

# Effect of Soil Solids Concentration and Temperature in Batch Tests on the Adsorption of Cr(VI) onto Clay Landfill Liners

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## ABSTRACT

The effect of soil solids concentration and temperature in batch tests on the adsorption of Cr(VI) onto landfill liner-soil materials was investigated. The results of the study show that the soils specimen sorption to Cr(VI) is characterized by a Langmuir isotherm model. The values of the isotherm parameters ( $q_m$ ,  $b$ ) and soil solids concentrations have a log-log linear relationship at low soil solids concentrations. The values of measured the isotherm parameters decreased strongly as soil solids concentration increased, and finally stabilized when the soil solids concentrations were over the critical values. The values of measured isotherm parameters ( $q_m$ ,  $b$ ) increased linearly with increasing temperature. It was concluded that the values for isotherm parameters measured using batch tests under low soil solids concentration will not properly simulate the field situation, and retardation factors of clay landfill liners systems will be overestimated. Temperature of landfill has obvious influence on the transport of pollutants through clay landfill liners.

**KEYWORDS:** Landfill; Pollutants; Adsorption; Clay; liner; Temperature

## INTRODUCTION

Leachates from landfill have been found to contain a wide range of potential environmental contaminants, including heavy metals. Due to their high toxicity and migration, these heavy metals may cause impact to the aquifer underlying the landfill and thereby may pose potential risk to human health and surrounding environment (Zhang *et al.*, 2004; Du *et al.*, 2006). One way for reducing the risk is to use clay liners to control heavy metals migration. In order to predict the movement of heavy metals through clay landfill liners, mass transport parameters such as seepage velocity, dispersion coefficient of the pollutant and isotherm parameters need to be evaluated

(Chang *et al.*, 2005; Zhang *et al.*, 2005). Among of mass transport parameters, isotherm parameters are most commonly estimated in the laboratory using batch tests. Some factors controlling sorption of heavy metals onto clays such as soil solids concentration or solid: solution ratio (S/L), temperature of solution should be considered.

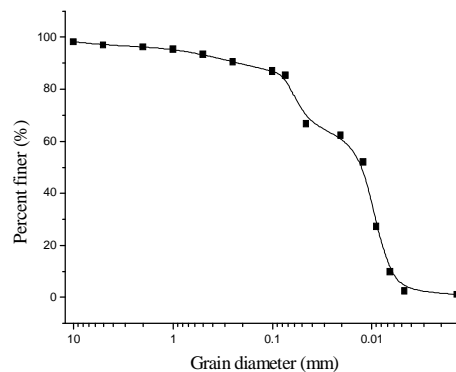
Some researchers (Shackelford and Redmond 1993; Kim *et al.*, 2003) have investigated the effect of soil solids concentration in batch tests on the partition coefficients. Kim *et al* observed partition coefficients strongly decreased as soil solids concentration increased. However, the above studies are most focus on organic pollutants, studies on sorbing heavy metals are relatively few. Temperature at the base of landfill in the range of 293K-333K have been reported (Southen and Rowe 2002, Southen and Rowe 2005; Koerner 2006). Studies on effect of the temperature on isotherm parameters of heavy metals are relatively few.

The main objectives of the study were (1) to evaluate the effect soil solids concentration, temperature of solution on the measured isotherm parameters in batch tests, (2) to identify the critical soil solids concentration at various temperature for measurement of isotherm parameters in landfill liner-soil materials using batch tests, and (3) to compare transport of Cr(VI) through landfill liner at various isotherm parameters.

## MATERIALS AND METHODS

### SORPTION MATERIALS AND SOLUTES

The red clay sample was obtained from Maoyingzi zone in Dalian city. The soil specimen can be considered to have no history of exposure to Cr(VI). The characteristics of the clay are given in Table 1. Grain size distribution of red clay sample is given in Figure 1. The standard Cr(VI) solutions used in the experiments were prepared from potassium dichromate. Cr(VI) was selected for testing because of its rife and toxicity in landfill leachates.



