

ADSORPTION BEHAVIOUR OF THIOPHENE DERIVATIVES ON SOIL MATERIALS

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Abstract: A laboratory batch test was conducted to determine the mechanisms by which sulfolane and thiolane adsorb on soil materials obtained from an alluvium/weathered rock aquifer. The site is a former Sulfinol waste sludge disposal site near Brisbane, Australia. Groundwater samples directly beneath a waste disposal site have been shown to contain higher concentration of sulfolane and relatively low concentration of thiolane from all of monitoring wells in the study area. The sulfolane is a source compound of thiolane, a reduced form of sulfolane. Thiolane is a non-polar heterocyclic organic molecule whereas sulfolane is a weakly acidic dipolar solvent.

The effect of pH on adsorption showed that adsorption was affected by the surface charge of the clay related to the polarity of sulfolane and thiolane. Higher temperatures increased the chemical potential of the solutes, which would normally act to decrease the level of adsorption. Remainder of the organic fraction of the soil following heating was associated with physical adsorption of uncharged solutes. Since these compounds were present together in the aquifer, competition might be possible in this system. Competitive adsorption on clay, which indicated the extent to which the solutes competed for the same adsorption sites as adsorption of sulfolane was comparatively suppressed by predominant adsorption of thiolane.

Key Words: adsorption, contaminated soil, desorption, sulfolane, thiolane

INTRODUCTION

Extensive and persistent contamination of the subsurface environment has occurred at a Liquid Waste Treatment Facility (LWTF) in Brisbane, Australia due to disposing of sulfolane waste sludge over 20 years period. The disposal of sulfolane ceased in 1991.

Sulfolane has been used in the Sulfinol process to remove CO₂ in the air stream at an ammonia plant in Brisbane, Australia. Sulfolane is also used for various industrial purposes, such as the industrial extraction of

aromatic hydrocarbons, normal and branched aliphatic hydrocarbons, fatty acids, and fatty acid esters.¹⁾ It is also used in wood delignification, as a polymer plasticizer, and as a polymer and polymerization solvent.²⁾

In the chemical analysis of groundwater from monitoring wells, the highest concentration of sulfolane detected was 4,344 mg/L. Subsequent analyses of groundwater samples suggest that little degradation and migration of sulfolane have occurred during the past 20 years. Over this period, sulfolane has been transformed into thiolane, a reduced form via unknown mechanisms. Thiolane is believed to originate from sulfolane by facultative anaerobic bacteria, which use sulfolane as an electron acceptor.³⁻⁶⁾ Thiolane is a reduced form of sulfolane. These

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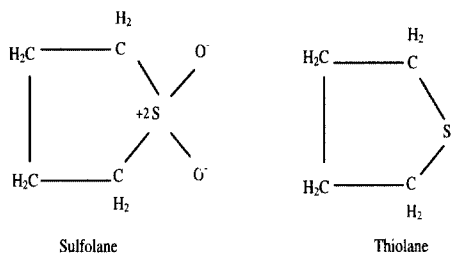
two contaminants are catalogued as saturated heterocyclic sulphur compounds⁷⁾ as shown in Figure 1.

Thiolane is a malodorous heterocyclic sulphur compound and moderately toxic,⁸⁾ which can be sensitively detected at concentrations 0.5 ng/L in the gaseous form as noted in reports on Superfund sites.^{9~12)} It is also used as a herbicide,⁸⁾ and insecticide.¹³⁾ In addition, it is naturally detected as impurities in various sources of crude oil.¹⁴⁾

Most of the earlier works were performed on gaseous thiolane adsorption to estimate the migration of thiolane occurring from natural gas leaks in underground storage tanks.^{15~19)} Additionally, adsorption and desorption on pipeline dust were studied.²⁰⁾

Luther *et al.*²¹⁾ examined the adsorption of sulfolane on a variety of soils containing a range of clay and organic carbon content. They found that the linear adsorption parameter for sulfolane, k_d [L/kg], correlated with the CEC of the soils studied, namely montmorillonite, kaolinite as well as soils from three different Canadian sites.

The experiments aim to determine the adsorption mechanism of soil at the LWTF, specifically for the predominant contaminants at the site (e.g. sulfolane and thiolane). The competitive effect between the two contaminants was evaluated over the entire range of concentrations detected from previous groundwater samples.



