Adsorption (2009) 15: 461–475
DOI 10.1007/s10450-009-9195-4

Adsorption of toluene and 1,1,1-trichloroethane on selected adsorbents under a range of ambient conditions

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Received: 23 January 2008 / Accepted: 28 September 2009 / Published online: 13 October 2009
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Abstract The effects of ambient temperature (25°C to 40°C) and relative humidity (0% to 30%) on the adsorption of toluene, and 1,1,1 trichloroethane on silica alumina, silica alumina impregnated with $KMnO_4$, and activated carbon granules and pellets were determined. VOC concentrations in the range 1–1000 ppm were studied. Measurements of the weight of the adsorbed VOCs as a function of time were made in a thermogravimetric analyzer (TGA). Linear isotherms were tested in all cases. Values of the Henry coefficient H were in the range 0.01–0.10 mm^3 air/mm^2 BET area; they decreased with both increasing temperature and relative humidity. The highest values of H were consistently observed with $KMnO_4$-impregnated silica alumina. Empirical correlations relating H to the parameters employed in this study were derived. There was good agreement between the values of H calculated from equilibrium and kinetic data obtained in the TGA and corresponding values measured in a glass test chamber. Improved correlation of the data was obtained using the nonlinear Freundlich, Toth and Dubinin isotherms. The determined fitting parameters for toluene and 1,1,1-trichloroethane on activated carbon were in good agreement with data published in the literature.

Keywords Adsorption · VOC · Activated carbon · Silica alumina · Activated silica alumina · Relative humidity · Isotherms

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Abbreviations

A_{BET}	BET surface area of the adsorbent (TGA experiments) (m^2/g)
A_D	Empirical constant in Dubinin isotherm $(mol/J)^2$
A_{si}	BET surface area of the adsorbent (test chamber experiments) (m^2)
A_{so}	Surface area of VOC source (m^2)
C_b	Bulk VOC concentration in the TGA chamber (mg/m^3)
C_i	Concentration of VOC within (and exiting from the test chamber) (mg/m^3)
C_o	VOC concentration in the inlet zero air (mg/m^3)
C_s	Sorbed weight per unit surface area (mg/m^2)
C_{sm}	Empirical constant in Toth isotherm (mg/m^2)
H	Henry constant calculated from TGA equilibrium tests (mm^3 air/mm^2 BET area)
H'	Henry constant calculated from TGA dynamic tests (mm^3 air/mm^2 BET area)
H''	Henry constant calculated from test chamber tests (mm^3 air/mm^2 BET area)
I_{ads}	Adsorbent index (–)
I_{voc}	VOC index (–)
k	Dimensionless mixing factor (–)
k_a	Adsorption rate constant, TGA (m/h)
k'_a	Adsorption rate constant, test chamber (m/h)
k_d	Desorption rate constant, TGA (h^{-1})
k'_d	Desorption rate constant, test chamber (h^{-1})
k_F	Empirical constant in Freundlich isotherm (mg/m^2)
k_T	Empirical constant in Toth isotherm (bar^τ)
k_s	Decay rate constant (h^{-1})
Mw	VOC molecular weight (g/mole)
n	Empirical constant in Freundlich isotherm (–)
N	Actual air exchange rate (h^{-1})
NMSE	Normalized mean square error (–)
P	Partial pressure of VOC (bar)

P_t	Total pressure (bar)
P^o	Vapor pressure of VOC (bar)
Q	Volumetric flowrate of air entering the test chamber (m^3/h)
R	Universal gas constant (cm^3 bar/mol.K)
R^2	Correlation coefficient (–)
R_o	Initial emission rate of VOC (mg/m^2.h)
$R_s(t)$	Evaporation rate of VOC (mg/m^2.h)
RH	Relative humidity (%)
t	Time (h)
t_{evap}	Time taken for the VOC to completely evaporate from the dish (h)
T	Temperature (°C, K)
v	VOC liquid molar volume (cm^3/g)
v_o	Empirical constant in Dubinin isotherm (m^3/kg)
V_{tga}	Volume of TGA chamber (m^3)
V_{tc}	Volume of test chamber (m^3)
ΔU_o	Activation energy (kJ/mol)
τ	Empirical constant in Toth isotherm (–)

1 Introduction

Volatile Organic Compounds (VOCs), many of which are classified as carcinogens, may give rise to indoor air quality problems when individual compounds or their mixtures exceed certain concentrations. In theory, the removal of gaseous contaminants from indoor air, or from outdoor air drawn into ventilation systems, can be achieved by adsorption. In this process, adsorbate species are transported via convection and molecular diffusion from the bulk air phase to locations near the adsorbent boundaries. Diffusion processes then take over to move the adsorbate first through the boundary layer surrounding the adsorbent and then through the porous interstices of the solid. Finally, physical or chemical processes bind the adsorbate to the surface of the adsorbent.

The large internal surface area of sorbents provides a favorable medium for chemical reactions. These surfaces can be coated or impregnated with chemicals that may selectively react with or chemisorb molecules from a gas stream. Activated alumina impregnated with potassium permanganate ($KMnO_4$) is one such example. It is used in air-cleaning systems and is best known by the trade names Purafil and Carasorb. Adsorption on activated alumina is irreversible until the operating conditions are changed in an appropriate manner.

