Korean J. Chem. Eng., **16**(2), 215-220 (1999)

COMPETITIVE ADSORPTION OF SULFOLANE AND THIOLANE ON CLAY MATERIALS

Chang Gyun Kim†, **William P. Clarke*** and **David Lockington****

Water Protection Research Team, RIST, P.O. Box 135, Kyungpook 790-330, Korea
*Department of Chemical Engineering, **Department of Civil Engineering,
University of Queensland, Brisbane, Queensland 4072, Australia

(Received 11 August 1998 • accepted 16 January 1999)

Abstract–Groundwater samples directly beneath a waste disposal site have been shown to contain a higher concentration of sulfolane and a relatively low concentration of thiolane. The sulfolane is a source compound of thiolane, a reduced form of sulfolane. In subsequent analyses of groundwater samples, these compounds have been detected from all of the monitoring wells in the study area. Since these compounds are present together in an aquifer, a possible competition, that can happen in such a system, has been investigated. Thiolane is a nonpolar heterocyclic organic compound whereas sulfolane is a weakly acidic dipolar solvent. As expected, thiolane adsorbs more strongly onto clay than sulfolane in a single solute system. For regression of bisolute system using Matlab to obtain Q (maximum number of moles of solute adsorbed per unit weight of adsorbent), k_1 (constants related to the energy of adsorption for sulfolane), and k_2 (constants related to the energy of adsorption for thiolane), the k_1 value (sulfolane) is smaller than the k_2 value (thiolane) which reflects that thiolane is more strongly adsorbed than sulfolane. This is strongly consistent with the result obtained from single solute system. The Q for the sulfolane and combined data is the same that indicates that the sulfolane data is dominantly fitted because the concentrations of sulfolane are much greater than those of thiolane in the experiments. In combined data regression, the suppression of sulfolane adsorption on clay was also observed by the presence of thiolane.

Key words : Competitive Adsorption, Sulfolane, Thiolane, Clay

INTRODUCTION

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

Sulfolane has been used as in Sulfinol process to remove CO_2 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 [Choo et al., 1998]. It is also used in wood delignification, as a polymer plasticiser, and as a polymer and polymerization solvent [Kirk-Othmer, 1983]. Toxicity of sulfolane reveals that LD_{50} for rats is 1,941 mg/kg [Chapman and Hall, 1996], which is considerably toxic than that of chlorophenols ranging between 130 and 4,000 mg/kg body weight [Kirk-Othmer, 1983]. The sulfolane chronic toxicity test with guinea pigs has shown that the threshold dose of sulfolane was 2.5 mg/kg, whereas the non-effective dose was 0.25 mg/kg. By extrapolation this experiment result to humans, the maximum allowable concentration of sulfolane in surface water has been recommended as 5 mg/*l* [Zhu et al., 1987]. Sulfolane was regulated as a toxic organic compound at the Federal Toxic Substances Control Act of EPA [Federal Register, 1991] and as a prescribed substance in HMSO [Environmental Protection, 1994]. Sulfolane was also reviewed on the effect of human health and environmental ecotoxicology [ECETOC, 1994].

In the chemical analysis of groundwater from monitoring wells, the highest concentration of sulfolane was detected as high as 4,344 mg/*l*. Subsequent analyses of groundwater samples suggest that little degradation and migration of sulfolane have occurred during the past 20 years and thiolane was also detected as one of major contaminants. Over this period, sulfolane has been transformed into thiolane via unknown mechanisms. Thiolane is believed to be originated from sulfolane by facultatively anaerobic bacteria, which use sulfolane as an electron acceptor [Zinder and Brock, 1978; Schrementi and Meganathan, 1986, 1987]. Thiolane is a reduced form of sulfolane that has a very strong smell. These two contaminants are catalogued as saturated heterocyclic sulphur compounds [Gutsche and Pasto, 1975] as shown in Fig. 1.

Thiolane is a malodorous heterocyclic sulphur compound which is mainly used as a warning odorant of odourless fuel, city and natural gas [Carlucci et al., 1984], which is sensitively detected as low as 0.5 ppb in the gaseous form [Bradstreet et al., 1985]. It is also used for herbicides [Carlucci et al., 1984], and insecticide [Afifi and Abdulla, 1977]. In addition, it is naturally detected as impurities in various sources of crude oil [Lorprayoon and Condrate, 1983].

