

지반오염물질의 흡에 대한 흡착특성

Adsorption Characteristics of Contaminants on Test Soil

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개요(SYNOPSIS) : 흡착현상은 오염물질의 지반내 거동에 영향을 준다. 본 연구에서는 흡속의 고유유기물 함량에 따른 오염물질의 흡착특성을 알아 보았다. 회분식 실험을 실시한 결과, 페놀 20mg/L 용액은 유기탄소함량이 0.34%인 흙에서 분배계수가 0.15, 유기탄소함량이 2.50%인 흙에서는 분배계수 0.57을 나타내어 고유유기물 함량과 오염물질의 흡착량이 선형성을 보였다. 고유유기물량이 증가함에 따라 오염물질의 지반내 이동의 지표가 되는 저감계수도 크게 증가하였다.

주요어(Key Words) : Adsorption, Contaminants, Distribution Coefficient, Organic-Carbon Content, Organic-Carbon Partition Coefficient.

1. Introduction

Adsorption is the process in which chemical compounds become associated with solid phase, which includes primarily clay minerals, indigenous soil organic matter, and amorphous oxides-hydroxides of metals. Adsorption is extremely important because it may affect the fate and impact of chemicals in the environment. Adsorption processes can be driven by a variety of forces and mechanisms as follows(Park et al., 1996); (1)hydrophobic sorption, (2)hydrogen bonding, (3)ion exchange, (4)physical adsorption, (5)coordination, and (6)chemisorption.

One of the most important characteristics of an adsorbent is the quantity of adsorbate that it can accumulate. The constant temperature equilibrium relationship between the mass of adsorbate per adsorbent, X/M , and the equilibrium concentration of adsorbate in solution C_e is called the *adsorption isotherm*. The most common equation is the Freundlich equation, which has the form,

$$X/M = KC_e^{1/n} \quad (1)$$

and can be linearized as

$$\log(X/M) = \log K + 1/n \log C_e \quad (2)$$

If the slope of the Freundlich isotherm, $1/n$, is found to be equal to 1, then the isotherm is said to be linear and the Freundlich coefficient K is identical to the distribution coefficient K_d . The constant K is related to the capacity of the adsorbent to sorb the compound, and $1/n$ is a function of the strength of adsorption.

Some dissolved contaminants may interact with the soil solids encountered along the flow path through adsorption, ion exchange, and other processes. These interactions result in the contaminants' distribution between the aqueous phase and the solids, diminution of concentration in the aqueous phase, and *retardation* of the movement of the contaminant relative to groundwater flow (Mackay and Roberts, 1985). The higher the fraction of the contaminant adsorbed, the more retarded is its transport (Freeze and Cherry, 1979). The retardation factor, R , is expressed as

$$R = 1 + (\rho K_d)/n_e = 1 + (1-n)\rho_s K_d/n = V/V_c \quad (3)$$

where ρ is soil bulk density, K_d is the distribution coefficient, n_e is effective porosity, n is porosity, ρ_s is solid particle density, V is average linear pore water velocity, and V_c is average velocity of the retarded constituent. To get the R value, the determination of K_d is essential to the evaluation of the mobility of compounds in the water.

Schwarzenbach and Westall (1981) elucidated the sorption behavior of organic compounds in soil through lab batch and column tests. They found that linearity of isotherms can be used for low concentrations, as $S = K_d C$, where S is concentration in the solid phase and C is concentration in the liquid phase. If the organic-carbon content in the soil, f_{oc} , is larger than 0.001, $K_d = f_{oc} K_{oc}$, where K_{oc} is the organic-carbon partition coefficient. They suggested that

$$\log K_{oc} = 0.72 \log K_{ow} + 0.49 \quad (4)$$

where K_{ow} is the octanol-water partition coefficient. The values of f_{oc} and K_{ow} are available in the literature. Through these relationships, the distribution ratio in water and soil for a certain contaminant was easily found, and the retardation factor was also found from (3) for a certain contaminant in groundwater contamination.

