Desorption kinetics of polycyclic aromatic hydrocarbons in soil using lab-scale rotary desorber

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Abstract−Thermal desorption of fluorene, anthracene, pyrene, and benzo(a)pyrene in soil contaminated with PAHs was performed using a rotary desorber at temperatures of 300-500 °C, and the dependency of the PAH removal efficiency on the percentage water content, residence time, and thermal desorption temperature was investigated. The removal efficiencies were inversely proportional to the boiling points of PAHs, and the removal efficiencies decreased with decreasing residence time and heating temperature. The reaction rate constant and activation energies (E_A) were estimated to determine the thermal desorption properties of each substance, and the activation energies were found to be 29.50-34.48 kJ mol^{-1}. Freeman-Carroll's law was applied along with the Arrhenius equation to extract the thermal desorption properties from the data obtained in this experiment.

Key words: PAHs, Thermal Desorption, Rotary Desorber, Desorption Kinetic, Activation Energy

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of one or more aromatic rings arranged in a linear or clustered sequence [1-3]. Large proportions of PAHs are contained in substances such as crude oil, coal and the residue of fossil fuel combustion [4-6].

Based on their harmful effects on human health, the United States Environmental Protection Agency (US EPA) included 16 PAHs in the list of priority pollutants and recently defined 32 kinds. The 16 PAH compounds are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k)flouranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, and Indeno (1,2,3-cd) pyrene, and these substances are often used to evaluate environmental pollution [7].

Rotary desorbers are commonly used to remediate hazardous material in the soil. In the rotary desorber, the contaminants such as organic material are desorbed by vaporization and combustion. PAH compounds have various physical properties; the removal efficiencies decrease with molecular structure, so it is difficult to remove from soil by thermal treatment. It is difficult to understand mass- and heat-transfer mechanism in the rotary desorber processes; however, it is important to understand thermal desorption properties in order to optimize desorber design and operating conditions. This paper focuses on the thermal desorption properties of PAHs from soil particles in the lab-scale rotary desorber.

Thermal desorption is a separation process that has been frequently used in the remediation of numerous superfund sites which have employed a variety of remediation techniques to treat the high concentrations of hazardous material for the following reasons: (1) a wide range of organic contaminants are effectively treated; (2) availability and mobility of commercial systems; and (3) the public acceptance of the approach. Superfund sites are any land in the U.S that have been contaminated by ncontrolled hazardous waste and identified by the U.S Environmental Protection Agency (USEPA) as a candidate for cleanup because they pose a risk to human health and the environment.

Thermal desorption is suitable for the treatment of organic wastes but not for that of metals or non-organic substances [8]. To achieve the optimal thermal desorption efficiency and determine appropriate reactor operating conditions, it is important to understand the rate of thermal desorption of PAHs from the soil.

A first-order desorption model to describe PAHs loss from sediment particles is described in Eqs. (1)-(2).

$$\frac{dC}{dt} = -kC \tag{1}$$

$$-r = kC \tag{2}$$

where C is the concentration of PAHs, k is the first-order rate constant, and r_A is reaction rate.

The concentration of PAHs can be described as follows:

$$C_{PAH} = C_{PAH0}(1-X) \tag{3}$$

where C_{PAH0} is initial concentration, C_{PAH} is final concentration, and X is conversion rate of PAHs. The thermal desorption rate constant in terms of the reaction temperature can be expressed through the Arrhenius equation:

$$k = \alpha \exp\left(-\frac{E_A}{RT}\right) \tag{4}$$

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$$\frac{dX}{dt} = \alpha \exp\left(-\frac{E_A}{RT}\right)(1-X) \qquad (5)$$

where t is the reaction time, A is the pre-exponential frequency factor, T is the temperature, E_A is activation energy of desorption, and R is the gas constant [9-11].

Since the Arrhenius equation cannot provide accurate information on the pyrolysis mechanism, the Freeman-Carroll method has been previously suggested [12-14].

$$\frac{dX}{dt} = \frac{\alpha}{\beta} \exp\left(-\frac{E_A}{RT}\right)(1-X) \qquad (6)$$

where β is the linear heating rate.

In this study, a series of experiments were conducted using a lab-scale rotary desorber usually used to measure thermal desorption processes of soil to investigate the removal efficiency of PAHs with 3-5 rings from soil. Dynamical data for the PAHs were determined by carrying out experiments in the temperature range 300 to 500 °C.

MATERIALS AND METHODS
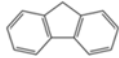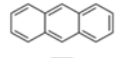
1. Preparation of the Contaminated Soil

The soils were obtained from the military base at Paju in Korea that was contaminated by oil for several years. To prepare the contaminated soil, gravel larger than 2 mm was removed by sieving, and the sieved soil was dried in an oven. The dried soil was analyzed for texture and other particular characteristics. The values are reported in Table 1.