**Figure 1:** Grain size distribution of red clay sample

**Table 1:** Characteristics of the soil samples used in the tests

Soil samples	$W_L$	$W_P$	$\rho_{dmax}$ /(g/cm <sup>3</sup> )	$W_{opt}$ /(%)	$e$	$G_s$	$K_s$ /(cm/s)	$\theta_s$
Natural clay	41.67	20.56	1.68	16.2	0.59	2.68	4.18E-9	0.350

## BATCH TESTS

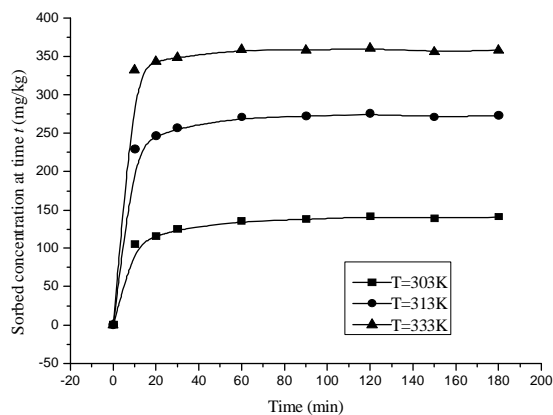
Batch tests were carried out in 100ml flasks immersed in a thermostatic shake bath. Dry soil samples (2g-8g) were mixed with 25ml of the aqueous solutions of the various initial concentrations (20mg/L-300mg/L) of Cr(VI) in each flask. The flasks were shaken for 48h at 295K, 313K, 323K, 333K. The pH of the solutions was adjusted to 7.0 with PHS-2C acidometer. In the experiments, the stirring speed was kept constant at 80rpm. After adsorption equilibrium was reached, the supernatants in flasks were centrifuged at 4000rpm for 30min with LDZ 4-0.8 centrifuge. The concentration of Cr(VI) in the supernatant solutions were measured with 721 spectrophotometer. The measurements were made at the wavelength  $\lambda=540\text{nm}$ , which corresponds to maximum absorbance. Using a mass balance, the concentrations of Cr(VI) adsorbed in soil solids was calculated. Blanks tests on Cr(VI) were used for each series of experiments.

## RESULTS AND DISCUSSION

### SORPTION EQUILIBRIUM TIME

The Changes in the concentration of Cr(VI) was observed over time to determine the time taken to attain sorption equilibrium. The soil solids concentration used in the experiment was 80g/L. The initial concentration of Cr(VI) was 100mg/L. Aqueous phase concentration of Cr(VI) Change over time at 303K, 313K, 333K in the testing are given in Figure 2.

The Figure 2 shows that Cr(VI) adsorption onto red clay are consisted of two phases: an initial rapid phase at firstly 20min that the adsorption is fast and contributed significantly to reach equilibrium sorption, a slower second phase whose contribution to the Cr(VI) adsorption is relatively small. The first phase is the instantaneous adsorption process by the surface adsorption(Zou *et al.*, 2006). The second phase is a gradual adsorption process, the intraparticle diffusion controls the adsorption rate and finally the adsorption process reaches equilibrium after about 120min. Following the result, equilibrium sorption time was determined to attain after 48h of solute-sorbent contact.



**Figure 2:** Aqueous phase concentration of Cr(VI) Change in the batch tests

## EQUILIBRIUM SORPTION ISOTHERMS

The equilibrium sorption isotherms of Cr(VI) are given in Figures 3.