---

†To whom correspondence should be addressed.
E-mail : CGKIM@RISNET.RIST.RE.KR

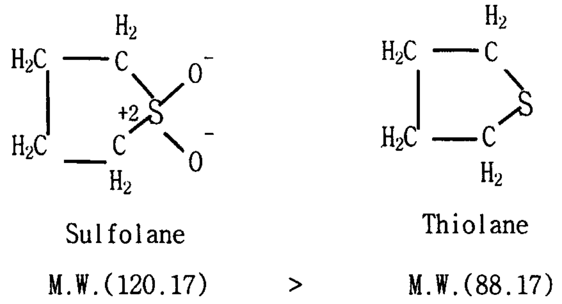

Fig. 1. Structure of sulfolane and thiolane.

Thiolane appears to be moderately toxic, but has a strong smell which is offensive to humans at very low concentrations (i.e. headache, vomiting, and nausea), as previously noted in reports on Super fund sites in USA [Moschandreas et al., 1982; Bradstreet et al., 1985; Schmidt and Meyer-Schmidt, 1985; Coy, 1987]. Site geology investigations show that the site consists of alluvial sediments overlying weathered rock, typically less than 10 m thick consisting of residual clayey silt, silty clay, and a trace of sand and gravel layers.

There have not been performed enough investigations on evaluation of adsorption behaviour of liquid phase of thiolane and sulfolane on aquifer materials as well as on competitive adsorption even though, in reality, adsorption should always be occurred as a competitive process between organic contaminants in mixed solvent systems [Lawrence and Parsons, 1969]. In order to clarify this competitive effect between nonpolar and polar solvents, the present study was undertaken over entire range of concentrations of thiolane and sulfolane that has been detected from the analyses of groundwater samples. The following experiments aim to determine the adsorption capacity of the Willawong clay, specifically for the predominant contaminants at the site, e.g. sulfolane and thiolane.

MATERIALS AND METHODS

1. Soil Sample Preparation

Soil samples used in this study were obtained using a split spoon sampler during drilling with a hollow stem auger to install the nest monitoring wells in the study area. The soil samples were air dried for 5 days and then crushed with a mortar and pestle followed by grinding with a ring mill. The samples were crushed such that 95 % passed through a 1 mm sieve. The samples were analysed for size distribution and clay content with laser and XRD analyses. Particles less than 2 μm consist of 13.4 %, while the particles ranging from 2 to 40 μm consist of 79.6 %. By XRD analysis, clay contains 20 to 30 % of kaolinite and 5 to 10 % of smectite/illite and montmorillonite. Cationic exchange capacity and organic carbon (LECO combustion method) were also determined. The clay contained 0.21 % of organic carbon and 30 meq/100 g of cationic exchange capacity.

2. Standard Solution

Contacting solutions for adsorption studies were prepared from standard stock solutions, and 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 membrane filter [Davis et al., 1994]. Groundwater stocks were then purged with N_2 gas for 1 hour to remove dissolved air immediately prior to use in the experiments in order to prevent quick diffusion of solutes into gaseous phase.

2,000 ppm stock solutions of thiolane and sulfolane were prepared and stored in 2 L volumetric flasks. Both the groundwater and stock solutions were stored at 4 °C. The thiolane and sulfolane stock solutions were diluted with the background solution according to the desired concentrations of thiolane and sulfolane in the adsorption tests.

3. Control Experiment to Monitor Microbial Activity

20 g of clay and a filtered groundwater sample were autoclaved at 121 °C and 104 kPa for 15 min on three consecutive days and then spiked with 40 ppm of sulfolane and thiolane. The sample was placed in a shaker bath amongst unsterilised samples. The effect of microbial activity was checked by comparing adsorption results with the unsterilised tests by contacting solutions of 40 ppm levels.

4. Adsorption Experiment

20 g of soil samples were pre-mixed with 100 ml of filtered groundwater for 30 min in a water shaker bath at 18 °C to remove any air trapped in the soil particles. Batch tests were carried out at 18 °C and pH 6.5, typical of the temperature and pH observed in the study area. The adsorption tests were performed on 20 g of soil sample in 100 ml of filtered groundwater, spiked with 100 ml of dilute stock solution. The experiments were performed in 250 ml bottles capped with a puncturable self sealing rubber septum. 5 ml sample was collected after 24 hours from each bottle through the septum using a needle and a syringe. The sample was centrifuged at 1,500 rpm and the supernatant filtered through a 0.2 μm membrane filter. 2 ml of the supernatant was kept in a vial capped with a PTFE septum. Another 2 ml of supernatant was mixed with 2 ml of methylene chloride in a small glass vial by hand-shaking for 1 minute [Ying et al., 1995]. The separated aqueous layer was discarded. Any moisture retained in the methylene chloride that could not be removed by pippetting was adsorbed by Na_2SO_4.