To remove other organic compounds, the soil was washed with acetone and volatilized at room temperature. The standard substances of fluorene, anthracene, pyrene, and benzo(a)pyrene with 3-5 benzene rings were selected as the target substances in this experiment.

Table 1. Characteristics of soil from the contaminated site at Paju

Parameter	Value	Soil texture	Sandy loam
Soil pH	6.46	Sand (%)	69.52
Soil porosity (%)	0.46	Silt (%)	26.37
Organic matter (%)	9.05	Clay (%)	4.11
Particle density (g/cm³)	2.15		
Bulk density (g/cm³)	1.16		
Moisture contents (%)	7.34		

Soil samples were uniformly distributed on the bottom surface of a steel rectangular box (0.50 m length, 0.30 m width, 0.08 m height) to prepare the contaminated soil [15]. Each standard substance was weighed and put into a flask with methylene. After shaking them well to ensure they had dissolved, they were left to stand for a period of time. Several hours later, they were mixed with pre-washed soil in the steel box, left for about two days at room temperature, and then the solvent was volatilized. At this time, they were contaminated with fluorene, anthracene, pyrene, and benzo(a)pyrene at concentrations of about 100 mg/kg, respectively. The PAHs used in this research and the concentrations measured by GC-FID are listed in Table 2.

2. Thermal Desorption of PAHs

The thermal desorption experimental device consisted of an inlet hopper, cylindrical reactor body, outlet screw cap discharge pipe and valve-type stopper, motor, and belt. Outside the reactor, there was an electric heater, insulating material, K-type thermocouple, temperature controller, rpm controller, angle controller, and Y-type shaft. The rotary desorber was designed with indirectly heated system. The indirect heat transfer allows a slower warming-up of the material in the kiln, so no crust formation occurs and volatilization of all the organic constituents is enhanced. The supply of heat to the indirectly heated desorber can be controlled by heating in sections, giving a higher degree of material temperature control.

Fig. 1 shows a general layout and some particular views of the rotary desorber thermal-desorption experimental set-up. The reactor body is cylindrical (Stainless Use Steel (SUS) 304; thickness, 3 mm; diameter, 0.15 m; length, 0.40 m; volume, 7.07 L) and inside four baffles of length 0.03 m were installed to mix the soil in the reactor. Sixteen heating wires of length 0.30 m were attached along the central axis of the cylinder, and a plaster insulating material was placed over the heating wires. The temperature of the outside wall of the reactor was measured with a K-type thermocouple of length 0.05 m and diameter 1 mm, and a temperature controller (Autonics, TZ4M) was also attached. The rotation and angle (in the range 0-30°) of the reactor were controlled by a motor (Panasonic M8GA5OM) and rpm controller.

Dry heated purge air was applied to the apparatus by air pump. The air was dried before entering the desorber by passing through glass impingers. To identify the optimal operating conditions of the thermal desorption reactor, 500 g of artificially contaminated soils with the PAH compounds fluorene, anthracene, pyrene, and benzo(a) pyrene were injected into the reactor. Their concentrations in the
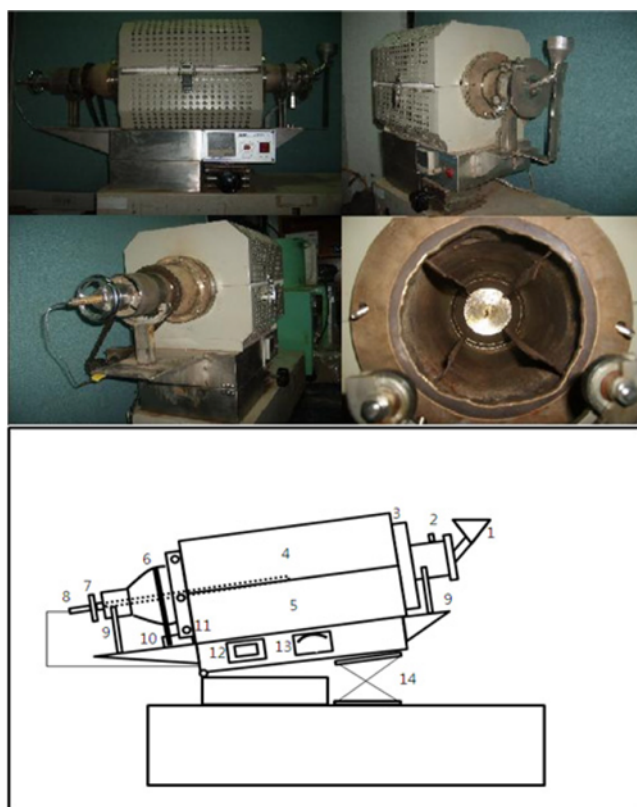
Table 2. List and pollution concentration of PAHs used in this study

PAHs	Structure	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Concentration[a] (mg/kg)
Fluorene		128.17	116	295	98.42±0.23
Anthracene		154.21	216	334	99.63±0.11
Pyrene		202.25	156	404	98.08±0.13
Benzo(a)pyrene		252.31	79	496	101.38±0.15

[a]Error represents one standard deviation from mean value from five replicates

Fig. 1. Image and schematic diagram of lab-scale rotary desorber.

