

Estimation of the Desorption Characteristics of Organic Compounds by Freundlich Isotherm Tests

후렌드리히 등온시험을 통한 유기화합물의 탈착특성 조사

박준범¹⁾, Junboun Park,
서민우²⁾, Minwoo Seo, 오명학²⁾, Myounghak Oh

¹⁾ 서울대학교 공과대학 토목공학과 조교수, Assistant Professor, Dept. of Civil Engineering,
Seoul National University

²⁾ 서울대학교 공과대학 토목공학과 대학원, Graduate Students, Dept. of Civil Engineering,
Seoul National University

개요(SYNOPSIS) : 유기화합물로 오염된 지반에 약액을 주입하여 정화하는 경우, 흡입자에 흡착된 오염물질은 그 흡착강도에 따라 정화율이 다르게 된다. 즉 흡착 강도가 강한 물질은 그렇지 않은 물질에 비하여 상대적으로 정화하기가 난해하다. 이러한 이유로 오염지반 정화시, 오염물질의 상대적 흡착강도에 따라 약액의 농도, 주입량등이 결정될 수 있다. 따라서 각 오염물질의 흡착강도를 파악하는 것은 오염지반정화 설계에 필요하다고 할 수 있다.

각, 유기화합물의 흡입자에 대한 흡착강도는 일반적으로 후렌드리히 등온흡착시험(Freundlich Isotherm Tests)을 통하여 등온흡착계수 $1/n$ 으로 표시된다. 즉 이 값의 크기가 작을수록 탈착이 난해하게된다. 본 연구에서는 aniline, quinoline, phenol, 및 2-naphthol을 이용하여 조립토와 세립토의 비가 60:40인 흙에 흡착시켜 그 흡착특성을 알아보았고, 여기서 구한 흡착특성계수 $1/n$ 과 탈착특성을 비교하여 보았다. 탈착특성은 연속역등온시험(Successive Reverse Isotherm Tests)을 통하여 조사하였다. 시험결과 $1/n$ 이 가장 작은 aniline이 예측된바와 같이 가장 탈착량이 작았다 (20%). 이와는 반대로 계수가 가장 큰 2-naphthol은 45%가량 탈착되어 후렌드리히 등온시험에서 구한 계수가 정화율을 비교적 정확하게 예측할 수 있음을 보여주었다.

Key Words(주요어) : Freundlich Isotherm, Desorption, Adsorption, Organic Compounds, Successive Reverse Isotherm Tests, Remediation

1. Introduction

Solvent extraction using aqueous solutions is presumed as one of the most effective methods applicable to the in situ clean up for contaminated subsurface. Since early 1980's, various remediation techniques have been tested and developed for the hazardous waste contaminated sites for cleanup. In most remediation processes, physical removal or cutoff of the contaminant source is done initially for the preventing further contamination. Once the contamination source is successfully controlled, the next step is to clean up the contamination plume or reduce the concentration of the contaminants by implementing various types of remediation technologies available for organic compounds. These techniques include: pump-and-treat method¹⁾²⁾³⁾⁴⁾, biodegradation⁵⁾⁶⁾⁷⁾, soil venting⁶⁾⁸⁾, and solvent extraction. But each treatment method has its own inherent disadvantages and limits; thus, the appropriate

method should be carefully chosen depending on the hydro-geological conditions of the site and the characteristics of the contaminants.

Adsorption can be defined as the interaction of a contaminant with solid particles. Adsorption is the process in which chemical compounds become associated with solid phase, which includes primarily clay mineral, indigenous soil organic matter, and amorphous oxides-hydroxides of metals. One of the most important characteristics of an adsorbent (soil) is the quantity of adsorbate (contaminant) 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 isotherm* 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 1, then the isotherm is said to be linear and the Freundlich isotherm coefficient K is identical to the distribution coefficient K_d . The constant K is related to the capacity of the adsorbent to sorb the compounds, and $1/n$ is a function of the strength of adsorption.

This paper focuses on the relationship between the coefficients of the Freundlich isotherm and the desorption tests of the successive reverse isotherm. The test results provide a quantitative description of potential difficulty of extraction caused by a given contaminant.