VOCs are often the principal cause of poor indoor air quality (IAQ), particularly in homes. Previous studies by Bouhamra et al. (2000) and BuHamra et al. (1998) published by the present research team showed the presence of high levels of benzene and chlorinated VOCs in 100 houses in Kuwait. The health risk calculated on the basis of the detected concentrations was high compared to international levels. The objective of the present study is to determine the adsorption and desorption characteristics of two typical VOCs on four selected adsorbents under a range of typical ambient (temperature and humidity) conditions. This represents a step towards building stand-alone units with adsorbent filters to remove VOCs from indoor air.

2 Experimental

2.1 Materials

Four adsorbents were employed in this study: silica alumina, silica alumina impregnated with potassium permanganate, activated carbon pellets and activated carbon granules. Reagent silica alumina grade 135 was obtained from Aldrich Chemical Co, UK, and was used as received. It was a fine amorphous powder with an alumina content of 13% and a pore volume of 0.77 cm^3/g. According to the manufacturer, $> 90\%$ of the particles were smaller than 100 mesh (149 μm). Its measured N_2-BET surface area was 496 m^2/g. The impregnated silica alumina was prepared with reagent grade $KMnO_4$ (BDH, UK) using a technique similar to that described by Ott and Baiker (1983); full details are given elsewhere (Alkandari 2001). The N_2-BET surface area of the $KMnO_4$-impregnated silica alumina was 276 m^2/g.

The activated carbon used in this research was supplied by Norit of the Netherlands (Type PK-1-3). The 1–2 mm sized granules were irregularly shaped. The pellets were cylindrical, measuring around 2 × 3 mm. The N_2-BET surface areas of the granules and pellets were 828 and 670 m^2/g, respectively. Two analytical reagent-grade VOCs were used in the experiments: toluene (PRS, Spain), and 1,1,1-trichloroethane (Ajax Chemicals, Australia).

2.2 TGA experiments

Adsorption isotherms Measurement of the adsorption isotherms was performed on a TGA-51 thermogravimetric analyzer (Shimadzu Corporation, Japan) having a chamber volume of 73.63 cm^3. The experiments were typically carried out at four different temperatures in the range 25–40°C and a range of VOC concentrations (1–1000 ppm) measured to around $\pm 1\%$ by gas chromatography. Fresh adsorbent was used in each experiment. Before use, it was refreshed by passing "zero" air over it for 24 h at the temperature of the particular experiment. The zero air (Kuwait Oxygen & Acetylene Co) contained < 5 ppm water vapor and < 1 ppm hydrocarbons.

Each experiment was performed as follows. The desired concentration of the organic vapor in zero air was prepared in the laboratory by injecting a known amount of VOC into a one-liter polypropylene gas sampling bag (Supelco) using an appropriate microvolume syringe (Hamilton). Full details are given elsewhere (Elkilani et al. 2003). The TGA balance pan was first zeroed. A known quantity of adsorbent (70–200 mg) was then placed in the pan and its initial weight recorded. One liter of the VOC/air mixture was injected into the balance chamber with the outlet valve open to flush out the existing air and to ensure that the concentration inside the TGA was the same as that in the tedlar air bag. The inlet and outlet valves were then closed and the adsorbent weight and temperature were measured as a function of time until constant values were attained. Each run took around two hours.

Effect of relative humidity In one set of experiments, the effect of relative humidity on the adsorption of the VOCs was determined on the TGA. The humidity of the air was varied from 0% to 30% using a Hovacal (IAS GmbH, Germany) humidifier. Zero air and distilled water was supplied to generate a pure air-water vapor mixture. Each experiment consisted of two parts. First, the tedlar bag was filled solely with air of the desired humidity and injected into the TGA in the manner described above. The purpose of this test was to determine the equilibrium quantity of moisture adsorbed by the adsorbent (either activated carbon granules or untreated silica alumina) at the prescribed relative humidity. In the case of the activated carbon, this was found to range between 0.012% and 0.033% of the adsorbent weight, depending on the conditions employed. The percentage of moisture adsorbed increased with increasing relative humidity and decreased with increasing temperature. In the case of silica alumina, the quantity of adsorbed moisture was essentially constant ($0.02 \pm 0.0037\%$ of the adsorbent weight), irrespective of the experimental conditions employed. Secondly, the experiment was repeated using air of the same temperature and relative humidity containing the required concentration of VOC. The quantity of VOC adsorbed was calculated by subtracting the adsorbed weight of moisture obtained in the first part of the experiment from that of the VOC plus moisture measured in the second. In all cases, it greatly exceeded that of the adsorbed moisture ($< 1\%$ and $< 1.2\%$ of the adsorbent weight in the cases of activated carbon and silica alumina, respectively).

2.3 Test chamber experiments

A 50.3-cm long × 45.0-cm wide × 14.8-cm high glass test chamber was used to study the decay of VOC concentration under controlled conditions. It had 6-mm diameter diametrically opposed openings for the inlet and outlet air, a fan to mix the air thoroughly, and a heating tape to control the temperature. The VOC was placed inside a 7-cm diameter petri dish centrally located on the floor of the chamber.