1. Hopper	7. Thermocouple
2. Gas inlet	8. Gas outlet
3. Reactor	9. Motor
4. Electric heater	10. Temperature controller
5. Belt	11. rpm Controller
6. Valve	12. Angle controller

Table 3. The experimental conditions of thermal desorption

Variables	Experimental conditions
Soil amount (g)	500
Temperature (°C)	300, 350, 400, 450, 500
Residence time (min)	5, 10, 15, 30
Initial water content (wt%)	0, 5, 10, 15, 20, 25, 30
Each PAHs concentration (mg/kg)	100
Rotating velocity (RPM)	3.58
Purge gas flow (L/min)	0.4

soils were monitored to determine their removal efficiency while varying the residence time from 5 to 30 min, the heating temperature from 300 to 500 °C, and the initial soil water content from 0 to 30 wt%. The variables in this experiment are reported in Table 3.

Also, based on the results of experiments at thermal desorption reaction temperatures of 300, 350, 400 and 500 °C, the energy at which the thermal desorption reaction occurred was estimated and compared for each substance. The contaminated soil was analyzed five times to quantify the errors in the measurements.

3. Extraction and Analysis of PAHs

All soil samples were extracted using a Soxhlet extraction apparatus for 48 h with 150 mL of dichloromethane (DCM). The extracted

specimens underwent alumina column refinement to remove chemicals with low polarity, dioxins, or PCN, which can interfere with the analysis. The elution conditions of the alumina column were those of the US EPA (United States Environmental Protection Agency) Method 3611B [16]. The refined solution was condensed to about 1 mL with a rotary evaporator for analysis.

The extracted solution was analyzed with a gas chromatograph (GC) with He as carrier gas. The instrument was an Agilent 7890A GC-FID (flame ionization detector), and for the column, a HP-5 (Crosslinked 5% PH ME siloxane, 30 m×0.32 mm×0.25 μm film thickness) was used. For the analysis, an external standard method was used; 1 μl of the extracted solution was injected. The injection and detector port temperatures were 270 and 325 °C, respectively. The oven temperature was ramped from 60 K to 325 K. The total procedure was carried out in duplicate, and calibration curves were used as the basis of the quantitative analysis [17,18].

RESULTS AND DISCUSSION

1. Calibration Curves and Quantitation

Calibration curves were constructed by the analysis of 1 μl samples containing known amounts of fluorene, anthracene, pyrene and benzo(a)pyrene, respectively. To prepare these standards, PAHs samples were spiked with the studied compounds to the following concentration: 0; 10; 50; 100 mg/l. Fig. 2 reports a calibration curve of the investigated compounds and the corresponding regression coefficients R^2 after GC-FID analysis. The areas of the PAHs were used for quantitation. These results show that, in the range of considered concentrations, the R^2 values, which were goodness of fit, were above 0.9998.

2. Effect of Water Content in the Soil

The quantity of water in the soil can significantly affect the thermal desorption efficiency, and pre-processing to remove water would affect the entire processing cost. Thus, to determine the optimum water content in the thermal desorption process, 10-30 wt% water was injected artificially into completely dried PAHs-contaminated soil, and the thermal desorption efficiency experiment was performed using the rotary desorber at a temperature of 400 °C and residence time of 15 min. Table 4 shows the condition of PAHs thermal desorption and removal efficiency of PAHs with respect to the water content. From the results, it appears that as the water content increased, the removal efficiency of PAHs decreased, as shown in Fig. 3. If there was no moisture in the soil, all substances exhibited over 90% desorption efficiency, which is because most of the heat generated in the reactor was transmitted to the soil and most of the PAHs were desorbed, dissolved, and vaporized from the soil into the air. However, as the water content increased, reactor heat was used as vaporization heat by water, thus causing a decrease in desorption efficiency. For the rotary desorber used, the water content had to be maintained at about 10% to achieve a processing efficiency of 85%. If an actual thermal desorption process were operated below 10%, the economic efficiency would decrease due to the costs associated with the water preprocessing, so it is important that an appropriate water content is maintained.

