

Low-temperature thermal desorption of aromatic compounds from activated carbon

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Abstract

Low-temperature thermal desorption of three aromatic compounds (toluene, chlorobenzene, and nitrobenzene) loaded on activated carbon was investigated. Desorption kinetics of these compounds followed an exponential-decay-type model assuming a distribution of sites over a range of activation energies. The activation energies of toluene, chlorobenzene and nitrobenzene were 17.6, 26.0, and 35.6 kJ mol⁻¹, corresponding to initial surface concentrations of 190, 300, and 610 mg g⁻¹, respectively. The desorption parameters determined using a simplified model predicted the aqueous phase adsorption of toluene and nitrobenzene and were used to estimate the residual contaminant concentrations as a function of time and temperature. The presence of electron-withdrawing functional groups increases the activation energy and thus the higher temperature required for desorption. © 1997 Elsevier Science B.V.

Keywords: Activated carbon; Desorption; Kinetic model; Low temperature; Regeneration

1. Introduction

Activated carbon is widely used for the removal of aqueous toxic organics and gaseous contaminants. The economic feasibility of this process is highly dependent upon regeneration costs of the used carbon. Currently, spent carbon is regenerated by thermal treatment, chemical treatment, or solvent extraction. Chemical regeneration is rather selective, achieving only partial regeneration [1], and solvent extraction is not cost effective and is inadequate for aromatic compounds possessing electron-donating func-

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tional groups [2]. Thermal regeneration is the most common process [3] in which temperatures close to 1000°C are used to desorb weakly bound pollutants (i.e., adsorption energies 40–170 kJ mol⁻¹). Such high temperatures not only increase the fuel cost but also reduce the adsorption capacity of regenerated carbon.

It has been demonstrated that 90% desorption of aromatic compounds with polar functional groups from activated carbon occurs below 450°C [4–6]. As a result, low-temperature thermal desorption (LTTD) processes have been proven useful to treat soils contaminated with various organics [7–9]. The LTTD process uses relatively low temperatures (110–400°C) to desorb organics from soil surfaces, resulting in a significant cost saving. LTTD is particularly applicable to the regeneration of activated carbon contaminated with organics with low boiling points, such as organic solvents [10,11]. In addition to low energy consumption, low temperature regeneration further provides other advantages:

1. solvents can be recovered, and
2. destruction of carbon pore structure is minimized, resulting in an insignificant loss of adsorption capacity.

Unlike adsorption, information on desorption from activated carbon in general and thermal desorption in particular is rather limited. There are very few citations in the literature concerning the low-temperature regeneration of activated carbon. To date the most comprehensive study was conducted by Suzuki et al. [12] who used 32 selected compounds and proposed a model based on Langmuir isotherms to describe the thermogravimetric desorption curves of volatile organics. This model, however, involves many assumptions and cumbersome graphical determination of some parameters. Hori et al. [13] described the thermal desorption of benzene using an empirical two-stage, first-order type equation. The desorption of a single component (toluene) and a multi-component system was further modeled on the basis of empirical mass-transfer correlations by using a linear adsorption isotherm [14,15]. However, these models failed to predict desorption rates. Krebs and Smith [16] used a simplified exponential decay type model to describe LTTD of phenol. All of these studies used thermogravimetric analysis to monitor the contaminant weight loss, with possibly erroneous results due to the formation of byproducts that remained adsorbed.

For optimum process design, the fundamentals of regeneration need to be studied more extensively, particularly the kinetics of the thermal desorption process. Consequently, this paper addresses the LTTD desorption kinetics of toluene, chlorobenzene, and nitrobenzene loaded on to activated carbon. Specifically, the capability of the existing exponential decay model [16] to estimate the residual sorbed concentration as a function of time and temperature was evaluated. Unlike other LTTD studies where thermogravimetric analysis was used to monitor the contaminant mass loss, the present study used solvent extraction, allowing a contaminant mass balance.