5. Analysis

The methylene chloride extracts were analysed 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 DB5 (5 % phenyl methyl poly siloxane) column was used for sulfolane analysis. High purity helium (CIG) was used as the carrier gas at a flow rate of 1.7 ml/min. The injector and detector temperatures were 300 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 ID) symmetrical C_{18} column was used and $CH_3CN:H_2O$ (50:50) was applied as the eluent at a flow rate of 1 ml/min. UV response was recorded with a Waters 740 emulator. Thiolane concentrations were determined by comparing peak areas against calibration curves.

RESULTS AND DISCUSSION

A total of 46 adsorption tests were performed on thiolane and sulfolane mixed in varying proportions. The tests were designed such that the soil was contacted with a range of sulfolane or thiolane concentrations while holding one of the species at a constant concentration.

1. Noncompetitive Adsorption

Adsorption behaviour was first analysed on solutions of either sulfolane or thiolane only. The results of the experiments on the single component systems are shown in Fig. 2. The error bars indicate standard deviations calculated from two isotherm determinations.

Fig. 2 shows that thiolane adsorbs more strongly than sulfolane. A difference of the adsorption behaviour between sulfolane and thiolane is expected as the physical and chemical properties of these compounds are quite different. Thiolane is a nonpolar heterocyclic organic molecule that is held to adsorption sites on clay by van der Waals forces. Bradley [1945], Macewan [1950], and Greenekelly [1955] 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 [Morrison and Boyd, 1987]. The sulfolane molecule is polar with a negative charge on the oxygen and a positive charge on the sulfur. As shown in Fig. 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 soil is clay consisting of 22.5 % montmorillonite. The CEC of the soil sample was approximately 30 meq/100 g suggesting that constituents other than montmorillonite did not significantly add 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. It is one of unique features of dipolar aprotic solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), and hexamethylphosphorotri-amide (HMPT), which have several times higher dipole moments than that of water [Morrison and Boyd, 1987]. The diminished adsorption capacity of sulfolane in comparison to thiolane suggests that the thermodynamic stability of sulfolane-water interactions is greater than the electrostatic attraction between the negative exchange sites and sulfolane [Spangler, 1980]. Consistent with this interpretation, Lorprayoon and Condrate [1981] found that the adsorption of sulfolane onto montmorillonite is enhanced by increasing the CEC of the montmorillonite by cation substitution.

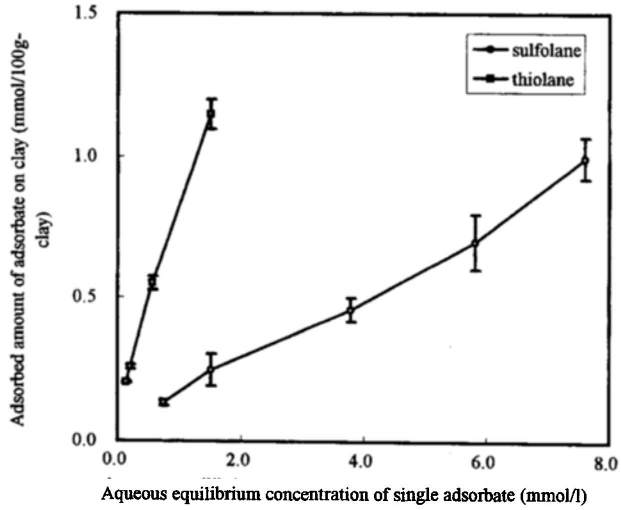

Fig. 2. Single solute isotherms for sulfolane and thiolane.

