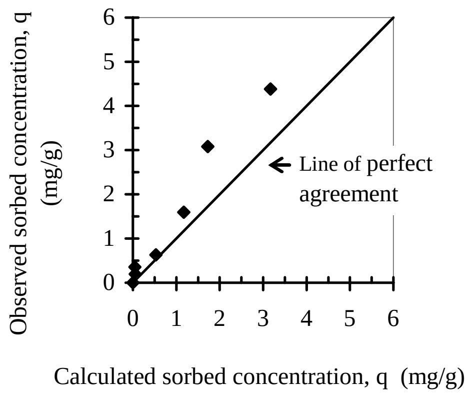


Fig. 3 (a) Comparison of observed sorbed concentration of Zn++ with Linear model

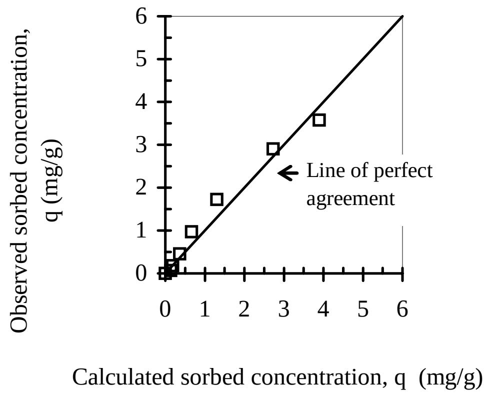


Fig. 3 (b) Comparison of observed sorbed concentration of Mn++ with Linear model

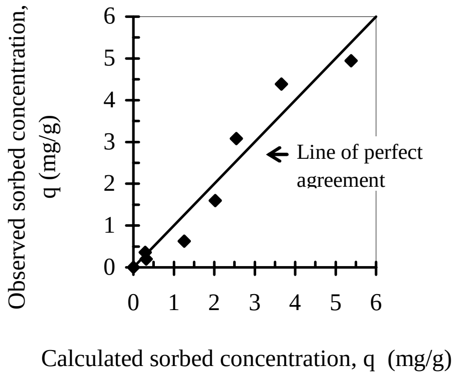


Fig. 4(a) Comparison of observed sorbed concentration of Zn++ with Freundlich model

In Eqs. (10), (11) and (12), the models parameters are termed as α and β. To evaluate these parameters, Mean Square Error (MSE) is used as a minimization criterion. The MSE is defined as the average of square of residual errors between observed and computed q values. Based on the analysis of data, a set of parameters are obtained for the case of $ZnCl_2$ and $MnCl_2$. MSE along with R^2 value is given in Table 3.Using the set of parameters given in Table 3, Figs. 3, 4 and 5 are developed. The agreement diagram between observed and computed q values using various models indicates that Langmuir model performs better than rest of the models as it has the least value of MSE. In general, Freundlich model also works well in preference to linear model.

CONCLUSIONS

The study indicates that Bangkok clays does exhibit sorption characteristics. The sorption characteristics are observed to be sensitive to the type of influent being removed. Sorption characteristic of Zn^{++} is more than Mn^{++} in the soft Bangkok clay. The nature of removal of

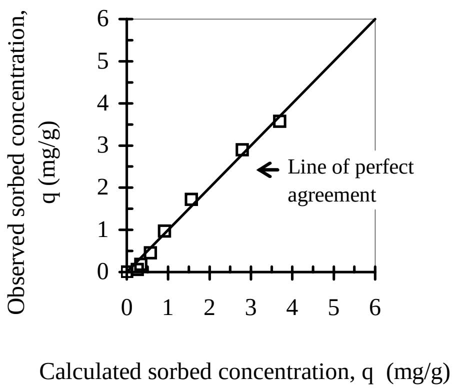


Fig. 4 (b) Comparison of observed sorbed concentration of Mn++ with Freundlich model