A Domnick Hunter ANG 600/2 air/nitrogen generator was used to supply the test chamber with purified air, which was essentially free of water (< 2.5 ppm) and hydrocarbons. A Monostat Size 4 flowmeter located between the purified-air generator and the test chamber was used to control the air flow at a constant 0.9 l/min, which corresponded to an air exchange rate in the chamber of around 1.6 h^{-1}.

Two sets of experiments were performed with air/toluene and air/1,1,1-trichloroethane mixtures at 20° and 40°C. The first set was carried out with the test chamber containing no adsorbent material. In the second set, a known weight (5–69 g) of adsorbent (untreated silica alumina, silica alumina impregnated with $KMnO_4$, or activated carbon granules) was placed in a 9.2 cm-diameter dish inside the test chamber. Before use, the adsorbents were stored with silica gel and subsequently exposed to a constant flow of zero air for 24 h in the test chamber to remove any pre-sorbed compounds.

At the start of each experiment, the VOC was added to the petri dish through a rubber tube. During the run, purified air was pumped from the Domnick Hunter generator through the inlet-air opening at the specified constant flow rate. Air samples were taken at 5-minute intervals at the outlet from the chamber using an airtight gas syringe. These were injected into a gas chromatograph for analysis of the hydrocarbon content. Measurements were continued until the VOC concentration had dropped to essentially zero.

3 Modeling

3.1 TGA chamber

Adsorption in the TGA was modeled using four well-known isotherms: Henry, Freundlich, Toth and Dubinin (Ruthven 1984). It is well established that for physical adsorption on a uniform surface at sufficiently low concentrations such that all molecules are isolated from their nearest neighbors, the equilibrium relationship between the fluid phase and adsorbed phase concentrations (isotherms) should be linear. This relationship is commonly referred to as Henry's Law. In the present study, the adsorption isotherms were indeed approximately linear. However, in a number of the cases, there was significant scatter about the straight lines. Therefore, the nonlinear Freundlich, Toth and Dubinin isotherms were also tested to determine whether these yielded a better fit, and to compare the derived and published values of the fitting parameters.

Henry's law Henry's law may be written as

$$C_s = HC_b \tag{1}$$

in which C_s is the sorbed weight of VOC per unit surface area and C_b is the bulk VOC concentration. The proportionality constant H is referred to as the Henry constant.