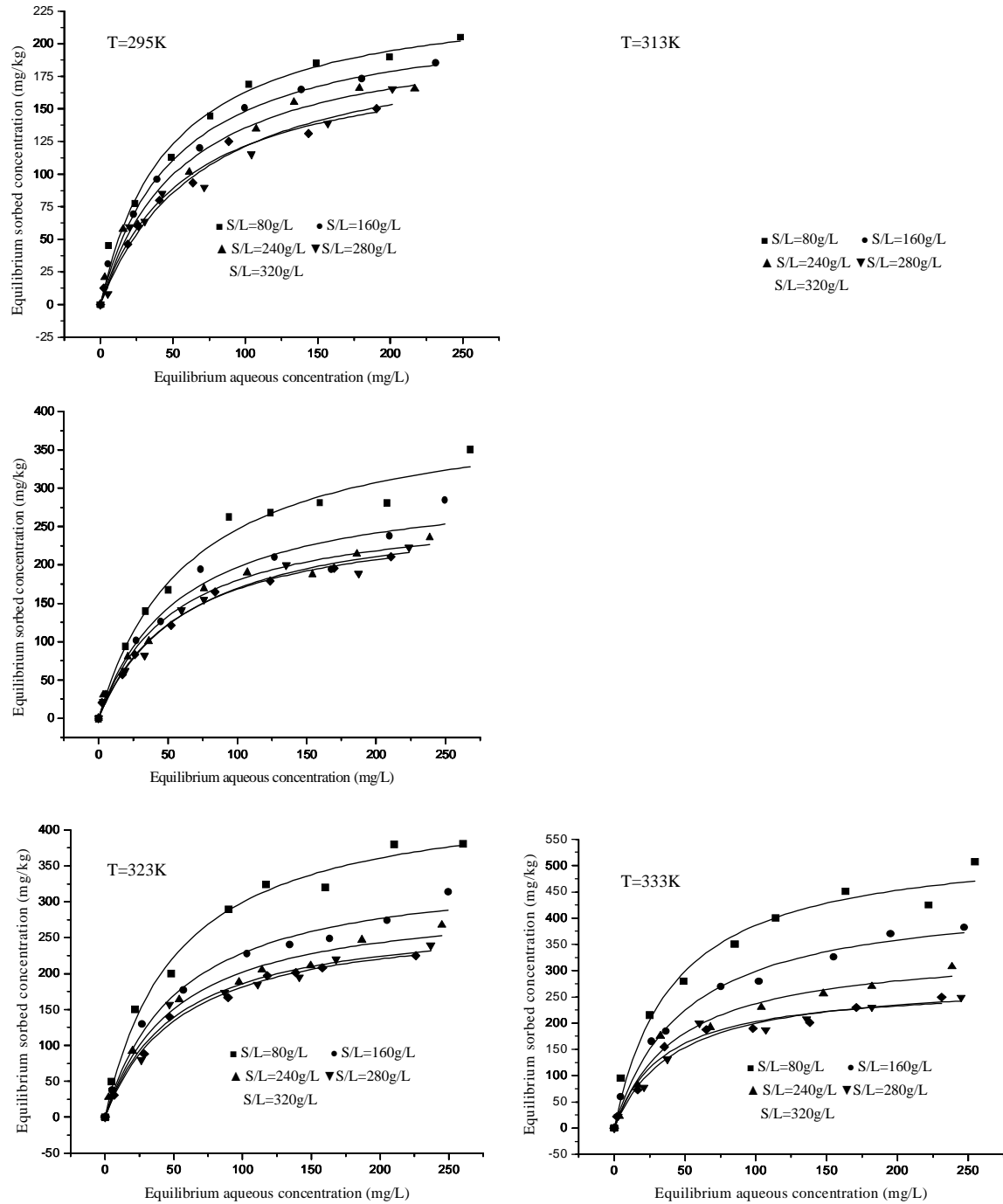


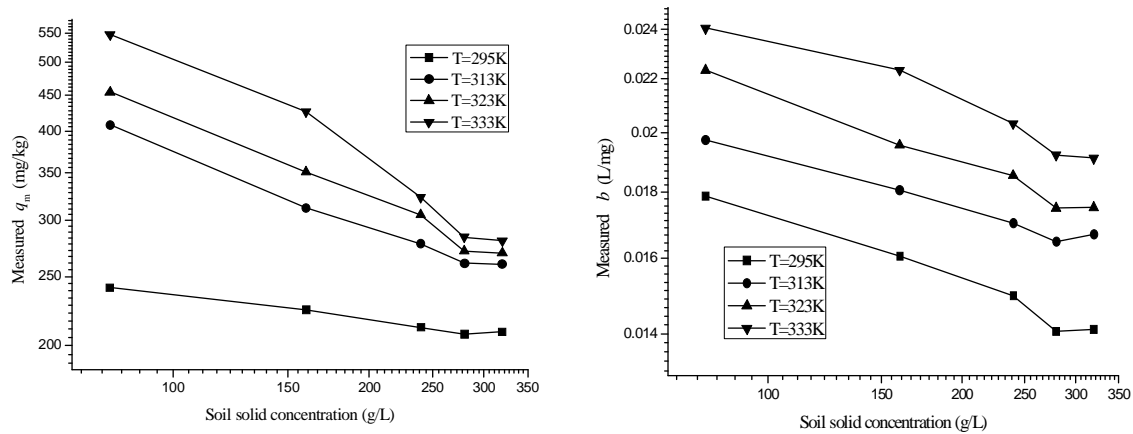
Figure 3: The equilibrium sorption isotherms of Cr(VI)

