

# A Comparison of the IAS and Langmuir Models for Multisolute Adsorption of Organic Compounds in Soil

유기화합물들이 혼합상태에서 토양입자에 흡착하는 정도를  
IAS와 Langmuir Model을 이용한 예측비교연구

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## 요 지

여러종류의 화합물질들이 동시에 토양에 유출되었을 때 이들이 토양에 흡착하는 정도를 예측함에는 Langmuir Competitive Model과 IAS(Ideal Adsorption Model) 등이 널리 사용되고 있는데, 5개의 유기화합물질(Phenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophenol, Brucine, Thiourea)과 2종류의 토양을 이용한 흡착실험을 통해서 이 Model들의 예측도를 비교분석하였다. 흡착실험은 이 화합물질들이 독자적인 상태에서 그리고 혼합상태에서 각각 구분하여 실험하였다. 일반적으로 IAS Model이 Langmuir Model보다 혼합상태에서 각 구성 화합물질들의 흡착을 더 정확히 예측하였다. Langmuir Model은 Phenol과 함께 섞여있는 다른물질의 농도가 높을 때 Phenol의 흡착을 낮게 예측하였다. 두가지 Model 모두 Thiourea가 혼합상태에 있을때 흡착정도를 만족스럽게 예측하지 못했는데 Thiourea는 Aliphatic화합물이고 나머지 4개는 Aromatic화합물이다.

## Abstract

The Langmuir competitive model and the IAS(ideal adsorption solution) model were evaluated and compared in a multisolute adsorption study using five organic compounds (phenol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol, brucine, and thiourea) and two soils. The chemicals were evaluated individually and in mixtures. In general, the IAS model predicted the equilibrium concentration of a chemical in a mixture better than the Langmuir model. The Langmuir model underestimated the sorption of phenol when the concentration of another compound in a mixture with phenol was high. Neither of the models predicted satisfactorily the equilibrium concentration of thiourea in the mixtures. Thiourea is an aliphatic compound while the other four chemicals are aromatic compounds.

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## 1. INTRODUCTION

When organic pollutants are introduced to soil as a mixture, the adsorption of an individual compound in the mixture can be different from what would occur in a single solute system. Since chemical mixtures are more common in soils than a single chemical, knowledge of the sorption and equilibrium concentration characteristics of chemicals in mixtures is important. Such characteristics impact the results of transformation and transport models as well as remediation decisions. Several mathematical models have been developed to describe multisolute adsorption characteristics. The IAS and Langmuir competitive models are widely used and these two models were evaluated using batch adsorption experiments in this study.

The Langmuir competitive model was developed by Butler and Ockrent<sup>(1)</sup>. The fundamental postulate of this theory is that the greatest amount of adsorption occurs when the surface is covered completely by a single layer of adsorbed molecules. Jain and Snoeyink<sup>(2)</sup> proposed a modified version of the Langmuir model for a bisolute system. While Murin and Snoeyink<sup>(3)</sup> found that the Langmuir competitive model did fit observed data well, Fritz et al.<sup>(4)</sup> and Rao et al.<sup>(5)</sup> found that it was not satisfactory.

The Langmuir model for competitive adsorption uses two basic equations, a single solute equation and a multisolute equation, Eqs. (1) and (2), respectively.

$$q = \frac{XbC}{1 + bC}, \text{ for single solute} \quad (1)$$

$$q_i = \frac{X_i b_i C_i}{1 + \sum b_k C_k}, \text{ for multisolute} \quad (2)$$

where,  $q$ =amount adsorbed, mg/g

$C$ =solution phase concentration, mg/L

$X$ =Langmuir coefficient related to surface coverage corresponding to a monolayer of adsorbate molecules on the adsorbent surface, mg/L

$b$ =Langmuir coefficient related to adsorption energy, L/mg

$C_i$ =solution phase concentration of solute  $i$ , mg/L

$q_i$ =solid phase concentration of solute  $i$ , mg/g

$i, k=1$  to  $N$ ,  $N$ =number of adsorbate species.

The parameters  $X$  and  $b$  can be determined by the intercept and slope using Eq.(3) which is rearranged from Eq.(1).

$$\frac{1}{q} = \frac{1}{X} + \frac{1}{Xb} \frac{1}{C} \quad (3)$$

The amount of a solute that is adsorbed can be determined by Eq.(4)

$$q_i = \frac{V(C_{oi} - C_i)}{M} \quad (4)$$

where,  $C_{oi}$  = concentration of solute  $i$  before contacting soil, mg/L

$M$  = mass of soil, gram

$V$  = volume of solution, liter.

After algebraic manipulation of Eq.(2) and Eq. (4) for each adsorbate, Eq.(5) can be derived :

$$C_i = \frac{-BB_i + \sqrt{BB_i^2 - 4 AA_i CC_i}}{2AA_i} \quad (5)$$

where,  $AA_i = b_i$ ,

$$BB_i = 1 + \sum(b_k C_k) + \frac{MX_i b_i}{V} - C_{oi} b_i$$

$$CC_i = -C_{oi} \{1 + \sum(b_k C_k)\}$$

$i = 1$  to  $N$ , and

$k = 1$  to  $N$  except  $i$ .

