

Determination of Partitioning Coefficient and Desorption Rate for Subcritical Water Extraction of PAHs

Mohammad Nazrul Islam, Young-tae Jo and Jeong-Hun Park⁺

Department of Environmental Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea

Abstract. Four models were used to describe the subcritical water extraction' (SCWE) kinetics of polycyclic aromatic hydrocarbons (PAHs) at elevated temperatures in this work. The subcritical water extraction profile obtained at a temperature of 200 °C and 250 °C were fitted with four models to presume the extraction mechanism parameters which could provide conceptual design to develop scale up methodology from laboratory SCWE devices. Two-site kinetic desorption model gave a best description of SCWE of phenanthrene, fluoranthene, and pyrene. The results of the study revealed that the highest amount of contaminants extraction was obtained at a temperature of 250 °C for 60 min extraction; and the partitioning coefficient and desorption rate constant were greatly affected by water temperature. Also, both of model and experimental data analysis results suggested that the first step desorption is more important for PAHs extraction than mass transfer process.

Keywords: Subcritical Water, Temperature, Extraction, Model

1. Introduction

The use of supercritical fluid extraction (SFE) has become increasingly apparent when cleaning of organic contaminated soils such as polychlorinated biphenyls (PCBs), PAHs, and pesticides. Unfortunately, supercritical water requires a temperature of >374 °C and a pressure of >221 bar and is corrosive [1]. Subcritical water extraction (SCWE) is one of the most recent techniques developed based on the use of superheated water (temperature 100 °C to 374 °C and pressure <221 bar) as a solvent instead of organic solvent. A number of researchers have been studied the remediation of PAHs using subcritical water and have shown the feasibility of extracting from contaminated soil [1-2]. However, to presume the extraction parameters, the extraction mechanism of PAHs using subcritical water has not been studied enough.

In this study, four models were used to determine the partitioning between the soils and solvent and the rates of PAHs desorption from the soil at two different temperatures.

2. Experimental and Models

2.1. Extraction Process

Heukeumgi soil, which was collected from Jeju Island in Korea, has been used in this study. Naphthalene, phenanthrene, fluoranthene, and pyrene (PAHs purity > 98%) have been spiked to prepare a contaminated soil. All of chemicals used in this experiment were HPLC grade. Distilled water was used for the extraction as a solvent. 8g of contaminated was packed into the reactor and the purged distilled water was flowed through the pre-heater and reactor under a moderate pressure of 100 bar. The water was passed vertically through the extraction reactor for up-flow extraction. In order to fitting the experimental data to models, experiments were done at 200 °C and 250 °C for 15, 30, 45 and 60 min extraction and a water flow rate of

⁺ Corresponding author. Tel.: +82 62 530 1855; fax: +82 62 530 1859
E-mail address: parkjeo1@chonnam.ac.kr

1.5 ml/min. After the desired extraction, the pump and heater were stopped and the pressure was released to atmospheric pressure. The reactor was left to cool to room temperature and packed soil was collected to analyze the remaining concentrations of contaminant.

2.2. Extraction Mechanism and Mathematical Models

The efficiency of SCWE is strictly controlled by four mechanisms: desorption, diffusion, concentration gradient that may be described by partitioning coefficient and mass transfer [3].

- Partitioning coefficient (K_d) model

The partitioning coefficient model, describes the extraction process that is controlled by distribution of solute between matrix and fluid, adopted from Kubátová *et al.* [4] and Khajenoori *et al.* [5]. The model equation could be express as follows:

$$\frac{C_b}{C_o} = \left(1 - \frac{C_a}{C_o}\right) \div \left(\frac{K_d}{(V_b - V_a)\rho} + 1\right) + \frac{C_a}{C_o} \quad (1)$$

where, C_a and C_b is the cumulative mass of the contaminant extracted after certain amount of volume V_a and V_b , respectively, mg/kg; C_o is the total initial mass of contaminant in the matrix, mg/kg; ρ is the density of water under given condition, mg/ml.

- Partitioning coefficient with external mass transfer model

This model describes extraction which is controlled by external mass transfer whose rate is described by type model of the following form [5].

$$\frac{C_t}{C_o} = 1 - \exp\left(-\frac{k_e a_p t}{K_d}\right) \quad (2)$$

where, C_t is the mass of contaminant removed by the subcritical water extraction after time t , mg/kg; $k_e a_p$ is the overall volumetric external mass transfer coefficient (min^{-1}).

- One-site kinetic desorption model

One-site kinetic desorption model describes the extractions that are controlled by intra-particle diffusion. a one-site kinetic desorption model, can be written for the ratio of mass of contaminant removed after time t (C_t) to the initial mass C_o as given by:

$$\frac{C_t}{C_o} = 1 - e^{-kt} \quad (3)$$

where, k is the first order desorption rate constant, min^{-1} .