(Tetrahydrothiophene 1,1-dioxide, M.W.(120.17))

(Tetrahydrothiophene, M.W.(88.17))

Figure 1. Structure of sulfolane and thiolane.

MATERIALS AND METHODS

Chemicals

Sulfolane and thiolane (AR) were purchased from Aldrich Chemicals (USA). A background solution was collected from a reference well beyond the extent of the contaminant plume. The background solution was filtered with a 0.45 μm poly acrylamide membrane filter.²²⁾ It was then purged with N_2 gas for 1 hr to remove dissolved air immediately prior to use in the experiments. Contacting solutions for adsorption studies were prepared from 2 g/L of standard stock solutions. Thiolane and sulfolane stock solutions were diluted with the background solution according to the desired concentrations of thiolane and sulfolane in the adsorption tests.

Soil Sample Preparation

Soil samples were selected to represent typical clay, silt and sand at the disposal site. The soils were obtained using a split spoon sampler while drilling with a hollow stem auger to install the nested monitoring wells in the study area. The soil samples were air dried for 5 days, then crushed with mortar and pestle followed by grinding with a ring mill. The soil characteristics were addressed using XRD diffractor equipped with PW 1840 diffractometer (Philips). The response was monitored with an ECM-5400 integrator. These samples were also analyzed for cationic exchange capacity²³⁾ and organic carbon (LECO combustion method). Organic carbon content of 1 mm sieved aquifer materials was determined by acidifying samples with 1.0 mole/L HCl to remove carbonates followed by combustion of the samples in a Leco WR-112 Carbon Determinator.

Batch Test Procedure

The effect of microbial activity was checked by comparing the unsterilized and sterilized tests at the 40 mg/L level. A 20 g sample of clay and 200 mL of filtered groundwater were

autoclaved at 121°C (101.4 kPa gauge pressure) for 15 min (Tomy high pressure steam sterilizer, ES-315) on three consecutive days and then spiked with 40 mg/L of sulfolane and thiolane. The sample was monitored in a shaker bath for 24 hr.

The soil slurry was allowed to equilibrate prior to adding 100 mL of stock solution, which subsequently diluted to achieve a range of concentrations in 100 mL of soil slurry. The bottles were capped with a puncturable self sealing rubber cap and then agitated for 24 hr in a temperature controlled water bath. After 24 hr, a 5 mL sample was collected using a 5 mL of glass syringe. The sample was then centrifuged at 1,500 rpm and filtered through a 0.22 µm polyacrylamide membrane filter. Separate 2 mL samples were required for sulfolane and thiolane analyses. 2 mL was set aside in a vial with 2 mL PTFE septum for thiolane analysis. Another 2 mL of sample was extracted with methylene chloride for sulfolane analysis.

The methylene chloride extracts were analyzed using a Perkin Elmer AutoSystem Gas Chromatography equipped with a flame ionization detector (FID). A 30 m long (0.25 mm I.D.) and 0.25 µm thick, stationary phase DB-5 (5% phenyl methyl poly siloxane) column, was used for sulfolane analysis. High purity helium (99.999%) was used as the carrier gas at a flow rate of 1.7 mL/min. The injector and detector temperatures were 300°C and 350°C, respectively. FID response was monitored with a Perkin-Elmer LCI-100 integrator. Sulfolane concentrations were determined by comparing peak areas against calibration curves.

The concentration of thiolane was determined by injecting 25 µL into a Waters High Performance Liquid Chromatography (HPLC) equipped with an UV spectrophotometer at 215 nm. A 150 mm long (3.9 mm I.D.) symmetrical C₁₈ column packed with 5 µm particles was used with a mobile phase of CH₃CN: H₂O (50:50) at a flow rate of 1 mL/min. UV response was recorded with a Waters 740 emulator. Thiolane concentrations were deter-

mined by comparing peak areas against calibration curves.