2. Competitive Adsorption

The trends in Figs. 3 and 4 (Exp.) show the evidence of competition for adsorption sites. Competition is apparent because the adsorption of either thiolane or sulfolane is restricted by the presence of the other compound (e.g thiolane in presense of sulfolane vice versa). One of the most common adsorption models that incorporates a site limitation is the Langmuir isotherm :

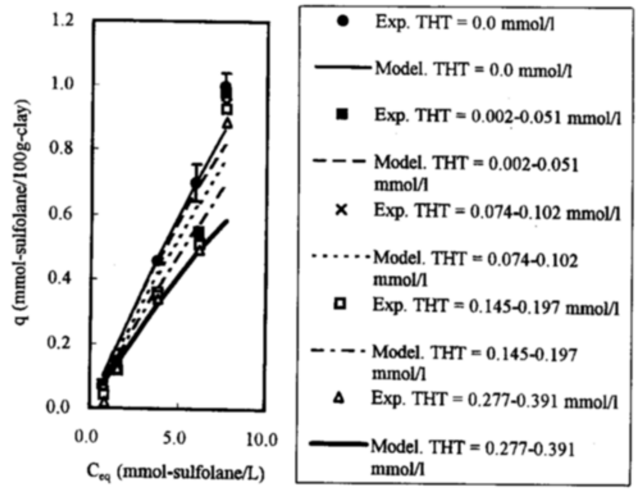

Fig. 3. Nonlinear regression of competitive adsorption of sulfolane in presence of thiolane using Metlab (THT2: thiolane)

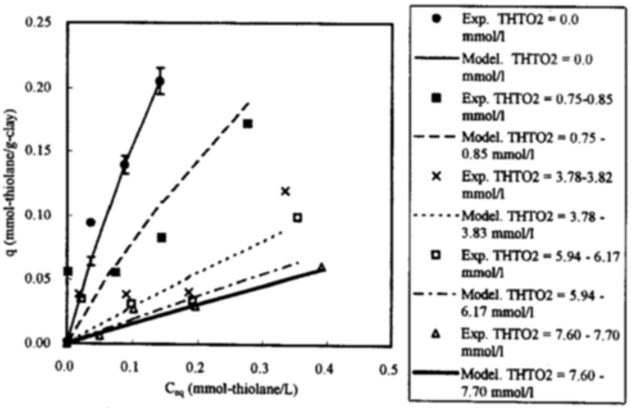

Fig. 4. Nonlinear regression of competitive adsorption of thiolane using Metlab in presence of sulfolane (THTO2 : sulfolane).

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

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/*l*] ;

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 above equation can be rearranged to determine Q and k by plotting 1/q against $1/C_{eq}$ in the following form :

$$\frac{1}{q}=\frac{1}{Q}+\frac{1}{(kQ)}\frac{1}{C_{eq}} \qquad (2)$$

The Langmuir isotherm has often been used to describe competitive adsorption effects of organic species. Srivastava and Tyagi [1995] employed a modified Langmuir isotherm [Butler and Ockrent, 1936] to evaluate the competitive adsorption of substituted phenol compounds on a converted carbonaceous adsorbent material :

$$q_i=\frac{Qk_iC_{eq_i}}{1+k_1C_{eq_1}+k_2C_{eq_2}} \qquad (3)$$

where Q, k_1 (thiolane in presense of sulfolane vice versa) and k_2 (thiolane in presense of sulfolane vice versa) are determined from single solute adsorption tests and C_{eq1} and C_{eq2} are the aqueous equilibrium concentrations of the competing solutes.

In order to justify the parameters, such as Q, k_1, and k_2, for a competition isotherm to describe the adsorption trends, a nonlinear regression using Matlab (The Math Works, Inc., USA) is presented by employing Eq. (3). Evidence of competition indicates that the adsorbates are attracted to the same adsorption sites. This suggests that molecular attractions rather than electrostatic interactions dominate the adsorption of sulfolane and that both solutes compete for uncharged surface sites.

3. Nonlinear Regression

A more empirical approach was performed using Matlab (The Math Works, Inc., USA) to obtain more accurate parameters such as Q, k_1 and k_2. As expected, the parameters, Q_1 and k_1, can be adjusted to obtain a good fit for both solutes against observed data as shown in Figs. 3 and 4.

The parameters were obtained as presented in Table 1 :

Table 1. Estimated parameters of Q, k_1, and k_2

	Q (mmol/100 g)	k_1 (L/mmol)	k_2 (L/mmol)
Sulfolane	1.863	0.102	0.953
Thiolane	1.662		
Sulfolane/Thiolane	1.291	0.026	1.468
Thiolane/Sulfolane	0.872	1.403	2.179
Thiolane+Sulfolane	1.291	0.116	0.450

*Sulfolane/Thiolane : Sulfolane in presence of thiolane
Thiolane/Sulfolane : Thiolane in presence of sulfolane
Thiolane+Sulfolane : combined
k_1 : constants for sulfolane, k_2 : constants for thiolane