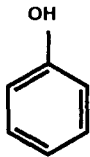
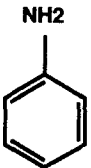
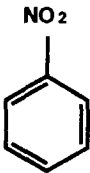
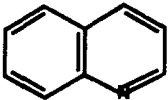
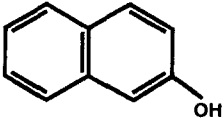
2. Materials and Methods

Natural silty clay (called 'soil A') of low plasticity was prepared to blend with uniform, fine siliceous sand (called 'soil B') to make test soil. Sieve and hydrometer test (ASTM D421-85, D422-63) results show that the soil A is composed of 15% sand, 48% silt, and 37% clay (by the soil size definition of the Unified Soil Classification System). Organic content of test soil is 2.6% (by ASTM D2974-87), cation exchange capacity is 29.3 meq/100g (Soil Waste 846 test method), and the pH of the soil A is 7.6. Its liquid limit is 39%, plastic limit is 25%, and plasticity index is 14. This soil was blended with uniform, fine siliceous sand. The cation exchange capacity of the soil B is 6.2 meq/100g, organic content is 0.34%, and 100% sand.

Five organic contaminants were chosen for adsorption tests: phenol, aniline, nitrobenzene, quinoline, and 2-naphthol. These contaminants were added to test soil for the laboratory studies because these five compounds are important organics that are each representative of major organic contaminant groups. Phenol is representative of *phenol* compounds; aniline is representative of *amine*

group; nitrobenzene is representative of *nitro* compounds; quinoline is representative of *fused-ring heterocyclic amines*; and 2-naphthol is a *double-ring structure phenol* compound. The phenol compounds are important aromatic compounds. Phenol is the monohydroxyl derivative of benzene. The amine are alkyl derivatives of ammonia. The amines are the simple aliphatic compounds containing nitrogen. The nitro compounds contain the nitro(-NO₂) group attached to an aromatic ring. Chemical and physical properties of the five contaminants are outlined further in Table 1.

Table 1. Chemical and Physical Characteristics of Contaminants.
(Source: CRC Handbook of Chemistry and Physics 1993-1994)

	phenol	aniline	nitrobenzene	quinoline	2-naphthol
Molecular formula	C ₆ H ₅ OH	C ₆ H ₅ NH ₂	C ₆ H ₅ NO ₂	C ₉ H ₇ N	C ₁₀ H ₈ O
Molecular weight	94.11	93.12	123.11	129.15	144.16
Boiling point (°C)	181.7	184.4	210.5	237.7	295.0
Melting point (°C)	43	-6.2	6	-15	122.0
Specific gravity	1.058	1.022	1.205	1.09	1.22
Water solubility (mg/L @ 15 °C)	66,700	34,900	1,900	6,000	1,000
Log K _{ow} (octanol-water partition coeff.)	1.49	1.18	2.15	2.97	3.32
pK _a	9.89	4.58	3.98	4.90	9.51
Structure					

2.1 Adsorption Rate Test

Batch adsorption rate experiments were carried out in establishing the adsorption equilibrium time required for adsorption of the each contaminant onto the Test soil(40% soil A + 60% soil B). Test procedures were as follows:

(1) Test soil was autoclaved to prevent undesirable biodegradation, which affects the remediation test results. Biodegradation checks were performed even though the soil was autoclaved. Autoclaving was performed for an hour at 250°C and 138 kPa.

(2) Ten accurately weighed ($\pm 1.0\text{mg}$) 6g samples of autoclaved and dried Test soil were placed in clean autoclaved 8mL Pyrex[®] vials and mixed with 5 mL of aqueous contaminant solution at a concentration of 50.0mg/L. The vials were sealed with Teflon[®] lined caps.

(3) The vials were stored in the refrigerator at 4°C in a shaking position (with Fisher Shaking Water Bath Model 129[®]). Physical shaking or agitation can reduce the thickness of the adsorbent, so that the organic compound can diffused through the layer more easily, and the rate of adsorption will increase.

(4) Two mixture samples were withdrawn after every 24 hours of contact time and centrifuge (Damon Model CRU 5000 Centrifuge[®]) in order to separate the solid from the liquid phase. Supernatant liquid of 4.2 μL from each sample was extracted with syringes and analyzed for the concentration of organic compound on a gas chromatography (GC).