The reversibility of adsorption was examined for 24 hr by replacing with the same volume of filtered groundwater as removed for analysis in adsorption study. The concentration of adsorbed phase is calculated as:

$$\bar{C} = \frac{(C_0 - C_{eq})}{W} V \quad (1)$$

where \bar{C} : adsorbed amount [mg/g]

C_0 : initial concentration of adsorbate in liquid phase [mg/L]

C_{eq} : final concentration of adsorbate in liquid phase [mg/L]

W : dry weight of soil samples [g]

V : volume of liquid phase [L]

RESULTS and DISCUSSION

The cationic exchange capacity (CEC) and organic carbon content for clay, silt and sand were shown in Table 1. The XRD analyses showed that the clay was dominated by kaolinite with lesser amounts of smectite, illite and montmorillonite. The organic carbon content of the clay is low compared to silt, because the clay samples were obtained from the deeper, less permeable zone (i.e. alluvium). In contrast, silt was present at shallow depths (i.e. weathered rock), which were flushed regularly and penetrated by vegetation.

Adsorption on Clay Fraction at a Set pH and Temperature

Batch adsorption tests were first conducted at 18°C and pH 6.5, typical of the temperature and pH of the study area, on solutions of either

Table 1. Cationic exchange capacity and organic carbon content for different soil types

	Clay	Silt	Sand
CEC (meq/100 g-soil)	26.25	3.06	1.04
f _{oc} (%)	0.082	0.211	0.078

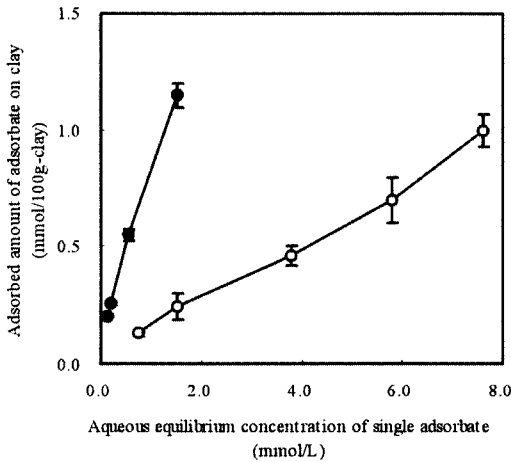


Figure 2. Single solute isotherm for sulfolane and thiolane. ●: thiolane, ○: sulfolane.

sulfolane or thiolane only as shown in Figure 2.

The adsorbed concentration increased linearly with aqueous concentration, for both sulfolane and thiolane. Thiolane adsorbed more strongly than sulfolane. The k_d value was obtained from regression of observed values in Figure 2, thereafter thiolane was 9.1 ± 0.41 L/kg, while the k_d value for sulfolane was 1.14 ± 0.16 L/kg. The errors signified the 95% confidence interval, assuming normally distributed data. Such difference of adsorption coefficients between sulfolane and thiolane attributed that the physical and chemical properties of these compounds are quite different, as sulfolane is more miscible with water.

Adsorption on Clay Fraction under Effect of pH

The effect of pH on the adsorption of sulfolane and thiolane was investigated at 18°C as shown in Figure 3(a) and (b). Equilibrium for adsorption/desorption of sulfolane and thiolane was reached in less than 3 hr. It showed sulfolane adsorbed to a marginally greater extent at pH 6.5 than at pH 4.5. The adsorbed concentration of sulfolane and thiolane at pH 6.5 was 0.92 and 1.35 mmol/kg, respectively, compared with sulfolane and thiolane adsorbed concentrations of 0.81 and 0.58 mmol/kg at