3. Effect of Residence Time and Temperature

In the thermal desorption process, a large amount of energy is consumed to increase the temperature of the reactor, so it is essen-
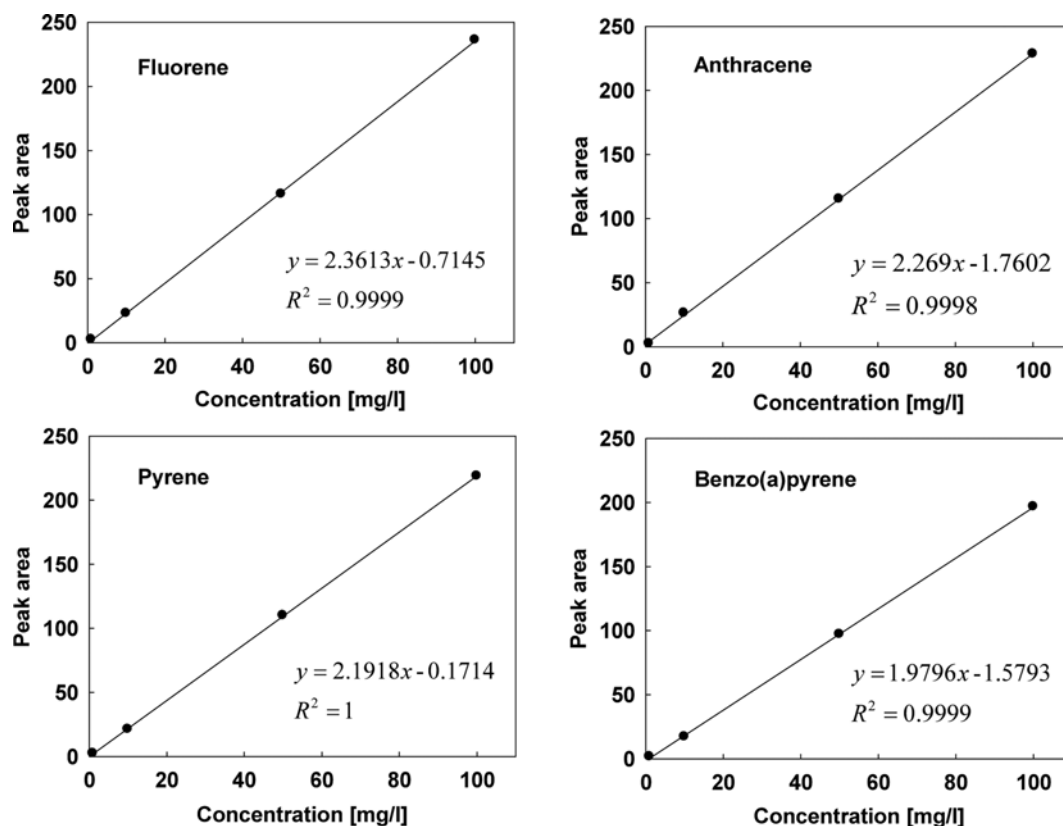
Fig. 2. Calibration curves and regression coefficients R² of PAHs analyzed by GC-FID.

Table 4. Removal efficiency and concentration of PAHs with respect to the water content of the soil

Residence time (min)	Temp. (°C)	Water content (%)	Fluorene		Anthracene		Pyrene		Benzo(a)pyrene	
			Final concentration (mg/kg)	Removal efficiency (%)	Final concentration (mg/kg)	Removal efficiency (%)	Final concentration (mg/kg)	Removal efficiency (%)	Final concentration (mg/kg)	Removal efficiency (%)
15	400	0	0.43	99.6	1.72	98.3	3.92	96.0	6.84	93.3
15	400	5	3.28	96.7	4.83	95.2	7.66	92.2	11.64	88.5
15	400	10	3.38	96.6	4.99	95.0	9.86	89.9	13.17	87.0
15	400	15	4.31	95.6	6.42	93.6	14.04	85.7	16.68	83.5
15	400	20	5.84	94.1	8.69	91.3	17.73	81.9	21.13	79.2
15	400	25	7.39	92.5	10.80	89.2	19.45	80.2	25.29	75.1
15	400	30	8.97	90.9	12.41	87.5	20.38	79.2	26.30	74.1

tial that the optimum operating conditions to achieve sufficient efficiency are determined. To this end, the effects of changing the thermal desorption temperature and residence time were investigated, and the results are shown in Figs. 4 and 5. As the temperature in the rotary desorber and the residence time of the specimens increased, the thermal desorption efficiency increased. The obtained removal efficiencies were decreasing at given temperature passing from fluorene to benzo(a)pyrene. This ordering tended to be in proportion to the number of rings in the substance; the more rings there were, the greater the molecular weight and higher the boiling point, which leads to a decrease in the thermal desorption efficiency.

To examine the impact of the residence time on the rotary desorber, the rpm of the baffles in the reactor was varied. As seen in the results in Fig. 4, for a short residence time of 5 min, the differ-ence in the thermal desorption efficiency of benzo(a)pyrene, which has a high boiling point, and fluorene, which has a low boiling point, was over 15%, which is large. However, as the residence time in-creased, the thermal desorption efficiency of all substances increased, and after 15 min, they all showed an efficiency of over 90%.

To investigate the effect of the reaction temperature, the speci-men was put into the desorber after an appropriate temperature was maintained for a given time using the temperature controller. The results in Fig. 5 show that fluorene and anthracene, which have rela-tively low boiling points, exhibit removal efficiencies of over 95% even at low temperature of 300 °C; however, pyrene and benzo(a) pyrene have thermal desorption efficiencies of over 90% only at temperatures above 400 °C.