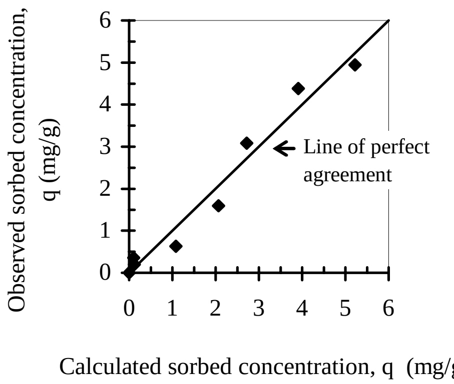


Fig. 5 (a) Comparison of observed sorbed concentration of Zn++ with Langmuir model

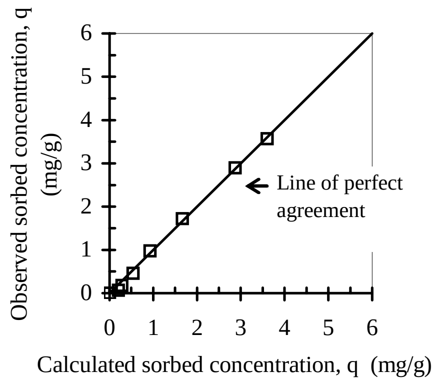


Fig. 5(b) Comparison of observed sorbed concentration of Mn++ with Langmuir model

the two ions tested in this work indicates that a non-linear adsorption isotherm is the most appropriate one for describing the removal of impurities. The Langmuir model is found to work well for Zn and Mn ions. A knowledge about sorption properties may enable better removal of ions during their passage through soft Bangkok clay.

ACKNOWLEDGEMENTS

The authors express their sincere gratitude for the support from the European Commission under the Asia-Pro-Eco Programme, Contract No. ASI/B7-301/2598/16-2004/79010 for the experimental work presented here.

REFERENCES

Asavadorndeja, P. and Glawe, U. (2004). Preliminary Results of Studies into Electrokinetic Remediation Technologies in the soft Bangkok clay. Proceedings of the Fifteenth Southeast Asian Geotechnical Conference (15^{th} SEAGC), Bangkok, Thailand.1: 653-658.

Crooks, V. E. and Quigley, R. M. (1984). Saline leachate migration through clay: a comparative laboratory and field investigation. Canadian Geotech J. 21(2):349-362.

Du, Y. J., Hayashi, S., Hini, T. and Tanaka, K, (2000). Contaminant adsorption characteristics of Kyushu regional soils. Lowland Technology International (IALT). 2 (2): 31-41.

Jang, Y. S and Hong, G. T. (2003). An experimental study on diffusion characteristics of hardened liner materials to inorganic chemicals. Environmental Geology. 44:599-607.

Ogata, A. (1970). Theory of dispersion in a granular medium. U.S. Geol. Surv. Prof. Paper 411-I.

Ogata, A. and Banks, R.B. (1961). A solution of the differential equation of longitudinal dispersion in porous media. U.S. Geol. Surv. Prof. Paper 411-A.

Reddy, L. N. and Inyang, H. I. (2000). Geoenvironmental Engineering: Principles and Applications. Marcel Dekker, Inc. New York.

Rowe, R. K., Caers, J. C. and Barone, F. S. (1988). Laboratory determining of diffusion and distribution coefficients of contaminants using undisturbed clayey soils. Canadian Geotech J. 25(1):108-118.

Rowe, R. K. and Badv, K. (1996). Advective-diffusive contaminant migration in unsaturated sand and gravel. Journal of Geotechnical Engineering ASCE, 122 (12):965-975.

Shackelford, C. D. and Daniel, D. E. (1991). Diffusion in Saturated Soil. II: Results for Compacted Clay. Journal of Geotechnical Engineering (ASCE). 117 (3): 485-506.

Yong, R. N., Mohamed, A. M. O. and Warkentin, B. P. (1992). Principles of Contaminant Transport in Soils. Elsevier, New York.