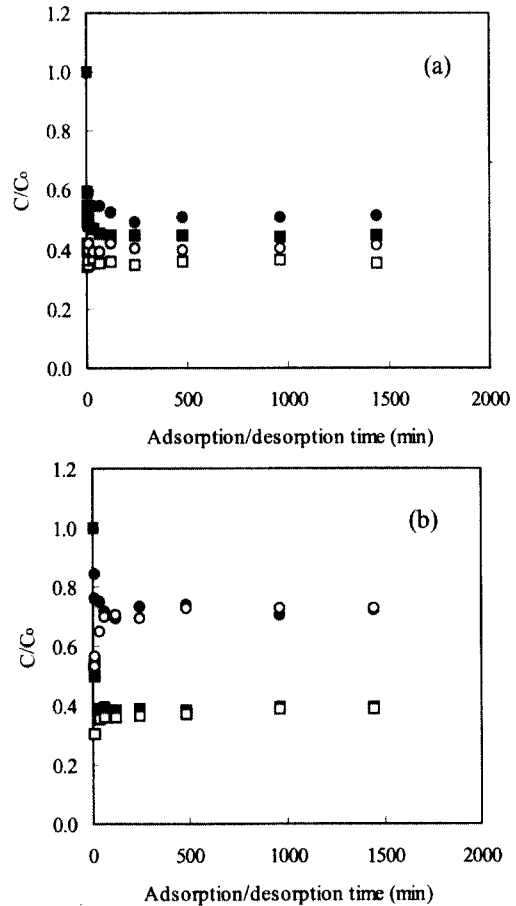


Figure 3. Adsorption/desorption of solutes on clay at different pH (18°C): (a) 0.167 mmol/L sulfolane, (b) 0.226 mmol/L thiolane. ■: adsorption (pH 6.5), □: desorption (pH 6.5), ●: adsorption (pH 4.5), ○: desorption (pH 4.5).

pH 4.5.

Adsorption on Clay Fraction under Effect of Temperature

It is likely that a separate solid phase will appear when water is cooled below 27°C as melting point of pure sulfolane is 27°C.^{24,25)} Adsorption experiment was thus conducted at 30°C above the melting point and at 18°C of the observed groundwater temperature.

The adsorbed concentration of sulfolane and thiolane on clay at 30°C was 1.29 and 1.18

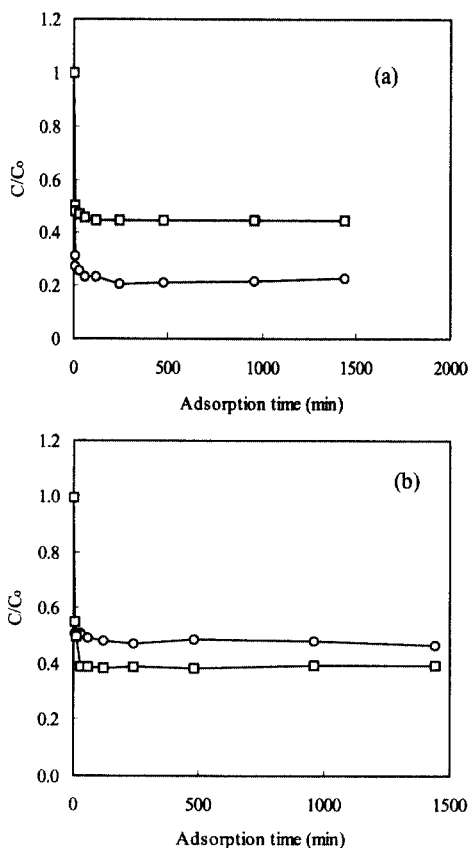


Figure 4. Adsorption of solutes on clay at different temperature (pH 6.5): (a) 0.167 mmol/L sulfolane, (b) 0.226 mmol/L thiolane. \circ : 30°C, \square : 18°C.

mmol/kg compared to 0.92 and 1.34 mmol/kg at 18°C, respectively (Figure 4). Sulfolane was adsorbed to a great extent on the clay at 30°C, compared to the level of adsorption at 18°C. This may reflect a reduction in viscosity of the sulfolane solution. In contrast, raising temperature reduces the level of thiolane adsorption. These trends in temperature alone indicate that adsorption of sulfolane and thiolane may attribute to different properties such that sulfolane is polar while thiolane is non-polar even though it has the similar chemical structure.¹⁵⁾

Adsorption on Silt and Sand

The level of sulfolane and thiolane adsorption on the silt and sand fractions over that of clay was compared as shown in Figure 5. The