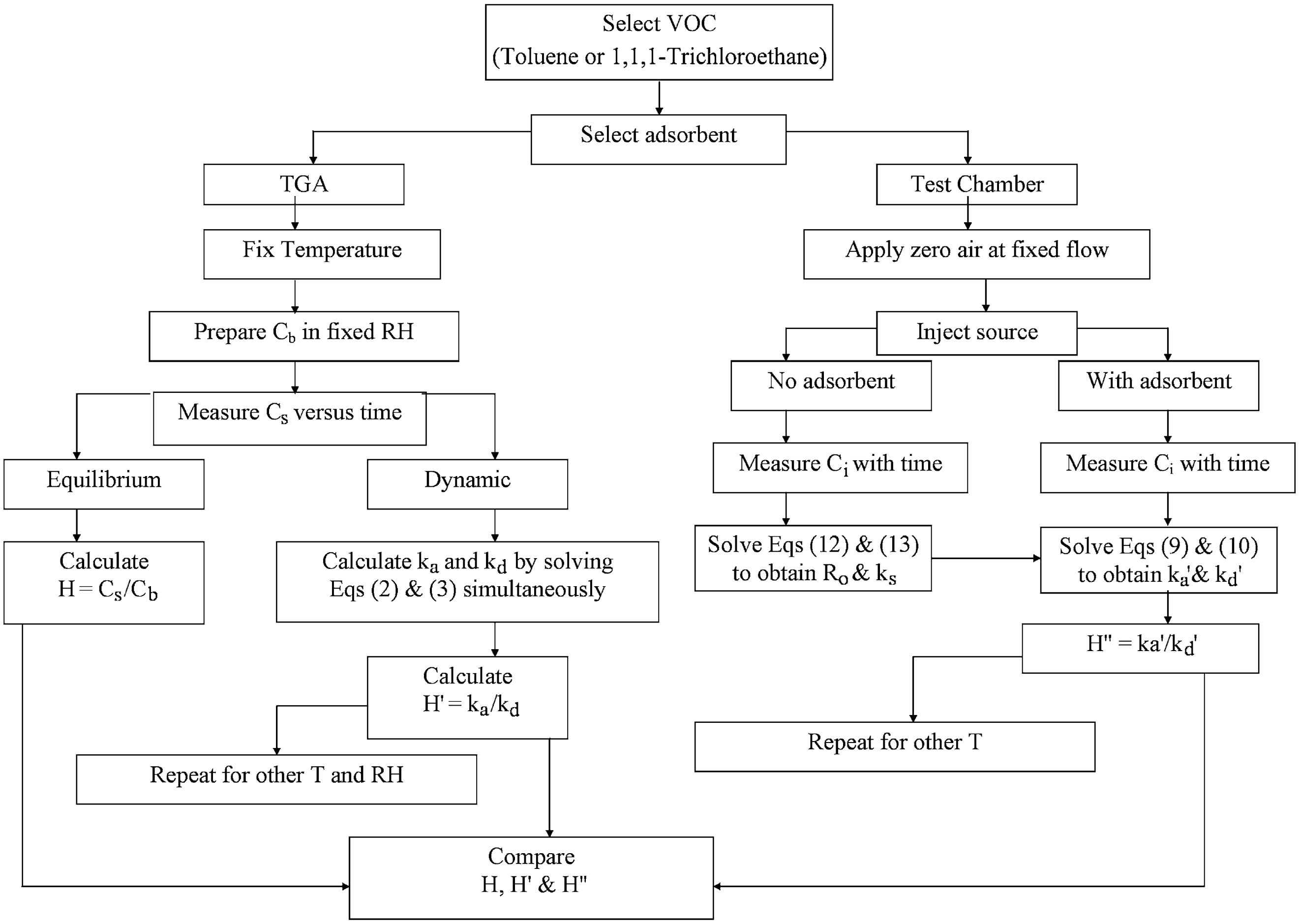


Fig. 1 Calculation procedure to evaluate adsorption parameters in TGA and test chamber experiments

The value of H was calculated from both equilibrium and dynamic data obtained in the TGA experiments. In the former case, the Henry constant was deduced from the slope of the linear adsorption isotherms. In the latter case, the dynamic model formulated by Elkilani (1999) and described briefly below was employed. Figure 1 illustrates the calculation procedures used.

The rates of change of bulk air concentration and sorbed weight per unit surface area are given by the following equations:

$$\frac{\mathrm{d}C_b}{\mathrm{d}t} = -k_a(A_{BET}/V_{tga})C_b + k_d(A_{BET}/V_{tga})C_s \tag{2}$$

$$\frac{\mathrm{d}C_s}{\mathrm{d}t} = k_a C_b - k_d C_s \tag{3}$$

in which the symbols are defined in the Nomenclature.

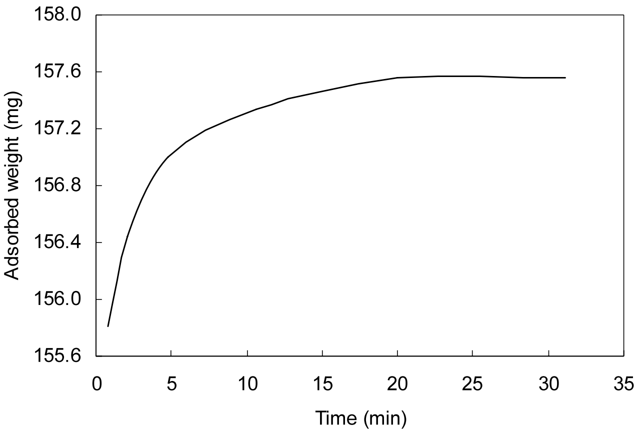


Fig. 2 Typical plot of weight of adsorbate plus adsorbed VOC as a function of time for 1,1,1-trichloroethane on activated carbon granules (TGA experiments)

In the TGA experiments, the mass of the adsorbent plus adsorbed VOC was recorded as a function of time; a typical example of such plots are shown in Fig. 2. Mathematica® software was used to fit these data to (2) and (3) and thereby to yield optimum values of k_a and k_d. It follows from (1) and (3) that the Henry constant, denoted H' in this case, is equal to the ratio k_a/k_d since, at equilibrium, $\mathrm{d}C_s/\mathrm{d}t = 0$.

Nonlinear isotherms The Freundlich isotherm, (4), can be applied for the adsorption of certain VOCs:

$$C_s = k_F P^{1/n} \tag{4}$$

where P, the partial pressure of the VOC, is calculated from the bulk concentration C_b:

$$P = C_b \frac{RT}{Mw} \tag{5}$$

k_F and n are empirical constants, which are determined by classical nonlinear curve fitting.

The Toth isotherm is a semi-empirical expression used to describe monolayer adsorption. It is a three parameter model, which usually written as:

$$C_s = \frac{C_{sm} P}{(k_T + P^\tau)^{1/\tau}} \tag{6}$$

Here k_T, C_{sm} and τ are again determined by classical nonlinear curve fitting. At low partial pressures ($P \to 0$), (6) reduces to

$$C_s = \left[\frac{C_{sm} RT}{1000 k_T^{1/\tau} Mw}\right] C_b \tag{7}$$

Comparison of (1) and (7) indicates that the term in square brackets (above) can be equated to the Henry constant H.

Finally, the Dubinin isotherm, which is based on the potential theory, can be expressed as:

$$\ln(C_s A_{BET} v) = \ln v_o - A_D [RT \ln(P/P^o)]^2 \tag{8}$$

In this equation, the liquid molar volume of the VOC v is calculated from its critical properties at the experimental temperature. A_D and v_o are the Dubinin isotherm empirical parameters which are determined by curve fitting of the experimental data for each system.