2. Theory

It is well known that activated carbon has a distribution of sites with varying activation energies [17]. According to Polanyi's potential theory, the adsorbate is loaded

first on the high-energy sites and subsequently on lower energy sites [10]; the contaminants sorbed on the lower activation energy sites desorb more quickly than those at higher energy sites and the desorption rate at any time can be approximated by:

$$r = k_a C_a + k_b C_b + k_c C_c + \dots + k_n C_n \tag{1}$$

where C_n represents the concentration of contaminant sorbed on sites n and k_n is the desorption rate from these sites. Krebs and Smith [16] developed a model based on the distribution of sites over a wide range of activation energies:

$$\frac{d\theta}{dt} = A \cdot n \cdot \theta^{[1 - \frac{1}{n}]} \tag{2}$$

where $\theta = q/q_0$, q being the sorbed concentration at time t and q_0 the initial sorbed concentration. The constants A and n are defined by the following equations:

$$A = \frac{\nu_0}{-\ln(0.5)} \exp\left(\frac{-E_0}{RT}\right) \tag{3}$$

$$n = \frac{C_1 RT}{C_2 RT - E_0} \tag{4}$$

where E_0 is the activation energy (kJ mol^{-1}) corresponding to the initial concentration; ν_0 is the frequency factor (min^{-1}) associated with E_0 ; R is the universal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}$); T is the absolute temperature (K); and C_1 and C_2 are dimensionless constants. The model assumes that:

1. the desorption rate is first-order for each site,
2. the minimum activation energy required for desorption is E_0 , and
3. the frequency factor increases with activation energy.

Integration of Eq. (2) at the initial conditions ($\theta = \theta_0$ at $t = 0$) yields:

$$\frac{\theta}{\theta_0} = \left\{ \left[A(\theta_0)^{-\frac{1}{n}t} + 1 \right]^n \right. \tag{5}$$

Krebs and Smith [16] further extended this model to derive an adsorption isotherm from aqueous phase adsorption as:

$$\theta = \left(\frac{C}{C^*} \right)^{-n} \tag{6}$$

which in its logarithmic form has a Freundlich's expression:

$$\log \frac{q}{q_0} = -n \log C + n \log C^* \tag{7}$$

where C is the aqueous phase concentration, C^* is K_0/H where $K_0 = \nu_0/\nu^*$, and n is given by Eq. (4). The slope of Eq. (7) ($-n$) and the slope of the Freundlich equation ($1/n$) are the same; however the intercept term is not comparable [16].

3. Methodology

3.1. Adsorption

HPLC grade toluene and *n*-hexane (Fisher) and reagent grade dichloromethane, chlorobenzene, and nitrobenzene (Baker) were used as supplied. A lignite-coal-based carbon, US mesh 16×20 (Darco), was loaded with the organic solvent of interest by soaking the carbon particles (5 to 10 g) with 100 mL of the organic solvent in a 125-mL flask overnight, filtering excess solvent and drying the carbon at 60°C for 15–20 min. Samples taken randomly from different locations of the carbon were extracted and analyzed for solvent, and a relatively constant solvent concentration was observed throughout the carbon mass. Deionized water was used whenever necessary.

3.2. Extraction efficiency evaluation

The equilibrium partitioning method described by Dommer and Melcher [18] was followed. Toluene was extracted with *n*-hexane, whereas chlorobenzene and nitrobenzene were extracted with dichloromethane. For toluene, the extraction efficiencies ranged from 93–98% corresponding to solid-phase concentrations of 33 to 225 mg g⁻¹; the range was from 93–95% for chlorobenzene with solid-phase concentrations from 25 to 312 mg g⁻¹ and 98–99% with solid-phase concentration of 25–263 mg g⁻¹ for nitrobenzene.

3.3. Adsorption isotherms

Different masses of carbon were added to deionized water in 35-mL vials and a predetermined amount of toluene was injected into each vial. After 72 h shaking at 25°C, samples were filtered. Filtrate and carbon collected on the filter were separately extracted and analyzed for toluene to determine its solid and solution concentrations. This approach facilitated a mass balance for toluene, thereby verifying the overall technique including the method of extraction. Mass balances accounted for 93–103% of the added toluene. The same procedure was followed for nitrobenzene.