2.2 Adsorption Isotherm Test (Freundlich Isotherm Test)

Once the equilibrium time was established, adsorption equilibrium tests(isotherm tests) for each organic compound were conducted, in which vials containing 6 g of autoclaved and oven-dried Test soil and 5 mL of aqueous contaminant solution varying in concentrations from 1 to 100mg/L were agitated for the desired equilibrium time and then centrifuged. The initial concentration of the solutions, C_0 (four or five different concentrations from 1 to 100 mg/L) were varied, with a constant weight of adsorbent, M , which was 6 g. Samples were taken out of the supernatant liquid and analyzed in the gas chromatography for defining the distribution of each contaminant between the liquid and solid phase. The relationship between the equilibrium adsorbate concentration in the liquid phase (C_e) and the amount of substance adsorbed per unit of adsorbent expressed as X/M , where X , the amount of solute adsorbed per unit mass of adsorbent M , was calculated and plotted on a log-log scale to permit description by the Freundlich isotherm equation (2).

3. Test Results

3.1 Adsorption Rate Test

The results of adsorption rate tests shown in Fig. 1 demonstrate that equilibrium of each organic compound was closely approached within 24 hours. The initial aqueous solution concentration was 50.0 mg/L and the mass of the adsorbent, M , was 6g. The concentration of phenol reaches equilibrium at about 39.0 mg/L, nitrobenzene at 18.0 mg/L, quinoline at 23.0 mg/L, and 2-naphthol at 24.9 mg/L within 24 hours. Based on this result, an equilibrium time of 24 hours was selected for adsorption isotherm testing for these organic compounds. A 24-hour contact period is a conservative period to reach equilibrium; however, nitrobenzene did show a slight decrease in

concentration with additional time. Nitrobenzene needs further study to explain this decrease of concentration. For other organic compounds, with the exception of nitrobenzene, no evidence for biodegradation existed because equilibrium concentrations were well maintained after equilibrium was established.

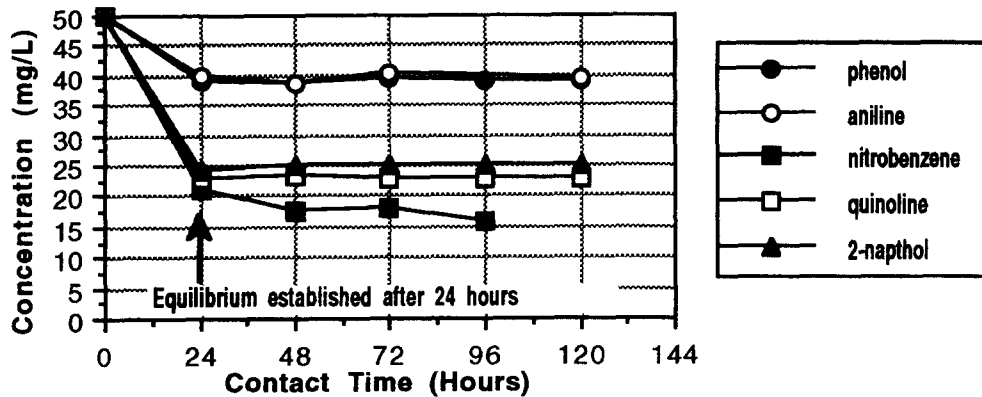


Fig. 1. Adsorption Rate Test for Organic Compounds

3.2 Adsorption Isotherm Test

Adsorption isotherm tests with varying concentrations (four or five different concentrations between 1 mg/L and 100 mg/L) at a constant weight of adsorbent, 6 g, were conducted to observe general adsorption characteristics of the organic compounds. Each sample was analyzed after the established equilibrium time of 24 hours. The Freundlich isotherm equation was used to provide a relatively accurate means of evaluating the strength ($1/n$) and degree of contaminant capture (K) and to provide a quantitative description of potential difficulty of extraction caused by a given contaminant.