Radke and Prausnitz<sup>(6)</sup> established a IAS model for calculating multisolute adsorption equilibria using an extension of the method of Myers and Prausnitz<sup>(7)</sup> for mixed gas adsorption to the multisolute adsorption from a dilute liquid solution. The IAS model is based on an exact formulation of the thermodynamics of adsorption from a dilute solution. After being developed by Radke and Prausnitz<sup>(6)</sup>, this model has been found by many researchers<sup>(8-14)</sup> to be satisfactory to predict equilibrium concentrations of chemicals in multisolute systems. In the IAS model, the following equations are used to predict multicomponent behavior :

$$q_T = \sum_{i=1}^N q_i \quad (6)$$

$$Z_i = \frac{q_i}{q_T} \quad (7)$$

$$\sum_{i=1}^N Z_i = 1 \quad (8)$$

$$C_i = Z_i C_i^o \quad (9)$$

$$\frac{1}{q_T} = \sum \frac{Z_i}{q_i^o} \quad (10)$$

$$\int \frac{d \ln C_i^o}{d \ln q_i^o} dq_i^o = \int \frac{d \ln C_k^o}{d \ln q_k^o} dq_k^o, \quad k=2 \text{ to } N \quad (11)$$

$$q_i = \frac{V(C_{oi} - C_i)}{M} \quad (12)$$

$$q = f(C) = K C^{\frac{1}{n}} \quad (13)$$

where,  $C_i^o$  = liquid phase concentration of a chemical in a single-solute system which

gives the same spreading pressure as that of mixture, mg/L

$q_i^0$  = corresponding  $q$  value of  $C_i^0$ , mg/g

$K$  = Freundlich isotherm constant, L/g

$n$  = Freundlich constant, dimensionless

$q_T$  = total solid phase concentration of solutes, mg/g

$Z_i$  = adsorbed concentration fraction of solute  $i$ , dimensionless

and the other notations are same as in Langmuir model. If the Freundlich isotherm equation is used to represent single solute behavior in Eq.(11), then Eq.(11) simplifies to:

$$n_i q_i^0 = n_k q_k^0, k = 2 \text{ to } N \quad (14)$$

After algebraic manipulation, the following equation for each adsorbate was derived<sup>(11)</sup> :

$$C_i = \frac{q_i}{\sum q_k} \left( \frac{\sum n_k q_k}{n_i K_i} \right)^{n_i} \text{ for } i, k = 1 \text{ to } N \quad (15)$$

## 2. Material and Methods

Five organic compounds and two different soils were used to evaluate the IAS and Langmuir competitive models with various combinations of compounds and soils in batch adsorption studies. Phenolic compounds are prevalent in the environment and can impart objectionable taste and odor to drinking water at concentration as low as 0.005 mg/L<sup>(16)</sup>. Three phenolic compounds (phenol, 2, 4-DCP, 2,4,6-TCP), and two quite different compounds, brucine, and thiourea were used in this research. Phenols are widely used in industry and these substances occur in the environment in air, groundwaters, wastewaters, and soils. Phenols show relatively greater toxicity compared to many other classes of organic compounds. Brucine is used for denaturing alcohol and oils, separating mixtures, and

Table 1. Characteristics of two soils selected

Characteristics	Texas Soil*	Mississippi Soil**
texture	fine sandy loam	sandy loam
pH(1:1 ratio of soil to water)	7.8	4.8
organic carbon(%)	3.25	0.94
CEC(meq/100g)	10.8	6.35
<u>particle size fraction(%)</u>		
sand(2~0.05mm)	61.5	68.0
silt(0.05~0.002 mm)	31.1	23.4
clay(<0.002 mm)	7.4	8.6

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as an additive to lubricants. It is very poisonous alkaloid and stimulates all portions of the central nervous system. Thiourea is used for photographic fixing agent and to remove stains from negatives. The acute oral toxicity of thiourea in most animals is of low order, and oral administration of it resulted in tumors in the liver and thyroid in rats. All of these chemicals can be toxic to human and are listed on the EPA Hazardous Waste List and Appendix IX Groundwater Monitoring List<sup>(17, 18)</sup>. Two soils were used: (a) a sandy loam from Wiggins, Mississippi, and (b) a fine sandy loam from near Austin, Texas. Physical and chemical properties of these soils are presented in Table 1.

Five data points were used to construct the adsorption isotherms and each data point resulted from four samples, one blank sample (only the chemical in solution) and the other three for the triplicated soil samples (soil with chemical in solution). The samples were shaken at 29 rpm for 24 hours and centrifuged, and the supernatant was filtered through a

Table 2. Summary of experimental procedure

Procedure	Description
samples	<ul style="list-style-type: none"> <li>• Soils which were air-dried and passed through 2-mm sieve (#10 sieve) and stock solutions of the compounds were stored at 4°C until use.</li> <li>• 50 grams of dry soil and 50 mL of solution in 120 mL glass bottle.</li> <li>• triplicated samples for each data point.</li> </ul>
solvent	<ul style="list-style-type: none"> <li>• distilled deionized water(DDW).</li> </ul>
mixing	<ul style="list-style-type: none"> <li>• 24 Hrs in rotating tumbler, 29 rpm, 25°C</li> </ul>
filtering	<ul style="list-style-type: none"> <li>• vacuum filtering with 0.45µm membrane filter.</li> </ul>
analysis	<ul style="list-style-type: none"> <li>• HPLC, Water Model 440.</li> <li>• 50µL injection.</li> <li>• eluted with 50:50.1 of acetonitrile:DDW:acetic acid.</li> <li>• UV adsorption detector wavelength of 254 nm</li> <li>• eluted solution flow rate of 3.0 mL/min.</li> <li>• attenuation varied 0.01 to 2.0 depending on compound adsorption spectra.</li> </ul>

Table 3. Experiments for single solute study

Compound(soil)	*Concentrations(ppm) Evaluated				
	a	b	c	d	e
Phenol(Texas)	1,000	2,000	3,000	6,000	10,000
Phenol(Miss.)	1,000	2,000	3,000	6,000	10,000
2,4-DCP(Texas)	20	30	130	700	2,400
2,4-DCP(Miss.)	20	70	200	200	2,500
2,4,6-TCP(Texas)	20	40	80	700	400
2,4,6-TCP(Miss.)	30	50	90	250	400
Brucine(Texas)	—	100	200	350	550
Brucine(Miss.)	30	60	100	150	300
Thiourea(Texas)	30	100	350	1,500	5,000
Thiourea(Miss.)	30	100	350	1,500	5,000