3.4. Thermal desorption experiments

All thermal desorption experiments were conducted in an oven (model OV-12A, Blue-M Electric Co.) with an external temperature controller as shown in Fig. 1. Contaminated carbon was placed into 35-mL pre-weighed borosilicate vials. To minimize temperature gradient within the carbon mass, small samples of contaminated carbon (0.15–0.2 g) were used [19]. Nitrogen gas was used to create an oxygen-free atmosphere in the oven and to flush the desorbed contaminants to increase the mass-transfer. Nitrogen gas was introduced at the bottom of the oven and exhaust was released into a fume hood. A test was designed to evaluate the mass- and heat-transfer in the oven. Samples of different mass were placed at different locations of the rack. Samples analyzed at the end of a particular time period showed essentially the same

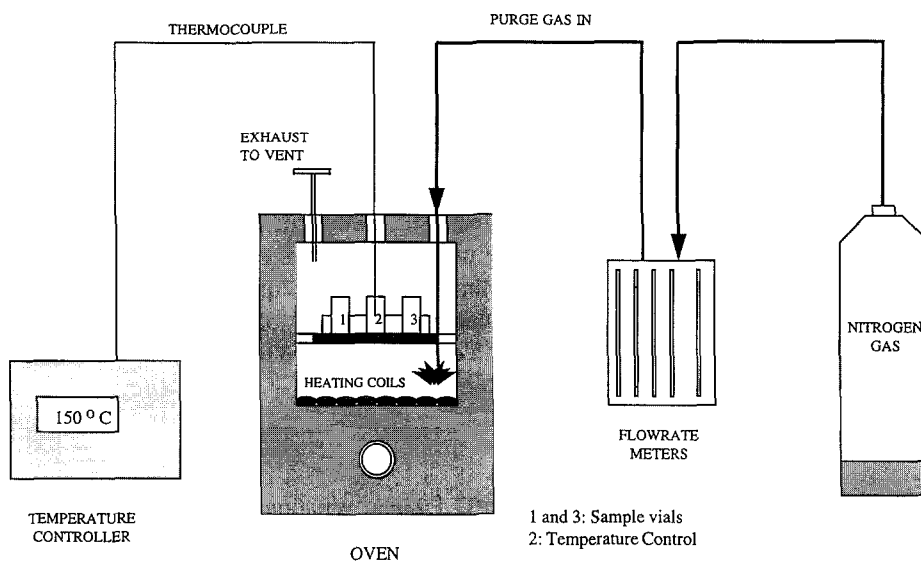


Fig. 1. Thermal desorption experimental set-up.

toluene concentration (Fig. 2). The results indicated that heat- and mass-transfer inside the oven were relatively uniform.

For the desorption experiments, the oven was initially preheated to the desired temperature. Caps of the vials were quickly removed and test tubes containing the sample vials were introduced into the oven. A thermocouple equipped with a digital

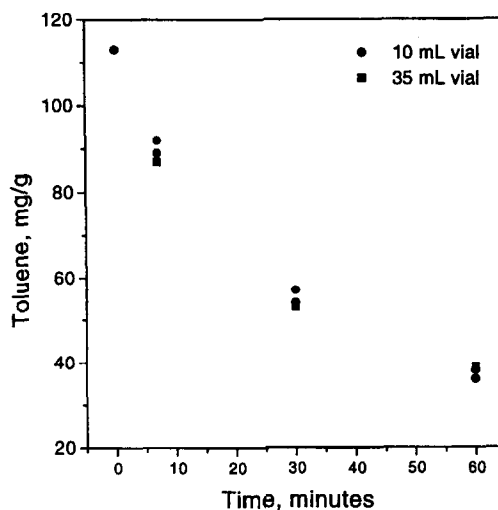


Fig. 2. Mass- and heat-transfer test where the vials were randomly located. Time = 0 indicates the time that the oven reached 150°C. Each point represents a single vial sample.

temperature display (Model 4842, Parr Instruments) was used to monitor the temperature. The thermocouple was inserted into the carbon mass in the control vial (without contaminant) located at the center of the oven. A temperature drop was always observed when the samples were introduced into the oven. It generally took 20 min for the system to reach the pre-set temperature. As soon as the target temperature was reached (termed $t = 0$), a sample vial was taken out for determining the initial contaminant concentration. Random samples were then removed at different time intervals for 2 h for measuring the contaminant concentration. After removing the vials from the oven, they were immediately capped with Teflon-coated rubber septum caps and were quenched in an ice bath to inhibit further desorption. A measured volume (30–35 mL) of extraction solvent was then added. The vials were vortex mixed (Vortex Genie, VWR Scientific) for 2 min at full speed and shaken for 72 h, before contaminant analysis.

3.5. Analytical methods

The samples were filtered through a GF/C 1.2 μm Whatman filter, using a filtration cartridge. Samples were extracted and analyzed for toluene, chlorobenzene, and nitrobenzene in a Perkin–Elmer 8500 gas chromatograph equipped with a flame ionization detector. Chlorobenzene was used as internal standard for the analysis of toluene and nitrobenzene, and toluene was the internal standard for chlorobenzene analysis. A Hewlett–Packard HP-5 (5% phenylpolydimethylsiloxane) capillary column was used.