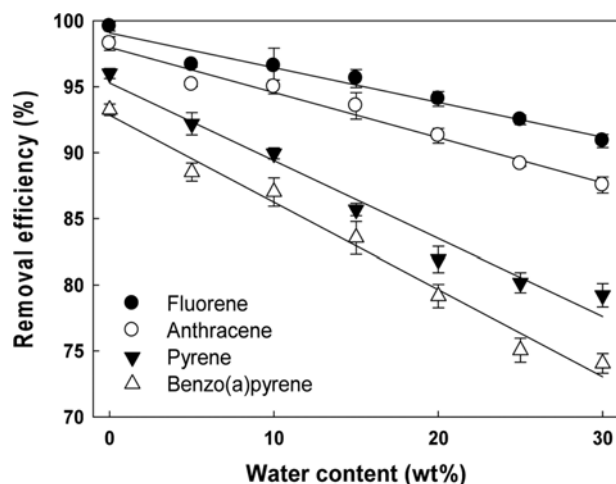To achieve the same removal efficiency for PAHs in the soil, a

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Fig. 3. Thermal desorption efficiency of PAHs with respect to the water content of the soil (residence time, 15 min; reaction temperature 400 °C).

Fig. 5. Thermal desorption efficiency of PAHs with respect to thermal desorption temperature (residence time, 15 min).
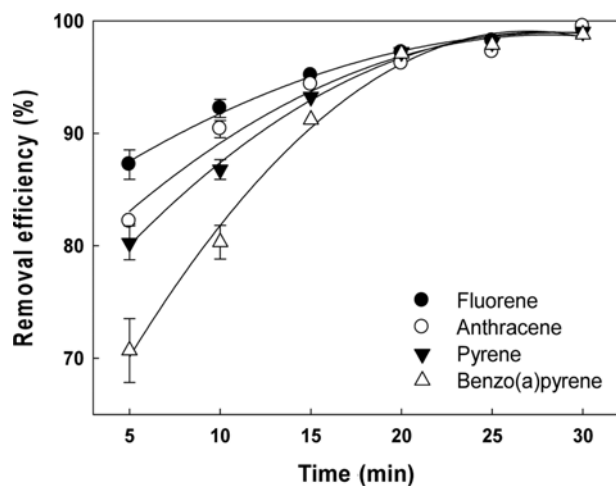

Fig. 4. Thermal desorption efficiency of PAHs with respect to the residence time of contaminated soil in the rotary desorber (reaction temperature, 400 °C).
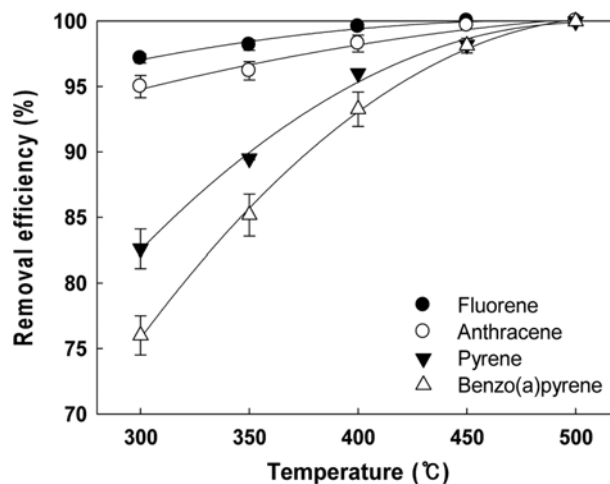
combination of the two main operating parameters of the thermal desorption process, i.e., heating temperature and residence time, can be used [15]. The combined operating parameter can be defined as T&T$_{combined}$ that is calculated as the product of corresponding heating temperature and residence time divided by 100 [15]. Table 5 shows the condition of PAHs thermal desorption and removal efficiency of PAHs for Soil S1 and S2. Figs. 6 and 7 show the achieved PAHs removal efficiency versus the composite T&T$_{combined}$ parameter for Soil sample 1 (no water content) and 2 (water content=10 wt%). The PAHs removal efficiencies increased with increasing values of the T&T$_{combined}$. In addition, the removal efficiencies of Soil 2 samples were lower than those of Soil 1 because of vaporization heat of water. However, the thermal desorption efficiencies had not achieved 100% as temperature and residence time increased. This is because a very long residence time is necessary to desorb the PAHs in the soil particle through evaporates, even if it has melted in the desorber.