- Two-site kinetic desorption model

Two-site kinetic model is a simple modification of the one-site kinetic desorption model. It is proposed by Kubatova *et al.* [4] and Hawthorne *et al.* [6] uses two steps to define an extraction curve: a certain fraction (F) of the solutes desorbs at a faster rate defined by k_1 , and the remaining fraction ($1-F$) desorbs at a slower rate defined by k_2 , thus:

$$\frac{C_t}{C_o} = 1 - [F e^{-k_1 t}] - [(1 - F) e^{-k_2 t}] \quad (4)$$

3. Results and Discussion

3.1. Partitioning Coefficient (K_d) Model

Naphthalene could not be detected only at 200 °C even after 15 min extraction. So, it was not possible to fit the experimental data into the mathematical models. The model Eq. (1) and the experimental data at two temperatures were used to determine the K_d values by minimizing the errors between the measured data and model regression data using EXCEL solver (Table 1). The K_d values decreases with increasing temperature. It means that the thermodynamic K_d model successfully predicts the extraction efficiency as a function of temperature. Fig. 1 shows the regression line and experimental data obtained at a temperature of 250 °C.

3.2. Partitioning Coefficient (K_d) with External Mass Transfer Model

The values of K_d and k_{ea_p} are shown in Table 1. Fig. 1 shows the experimental extraction efficiency of phenanthrene, fluoranthene, and pyrene versus time, with the regression lines which suggested that the lines are fitted reasonably experimental data. As could be expected, the k_{ea_p} increases when temperature of water is increased (Table 1), that is indicating the hydroscopicity of the extraction matrix is rapid at higher water temperature. The results suggest that the external mass transfer is improved at higher water temperature.

Table 1: K_d values of two thermodynamic models for PAHs extracted with SCWE process

PAHs	Partitioning coefficient model		Partitioning coefficient with external mass transfer model			
	K_d		K_d		k_{ea_p}/min	
	200 °C	250 °C	200 °C	250 °C	200 °C	250 °C
Phenanthrene	30.59	10.65	10.11	9.40	0.2026	0.6285
Fluoranthene	17.16	7.92	14.71	11.81	0.3730	0.7552
Pyrene	28.44	11.18	10.02	9.49	0.1860	0.5360

3.3. One-Site Kinetic Desorption Model

A desorption rate constant, k , is referred to as desorption of contaminant removal per unit weight of matrix and high values are preferable. The k values are presented in Table 2, which are indicated of degradability of those organic compounds. The kinetic desorption rate increased due to the viscosity and surface tension of water drop with increasing temperature. The numbers are similar to each other, suggesting similar release rate of three PAHs.

3.4. Two-Site Kinetic Desorption Model

Experimental results have shown that 60-65% of removal efficiency for three PAHs was obtained during the first 15 minutes. The remaining 35 to 40% of removal efficiency was detected from 15 to 60 minutes. This suggests that the fast and slow desorption was occurred. Table 2 summarizes the fast and slow kinetic desorption coefficient, as well as mole fraction at two temperatures of three PAHs. The results show that kinetic desorption coefficient (k_1 , k_2) increased with increasing the temperature for all of compounds.

Table 2: Predicted mole fraction (F) and kinetic coefficients (k_1 , k_2) obtained by fitting two-site and one-site kinetic desorption model

PAHs	Two-site kinetic desorption model parameters						One-site model	
	200 °C			250 °C			200 °C	250 °C
	F	k_1	k_2	F	k_1	k_2	k	k
Phenanthrene	0.3996	0.0682	0.0062	0.2558	0.9156	0.0519	0.0201	0.0668
Fluoranthene	0.5474	0.0752	0.0029	0.4280	0.9917	0.0376	0.0254	0.0639
Pyrene	0.4563	0.0625	0.0025	0.3411	0.9568	0.0383	0.0186	0.0565

This results are consistent with findings of Langenfeld *et al.* [7], who studied the PAHs extraction from railroad bed soil in SFE and demonstrated that increasing the temperature resulted in faster desorption for all of PAHs. Calculated F values based on the two-site kinetic model are summarized in Table 2.

4. Conclusion

This study has demonstrated that extraction efficiencies and mechanisms depend primarily on extraction temperature. The model fitting results suggested that the employed models have the potential to be used in such studies to gain information on the extraction of PAHs. Overall by considering average errors between the experimental data and the model data, two-site kinetic desorption model gave a best description of SCWE of representative PAHs which are suggesting that the desorption step (rate) is more important than other steps.