4. Results and discussion

4.1. Adsorption isotherm

The equilibrium aqueous and solid concentrations obtained for toluene and nitrobenzene are shown in Fig. 3. Adsorption appears to follow the pattern of Freundlich's isotherms ($q = KC^n$) where q is the solid-phase concentration (mg g^{-1}), C is the aqueous-phase concentration (mg L^{-1}), and K and $1/n$ are constants. The K values were found to be 58 and 102, respectively, for toluene and nitrobenzene; the corresponding $1/n$ values were 0.24 and 0.26. The slight difference between our results and those reported in other adsorption studies (e.g., 0.43 for nitrobenzene and 0.30–0.45 for toluene, [20–22]) could be the result of the nature of the activated carbon and/or the experimental method used. In those studies, the solid-phase concentration was determined as the difference in the aqueous-phase concentration before and after the addition of carbon. The solid-phase contaminant concentration obtained by extraction might be a better method, particularly for volatile organics where losses other than adsorption may take place.

4.2. Desorption kinetics

The solid phase contaminant concentration profiles at different temperatures are shown in Fig. 4. The desorption rate was rapid in the first few minutes, and eventually

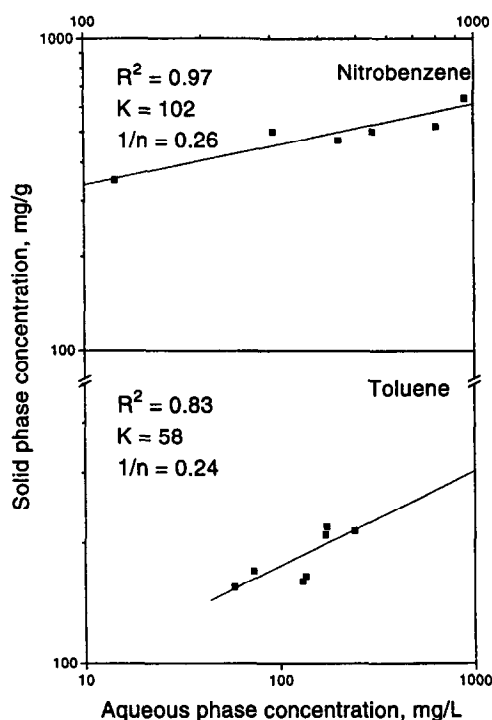


Fig. 3. Adsorption isotherms for toluene and nitrobenzene at $T = 25^{\circ}\text{C}$. Initial aqueous phase concentrations were from 61 to 345 mgL^{-1} for toluene and from 122 to 1021 mgL^{-1} for nitrobenzene.

desorption slowed and a contaminant concentration plateau was reached at each temperature. The higher the temperature (more energy input), the lower the residual concentration, as expected by Polanyi adsorption potential theory where adsorbate loaded on the low-energy sites desorbs first and the energy required increases as desorption progresses.

Data (θ versus t) were used according to Eq. (5) to obtain the parameters A and n , using non-linear least-squares fitting. The parameters are summarized in Table 1. The activation energies (E_0) corresponding to the initial concentration and the frequency factor ν_0 were then calculated using Eq. (3). The parameters A and $-\frac{1}{n}$ were plotted

Table 1
Parameters A and n in rate Eq. (5)

Temperature ($^{\circ}\text{C}$)	Toluene			Chlorobenzene			Nitrobenzene		
	A	$-n$	χ^2	A	$-n$	χ^2	A	$-n$	χ^2
120	0.09	0.41	4.98×10^{-5}	0.09	0.43	1.40×10^{-4}	–	–	–
150	0.12	0.55	1.22×10^{-4}	0.16	0.50	1.11×10^{-4}	0.13	0.45	3.88×10^{-5}
180	0.19	0.64	1.19×10^{-4}	0.26	0.61	1.07×10^{-5}	0.22	0.56	9.55×10^{-5}
210	–	–	–	–	–	–	0.45	0.61	1.10×10^{-4}