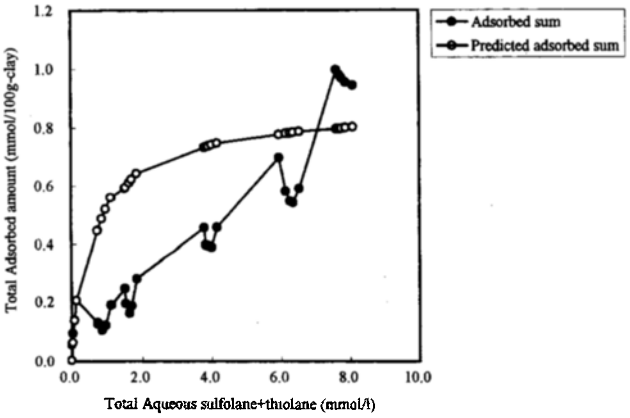

Fig. 5. Total adsorbed sulfolane+thiolane (combined) against observed total adsorbed sulfolane+thiolane (combined) on clay.

The maximum number of moles (Q) for the sulfolane/thiolane and combined data is the same. It simply means that the sulfolane data dominates the fitting routine simply because the concentrations of sulfolane are much greater than thiolane in the experiments. However, the k_1 value for sulfolane/thiolane is smaller than the k_2 value for thiolane/sulfolane that reflects that thiolane is more strongly adsorbed than sulfolane.

The estimated results for bi-solute system and combined data were plotted against the observed values as shown in Figs. 3, 4 and 5. Adsorption of sulfolane are not greatly influenced by varying concentrations of thiolane, while thiolane is greatly affected by the presence of sulfolane. It simply means that the bisolute system employed in this experiment was simulated to the analytical results obtained from field survey where sulfolane exists as approximately two order of magnitude higher concentration than that of thiolane. The experiment was initially designed to assess the effect of hydrophilicity of solutes on clay when they are present together, as sulfolane is much more polar than thiolane. As expected, thiolane could be more attracted onto clay while sulfolane more greatly solvates into water. However, thiolane (Fig. 4) is more sensitively varied for a range of concentrations of sulfolane due to biased concentrations of solutes. Fig. 5 presents that total amount adsorbed onto soil was not fitted with the estimated one. The discrepancy occurred from the regression can be postulated that solutes are supposed to adsorb into different adsorption sites on clay particles such as soil organic carbon (0.21 %) and mineral surface. Karickhoff [1984] has attempted to interpret organic carbon sites blockage, which layered on mineral sorption sites. In the bisolute system, a nonpolar compound can be adsorbed onto the organic carbon sorption sites and subsequently suppress mineral sorption sites which may be attracted by sulfolane molecules as Lorprayoon and Condrate [1981] demonstrated.

As the amount of thiolane was increased, thiolane repels more competitively the sulfolane molecules, which result in the reduction of total amount of adsorbates. Moreover, the observed plot for no-addition of thiolane keeps higher peaks through the whole range of summed values as presented in Fig. 5.

CONCLUSIONS

Thiolane is more strongly adsorbed onto clay materials than sulfolane. Thiolane is a nonpolar 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. A more empirical approach would be to readjust the adsorption parameters, Q, k_1 and k_2, to optimise the fit of the competitive isotherm to the data. This involves nonlinear regression analysis. The development of these approaches would form an extension to this study.

For regression of bi-solute system using Matlab, the k_1 value (sulfolane) is smaller than the k_2 value (thiolane) which reflects that thiolane is more strongly adsorbed than sulfolane. This is well consistent with the result obtained from single solute system. The maximum number of moles (Q) for both sulfolane and combined data is the same that implies that the sulfolane data is dominantly fitted because the concentrations of sulfolane are much greater than thiolane in the experiments. Through subsequent regression of combined data, the suppression of sulfolane adsorption on clay was also observed by varying concentration of thiolane

NOMENCLATURE

C_{eq}, C_{eq1}, C_{eq2} : aqueous equilibrium concentration
k, k_1, k_2 : equilibrium constant
q : number of moles of solute adsorbed per unit weight of adsorbent in equilibrium with solute concentration
Q : maximum number of moles of solute adsorbed as a monolayer per unit weight of adsorbent

REFERENCES

Afifi, A. F. and Abdulla, M. E., "Effect of the Insecticide Thiolane on the Spore-Germinating Potentialities of Artemisia Vulgaris Phyllospheric Fungi," *Egypt. J. Bot.*, **20**, 121 (1977).