\*The initial concentration before adsorption occurs, ppm=mg compound/kg water

Table 4. Experiments for mixture study\*

Experiment	Phenol	2,4-DCP	2,4,6-TCP	Brucine	Thiourea
reference	1,000	-	-	-	-
isotherm	2,000	-	-	-	-
	3,000	-	-	-	-
	6,000	-	-	-	-
	10,000	-	-	-	-
	Mix-1	1,000	100	-	-
Mix-1	2,000	100	-	-	-
	3,000	100	-	-	-
	6,000	100	-	-	-
	10,000	100	-	-	-
	Mix-2	1,000	1,000	-	-
Mix-2	2,000	1,000	-	-	-
	3,000	1,000	-	-	-
	6,000	1,000	-	-	-
	10,000	1,000	-	-	-
	Mix-3	1,000	-	100	-
Mix-3	2,000	-	100	-	-
	3,000	-	100	-	-
	6,000	-	100	-	-
	10,000	-	100	-	-
	Mix-4	1,000	-	500	-
Mix-4	2,000	-	500	-	-
	3,000	-	500	-	-
	6,000	-	500	-	-
	10,000	-	500	-	-
	Mix-5	1,000	100	100	-
Mix-5	2,000	100	100	-	-
	3,000	100	100	-	-
	6,000	100	100	-	-
	10,000	100	100	-	-
	Mix-6	1,000	1,000	500	-
Mix-6	2,000	1,000	500	-	-
	3,000	1,000	500	-	-
	6,000	1,000	500	-	-
	10,000	1,000	500	-	-
	Mix-7	1,000	-	-	100
Mix-7	2,000	-	-	100	-
	3,000	-	-	100	-
	6,000	-	-	100	-
	10,000	-	-	100	-
	Mix-8	1,000	-	-	500
Mix-8	2,000	-	-	500	-
	3,000	-	-	500	-
	6,000	-	-	500	-
	10,000	-	-	500	-

(Table 4. continued)

Experiment	Phenol	2,4-DCP	2,4,6-TCP	Brucine	Thiourea
Mix-9	1,000	-	-	-	100
	2,000	-	-	-	100
	3,000	-	-	-	100
	6,000	-	-	-	100
	10,000	-	-	-	100
Mix-10	1,000	-	-	-	1,000
	2,000	-	-	-	1,000
	3,000	-	-	-	1,000
	6,000	-	-	-	1,000
	10,000	-	-	-	1,000
Mix-11	1,000	500	500	500	500
	2,000	500	500	500	500
	3,000	500	500	500	500
	6,000	500	500	500	500
	10,000	500	500	500	500

\*Concentrations of specific chemicals(mg chemical/kg water) used in the noted experiments.

0.45  $\mu\text{m}$  membrane filter and analyzed by HPLC. 24 hours were proved to be sufficient for equilibrium from kinetic study and degradation was assumed to be not significant during this period. A summary of the experimental procedure is presented in Table 2. The chemicals and concentrations used in the single solute and mixture studies are presented in Table 3 and 4, respectively.

Adsorption at high concentrations was of interest since it was expected that any differences in sorption would be more noticeable at these concentrations. Typical Freundlich and Langmuir isotherms for the single solute studies are presented in Figure 1, and constants of the single solute adsorption isotherms are presented in Table 5.

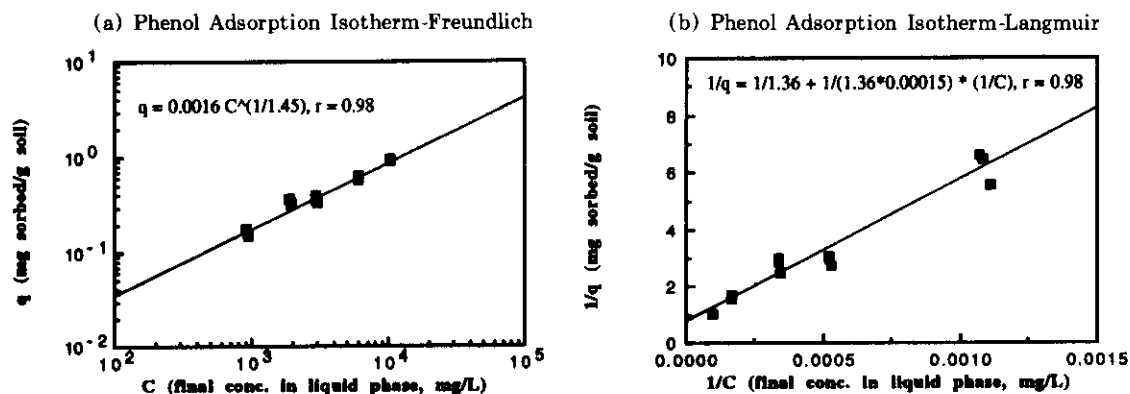


Fig 1. Freundlich (a) and Langmuir (b) Adsorption isotherms for phenol in Mississippi soil single-solute system.

Table 5. Freundlich and Langmuir constants for singlesolute system

Soil	Chemicals	Freundlich $q=KC^n$			Langmuir $=\frac{1}{X} + \frac{1}{bX} \frac{1}{C}$		
		K	n	r	X	b	r
Texas	Phenol	0.0014	1.35	0.98	1.41	0.00021	0.96
	2,4-DCP	0.0051	1.31	1.00	0.32	0.012	0.99
	2,4,6-TCP	0.0018	1.37	1.00	0.11	0.0091	0.99
	Brucine	0.14	1.37	0.99	0.35	0.93	0.89
	Thiourea	0.00027	1.19	0.99	0.15	0.0011	1.00
Miss.	Phenol	0.0016	1.45	0.98	1.36	0.00015	0.98
	2,4-DCP	0.0068	1.53	1.00	0.22	0.022	0.99
	2,4,6-TCP	0.0098	1.56	1.00	0.17	0.041	0.98
	Brucine	0.062	2.09	0.97	0.13	2.00	0.90
	Thiourea	0.00081	1.77	0.99	0.046	0.0046	0.97

\* r = correlation coefficient.