2. Test Material

Natural silty clay was prepared to blend with uniform, fine siliceous sand to make 65% sand, 20% silt, and 15% clay mixture, called the test soil. Organic content of the test soil is 1.2%. To exclude the effect of biodegradation, sodium azide (strong bactericide) was added to the test soil. Phenol, aniline, nitrobenzene, quinoline, and 2-naphthol were permeated into test soil. Phenols are single-ring compounds with a hydroxyl group directly bonded to an aromatic ring, $Ar-OH$. Aniline is weakly basic with an amine group (NH_2) attached to an aromatic ring. Nitrobenzene is representative of nitro compounds, in which the aromatic compounds contain nitrogen as a derivative of nitric acid. NO_2 attaches to an aromatic ring. Quinoline is a fused ring heterocyclic amine that contain both a benzene ring and a heterocyclic aromatic ring. 2-naphthol is a double ring structure phenol compound which includes hydrolaphacol, aminonaphthols, and bromonaphthols. The hydroxyl group attaches to the 2nd position of the two-benzene-ring structure.

3. Test Methods

3.1 Freundlich Isotherm Tests (FIT)

Freundlich Isotherm Tests(FIT) for each organic compound were conducted, in which vials containing 6g of autoclaved and oven-dried test soil and 5ml of contaminant solution varying in concentration from 1 to 100mg/L were agitated for the desired equilibrium time and then centrifuged. The initial concentration of the solutions, C_o (four or five different concentrations from 1 to 100mg/L), were varied with a constant weight of adsorbent, M , which was 6g. 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 was calculated and plotted on a log-log scale to permit description by the FIT.

3.2 Successive Reverse Isotherm Tests (SRIT)

Desorption tests were conducted to assess the effectiveness of the extraction solution for the five contaminants studied with the potential desorbing solutions by simple contact shaking of the contaminated soil with deionized water. This test method is termed the SRIT procedure. In the SRI test, oven-dry test soil (6g) was mixed with 5mL of contaminant solution at the concentration of 50mg/L. After a 24-hour contact time, the contaminated soil was cleaned successively by agitating the soil in the deionized water for five minutes, centrifuging, decanting half of the supernatant solution, replacing the decanted solution with fresh decontaminant solution, and repeating the process several times until the contaminant could not be measured in the decanted supernatant solution. The process required about 30 minutes. The cumulative weights of the desorbed contaminants, again determined through gas chromatography, were added to obtain the total weight of contaminant removed.

4. Test Results

FIT result for phenol is shown in Fig.1. Table 1 summarizes the FIT parameter K and $1/n$ for each compound. The FIT data given in Table 1 indicate the potential difficulty of removing the organic compounds attached on the soil particle at a certain equilibrium concentration, C_e . As $1/n$ becomes smaller, the adsorption bond becomes stronger, which means that recovering(or desorbing) the organics from the soil becomes more difficult. Aniline has the smallest value of $1/n$. Potential difficulty of desorbing aniline from the soil particle is possibly expected. The estimation of potential difficulty of desorbing organics from soil suggested by the FIT can be confirmed by the desorption of SRIT.

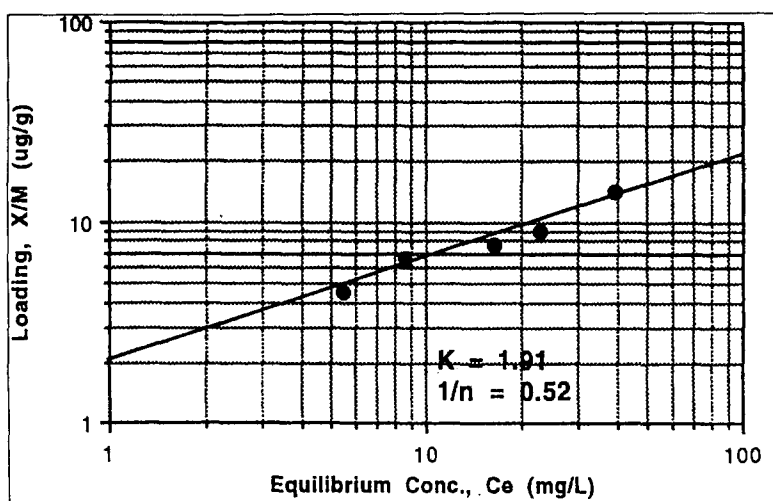


Fig.1. FIT for Phenol on the Test Soil

Table 1. FIT Parameters for Five Organic Compounds

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

Fig.2 shows the typical SRIT results with deionized water for phenol contamination. Table 2 summarizes the result. The bond strength, $1/n$, found in FIT was confirmed by the SRIT. SRIT results with deionized water for each organic contaminant were compared with the value of $1/n$ that were found in FIT. Deionized water is used for comparison because other decontaminant solutions may react with a specific contaminant and affect the remediation percentage.