4. Activation Energy and Desorption Rate Constant

For the thermal desorption of PAHs in the soil, a certain amount of energy is necessary, and to quantify this, the activation energy of

Table 5. Removal efficiency and concentration of PAHs with respect to the residence time and desorption thermal temperature of the soil

Test identification	Residence time (min)	Temp. (°C)	Water content (%)	T&T$_{combined}$	Fluorene		Anthracene		Pyrene		Benzo(a)pyrene	
					Final conc. (mg/kg)	Removal eff. (%)	Final conc. (mg/kg)	Removal eff. (%)	Final conc. (mg/kg)	Removal eff. (%)	Final conc. (mg/kg)	Removal eff. (%)
T1S1	15	300	0	45.0	2.82	97.1	4.99	95.0	17.05	82.6	24.33	76.0
T2S1	15	350	0	52.5	1.81	98.2	3.80	96.2	10.31	89.5	15.04	85.2
T3S1	15	400	0	60.0	0.43	99.6	1.72	98.3	3.92	96.0	6.84	93.3
T4S1	15	450	0	67.5	0.00	100.0	0.33	99.7	1.78	98.2	1.91	98.1
T5S1	15	500	0	75	0.00	100.0	0.00	100.0	0.02	100.0	0.03	100.0
T1S2	5	300	10	15.0	12.58	87.2	17.74	82.2	19.35	80.3	29.72	70.7
T2S2	10	300	10	30.0	7.66	92.2	9.58	90.4	12.96	86.8	19.95	80.3
T3S2	15	300	10	45.0	4.77	95.2	5.62	94.4	6.62	93.2	8.90	91.2
T4S2	20	300	10	60.0	2.79	97.2	3.77	96.2	2.73	97.2	2.95	97.1
T5S2	25	300	10	75.0	1.75	98.2	2.74	97.2	1.87	98.1	2.17	97.9
T6S2	30	300	10	90.0	0.74	99.2	0.48	99.5	0.94	99.0	1.24	98.8

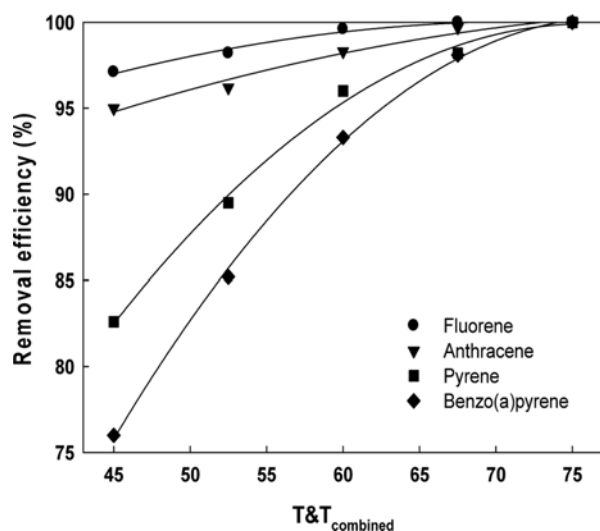Fig. 6. Thermal desorption efficiency of PAHs with respect to the operating parameter T&Tcombined (Soil S1).
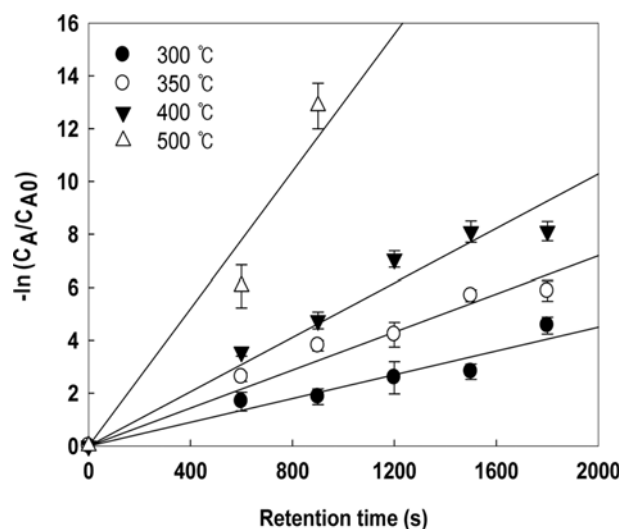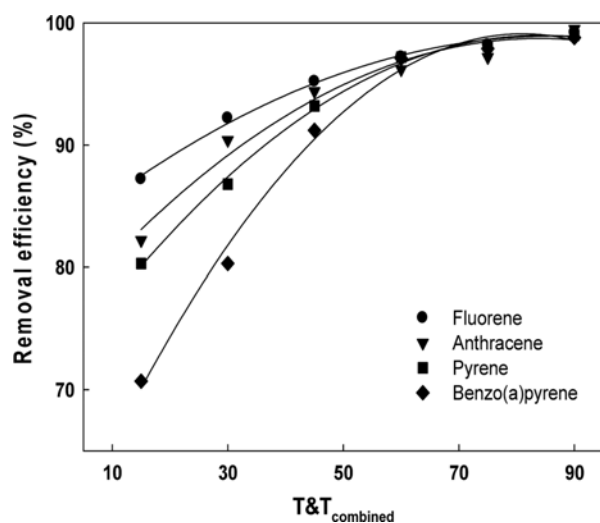