Adsorption isotherm test result for 2-naphthol presented in Fig. 2. Table 2 summarizes the Freundlich Isotherm test parameter K and $1/n$ for each compound.

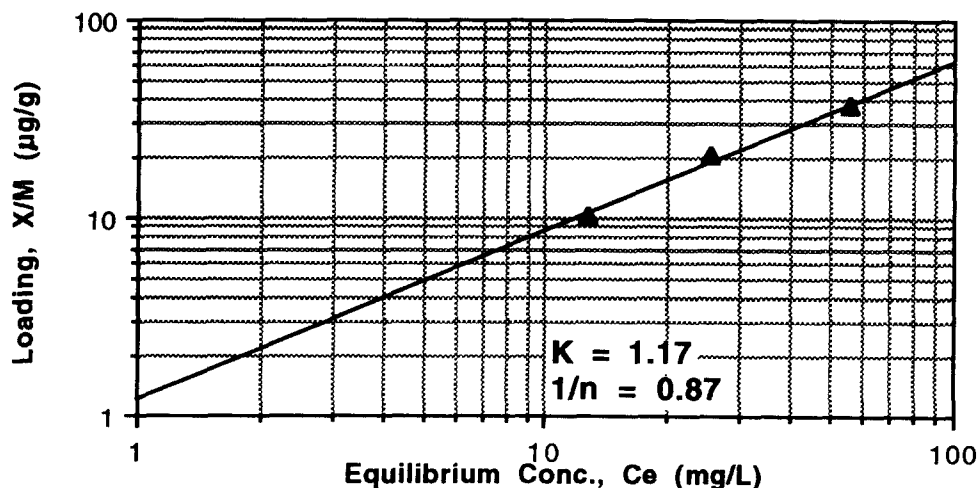


Fig. 2. Freundlich Isotherm Test for 2-Naphthol on Test Soil

Table 2. Adsorption Parameters for Freundlich Isotherm Test

	Phenol	Aniline	Nitrobenzene	Quinoline	2-Napthol
K	1.91	4.27	8.30	4.90	1.17
1/n	0.52	0.15	0.36	0.46	0.87

The distribution coefficient, K_d , is directly related to K_{oc} and f_{oc} , as $K_d = K_{oc}f_{oc}$, where K_o is the organic carbon partition coefficient, and f_{oc} is the fraction of organic carbon in the soil (Schwarzenbach and Westall 1981). This means that soil adsorption is linearly related to the amount of organic carbon in the soil as well as the characteristics of the organic compounds by K_{oc} . Figure 3 shows that the increase of the amount of organics in the test soil also increases the adsorption amount of organic compounds in soil. In the case of these tests, organic content of the mixtures decreased as the percent of sand, with virtually no organic content, increased. Phenol is adsorbed onto soilA-100 (100% soil A, $f_{oc} = 2.50\%$) about three times more strongly than soilA-0 (100% soil B, $f_{oc} = 0.34\%$). the initial phenol concentration of 20mg/L decreased to 13mg/L with soilA-100, while the phenol concentration decreased to 18mg/L with soilA-0 soil. Figure 3 indicates that the relationship between f_{oc} and the distribution coefficient K_d is approximately linear relationship. Soil A, B, and phenol satisfy the relationship, $K_d = K_{oc}f_{oc}$. K_{oc} is the slope of the curve, approximately 30(L/Kg) in this case.