The soils specimen sorption to Cr(VI) was nonlinear and characterized by a Langmuir isotherm model of the form:

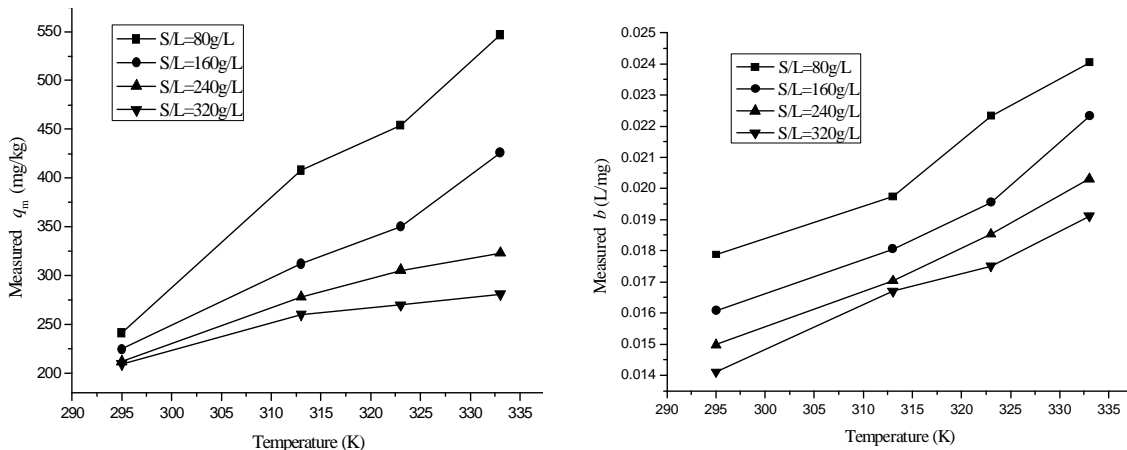
$$C_s = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where  $C_s$  is equilibrium sorbed concentration;  $q_m$  is total concentration of sorption sites available;  $b$  is Langmuir constant;  $C_e$  is equilibrium aqueous solute concentration.

Figures 3 show that the adsorption of Cr(VI) onto the clay decreases significantly as the soil solids concentration increases. However, the initial rapid decrease in adsorption capacity moderates as the soil solids concentration exceeds a critical value. The critical concentration was 280g/L for the clay at various temperatures. In the Figure 3, the increased strongly the values of measured adsorption capacity with increasing the temperature indicates that a high temperature favors the Cr(VI) removal by adsorption on the clay. The equilibrium conversion of Cr(VI) between soil solids and solution increased at highly temperature (Zou *et al.*, 2006). The adsorption is controlled by an endothermic process in nature (Al-Ghouti *et al.*, 2005). The effect is characteristic of a chemical reaction (Aksu, 2002).



**Figure 4:** Effect of soil solids concentrations on the  $q_m$  and  $b$



**Figure 5:** Effect of temperature on the  $q_m$  and  $b$ 

Fig. 4 show the relationships between isotherm parameters ( $q_m$ ,  $b$ ) and soil solids concentrations at various temperature. Isotherm parameters measured in the batch tests have the same tendency at various temperatures. The values of isotherm parameters decreased strongly with increasing soil solids concentrations. However, the initial rapid decrease of isotherm parameters moderated, and finally stabilized as the soil solids concentrations increased to the critical values, which is contrary to the proposition by O'Connor and Connolly that it converges to zero if the soil solids concentration increases to infinity (O'Connor *et al.*, 1980). Because adsorption is a surface phenomenon, so the higher adsorption rate and Cr(VI) adsorption onto the clay at low soil solids concentrations is attributed to greater accessibility to pores and larger surface area for adsorption per unit weight of the adsorbent at equilibrium. However, as soil solids concentration increased, the soil particle density increased, which decreases voids of among soil solids particle, resulting in a reduce Cr(VI) adsorption onto the clay.

Figure 5 shows the relationship between the values of measured isotherm parameter ( $q_m$ ,  $b$ ) and temperatures at various soil solids concentrations. In Figure 5, the temperature has exerted a profound influence on isotherm parameters. The values of measured  $q_m$  and  $b$  increased linearly with increasing temperature. Consequently, it is impossible to obtain reasonable retardation factor of landfill liner-soil material if the temperature is neglected in the batch tests.