Bradley, W. F., "Molecular Associations between Montmorillonite and Some Polyfunctional Organic Liquids," *J. Amer. Chem. Soc.*, **67**, 975 (1945).

Bradstreet, J. W., Duffee, R. A. and Zoldak, J. J., "Quantification of Odours from Waste Sites," The 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21, 85-79.4 (1985).

Butler, J. A. V. and Ockrent, C., "Studies in Electro-Capillarity," *J. Phys. Chem.*, **34**, 2841 (1930).

Carlucci G., Airoldi L. and Fanelli R., "Analysis of Tetrahydrothiophene in Water by Headspace High-Resolution Gas Chromatography-Mass Spectrometry," *J. Chrom.*, **287**, 425 (1984).

Chapman and Hall, "Dictionary of Organic Compounds," Electronic Publishing Division, London (1996).

Choo, J.-O., Yeo, Y.-K., Kim, M.-K., Kim, K.-S., Chang, K.-S., "Modeling and Simulation of a Sulfolane Extraction Process," *Korean J. Chem. Eng.*, **15**, 90 (1998).

Coy, C. A., "Regulation and Control of Air Contaminants during Hazardous Waste Site Remediation," The 80th Annual Meeting of the Air Pollution Control Association, New York, June 21-26, 87-18.1 (1987).

Davis, J. W., Klier, N. J. and Carpenter, C. L., "Natural Biological Attenuation of Benzene in Ground Water beneath a Manufacturing Facility," *Ground Water*, **32**, 215 (1994).

ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals), "Existing Chemicals : Literature Reviews and Evaluations Technical Report," Brussels, **30**, 1994. Environmental Protection, "The Environmental Protection (Prescribed Processes and Substances) Regulations 1991," no. 472, part 1/section 2, London : HMSO (1994).

Federal Register (EPA), "Twenty-Seventh Report of the Interagency Testing Committee to the Administrator ; Receipt of Report and Request for Comments Regarding Priority List of Chemicals," **56**, 9534 (1991).

Greene-Kelly, R., "Sorption of Aromatic Organic Compounds by Montmorillonite. I. Orientation Studies," *Trans. Faraday Soc.*, **51**, 412 (1955).

Gutsche, C. D. and Pasto, D. J., "Fundamentals of Organic Chemistry," Prentice-Hall (1975).

Karickhoff, S. W., "Organic Pollutant Sorption in Aquatic Systems," *J. Hydraulic Eng.*, **110**, 707 (1984).

Kirk-Othmer, "Encyclopedia of Chemical Technology," 3rd ed., John Wiley & Sons (1983).

Lawrence, J. and Parsons, R., "Adsorption Isotherms in Mixed Solvent Systems," *J. Phys. Chem.*, **73**, 3577 (1969).

Lorprayoon, V. and Condrate, R. A., Sr., "Infrared Spectra of Sulfolane Adsorbed on Cation-Substituted Montmorillonites," *Clays and Clay Minerals*, **29**, 71 (1981).

Lorprayoon, V. and Condrate, R. A., Sr., "Infrared Spectra of Thiolane and Tetramethylene Sulfoxide Adsorbed on Montmorillonites," *Clays and Clay Minerals*, **31**, 43 (1983).

MacEwan, D. M. C., "Complexes of Clays with Organic Compounds," *Trans. Faraday Soc.*, **44**, 349 (1948).

Morrison, R. T. and Boyd, R. N., "Organic Chemistry," 5th ed., 1987.

Moschandreas, D. J., Jones, D. and Martinus, J., "Detection and Recognition Threshold Values of Odorants Used in the Odorization of Natural Gas," The 75th Annual Meeting of the Air Pollution Control Association, New Orleans, Louisiana, June 20-25, 82-48.4 (1982).

Schmidt, C. E. and Meyer-Schmidt, J. K., "Assessment, Monitoring from a Superfund Site Remedial Action," The 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 20-25, 85-66.2 (1985).

Schrementi, J. and Meganathan, R., "Tetrahydrothiophene 1-Oxide as an Electron Acceptor for Anaerobic Growth of Bacteria," Abstracts of the Annual Meeting of the American Society for Microbiology, The 86th Annual Meeting, Washington D. C., March 23-28, K-128 (1986).

Schrementi, J. and Meganathan, R., "A Gas Chromatographic Method for the Determination of Tetrahydrothiophene Produced by Enzymatic Reduction of Tetrahydrothiophene-1-oxide," *Microbios Letters*, **35**, 79 (1987).

Spangler, C. W., "Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, New Jersey (1980).