3.2 Test chamber

Elkilani (1999) described an unsteady-state mass balance adsorption model to predict the concentration of VOC in the air exiting the test chamber as a function of time. The principal equations may be written:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = NC_o - NC_i - k_a' C_i (A_{si}/V_{tc}) + k_d' C_s (A_{si}/V_{tc}) + R_s(t) A_{so}/V_{tc} \tag{9}$$

$$\frac{\mathrm{d}C_s}{\mathrm{d}t} = k_a' C_i - k_d' C_s \tag{10}$$

where the symbols are again defined in the Nomenclature. The VOC concentration in the inlet zero air $C_o = 0$ mg/m^3. The parameters k_a' and k_d' are the adsorption and desorption rate constants (in m/h and h^{-1}, respectively) derived from the test-chamber data. Elkilani et al. (2003) showed that the actual air exchange rate in the chamber was given by:

$$N = kQ/V_{tc} \tag{11}$$

where $k = 0.871$ is a dimensionless mixing factor. The same value of k was employed in this study.

When there is no adsorbent present in the chamber, clean air is injected, and $t < t_{evap}$, (9) reduces to:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -NC_i + R_s(t) A_{so}/V_{tc} \tag{12}$$

in which $R_s(t)$ is best described by a first-order decay equation (Elkilani et al. 2001):

$$R_s(t) = R_o \exp(-k_s t) \tag{13}$$

Both R_o and k_s depend on the VOC employed and the temperature.

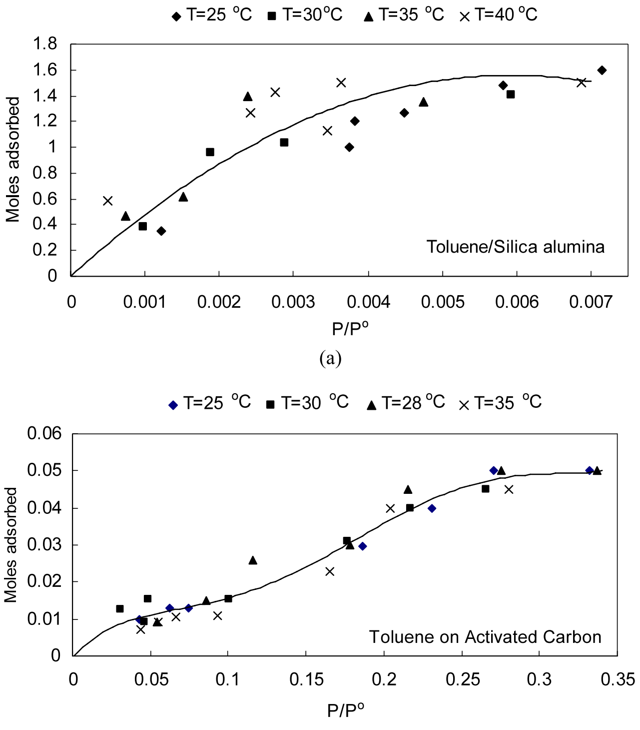
The four main parameters, k_a', k_d', k_s and R_o, were derived by fitting the experimental elution curves to the model equations using Mathematica® software. The calculation procedure is also illustrated schematically in Fig. 1. The Henry constant, denoted as $H'' = k_a'/k_d'$ in this case, can be determined from the calculated values of k_a' and k_d'.

4 Results and discussion

4.1 TGA experiments

In each experiment, the initial concentration of VOC inside the TGA chamber was measured and the adsorbent weight recorded as a function of time. The final concentration of VOC in the bulk air inside the TGA chamber and the corresponding sorbed weight of VOC per unit (BET) area were calculated from a material balance (Elkilani et al. 2003). A total of 336 experiments were performed at different temperatures and different VOC concentrations. About 25 experiments were duplicated to determine the reproducibility of the sorbed weight in the TGA measurements. The NMSE was found to be around 0.0012.

Figure 3 shows typical adsorption isotherms plotted as moles VOC adsorbed versus P/P^o. In all cases, the adsorbent was clearly unsaturated. For each system, the data obtained over the entire temperature ranges scattered about a single curve. Toluene-silica alumina, as shown in Fig. 3a, and toluene-KMnO$_4$-impregnated silica alumina both exhibited Type I isotherms (Ruthven 1984). These are characteristic of microporous adsorbents in which the pore size is of comparable size to the molecular diameter of the adsorbate. The maximum values of P/P^o were around 0.012. In contrast, the toluene-activated carbon and



(a)

(b)

Fig. 3 Typical adsorption isotherms plotted as moles VOC adsorbed versus P/P^o

1,1,1-trichloroethane-activated carbon systems, for which the maximum values of P/P^o were 0.075 and 0.35, respectively, exhibited Type IV isotherms. According to Ruthven (1984), such isotherms "suggest the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the sorbate." In the case of 1,1,1-trichloroethane-silica alumina and 1,1,1-trichloroethane-$KMnO_4$-impregnated silica alumina for which the maximum value of P/P^o was around 0.12, it was not possible to determine with certainty whether the isotherms were of Type I or Type IV.