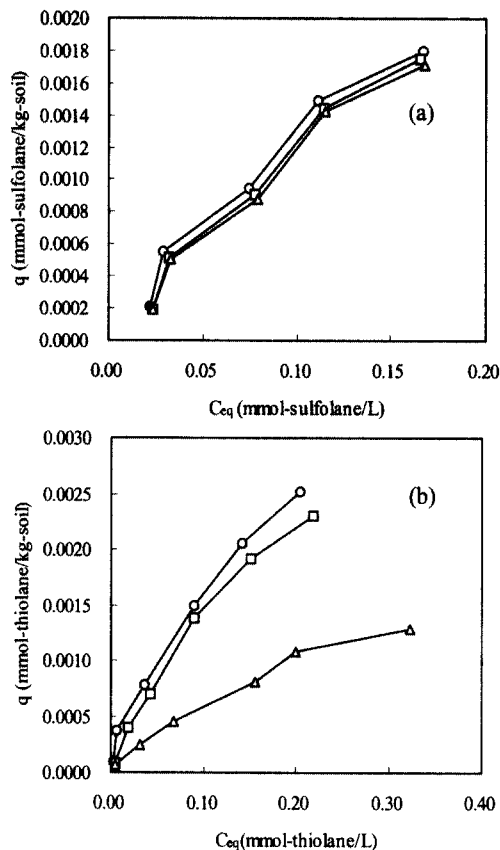


Figure 5. Amount of solute adsorbed on different soils, i.e., clay, silt, sand (pH 6.5 and 18°C): (a) sulfolane, (b) thiolane. \circ : clay, \square : silt, \triangle : sand.

adsorption of sulfolane is virtually independent of soil type, whereas the adsorption of thiolane is affected by soil types. This was first observed by Tarman and Linden.¹⁵⁾ They found that gaseous thiolane did not adsorb onto peat moss or sand, while it was significantly adsorbed by clay. Tarman and Linden¹⁵⁾ found that thiolane adsorption onto montmorillonite was approximately 16 times greater than adsorption onto kaolinite or illite, indicating that thiolane adsorption is correlated to CEC, as recently observed by Luther *et al.*²¹⁾ for thiolane adsorption onto various clays. The level of sulfolane adsorption was an order of magnitude less than thiolane, according to k_d values for clay (Figure 2). Sulfolane has a higher dipole moment of 4.81 D compared to

that of thiolane showing 1.9 D, which can increase the level of attraction to charged surfaces, but may also result in hydration, which would in turn rather reduce the attraction to the soil surface than that of thiolane. Regardless of soil type being varied, the same trend of adsorption showing clay > silt > sand on both sulfolane and thiolane may strongly ascribe to the extent of CEC values as shown in Table 1.

Effects of Heating Clays

The intention of these experiments was to remove organic carbon from the clay, thereby assessing its effect on adsorption properties. Initially an attempt was made to extract organic matter with 0.5 mole/L NaOH washes followed centrifugation.²⁶⁾ However, these washes had no impact on organic carbon levels. Instead, the clay soil was heated to 550°C for 5 min to burn out soil organic fraction.²⁶⁾

A heat treated clay sample was then contacted with 0.226 mmol/L of thiolane. Another sample was contacted with 0.167 mmol/L of sulfolane. The level of adsorption in these batch tests was 0.926 mmol/kg for thiolane and 0.757 mmol/kg for sulfolane (Figure 6), considerably less than the adsorption level for the untreated samples (Figure 2). This indicated that soil organic matters could more affect adsorption of sulfolane than that of thiolane due to the discrepancy of dipole moment between them. Further insight into the mechanisms of adsorption/desorption on soil organic matters can be gained by examining adsorption/desorption kinetics (Figure 6).

Thiolane was highly desorbed by 45.8% showing 0.032 mmol/L released for 24 hr. In contrast, the less amount of sulfolane was released by 7% showing 0.005 mmol/L desorbed. In desorbing solutes from the un-heated clay, thiolane and sulfolane were released at 28% (0.019 mmol/L) and 2.9% (0.002 mmol/L), respectively. It indicated that the differences of degree of release of solutes between heated and un-heated clay related to the extent of organic matter loss in heated clay, which in turn might