## TRANSPORT MODELING SIMULATIONS

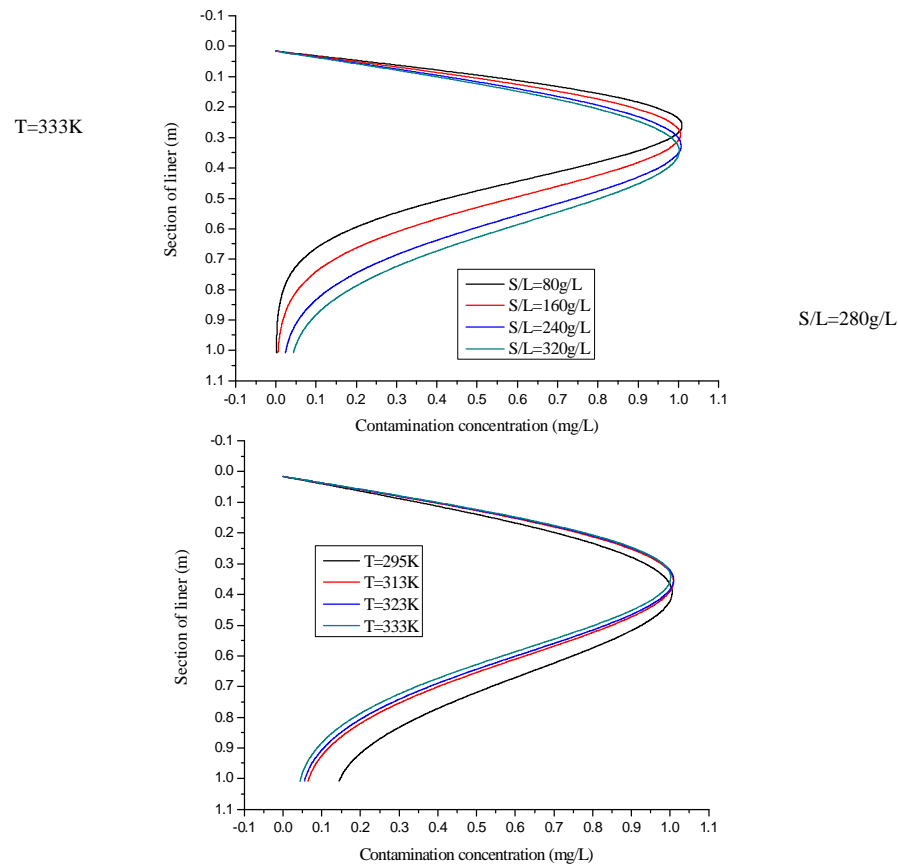
A one-dimensional solute transport equation was used to simulate the transport of Cr(VI) through landfill liner (Zhang *et al.*, 2004),

$$\left(1 + \frac{\rho q_m b}{n(1 + bC)^2}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial Z^2} - V \frac{\partial C}{\partial Z} \quad (2)$$

where  $C$  is contaminant concentration in the aqueous phase;  $t$  is time;  $D$  is dispersion coefficient;  $V$  is fluid velocity;  $n$  is porosity;  $\rho$  is bulk density and  $Z$  is distance from the domain entrance.

A hypothetical 1m thick liner is used to simulate transport of Cr(VI). The initial contaminant concentration was  $C(Z,0)=0\text{mg/L}$  for the transport simulation. The press head of leachate is 1m. Cr(VI) concentration of the upper boundary is 10mg/L at previous 10 years, then is 0 mg/L at consecutively 20 years.

The values of  $\rho$  and  $n$  are given in Table 1. The values of isotherm parameter ( $q_m$ ,  $b$ ) at various soil solids concentrations and temperatures can be seen in Fig. 4. A dispersion coefficient ( $D$ ) equal to  $3 \times 10^{-10} \text{m}^2/\text{s}$  was used for all the simulations (Xi *et al.*, 2006).



**Figure 6:** Transport of Cr(VI) through landfill liners

Results from the Cr(VI) transport simulations are presented in Fig. 6. In Fig. 6, the transport of Cr(VI) through clay liner was speeded up significantly with an increase soil solids concentrations. It was concluded that the values of isotherm parameters measured using batch tests under low soil solids concentrations will not properly simulate the field situation, and retardation factors of clay landfill liners systems will be overestimated. Therefore, a sufficiently high soil solids concentration should be conducted in batch tests in order to obtain isotherm parameters close to the results from the field situation. In addition, the transport of Cr(VI) through clay landfill liner was reduced as the temperature increases. In order to reasonable predict transport of pollutants, it is significant to consider the effect of temperature on adsorption capacity of pollutants onto landfill liners.