To calculate the equilibrium concentration of the compounds in mixture using the Langmuir competitive model, the Gauss-Seidel method<sup>(15)</sup> was used to solve the nonlinear simultaneous equations of Eq.(5) for each adsorbate. The needed input data were Langmuir constants for each solute from a singlesolute system -  $X_i$ (mg/L) and  $b_i$ , the volume of solution -  $V$ (liter), the mass of soil -  $M$ (gram), the initial concentration of each solute in the multisolute system -  $C_{oi}$ (mg/L), and the estimated liquid phase equilibrium concentration of each solute in the multisolute system -  $C_{i,guess}$ (mg/L). In the calculation of Eq.(5), The most appropriate estimate of  $C_{eq,i}$ , i.e.,  $C_{i,guess}$ , is used for the first calculation. In case of two compound mixture,  $C^{eq1}$ (the first subscript number indicates compound and the second one, the number of iteration) can be calculated first with initial input data in the first run. Always the latest value should be used in calculation, therefore, during the calculation of  $C_{eq21}$  in the first run,  $C_{eq11}$  should be used instead of  $C_{i,guess}$ . In the second run,  $C_{eq11}$  and  $C_{eq21}$  should be used to calculate  $C_{eq12}$ , and this  $C_{eq12}$  and  $C_{eq21}$  be used to calculate  $C_{eq22}$ . The successive iteration of Eq.(5) continues until the difference between  $C_{i,N}$  and  $C_{i,N-1}$  is less than  $10^{-5}$  mg/L. Usually less than five iterations were required. Once  $C_{eq,i}$  was determined,  $q_{eq,i}$  was calculated using Eq.(4).

For the IAS model, Eq.(16) was derived by manipulating Eq.(12) and Eq.(15) to eliminate  $C_{i(1)}$ . If  $F_i(q)$  is defined as in Eq.(16), then the root of this equation is the solution for the equilibrium state.

$$F_i(q) = F_i(q_1, q_2, \dots, q_N) = C_{oi} - \frac{M}{V} q_i - \frac{q_i}{\sum q_k} \left( \frac{\sum n_k q_k}{n_i K_i} \right)^{n_i} = 0 \quad (16)$$

where,  $q$ =vector  $q$ , which is  $(q_1, q_2, \dots, q_N)$ , and  $i, k=1$  to  $N$ . To distinguish vectors from scalars, the vectors are printed in boldface type. According to Eq.(16), the equilibrium state is determined by setting  $F_i$  equal to zero.  $N$  nonlinear simultaneous equations( $F_i$ )



with N unknown  $q_i$  values are solved by the Newton-Raphson algorithm(11, 15). The needed input data to define the equilibrium state are Freundlich constants  $K_i$  and  $n_i$  from a single-solute system, the initial concentration of each solute in the mixture system  $-C_{oi}$  (mg/L), the mass of soil  $-M$ (gram), the volume of solution  $-V$ (liter), and the estimated solid phase equilibrium concentration in mixture system  $-q_{i, guess}$  (mg/g). To solve the equation, let  $q_{new}$  be equal to the new guess of  $(q_1, q_2, \dots, q_N)^T$  and  $F$  be equal to  $(F_1, F_2, F_3, \dots, F_N)^T$  as transpose matrices. The  $q_{new}$  can be calculated by Eq.(17) from the second run, and the first  $q_{new}$  is the estimated  $q$  value of the input data,  $q_{i, guess}$ .

$$q_{new} = q_{old} + \Delta q \quad (17)$$

$$f(q)_{old} \Delta q = -F_{old} \quad (18)$$

Where (a) the matrix  $f(q)$  is defined with each derivatives,  $f_{ij}(q) = \partial F_i(q) / \partial q_j$ , (b)  $q_{new}$  and  $q_{old}$  are the new and old  $q$  guesses to Eq.(16), and (c)  $F_{old}$  is the numerical value of Eq. (16) which is evaluated at  $q_{old}$ . The increment,  $\Delta q$ , is a solution vector of Eq.(18) which can be solved by Cramer's rule<sup>(15)</sup>. In case of a three-component mixture system, a 3x3 matrix can be defined as

$$A(q) = \begin{vmatrix} \underline{\partial F_1 / \partial q_1} & \partial F_1 / \partial q_2 & \partial F_1 / \partial q_3 \\ \partial F_2 / \partial q_1 & \underline{\partial F_2 / \partial q_2} & \partial F_2 / \partial q_3 \\ \partial F_3 / \partial q_1 & \partial F_3 / \partial q_2 & \underline{\partial F_3 / \partial q_3} \end{vmatrix}$$

The off-diagonal elements of the matrix  $A(q)$  are

$$\frac{\partial F_i(q)}{\partial q_k} = \frac{q_i}{(\Sigma q_j)^2} \left( \frac{\Sigma n_j q_j}{n_i K_i} \right)^{n_i} - \frac{q_i n_i n_k}{\Sigma q_j} \frac{(\Sigma n_j q_j)^{n_i-1}}{(K_i n_i)^{n_i}} \quad (19)$$

The diagonal elements (underlined) of the matrix  $A(q)$  are

$$\frac{\partial F_i(q)}{\partial q_i} = -\frac{M}{V} - \frac{1}{\Sigma q_j} \left( \frac{\Sigma n_j q_j}{n_i K_i} \right) + \frac{q_i}{(\Sigma q_j)^2} \left( \frac{\Sigma n_j q_j}{n_i K_i} \right)^{n_i} - \frac{q_i n_i^2}{\Sigma q_j} \frac{(\Sigma n_j q_j)^{n_i-1}}{(n_i K_i)^{n_i}} \quad (20)$$

where,  $i, j$  and  $k=1$  to  $N$  for Eq.(19) and Eq.(20). Eq.(18) can be rewritten in the form of polynomial as below, and Eqs.(21), (22), and (23) can be solved using Cramer's rule to find the  $\Delta q$  as mentioned above.