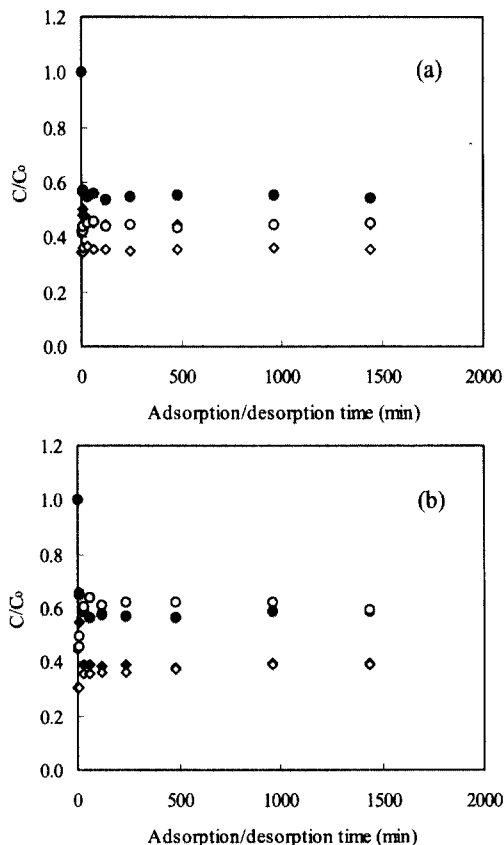


Figure 6. Comparison of adsorption/desorption properties on heated and not-heated clay (pH 6.5 and 18°C): (a) 0.167 mmol/L sulfolane, (b) 0.226 mmol/L thiolane. ◆: adsorption(not heated), ◇: desorption(not heated), ●: adsorption(heated at 550°C), ○: desorption(heated at 550°C).

more readily release solutes even though they had been more strongly adsorbed into organic matter on clay.

Competitive Adsorption between Sulfolane and Thiolane

Batch experiments were conducted with both sulfolane and thiolane in the contacting solutions. The levels of both solutes reflect site concentrations: with concentrations of sulfolane ranging up to 8 mmol/L and thiolane concentrations ranging up to 0.4 mmol/L. Each isotherm was designed such that soil was

contacted with a range of concentrations of one compound while holding the other compound at a constant concentration. Because concentrations were restricted to ranges that reflected site conditions, thiolane is always a minor fraction of the total adsorbate concentration. The trends in Figure 7(a) and (b) show evidence of competition for adsorption sites.

Competition is apparent because the adsorption of either thiolane or sulfolane is reduced by the presence of the other compound. Evidence of competition indicates that the adsorbates are attracted to the same adsorption sites.

Thiolane is a non-polar heterocyclic organic molecule that is held to adsorption sites in clay by van der Waals forces. Bradley,²⁷⁾ MacEwan,²⁸⁾ and Greene-Kelly²⁹⁾ demonstrated that van der Waals forces play a significant role in the adsorption of neutral polar and non-polar organic molecules onto montmorillonite.

In contrast, sulfolane is a weakly acidic dipolar solvent.³⁰⁾ The sulfolane molecule is polar with a negative charge on the oxygen and a positive charge on the sulfur. As shown in Figure 1, oxygen protrudes from the molecule forming a negative pole that is exposed and readily accessible. The charged nature of sulfolane suggests that it may be partially adsorbed by electrostatic forces. The XRD and CEC analyses performed on the soil samples used in these experiments showed that 13.4% of the clay subsample is $< 2 \mu\text{m}$, of which 20 to 25% montmorillonite. The CEC of the soil sample is approximately 26.25 meq/100 g suggesting that constituents other than montmorillonite do not significantly contribute to the CEC of the soil. Although sulfolane can be adsorbed onto CEC sites, presumably by the positive pole of the sulfur ion, the charged nature of unshared pairs of electrons of the oxygen ion makes it completely miscible in water. Miscibility is one of unique feature of dipolar aprotic solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), and hexamethylphosphorotriamide (HMPT), with dipole moments several times as large as that of water.³⁰⁾ The diminished adsorption capacity