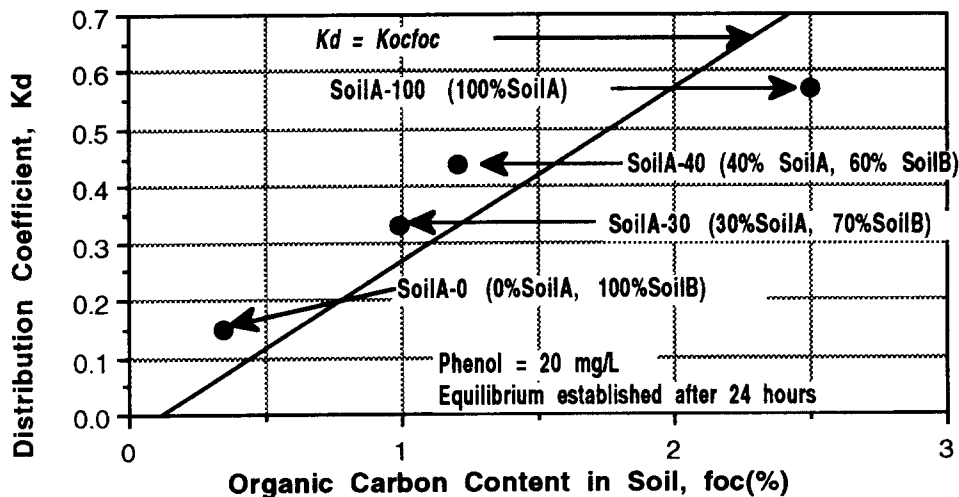


Fig. 3. Linear Relationship between K_d and f_{oc} for Test Soil

The value of K_{oc} can be estimated from the solubility, S , of the organic compounds. There are a number of equations that relate K_{oc} to K_{ow} and S for many potential contaminants. The best choice for estimating K_{oc} is an equation that is derived on the basis of chemicals similar to the contaminating organics of interest.

Once the K_{oc} values are obtained, the distribution coefficients, K_d , are also readily calculated from $K_d = K_{oc}f_{oc}$. The organic content of the soilA-40(40% soilA and 60% soil B) is estimated as 1.204%. Typical values for soil are between 0.5% and 3.5%. For evaluating K_d , K_{oc} for each compound was

obtained from the average value of the established equations. Table 3 shows the K_{oc} and K_d values calculated for each organic compound. The calculated K_d value for phenol with soilA-40 was 0.340. In Fig. 3, the K_d value for $f_{oc} = 1.204\%$ is 0.444. Thus, the K_d values obtained by the equations seem to match moderately well with the experimental values.

Table 3. Estimated K_{oc} and K_d Values (for SoilA-40, $f_{oc} = 0.01204$)

	Phenol	Aniline	Nitrobenzene	Quinoline	2-Napthol
K_{oc}	28.03	18.40	107.26	455.60	955.57
K_d	0.34	0.22	1.29	5.49	11.51

The value of K_d is important to determine, as it relates to the physical movement of the contaminants (eq. 3). As K_d increases, the retardation factor increases; thus, the mobility of the contaminant becomes reduced. The slope of the curve in Fig. 3, K_{oc} , is 30(kg/L.) for phenol. It matches well with the empirical equation value of 28.03 in Table 3. From Table 3 and the retardation equation (eq. 3), retardation factors for each contaminant can be obtained. Retardation factor for phenol is 2.77; aniline is 2.16; nitrobenzene is 7.77; quinoline is 29.75; and 2-napthol is 61.3 with $n=0.34$, and $\rho_s=2.70$. This means phenol can be transported approximately 20 times faster than 2-napthol under the same conditions.

4. Conclusions

1. The adsorption rate test for each organic compound shows that adsorption equilibrium is closely approached within 24 hours (Fig. 1). The Freundlich isotherm test provides an appropriate means of evaluating the strength and degree of contaminant adsorption onto the soil particles and gives an understanding of the potential difficulty of extraction. Table 2 summarizes the isotherm test results.

2. Adsorption is lineally related to the amount of organic carbon in the soil, f_{oc} , as well as the characteristics of the organic compound, expressed by K_{oc} . SoilA and SoilB also satisfy the relationship, where K_{oc} is the slope of the curve in Fig. 3, approximately equal to 30 for phenol. This gives an equation that also matches well with the empirical equation using values calculated using published K_{ow} or S values.

3. The value of the distribution coefficient K_d is a very important parameter to characterize the physical movement of the contaminants (eq. 3). As K_d increases, the retardation factor increases; thus, the mobility of the contaminant becomes reduced. Estimated K_d values based on the K_{oc} values in Table 3 indicate that 2-napthol will be retarded more than the other contaminants considered here. The Freundlich isotherm test also indicates that 2-napthol is adsorbed into the soil more readily than the other compounds; thus, its migration can be slower and more retarded.

5. References

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