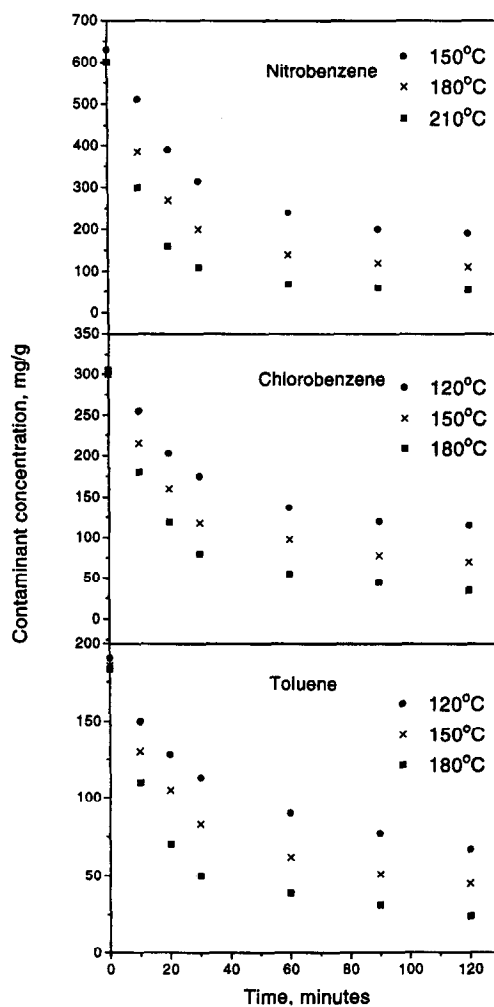


Fig. 4. Contaminant solid-phase concentration profiles as a function of time and temperature.

against the reciprocal of absolute temperature on a semi-log and linear plot, respectively. The constants E_0 , ν_0 , C_1 and C_2 were determined from the intercept and the slopes as shown in Fig. 5. The results are summarized in Table 2.

Table 2
Kinetic parameters

	E_0 ($/(kJ mol^{-1})$)	ν_0 ($/min^{-1}$)	C_1	C_2
Toluene	17.6	14	0.82	3.44
Chlorobenzene	26	182	1.5	4.42
Nitrobenzene	35.6	2100	2.17	5.4

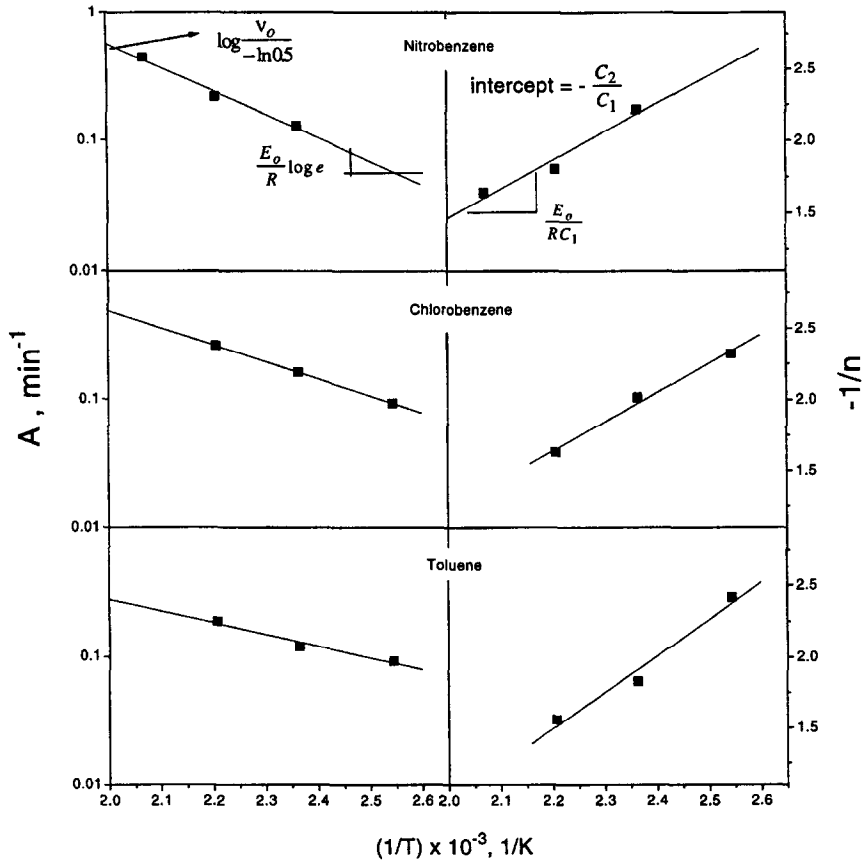


Fig. 5. Temperature-dependence of A and n . Determination of temperature-independent parameters E_0 and ν_0 .