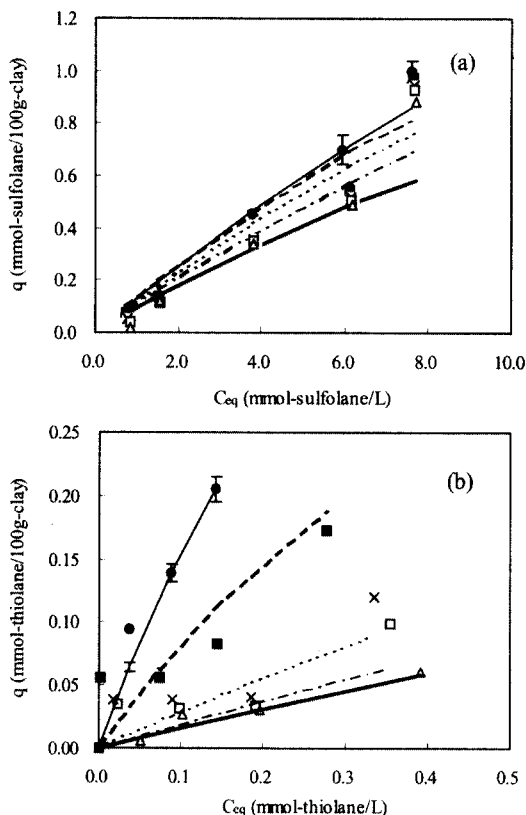


Figure 7. (a) Adsorption of sulfolane in a background of thiolane. The data points represent experimental data. Lines represent best fitting Langmuir competitive isotherm. ● : background thiolane level = 0.0, ■ : background thiolane level = 0.02 mmol/L, × : background thiolane level = 0.09 mmol/L, □ : background thiolane level = 0.18 mmol/L, △ : background thiolane level = 0.27 mmol/L. (b) Adsorption of thiolane in a background of sulfolane. The data points represent experimental data. Lines represent best fitting Langmuir competitive isotherm. ● : background sulfolane level = 0.0, ■ : background sulfolane level = 0.8 mmol/L, × : background sulfolane level = 3.8 mmol/L, □ : background sulfolane level = 6.0 mmol/L, △ : background sulfolane level = 7.6 mmol/L.

of sulfolane in comparison to thiolane suggests that the thermodynamic stability of sulfolane-water interactions are greater than the electrostatic attraction between the negative exchange sites and sulfolane.³¹⁾ Lorprayoon and Condrate³²⁾ demonstrated that adsorption of sulfolane onto clay was enhanced by increasing CEC.

Variations in pH and temperature do not provide any clear insight to the adsorption mechanisms. Removing organic carbon from the clay has the largest impact on thiolane adsorption (Figure 6(b)), implying that thiolane adsorption is associated with organic carbon more than sulfolane.

The clearest indication that sulfolane and thiolane compete for different sites comes from the competitive adsorption data. Figure 7(a) and (b) show that sulfolane and thiolane compete to some degree for adsorption sites.

If all adsorption sites on the surface of the clay are the same, then the sites will be equally accessible to sulfolane and thiolane, and equilibrated adsorbed concentrations will have a ratio equal to the ratio of the equilibration constants for the single solute isotherms. A competitive adsorption must necessarily incorporate a site limitation.

One of the most common adsorption models that incorporates a site limitations is the Langmuir isotherm:

$$q = \frac{QkC_{eq}}{1 + kC_{eq}} \quad (2)$$

where q [mmol/g] is the number of moles of solute adsorbed per unit weight of adsorbent in equilibrium with solute concentration; C_{eq} [mmol/g]; Q [mmol/g] is the maximum number of moles of solute adsorbed as a monolayer per unit weight of adsorbent; k [L/mmol] is the equilibrium constant, a function of the adsorption energy.

The Langmuir isotherm has often been used to describe competitive adsorption effects of organic species. Srivastava and Tyagi³³⁾ employed a modified Langmuir isotherm³⁴⁾ to

evaluate the competitive adsorption of substituted phenol compounds on a converted carbonaceous adsorbent material:

$$q_i = \frac{Qk_i C_{eqi}}{1 + k_1 C_{eq1} + k_2 C_{eq2}} \quad (3)$$

where Q , k_1 , and k_2 are determined from single solute adsorption tests and C_{eq1} and C_{eq2} are the aqueous equilibrium concentrations of the competing solutes.

Equation (3) was fitted to the data in Figure 7(a), and then to the data in Figure 7(b) by employing Matlab. The sum of sulfolane and thiolane, represented as the total amount of thiophene in the adsorbed phase (mmol/kg), is plotted against total thiophene in the aqueous phase shown in Figure 8.

A least squares fit of Equation (3) is also applied to Figure 8. Table 2 shows the values of Q , k_1 , and k_2 obtained from the fits to Figures 7(a), (b), and 8 by employing Matlab.

The saturated level of adsorption, based on best fits to Figure 7(a) and 8, are the same. This simply reflects the dominance of adsorbed sulfolane concentration in Figure 8. The equilibrium constant for thiolane, k_2 , is greater than the equilibrium constant for sulfolane, k_1 , which simply means that adsorption strength of thiolane is far stronger than that of sulfolane, thereby thiolane could more strongly be adsorbed onto clay. Table 2 clearly shows that the data in Figure 7(a) and (b) cannot be represented with one set of parameters. This suggests that sulfolane and thiolane compete for different sites, possibly with a group of sites accessible to both solutes.