$$\frac{\partial F_1}{\partial q_1} \Delta q_1 + \frac{\partial F_1}{\partial q_2} \Delta q_2 + \frac{\partial F_1}{\partial q_3} \Delta q_3 = -F_1 \quad (21)$$

$$\frac{\partial F_2}{\partial q_1} \Delta q_1 + \frac{\partial F_2}{\partial q_2} \Delta q_2 + \frac{\partial F_2}{\partial q_3} \Delta q_3 = -F_2 \quad (22)$$

$$\frac{\partial F_3}{\partial q_1} \Delta q_1 + \frac{\partial F_3}{\partial q_2} \Delta q_2 + \frac{\partial F_3}{\partial q_3} \Delta q_3 = -F_3 \quad (23)$$

To implement this algorithm, one must start with an initial value of  $q_{\text{guess}}$  and improve the guess using Eq. (16), (17), (18), (19), and (20) until Eq.(16) is satisfied. Usually less than 10 iterations were required to obtain greater than  $10^{-5}$ (mg/L) precision in the roots of Eq.(16).

### 3. Results and Discussion

In this study, the evaluation and comparison of the two models was done first by using the phenol adsorption data from the single solute and the mixture experiments. The averaged phenol adsorption data of the triplicates for each data point in the mixtures are compared with the predicted equilibrium concentration by the IAS and Langmuir competitive models in Table 6. the experimental  $q_{\text{phenol}}$  for the mixtures was calculated with the difference between the  $C_{i, \text{phenol}}$  and the  $C_{oi, \text{phenol}}$  in the mixture using Eq.(4). The predicted equilibrium concentration was calculated using the Freundlich and Langmuir constants for single solute system.

Table 6. (a) Phenol adsorption data—Mississippi Soil unit : mg sorbed/g soil

*		Data Point(ppm)—Texas Soil				
Experiment #		1,000	2,000	3,000	6,000	10,000
Mix.1	Exp.	0.191	0.312	0.306	0.541	0.748
	Lang.	0.137	0.236	0.294	0.473	0.736
	IAS	0.181	0.300	0.377	0.629	0.972
Mix.2	Exp.	0.176	0.353	0.396	0.513	1.174
	Lang.	0.017	0.034	0.044	0.069	0.145
	IAS	0.138	0.260	0.337	0.588	0.955
Mix.3	Exp.	0.168	0.348	0.348	0.441	0.571
	Lang.	0.118	0.226	0.273	0.414	0.592
	IAS	0.177	0.325	0.391	0.617	0.847
Mix.4	Exp.	0.147	0.206	0.351	0.485	1.698
	Lang.	0.025	0.036	0.051	0.127	0.159
	IAS	0.151	0.236	0.344	0.591	0.758
Mix.5	Exp.	0.122	0.256	0.233	0.448	0.689
	Lang.	0.087	0.137	0.181	0.249	0.439
	IAS	0.169	0.262	0.350	0.608	0.916
Mix.6	Exp.	0.094	0.109	0.145	0.292	1.932
	Lang.	0.0076	0.014	0.019	0.085	0.066
	IAS	0.103	0.187	0.259	0.494	0.849
Mix.7	Exp.	0.139	0.286	0.310	0.662	0.625
	Lang.	0.067	0.126	0.159	0.244	0.302
	IAS	0.143	0.266	0.355	0.635	0.978

Mix.8	Exp.	0.162	0.310	0.379	0.623	0.715
	Lang.	0.0012	0.0025	0.0037	0.0076	0.0126
	IAS	0.119	0.237	0.340	0.631	1.000
Mix.9	Exp.	0.145	0.196	0.299	0.426	0.496
	Lang.	0.137	0.247	0.336	0.547	0.731
	IAS	0.186	0.305	0.403	0.665	0.971
Mix.10	Exp.	0.189	0.228	0.269	0.406	0.689
	Lang.	0.050	0.090	0.125	0.305	0.463
	IAS	0.192	0.308	0.399	0.661	1.017
Mix.11	Exp.	0.117	0.206	0.178	0.426	0.651
	Lang.	0.00011	0.00039	0.00036	0.00107	0.00110
	IAS	0.056	0.106	0.158	0.324	0.525

\*Exp.= experimental data, Lang.=predicted by the Langmuir model, IAS=predicted by the IAS model.

Table 6. (b) Phenol adsorption data—Texas Soil

unit : mg sorbed/g soil

* Experiment #		Data Point(ppm)—Texas Soil				
		1,000	2,000	3,000	6,000	10,000
Mix.1	Exp.	0.088	0.160	0.273	0.822	0.731
	Lang.	0.103	0.168	0.261	0.457	0.603
	IAS	0.123	0.204	0.313	0.581	0.825
Mix.2	Exp.	0.114	0.196	0.467	0.940	0.547
	Lang.	0.023	0.040	0.066	0.128	0.190
	IAS	0.135	0.227	0.375	0.716	1.061
Mix.3	Exp.	0.181	0.352	0.534	0.820	1.444
	Lang.	0.184	0.336	0.434	0.577	0.893
	IAS	0.228	0.415	0.536	0.833	1.611
Mix.4	Exp.	0.235	0.293	0.446	0.933	1.308
	Lang.	0.090	0.139	0.197	0.379	0.453
	IAS	0.231	0.354	0.512	0.853	1.255
Mix.5	Exp.	0.202	0.319	0.395	0.721	1.359
	Lang.	0.153	0.215	0.302	0.501	0.740
	IAS	0.217	0.431	0.472	0.804	1.530
Mix.6	Exp.	0.204	0.277	0.358	0.820	1.766
	Lang.	0.030	0.063	0.074	0.144	0.269
	IAS	0.169	0.308	0.408	0.754	1.516
Mix.7	Exp.	0.186	0.284	0.394	0.852	1.066
	Lang.	0.198	0.336	0.430	0.678	0.840
	IAS	0.218	0.366	0.482	0.901	1.308
Mix.8	Exp.	0.179	0.314	0.421	0.736	1.557
	Lang.	0.096	0.175	0.254	0.393	0.453
	IAS	0.200	0.356	0.471	0.837	1.315
Mix.9	Exp.	0.161	0.339	0.423	0.865	1.362
	Lang.	0.167	0.377	0.481	0.752	0.957
	IAS	0.179	0.308	0.492	0.877	1.367