Experimental desorption rates were calculated by numerical differentiation of the data in Fig. 4. The temperature-independent constants E_0 , ν_0 , C_1 and C_2 from Fig. 5 were used to back-calculate the temperature-dependent parameters A and n , which were, in turn, used to determine the model-predicted desorption rate using Eq. (2). The experimental and predicted rates are shown in Fig. 6. The good agreement between the two indicates the accuracy of the model and its capability to estimate thermal desorption rates of three different aromatic compounds at different temperatures.

The LTTD kinetic model was further used to determine the residual contaminant concentrations on activated carbon as a function of temperature and time using the parameters from Table 2. The results are depicted in Fig. 7. Fig. 7(a) shows the residual toluene concentration as a function of time and oven temperature. Fig. 7(b) shows the residual concentrations of the three compounds studied as a function of temperature. The good agreement between the experimental residuals and the concentrations predicted by Eq. (7) indicates the applicability of the LTTD model to optimize temperature, time, and expected residual for thermal regeneration processes.

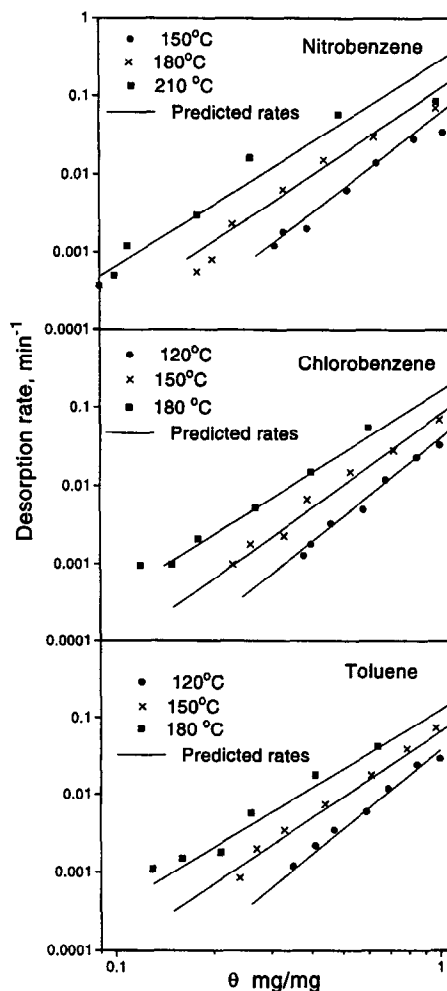
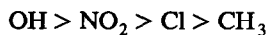


Fig. 6. Comparison of experimental and predicted initial desorption rates as a function of temperature and surface coverage. Toluene loading = 190 mg g^{-1} ; chlorobenzene loading = 300 mg g^{-1} ; nitrobenzene loading = 610 mg g^{-1} .

The frequency factor increases with the activation energy. Semi-log plots of ν_0 against E_0 for four substituted benzenes (phenol data were obtained from Ref. [16]) shown in Fig. 8 indicate that the frequency factor increases logarithmically with the activation energy as:

$$\nu_0 = 0.032(10^{0.143E_0})$$

and the activation energies follow the substituent order:



According to the donor–acceptor complex theory, the aromatic ring of the contami-

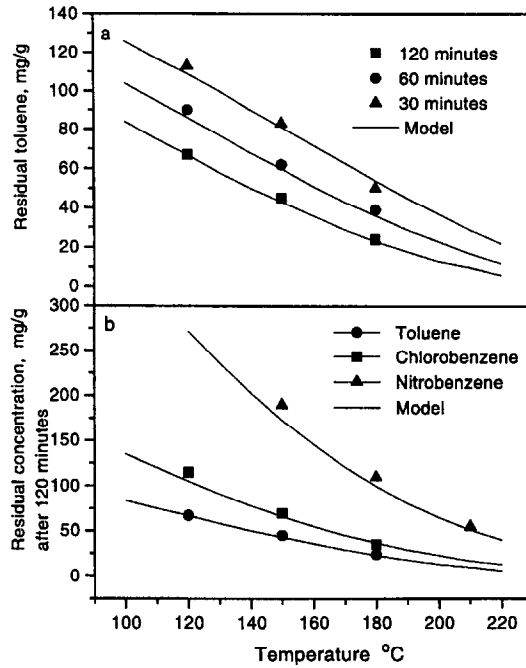


Fig. 7. Comparison of experimental and predicted contaminant solid-phase residual concentrations as a function of temperature. (a) Toluene residuals as a function of time. (b) Residuals as a function of contaminant structure.