Figure 7(a) shows that sulfolane adsorption is reduced by the introduction at a trace amount of thiolane, but further increases in thiolane concentration do not further reduce sulfolane adsorption. Karickhoff³⁵⁾ proposed that organic carbon adsorption sites, when occupied, could block access to mineral sites within a particle. Following previous observations that sulfolane is adsorbed onto cationic exchange sites associated with clay.^{21,32)} This

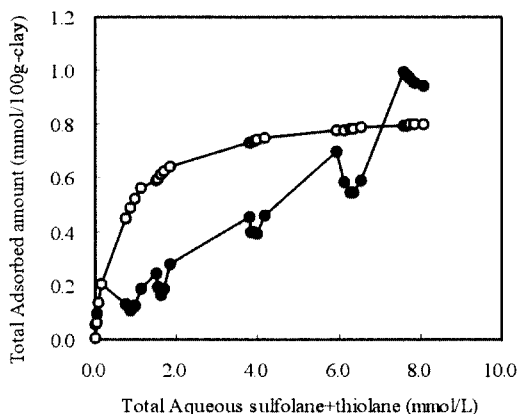


Figure 8. Predicted total adsorbed thiophene against observed total adsorbed thiophene on clay. ● : observed, ○ : predicted.

lane may act to block the sites by adsorbing onto superficial carbon on the surface of the clay particles. This hypothesis is also consistent with the tips in total adsorbed thiophene concentration, which correlate with additions of thiolane to the contacting solution.

The steady decline in thiolane adsorption with increasing concentrations of sulfolane background concentrations indicates that both solutes compete for the organic carbon sites. The Langmuir parameters for Figure 7(b) indicate that thiolane is preferably adsorbed to sulfolane on this material.

CONCLUSIONS

Thiolane is more strongly adsorbed onto clay materials than sulfolane as k_d showed 9.1 ± 0.41 L/kg and 1.14 ± 0.16 L/kg, respectively. Thiolane is a non-polar molecule, adsorbed to clay surfaces by van der Waals force, while sulfolane is a polar molecule, adsorbed by a combination of van der Waals and electrostatic forces. The interactions between solute and clay can be accounted for by considering the activity rather than the concentration of the competing molecules. Decreasing pH correspondingly reduced the degree of adsorption capacity of clay on solutes as clay became more protonated, thereby decreasing interaction between adsorbate and solute. The temperature above a melting point of sulfolane increased adsorption amount on clay as sulfolane molecules were more solvated. For a while, adsorption of thiolane was greatly dependent upon types of soils, e.g. clay, silt, sand, ascribing to differences in CEC. Adsorption capacity of thiolane was also significantly influenced by removing soil organic matters as thiolane more strongly interacted with them. A more empirical approach would be to readjust the adsorption parameters, Q , k_1 , and k_2 , to optimize the fit of the competitive isotherm to the data. This involves nonlinear regression analysis using Matlab. The development of these approaches would form an extension to this study.

For regression of bi-solute system, adsorption

Table 2. Estimated parameters of Q , k_1 , and k_2

	Q (mmol/100 g)*	k_1 (L/mmol)**	k_2 (L/mmol)***
Sulfolane/thiolane****	1.2909	0.0259	1.4680
Thiolane/sulfolane*****	0.8722	1.4026	2.1790
Thiolane+sulfolane*****	1.2909	0.1160	0.4497

* maximum number of molecules of solute adsorbed per unit weight of adsorbent

** constant for enthalpy change on the adsorption of sulfolane

*** constant for enthalpy change on the adsorption of thiolane

**** sulfolane in presence of thiolane

***** thiolane in presence of sulfolane

***** combined as thiophene

strength of sulfolane was smaller than that of thiolane showing greater value of enthalpy of adsorption constant such that sulfolane adsorption on clay was comparatively suppressed in the presence of thiolane. This was well consistent with the result obtained from single solute system. It was concluded that sulfolane and thiolane might compete for different sites as sulfolane was more attractive on organic fraction while thiolane was more readily accessible on CEC contents.

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