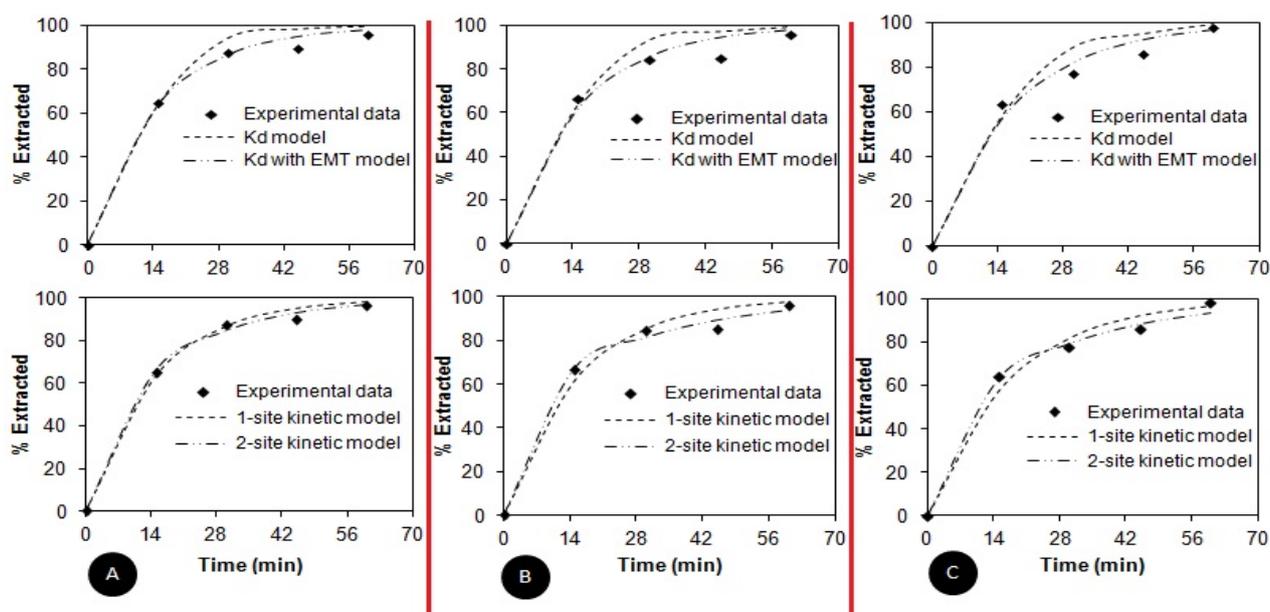


Fig. 1: Experimental fitting of partitioning coefficient (K_d), partitioning coefficient with external mass transfer (EMT), one-site kinetic desorption and two-site kinetic desorption model to SCWE data of (A) phenanthrene, (B) fluoranthene, and (C) pyrene obtained at a temperature of 250 °C, water flow rate of 1.5 ml/min and pressure of 100 bar. Symbols represent experimental data and dotted lines are based on curve fitting of experimental data.

5. Acknowledgement

Financial support is gratefully acknowledged to Korea Environmental Industry and Technology Institute (KEITI) through the GAIA project.

6. References

- [1] A. J. M. Lagadec, D. J. Miller, A. V. Lilke and S. B. Hawthorne. Pilot-Scale Subcritical Water Remediation of Polycyclic Aromatic Hydrocarbon- and Pesticide-Contaminated Soil. *Environmental Science & Technology*, 2000. **34**(8): p. 1542-1548.
- [2] S. B. Hawthorne, Y. Yang and D. J. Miller. Extraction of Organic Pollutants from Environmental Solids with Sub- and Supercritical Water. *Analytical Chemistry*, 1994. **66**(18): p. 2912-2920.
- [3] C. C. Teo, S. N. Tan, J. W. H. Yong, C. S. Hew and E. S. Ong. Pressurized hot water extraction (PHWE). *Journal of Chromatography A*, 2010. **1217**(16): p. 2484-2494.
- [4] A. Kubátová, B. Jansen, J.-F. Vaudoisot and S. B. Hawthorne. Thermodynamic and kinetic models for the extraction of essential oil from savory and polycyclic aromatic hydrocarbons from soil with hot (subcritical) water and supercritical CO₂. *Journal of Chromatography A*, 2002. **975**(1): p. 175-188.
- [5] M. Khajenoori, A. H. Asl and F. Hormozi. Proposed Models for Subcritical Water Extraction of Essential Oils. *Chinese Journal of Chemical Engineering*, 2009. **17**(3): p. 359-365.
- [6] S. B. Hawthorne, D. G. Poppendieck, C. B. Grabanski and R. C. Loehr. PAH Release during Water Desorption, Supercritical Carbon Dioxide Extraction, and Field Bioremediation. *Environmental Science & Technology*, 2001. **35**(22): p. 4577-4583.
- [7] J. J. Langenfeld, S. B. Hawthorne, D. J. Miller and J. Pawliszyn. Kinetic Study of Supercritical Fluid Extraction of Organic Contaminants from Heterogeneous Environmental Samples with Carbon Dioxide and Elevated Temperatures. *Analytical Chemistry*, 1995. **67**(10): p. 1727-1736.