4.1.1 Equilibrium tests

Henry's law Table 1 summarizes the values of the Henry constants H for the adsorption of toluene and 1,1,1-trichloroethane on silica alumina and silica alumina impregnated with $KMnO_4$. Corresponding values for the adsorption of these VOCs on activated carbon are given in Table 2. In both cases, the data were calculated from the slope of the C_s versus C_b plots. Values of the correlation coefficients R^2 ranged from 0.54 to 0.97. Given Ruthven's (1984) description of the different isotherms, it might be anticipated that Henry's law would provide the best fit for those systems that exhibited Type I curves. However, this was not the case. The highest values of R^2 (0.82–0.97) were obtained for the adsorption of toluene and 1,1,1-trichloroethane on activated carbon for

Table 1 Values of the Henry constant (mm^3 air/mm^2 BET area) for toluene and 1,1,1-trichloroethane on silica alumina and silica alumina impregnated with potassium permanganate

Temperature, °C	Toluene				1,1,1-trichloroethane			
	Silica alumina		Silica alumina/ $KMnO_4$		Silica alumina		Silica alumina/ $KMnO_4$	
	H	R^2, –	H	R^2, –	H	R^2, –	H	R^2, –
25	0.0298	0.86	0.1450	0.92	0.0275	0.94	0.1010	0.72
30	0.0283	0.75	0.0874	0.54	0.0254	0.74	0.0771	0.80
35	0.0280	0.67	0.0845	0.81	0.0170	0.82	0.0713	0.91
40	0.0228	0.66	0.0761	0.63	0.0119	0.68	0.0698	0.57

Table 2 Values of the Henry constant (mm^3 air/mm^2 BET area) for toluene and 1,1,1-trichloroethane on activated carbon granules and activated carbon pellets

Temperature, °C	Toluene				1,1,1-trichloroethane			
	Activated carbon granules		Activated carbon pellets		Activated carbon granules		Activated carbon pellets	
	H	R^2, –	H	R^2, –	H	R^2, –	H	R^2, –
25	0.0225	0.92	0.0224	0.91	0.0281	0.87	0.0282	0.85
28	0.0210	0.85	–	–	0.0227	0.92	–	–
30	0.0181	0.82	–	–	0.0205	0.90	–	–
35	0.0104	0.97	0.0105	0.87	0.0174	0.88	0.0174	0.93

which Type IV isotherms were observed. We do not have a totally satisfactory explanation for this behavior. However, at low values of P/P^o, the shape of the Type I and Type IV isotherms is quite similar (concave to the P/P^o axis) and it is possible that this is a sufficient requirement for Henry's law to be obeyed.

The results showed that H decreased with increasing temperature in every case. This is to be anticipated as a rise in temperature can be expected to decrease adsorption and increase desorption. The effect of impregnating the silica alumina with $KMnO_4$ is clear from the results shown in Table 1. The Henry constants for the impregnated silica alumina were in all cases significantly higher (by factors ranging from about 3–6) than those for the untreated adsorbent; this can be attributed to an increase in the number of active sites. The values of H obtained for the activated carbon granules and pellets (Table 2) were essentially identical despite the difference in their BET surface areas. This again suggests that the Henry constant is determined by the number of active sites. In the case of toluene, the values of H were consistently lower for activated carbon than for silica alumina. However, for 1,1,1-trichloroethane, the Henry constants for these two adsorbents were essentially the same. This again suggests that the number of active sites rather than surface area is the defining parameter in these adsorption processes.

Figure 4 shows the van't Hoff plots for all the systems studied apart from the carbon pellets, which were only tested at two temperatures. As might be anticipated, however, these data were coincident with the corresponding results for the activated carbon granules. Values of the activation energy (ΔU_o) calculated from the slopes of these plots, together with the corresponding correlation coefficients, are given in Table 3. There is good agreement between the value of ΔU_o obtained in this study for toluene/activated carbon (both granules and pellets), 61.1 kJ/mol, and the heat of adsorption reported by Pre et al. (2002) for the same system, 63.1 kJ/mol. The value of ΔU_o for toluene with different adsorbents increased in the following order: silica alumina, impregnated silica alumina, activated carbon. On the other hand, untreated silica alumina exhibited a higher heat of adsorption than both impregnated silica alumina and activated carbon for 1,1,1-trichloroethane. The authors have no explanation for this unexpected behavior. It is of interest to note that the values of ΔU_o obtained in this study (see Table 3) for the adsorption of both toluene and 1,1,1-trichloroethane on silica alumina/$KMnO_4$ (30.7 and 18.3 kJ/mol) were in the same range as those (36.6 and 20.3 kJ/mol, respectively) reported by Elkilani et al. (2003) for the adsorption of these VOCs on polyacrylonitrile fibers.