Fig. 7. Thermal desorption efficiency of PAHs with respect to the operating parameter T&Tcombined (Soil S2).
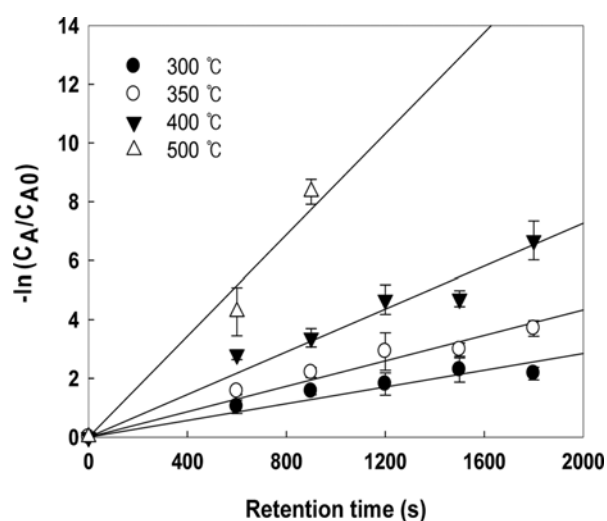

Fig. 8. Soil thermal desorption kinetics of fluorene with respect to reaction temperature and residence time.

Fig. 9. Soil thermal desorption kinetics of anthracene with respect to reaction temperature and residence time.
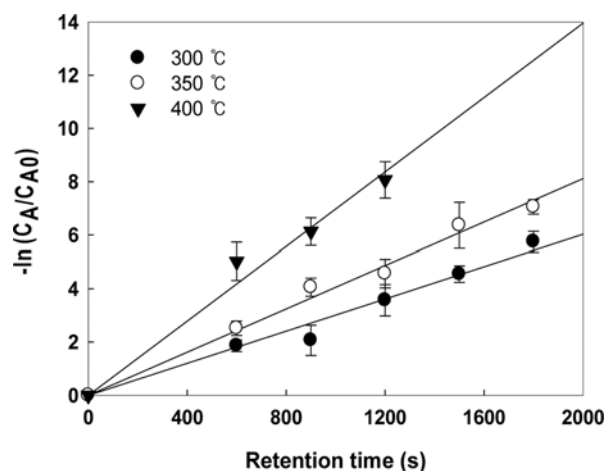

Fig. 10. Soil thermal desorption kinetics of pyrene with respect to reaction temperature and residence time.
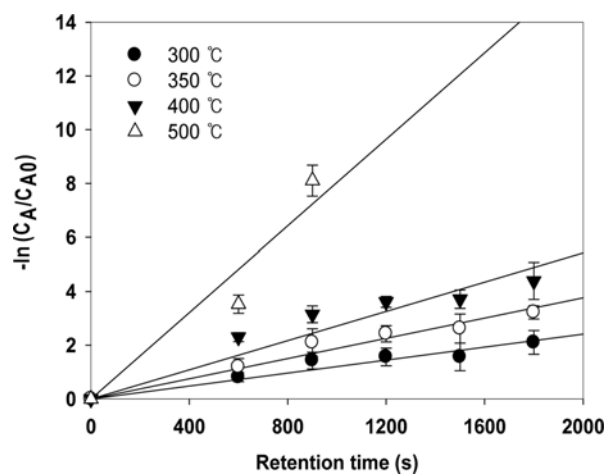

Fig. 11. Soil thermal desorption kinetics of benzo(a)pyrene with respect to reaction temperature and residence time.

desorption was estimated. For this, thermal desorption reaction rate constant (k_{des}) should be determined from the exponential fits to the experimental plots [19]. At low desorption rates the experimental plots could be described by first-order kinetics. To find k_{des} for each PAH, the slope of the desorption ratio vs. residence time was calculated, as shown in Figs. 8-11, and from this, k_{des} with respect to temperature was evaluated.

Formula (6) was rearranged as shown in formula (7), and the activation energy (E_A) was calculated from the slope of the graph of ln(dX/dt) against 1,000/T with the heating rate as a parameter [13, 14,19]. The absorbed contaminant was assumed to be an irreversible primary reaction and does not combine with other substances, and instead is desorbed.

$$\frac{dX}{dt} = \ln[A(1-X)] - \frac{E_A}{RT} \tag{7}$$

To compute the activation energy, the natural logarithm of the reaction rate constant was plotted against the reciprocal of the temperature and a linear fit was found. If the residence time is 0 sec, all lines will pass the starting point since the initial concentration C_{A0} and post-reaction concentration C_A are the same.