Mix.10	Exp.	0.146	0.322	0.468	0.855	1.556
	Lang.	0.109	0.255	0.355	0.615	0.841
	IAS	0.172	0.367	0.510	0.879	0.430
Mix.11	Exp.	0.187	0.258	0.292	0.473	0.749
	Lang.	0.00029	0.00069	0.00132	0.00305	0.00407
	IAS	0.054	0.098	0.155	0.337	0.572

\*Exp.= experimental data, Lang.=predicted by the Langmuir model, IAS=predicted by the IAS model.

combinations except Mix. 11. The predictions by the IAS model was slightly lower than the experimental data in Mix. 11 in both soils. Mix.11 was a mixture of the five compounds in high concentrations(Table 4). The Langmuir competitive model, generally underestimated the adsorption of phenol compared to the experimental data. This trend was more distinct when the concentrations of the added compounds was high such as Mix 2,4,6,8,10, and 11 (Table 4) in both soils. The worst prediction occurred with Mix. 6 and 11. Mix.6 was a mixture of three compounds, Mix.11 was a mixture of five compounds, and the others were mixtures of two compounds. As the number of the compounds in mixture increased, a poorer prediction was observed.

Figure 2 indicates the predictions of phenol adsorption by the IAS and Langmuir competitive models and experimental data for several mixtures. As the data in Table 6 indicated the prediction of phenol adsorption in mixtures by the Langmuir competitive model was slightly lower than the experimental data when the concentration of the added compound was low(Figure 2a), however, the prediction was far lower than the experimental data when the concentration of the added compound was high(Figure 2b). The prediction by the IAS model was close to the experimental data for both (a) and (b). This trend was consistent for almost all the mixtures in both soils.

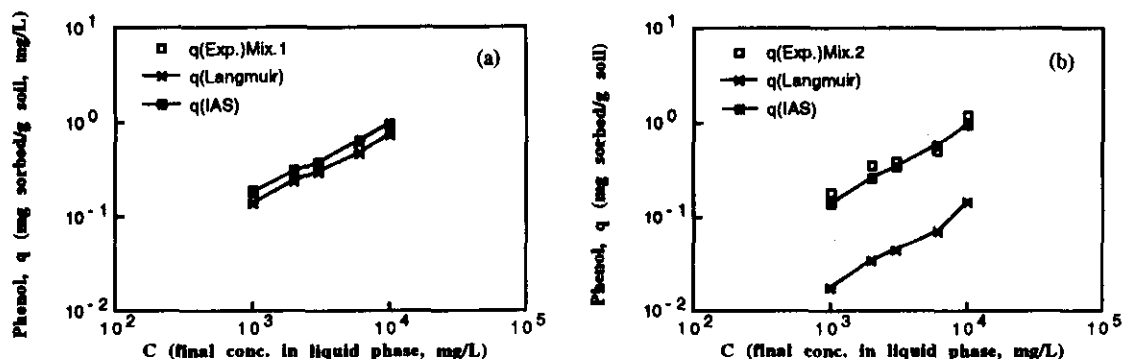


Fig 2. Experimental and predicted data by the Langmuir and IAS models for (a) phenol adsorption in Mix. 1 (phenol+100ppm of 2,4-DCP) and (b) phenol adsorption in Mix. 2 (phenol+1,000 ppm of 2,4-DCP) in Mississippi soil.

The IAS model, generally, was satisfactory for almost all the soil-compound

In the same way, the  $q$  values of the added compounds(2,4-DCP, 2,4,6-TCP, brucine, and thiourea) in the mixtures were compared to the equilibrium concentrations predicted by the IAS and Langmuir competitive models. The  $q_i(\text{Exp.})$  of each compound was calculated with the difference between the  $C_{oi}$  and  $C_i$  of each compound in the mixtures using Eq(4). The results are presented in Table 7. In general, the IAS model predicted the equilibrium concentration of 2,4-DCP, 2,4,6-TCP, and brucine in the mixture better than the Langmuir competitive model. The Langmuir competitive model predicted well when the concentration of 2,4-DCP, 2,4,6-TCP, and brucine was low (Mix.1, 3, 5, and 7), but it underestimated the adsorption when the concentration of added chemicals was high(Mix.2, 4, 6, and 11). Neither models predicted satisfactorily the equilibrium concentration of thiourea in the mixture system. Thiourea is an aliphatic compound while the other four chemicals are aromatic compounds.

Table 7. Multisolute adsorption data for 2,4-DCP, 2,4,6-TCP Brucine, and Thiourea-experiment, Langmuir, IAS.