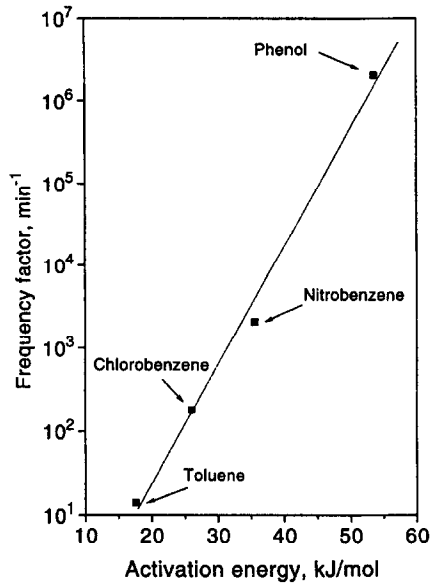


Fig. 8. Relation between activation energy and frequency factor for LTTD process.

nant, acting as an electron acceptor, forms a complex with the surface functional groups of the activated carbon. The presence of electron-withdrawing groups on the aromatic ring, such as NO_2 , Cl, and CH_3 , reduces the electron density in the π -system of the aromatic ring and leads to a much stronger interaction between the contaminant and the carbon [2]. In the case of phenol the OH group can specifically interact with activated carbon surface functional groups leading to a higher adsorption energy.

The parameters from the LTTD model obtained from desorption data at 120–210°C effectively predicted the $\frac{1}{n}$ of the Freundlich isotherm from aqueous phase adsorption at 25°C with predicted values of 0.22 and 0.24 (from Eq. (4)) compared with the experimental values of 0.24 and 0.26 for toluene and nitrobenzene, respectively. The fact that the Freundlich isotherm is based on exponential distribution of sites of different activities and that the parameters of the Freundlich equation can be obtained from the LTTD model indicates that the model could be applied to describe the desorption kinetics of systems in which adsorption isotherms follow Freundlich's equation. It has been reported that the Freundlich isotherm is accurate for describing the adsorption of several organic pollutants on soils and sediments [23–25]. Therefore, it seems possible to apply the LTTD model to predict the desorption of organics from soils as well as from activated carbon.

5. Conclusions

This study showed that the LTTD kinetic model can be used to estimate desorption rates for aromatic compounds loaded on to activated carbon, and the adsorption isotherms for toluene and nitrobenzene. The temperature-independent desorption parameters can be used to estimate residual contaminant concentrations as a function of time and temperature. Desorption efficiencies of over 90% were achieved with temperatures of 200°C in less than 2 h for toluene. The desorption efficiency decreased for contaminants possessing electron-withdrawing groups on the aromatic ring. For contaminants able to form a complex with activated carbon surface groups, higher temperatures and longer residence times are needed for adequate desorption. Our results indicate that the temperature and time requirements for LTTD regeneration of activated carbon will be a function of the sorbed contaminant.

6. Notation

A	= constant defined by Eq. (3), min^{-1}
C	= equilibrium liquid phase concentration, mg L^{-1}
C_1 and C_2	= constants in Eq. (4)
C_0	= initial liquid phase concentration, mg L^{-1}
C_n	= sorbed concentration at specific surface sites n
E_0	= activation energy, J mol^{-1}
H	= Henry's constant

k_n	= desorption rate from specific sites n
K	= adsorption equilibrium constant
n	= exponent defined by Eq. (4), and in the Freundlich isotherm
q	= sorbed concentration at time t , mg g^{-1}
q_0	= sorbed concentration at time $t = 0$, mg g^{-1}
r	= desorption rate, min^{-1}
R	= gas constant, J mol K^{-1}
T	= temperature °C or K
t	= time, min
Greek symbols	
θ	= sorbed fraction at time t , mg mg^{-1}
θ_0	= sorbed fraction at time $t = 0$, mg mg^{-1}
ν	= frequency factor for desorption, min^{-1}
ν^*	= frequency factor for adsorption, $(\text{Pa min})^{-1}$
ν_0	= frequency factor for desorption corresponding to E_0 , min^{-1}

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