For fluorene, at thermal desorption temperatures of 300, 350 and 400 °C, the reaction rate constants were found to be 0.00299, 0.00401, and 0.00759 s^{-1}, respectively, and at a reaction temperature of 400 °C, after a residence time of 1,200 sec, residual fluorene was no longer detected. The reaction rate constants at thermal desorption temperatures of 300, 350, 400, and 500 °C were 0.00235, 0.00352, 0.00504, and 0.01299 s^{-1}, respectively, for anthracene; 0.00140, 0.00224, 0.00357, and 0.00860 s^{-1} for pyrene; and 0.00123, 0.00191, 0.00283, and 0.00804 s^{-1} for benzo(a)pyrene.

Since the initial concentration of each PAH is the same, the reaction rate will be proportional to a constant k, and using this, the thermal desorption rate of each substance can be compared. According to the results of the experiment, the thermal desorption reaction rate of each substance increases as the temperature increases, and if the reaction rate of each PAH is compared, the reaction rate increases as the molecular weight and boiling point of the substance
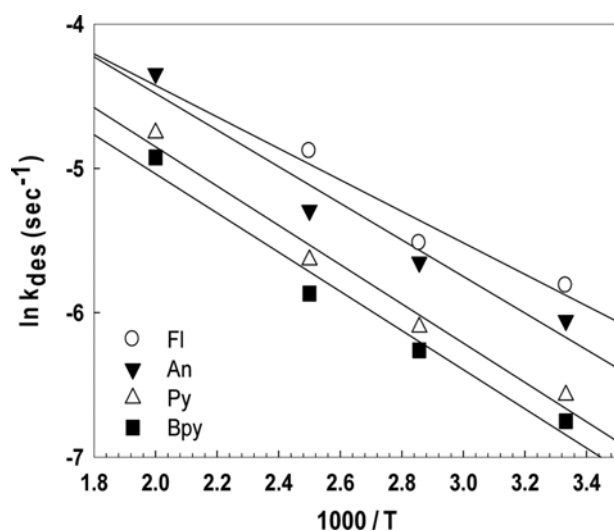

Fig. 12. Reaction rate constant with respect to temperature for each PAH.

Table 6. Results of thermal desorption experiment of PAH from soil

PAHs	1000/T (K^{-1})	k (s^{-1})	$\ln k_{des}$	E_A (kJ/mol)
Fluorene	3.333	0.00299	−5.8125	29.50
	2.857	0.00401	−5.5190	
	2.500	0.00759	−4.8809	
Anthracene	3.333	0.00235	−6.0533	31.40
	2.857	0.00352	−5.6493	
	2.500	0.00504	−5.2903	
	2.000	0.01299	−4.3436	
Pyrene	3.333	0.00140	−6.5713	33.56
	2.857	0.00224	−6.1013	
	2.500	0.00357	−5.6352	
	2.000	0.00804	−4.7560	
Benzo(a)pyrene	3.333	0.00123	−6.7007	34.48
	2.857	0.00191	−6.2607	
	2.500	0.00283	−5.8675	
	2.000	0.00804	−4.8233	

get lower.

By displaying the relationship between the reaction rate constant, reaction temperature reciprocal, and reaction rate estimated using the reaction time and concentration of desorbed PAHs, the activation energy needed for thermal desorption can be evaluated. Fig. 12 shows the reaction rate constant for the reaction temperature of each substance, and the activation energy of each pollutant can be calculated using the Arrhenius equation as follows.

Using the above formula and the reaction rate constants for each temperature, the activation energy can be estimated. As in formula (4), using the slope of reaction rate constant from Fig. 12 and the reaction temperature, the activation energy could be estimated and is listed in Table 6. The activation energies of the thermal desorption of naphthalene, fluorene, anthracene, pyrene, and benzo(a)pyrene were found to be 29.1, 29.5, 31.4, 33.6 and 34.5 kJ/mol, respectively, and these values are in proportion to the corresponding boiling points of 295, 338, 404, and 496 °C.

CONCLUSIONS

Thermal desorption experiments of soils contaminated with PAHs were performed using a lab-scale rotary desorber, and the removal efficiencies of fluorene, anthracene, pyrene, and benzo(a)pyrene were determined, Based on this, the reaction rate constants and activation coefficients were obtained. The results indicated that an increase in the water content of the soil caused an increase in the vaporization heat and a decrease in the thermal desorption efficiency; for pyrene and benzo(a)pyrene, which have a high boiling point, the thermal desorption efficiency was 90% or less when the water content was 10% or higher. Additionally, a thermal desorption efficiency experiment was conducted for residence times of 0-15 min and within a temperature range of 300-500 °C, and from this the reaction rate constants of the PAHs were calculated. From these rate constants at different temperatures, the activation energies were found to be in the range 29.50-34.48 kJ mol^{-1}.

Based on all the experimental findings, the reported kinetic data obtained for desorption of PAHs seem to represent a significant and useful support for operating parameter of thermal rotary desorber. The water content should be controlled about 10% for economic operation and effective thermal desorption efficiency. The optimum thermal desorption temperature and residence time for contaminated soil vary depending on the number of ring for PAHs. It is anticipated that the results of the experimental data could help to identify the optimal operating conditions for thermal desorption processes.

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