Experiment #	Data Point(ppm) - Texas Soil					Data Point(ppm) - Mississippi Soil				
	1,000	2,000	3,000	6,000	10,000	1,000	2,000	3,000	6,000	10,000
<b>2,4-DCP</b>										
exp.	0.083	0.081	0.074	0.072	0.064	0.057	0.056	0.057	0.047	0.044
Mix.1 Lang.	0.089	0.086	0.084	0.077	0.068	0.064	0.064	0.066	0.059	0.030
IAS	0.077	0.072	0.070	0.065	0.059	0.083	0.081	0.074	0.072	0.064
<b>Mix.2</b>										
Exp.	0.599	0.594	0.600	0.622	0.581	0.517	0.445	0.445	0.573	0.403
Lang.	0.283	0.280	0.276	0.264	0.252	0.205	0.202	0.201	0.200	0.185
IAS	0.598	0.584	0.592	0.573	0.557	0.368	0.3481	0.346	0.372	0.277
<b>Mix.5</b>										
Exp.	0.050	0.052	0.053	0.050	0.052	0.040	0.041	0.041	0.040	0.033
Lang.	0.047	0.048	0.049	0.043	0.036	0.047	0.047	0.047	0.043	0.039
IAS	0.042	0.043	0.044	0.039	0.038	0.037	0.036	0.034	0.030	0.027
<b>Mix.6</b>										
Exp.	0.485	0.309	0.439	0.417	0.434	0.293	0.254	0.282	0.263	0.270
Lang.	0.168	0.157	0.164	0.156	0.142	0.091	0.090	0.090	0.088	0.084
IAS	0.406	0.330	0.397	0.369	0.358	0.287	0.282	0.282	0.264	0.246
<b>Mix.11</b>										
Exp.	0.276	0.239	0.213	0.215	0.286	0.176	0.199	0.128	0.131	0.210
Lang.	0.0023	0.0021	0.0024	0.0024	0.0026	0.0010	0.0011	0.0011	0.0011	0.0011
IAS	0.123	0.110	0.112	0.106	0.143	0.101	0.097	0.096	0.087	0.103
<b>2,4,6-TCP</b>										
Exp.	0.023	0.026	0.017	0.047	0.031	0.066	0.064	0.065	0.059	0.058
Mix.3 Lang.	0.028	0.028	0.024	0.027	0.017	0.067	0.066	0.065	0.061	0.052
IAS	0.017	0.016	0.014	0.017	0.012	0.055	0.051	0.049	0.044	0.036
<b>Mix.4</b>										
Exp.	0.120	0.108	0.084	0.091	0.108	0.251	0.267	0.272	0.193	0.221
Lang.	0.075	0.074	0.072	0.057	0.058	0.151	0.153	0.152	0.139	0.139
IAS	0.080	0.077	0.075	0.052	0.062	0.214	0.230	0.233	0.167	0.183

Table 7. continued

Experiment #	Data Point(ppm) - Texas Soil					Data Point(ppm) - Mississippi Soil				
	1,000	2,000	3,000	6,000	10,000	1,000	2,000	3,000	6,000	10,000
Mix.5 Exp.	0.021	0.062	0.051	0.036	0.056	0.058	0.061	0.064	0.063	0.060
Mix.5 Lang.	0.029	0.060	0.047	0.037	0.048	0.062	0.063	0.064	0.059	0.056
Mix.5 IAS	0.017	0.024	0.020	0.015	0.016	0.052	0.050	0.050	0.044	0.040
Mix.6 Exp.	0.0032	0.017	0.030	0.000	0.000	0.235	0.238	0.263	0.217	0.266
Mix.6 Lang.	-0.220	-0.131	-0.221	-0.218	-0.226	-0.045	-0.044	-0.049	-0.051	-0.062
Mix.6 IAS	0.060	0.060	0.058	0.053	0.056	0.213	0.214	0.214	0.204	0.218
Mix.11 Exp.	0.000	0.000	0.000	0.0077	0.0061	0.037	0.020	0.034	0.087	0.237
Mix.11 Lang.	-0.376	-0.351	-0.285	-0.160	-0.056	-0.333	-0.344	-0.296	-0.149	-0.033
Mix.11 IAS	0.0047	0.0022	0.0062	0.0013	0.0029	0.027	0.014	0.028	0.067	0.130
<u>Brucine</u>										
Mix.7 Exp.	0.060	0.056	0.055	0.055	0.046	0.081	0.079	0.081	0.082	0.085
Mix.7 Lang.	0.061	0.056	0.056	0.055	0.047	0.081	0.079	0.081	0.081	0.083
Mix.7 IAS	0.033	0.028	0.025	0.021	0.016	0.080	0.076	0.076	0.074	0.073
Mix.8 Exp.	0.192	0.198	0.176	0.165	0.187	0.233	0.226	0.226	0.229	0.231
Mix.8 Lang.	0.220	0.208	0.183	0.175	0.188	0.125	0.125	0.125	0.124	0.124
Mix.8 IAS	0.112	0.097	0.081	0.067	0.063	0.217	0.211	0.208	0.201	0.192
Mix.11 Exp.	0.747	0.683	0.595	0.612	0.747	0.520	0.522	0.325	0.297	0.482
Mix.11 Lang.	0.353	0.352	0.352	0.352	0.352	0.134	0.133	0.133	0.132	0.134
Mix.11 IAS	0.881	0.838	0.786	0.736	0.792	0.836	0.761	0.743	0.661	0.761
<u>Thiourea</u>										
Mix.9 Exp.	0.0064	0.0060	0.0049	0.0037	0.0030	0.011	0.014	0.013	0.014	0.012
Mix.9 Lang.	0.011	0.0094	0.0084	0.0063	0.0044	0.012	0.011	0.0099	0.0079	0.0062
Mix.9 IAS	0.033	0.028	0.025	0.021	0.016	0.080	0.076	0.076	0.074	0.073
Mix.10 Exp.	0.0093	0.0097	0.0092	0.0076	0.0092	0.076	0.056	0.054	0.049	0.048
Mix.10 Lang.	0.065	0.057	0.053	0.034	0.025	0.035	0.034	0.033	0.025	0.022
Mix.10 IAS	0.055	0.047	0.045	0.031	0.029	0.013	0.0099	0.0082	0.0035	0.0036
Mix.11 Exp.	0.06	0.064	0.045	0.035	0.060	0.038	0.057	0.040	0.022	0.022
Mix.11 Lang.	-0.038	0.021	0.011	-0.090	-0.175	-0.027	0.020	0.018	-0.099	-0.188
Mix.11 IAS	0.0083	0.0084	0.0084	0.0058	0.0067	0.0011	0.0012	0.0011	0.0007	0.0061