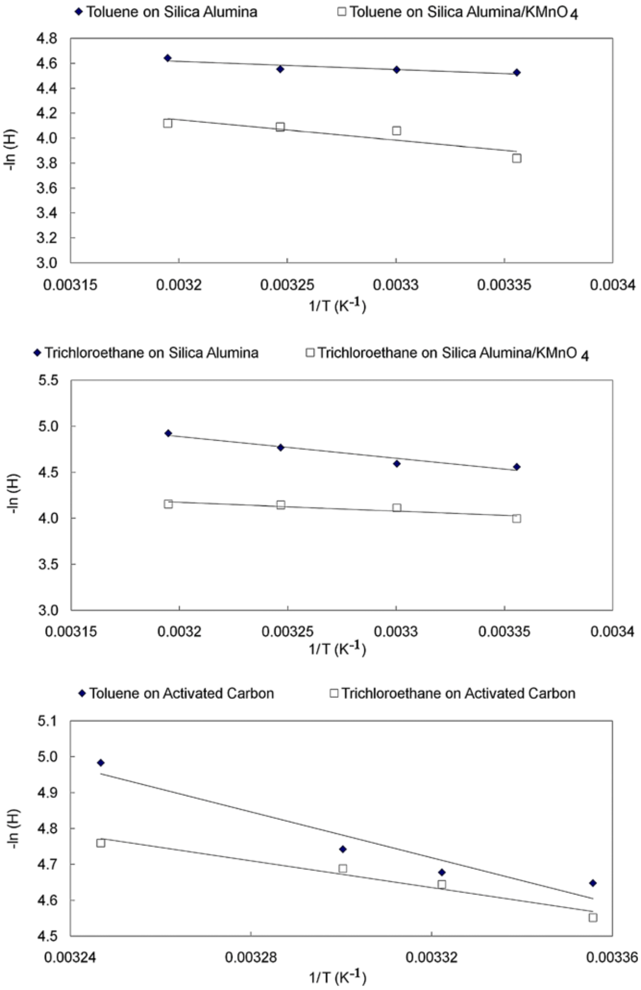


Fig. 4 van't Hoff plots

If the heat of adsorption is less than two or three times the latent heat of vaporization, the adsorption is physical; if it is greater, it is chemical in nature (Ruthven 1984). In all cases, the values of ΔU_o were of comparable order of mag-

Table 3 Heats of adsorption of toluene and 1,1,1-trichloroethane on silica alumina, silica alumina impregnated with $KMnO_4$, and activated carbon granules

Adsorbent	Toluene		1,1,1 trichloroethane	
	Heat of adsorption, ΔU_o (kJ/mol)	R^2, –	Heat of adsorption, ΔU_o (kJ/mol)	R^2, –
Silica alumina	12.54	0.78	45.03	0.94
Silica alumina/$KMnO_4$	30.72	0.79	18.34	0.82
Activated carbon granules	61.11	0.92	39.89	0.87

Table 4 Values of the Freundlich constants for toluene and 1,1,1-trichloroethane on silica alumina and silica alumina impregnated with potassium permanganate

Temperature, °C	Toluene						1,1,1-trichloroethane					
	Silica alumina			Silica alumina/ $KMnO_4$			Silica alumina			Silica alumina/ $KMnO_4$		
	n	k_F (mg/m^2)	R^2, –	n	k_F (mg/m^2)	R^2, –	n	k_F (mg/m^2)	R^2, –	n	k_F (mg/m^2)	R^2, –
25	1.07	0.017	0.74	1.14	0.005	0.84	1.19	0.026	0.97	2.38	6.2E-5	0.83
30	1.44	0.012	0.86	1.54	0.005	0.79	1.15	0.030	0.77	1.32	2.4E-5	0.53
35	1.58	0.010	0.82	2.20	0.003	0.93	1.14	0.035	0.66	1.44	1.3E-5	0.77
40	2.09	0.004	0.88	1.67	0.001	0.77	1.11	0.039	0.55	1.67	1.E-5	0.63

Table 5 Values of the Freundlich constants for toluene and 1,1,1-trichloroethane on activated carbon granules

Temperature, °C	Toluene			1,1,1-trichloroethane		
	Activated carbon granules			Activated carbon granules		
	n, –	k_F (mg/m^2)	R^2, –	n, –	k_F (mg/m^2)	R^2, –
25	8.2	2.4E-4	0.86	2.4	5.5E-3	0.94
28	8.1	2.35E-4	0.89	2.2	7E-4	0.97
30	8.0	2.33E-4	0.76	2.1	5E-4	0.86
35	7.9	2.3E-4	0.9	2.0	2E-5	0.91

Table 6 Values of the Toth constants for toluene and 1,1,1-trichloroethane on silica alumina and silica alumina impregnated with potassium permanganate

Temperature, °C	Toluene								1,1,1-trichloroethane							
	Silica alumina				Silica alumina/ $KMnO_4$				Silica alumina				Silica alumina/ $KmnO_4$			
	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –
25	0.12	0.79	2.4E-4	0.91	0.11	1.6	2.8E-4	0.94	0.2	0.81	2.5E-3	0.95	0.21	0.9	3.3E-3	0.85
30	0.14	1.64	2.7E-4	0.85	0.13	1.3	3.1E-4	0.87	0.29	0.97	3.7E-3	0.86	0.23	1.1	3.9E-3	0.89
35	0.11	1.38	2.8E-4	0.88	0.15	1.44	3.2E-4	0.91	0.21	1.11	3.9E-3	0.89	0.21	1.1	4.1E-3	0.95
40	0.16	1.33	2.9E-4	0.87	0.12	1.56	3.5E-4	0.89	0.24	1.25	4.5E-3	0.88	0.20	1.2	4.7E-3	0.86

nitude to the latent heats (38.0 and 32.3 kJ/mol at 25°C for toluene and 1,1,1-trichloroethane, respectively). It follows that physical adsorption occurred in all cases in this study.