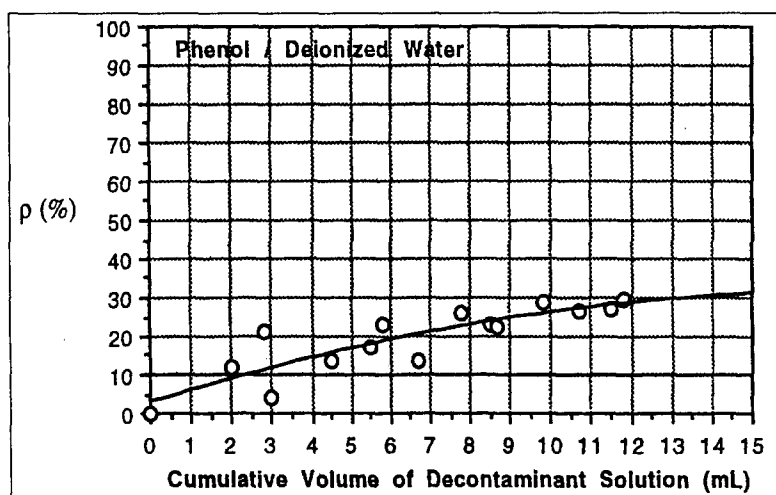


Fig.2. Typical SRIT Results with Phenol and Deionized Water

Table 2. Remediation Percentage from SRIT with Deionized Water

	Phenol	Aniline	Nitrobenzene	Quinoline	2-Napthol
1/n	0.52	~ 0.15	0.36	0.46	0.87
Remediation Percentage(%)	30	20	10	28	45

Fig.3. indicates that as 1/n becomes larger the remediation percentage with deionized water becomes larger. This means that as the bond strength becomes the weaker the desorbing activity becomes easier. Nitrobenzene might have been located between aniline and quinoline; however, it was remediated much less than expected from the value by the FIT. From this graph, the 1/n value can be estimated approximately from the SRIT. This can be an independent way to investigate the 1/n value of the contaminant previously obtained from the FIT.

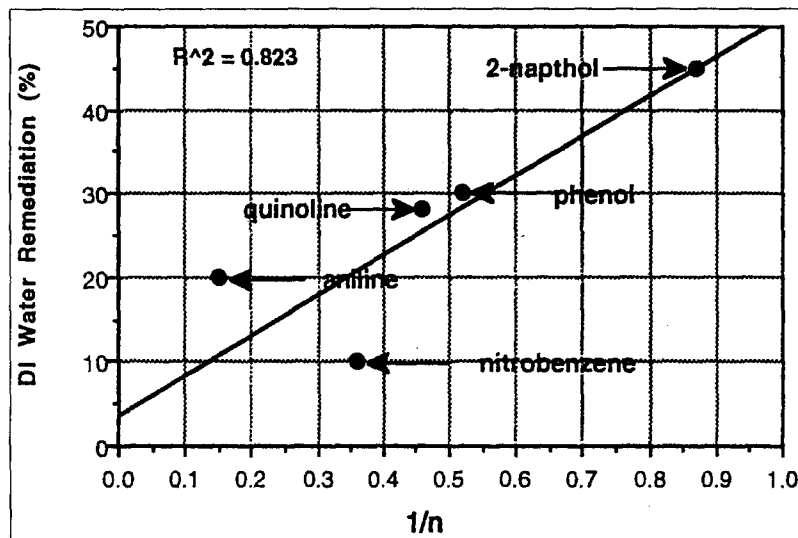


Fig.3. Relationship between 1/n and Deionized Water Remediation Percentage

5. Conclusion

The SRIT was originally developed as a screening technique for estimating the desorption potential of a given decontaminant solution. The SRIT consists of simple contact shaking of the contaminated soil with an extracting solution (deionized water for this study), primarily to assess the effectiveness of the extracting solution. The SRIT results with deionized water were given in Table 2. The FIT is a good indicator of the bond strength between the contaminants and the soil particles. As the 1/n value becomes smaller, the bond strength becomes stronger, thus desorption becomes more difficult.

The 1/n and the remediation percentage obtained from the SRIT show linear relationship (R square value of 0.823). The 1/n value of 2-napthol, which is the biggest value among five contaminants tested as 0.87, showed also the biggest remediation value of 45%.

The FIT and SRIT combined could be a predicting tool for the potential remediation

feasibility of the contaminated subsurface by organic compounds before performing a pilot level study.

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