## CONCLUSIONS

The study presents effect of soil solids concentrations and temperature in batch tests on Cr(VI) adsorption onto landfill liner-soil materials. The following conclusions can be attained from the study:

- (1) The values of isotherm parameters and soil solids concentrations have a log-log linear relationship at low soil solids concentrations.

- (2) The values of isotherm parameters( $q_m$ ,  $b$ ) decreased strongly as soil solids concentration increased, and finally stabilized when the soil solids concentrations were over the critical values.
- (3) The adsorption capacity of Cr(VI) onto the clay increased with increasing temperature. The adsorption is controlled by an endothermic process in nature.
- (4) The values of measured isotherm parameters( $q_m$ ,  $b$ ) increased linearly with increasing temperature.
- (5) The values for isotherm parameters measured using batch tests under low soil solids concentration will not properly simulate the field situation, and retardation factors of clay landfill liners systems will be overestimated.

## REFERENCES

1. Zhang Jin-li, Luan Mao-tian, Yang Qing (2004) "One-dimensional numerical analyses of pollutant migration process in solid waste considering bio-degradation effect of contaminants," *Journal of Dalian University of Technology*, 11, 44(6):870-876(in Chinese).
2. Du Y J, Hayashi S and Liu S Y (2006) "Sorption properties of  $Cd^{2+}$  and  $Pb^{2+}$  on Ariake clay," *Proceeding of Sessions of GeoShanghai 2006*, June 6-8, Shanghai, China:255-261.
3. Chang Fu-xuan, Wu Ji-chun, Xue Yu-qun (2005) "The fractional dispersion in the problem of solute movement in porous media," *Journal of Hydrodynamics, Ser. A*, 1, 20(1):50-55(in Chinese).
4. Zhang De-sheng, Chang An-ding, Shen Bing (2005) "Quasi-analytical solution and numerical simulation for advection-dispersion model of adsorbed solute transport through soils under steady state flow," *Journal of Hydrodynamics, Ser. A*, 3, 20(2): 226-232 (in Chinese).
5. Shackelford C. D, Redmond P. L. (1993) "Solute breakthrough curves for processed kaolin at low flow rates," *Journal of Geotechnical Engineering, ASCE*, 121(1):17-32.
6. Kim J Y, Shin MC, Park J R (2003) "Effect of soil solids concentration in batch tests on the partition coefficients of organic pollutants in landfill liner-soil materials," *J Mater Cycles Waste Manag.*, 5:55-62.
7. Southen J M and Rowe R K (2002) "Desiccation behaviour of composite landfill lining systems under thermal gradients," *Proc. International Symposium on Clay Geosynthetic Barriers*, A. A. Balkema, Nuremberg, Germany:311-320.
8. Southen J M and Rowe R K (2005) "Thermally induced desiccation of geosynthetic clay liners in landfill basal liner applications," *Proceedings of the Sessions of the Geo-Frontiers 2005 Congress*, January 24-26, Austin, Texas, USA:24-26.
9. Koerner G R, Koerner R M (2006) "Long-term temperature monitoring of geomembranes at dry and wet landfills," *Geotextiles and Geomembranes*, 24(1):72-77.
10. Zou Wei-hua, Han Run-ping, Chen Zong-zhang (2006) "Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 279:238-246.
11. Al-Ghouti M, Khraisheh M A M, Ahmad M N M *et al* (2005) "Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study," *Journal of Colloid and Interface Science*, 287: 6-13.

12. Aksu Z (2002) "Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of lead(II) ions onto *Chlorella vulgaris*," *Process Biochem*, 38:89-99.
13. O'Connor D J, Connolly J P (1980) "The effect of concentration of adsorbing solids on the partition coefficient," *Water Res*, 14:1517-1523.
14. Xi YongHui, Ren Jie, HU ZhongXiong (2006) "Laboratory determination of diffusion and distribution coefficients of contaminants in clay soil," *Chinese Journal of Geotechnical Engineering*, 3, 28(3):397-402.