\*Exp.-experimental data ; Lang. and IAS-predicted by Langmuir competitive model and IAS model, respectively

The differences in the experimental data for the individual compounds in Mix.11 with the predicted values by the IAS and Langmuir models are illustrated in Figure 3. Mix. 11 was a mixture of five compounds in high concentration (Table 4). A comparison for thiourea is excluded since neither models satisfactorily predicted the sorption of thiourea in mixtures. Thiourea is an aliphatic compound and thus has much lower  $K_{oc}$  (organic carbon partition coefficient) value than other aromatic compounds, therefore, less adsorption onto soil was assumed than others. Significantly low adsorption capacity might affect general adsorption theory in mixtures that prediction of thiourea adsorption by these models can be limited.

This effect could be expected by comparing K values in Table 5. The prediction by IAS model was close to the experimental data of adsorption for phenol, 2,4-DCP, 2,4,6-TCP, and brucine than that of the Langmuir model. Figure 3(c) shows the experimental and the IAS data only because the Langmuir prediction shows negative adsorption value which is not realistic. The Langmuir model underestimated the sorption of all the individual compounds in the mixture compared to the experimental data.

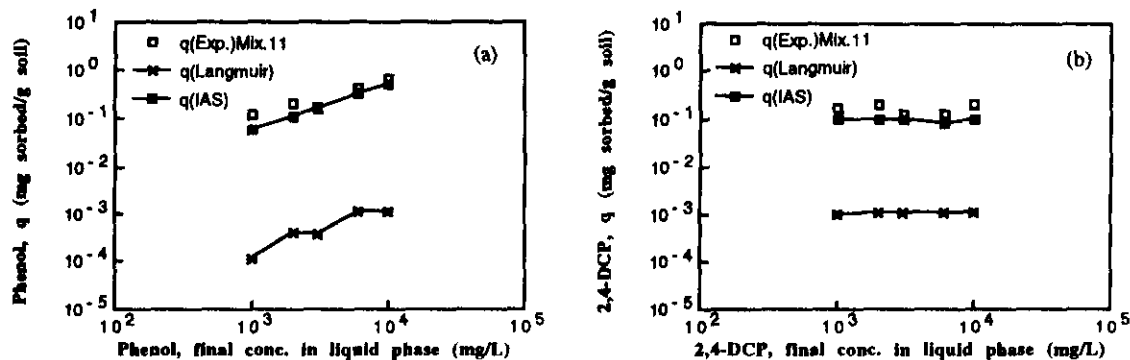


Fig 3. A comparison of the experimental data of the compounds ((a) : phenol and (b) : 2, 4-DCP) in Mix. 11, Mississippi soil, to the predicted values by IAS and Langmuir models.

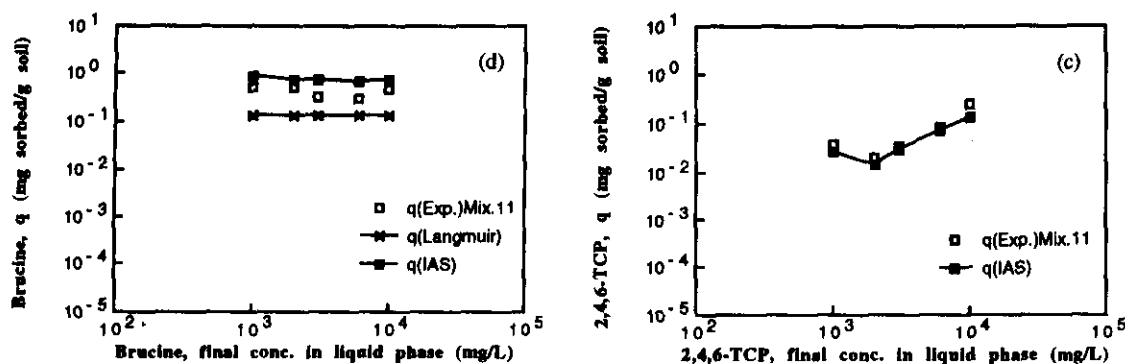


Fig 3. (continued)

A comparison of the experimental data of the compounds ((c) : 2, 4, 6-TCP and (d) : Brucine) in Mix. 11, Mississippi soil, to the predicted values by IAS and Langmuir models.

#### 4. Conclusion

- (1) The IAS model, in general, predicted the equilibrium concentration of the compounds in mixtures better than the Langmuir competitive model.
- (2) Even though the IAS model was developed based on ideal adsorption theory in dilute

solutions and nonidealities were expected in mixtures with high concentrations, it predicted phenol adsorption closely for all the concentrations used in this research, including high concentrations(1,000~10,000 mg/L).

- (3) The Langmuir competitive model underestimated the phenol adsorption in mixtures compared to the experimental data, and this trend was greater when the concentration of the added compound(s) was high.
- (4) When the concentration of the added compounds was high, there was more underestimation observed in phenol adsorption as the number of the compounds increased.
- (5) Neither of the models satisfactorily predicted the sorption of thiourea in mixtures. Thiourea is an aliphatic compound while the other four chemicals are aromatic compounds.
- (6) For 2,4-DCP, 2,4,6-TCP, and brucine in mixtures, the Langmuir competitive model predicted the sorption well when the concentration of these three chemicals was low (Mix. 1,3,5, and 7). However, the Langmuir model underestimated the sorption when the concentration of these chemicals was high(Mix.2,4,6, and 11).

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