Nonlinear isotherms Given the relatively low values of R^2 observed in some attempts to correlate the results using Henry's law, the data were also fitted against the Freundlich, Toth and Dubinin isotherms. Values of the Freundlich fitting parameters (n and k_F) for the adsorption of toluene and 1,1,1-trichloroethane on silica alumina and impregnated silica alumina are given in Table 4; those for adsorption on activated carbon are listed in Table 5. Corresponding fitting parameters for the Toth (τ, C_{sm}, k_T) and Dubinin (v_o and A_D) isotherm are given in Tables 6, 7, 8 and 9, respectively.

For the adsorption of toluene and 1,1,1-trichloroethane on silica alumina and impregnated silica alumina, the more complicated Toth and Dubinin isotherms provided a marginally better fit than Henry's law. The Freundlich isotherm normally yielded an intermediate result. It is of interest to note that the Henry constants calculated from the reduced form of the Toth isotherm, (7), for $P/P^o < 0.05$, were in good agreement ($< 10\%$) with those listed in Tables 1 and 2.

Figure 5 compares typical results for toluene on silica alumina at 40°C. In the case of the adsorption of both VOCs on activated carbon granules, there was little difference in

Table 7 Values of the Toth constants for toluene and 1,1,1-trichloroethane on activated carbon granules

Temperature, °C	Toluene				1,1,1-trichloroethane			
	Activated carbon granules				Activated carbon granules			
	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –	τ, –	C_{sm} (mg/m^2)	k_T (bar$^\tau$)	R^2, –
25	0.28	0.53	8.7E-4	0.86	0.26	0.65	1.6E-5	0.89
28	0.30	0.31	9.1E-4	0.89	0.26	1.15	1.7E-5	0.86
30	0.31	0.43	1.0E-3	0.89	0.24	1.08	2.3E-5	0.81
35	0.29	0.34	1.9E-3	0.89	0.18	0.92	2.1E-5	0.99

Table 8 Values of the Dubinin constants for toluene and 1,1,1-trichloroethane on silica alumina and silica alumina impregnated with potassium permanganate

Temperature, °C	Toluene						1,1,1-trichloroethane					
	Silica alumina			Silica alumina/ $KMnO_4$			Silica alumina			Silica alumina/ $KMnO_4$		
	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –
25	1.3E-3	4.7E-5	0.90	2.6E-3	3.5E-5	0.91	1.7E-4	1.9E-9	0.89	2.4E-4	1.7E-9	0.88
30	1.4E-3	4.1E-5	0.88	2.3E-3	3.2E-5	0.88	1.5E-4	1.6E-9	0.85	2.2E-4	1.1E-9	0.89
35	1.2E-3	4.5E-5	0.87	2.5E-3	3.2E-5	0.90	1.5E-4	1.7E-9	0.87	2.1E-4	1.2E-9	0.86
40	1.1E-3	4.1E-5	0.89	2.1E-3	3.0E-5	0.86	1.4E-4	1.1E-9	0.90	1.9E-4	1.1E-9	0.88

Table 9 Values of the Dubinin constants for toluene and 1,1,1-trichloroethane on activated carbon granules

Temperature, °C	Toluene			1,1,1-trichloroethane		
	Activated carbon granules			Activated carbon granules		
	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –	v_o (m^3/kg)	A_D (mol/J)^2	R^2, –
25	7.6E-3	5.2E-5	0.90	3.3E-4	2.1E-9	0.79
28	6.5E-3	4.7E-5	0.85	3.8E-4	2.5E-9	0.89
30	5.9E-3	2.2E-5	0.80	2.7 E-4	1.7E-9	0.83
35	5.8E-3	2.8E-5	0.94	3.1E-4	1.9E-9	0.89

the quality of the fit provided by the four isotherms. Consequently, most of the analysis described below was based on Henry's law as this provided a convenient means of comparing the equilibrium, dynamic, and test-chamber data. However, the nonlinear isotherm fitting parameters were employed to compare the present results with those published in the literature.

Table 10 compares the present data for the adsorption of toluene and 1,1,1-trichloroethane on activated carbon with previously published fitting parameters for the nonlinear isotherms. As may be seen, the agreement is generally satisfactory. Published results for the adsorption of these VOCs on silica-alumina and impregnated silica-alumina appear to be lacking.

Effect of relative humidity As indicated above, a series of experiments was conducted to determine the effect of relative humidity in the range 0–30% on the adsorption of toluene and 1,1,1-trichloroethane on activated carbon granules at temperatures of 25, 35 and 45°C. The data were fitted against Henry's law, which, as noted above, yielded a satisfactory fit for these systems. Typical results are shown in Fig. 6 for toluene on activated carbon granules. The error bars for those points for which duplicate runs were carried out are also shown in the figure. The slope of the plots, and the corresponding values of the Henry constant, progressively decreased as the relative humidity increased. This is presumably due to the fact that the moisture occupies some of the sites available for adsorption and hence decreases the VOC adsorption capacity.

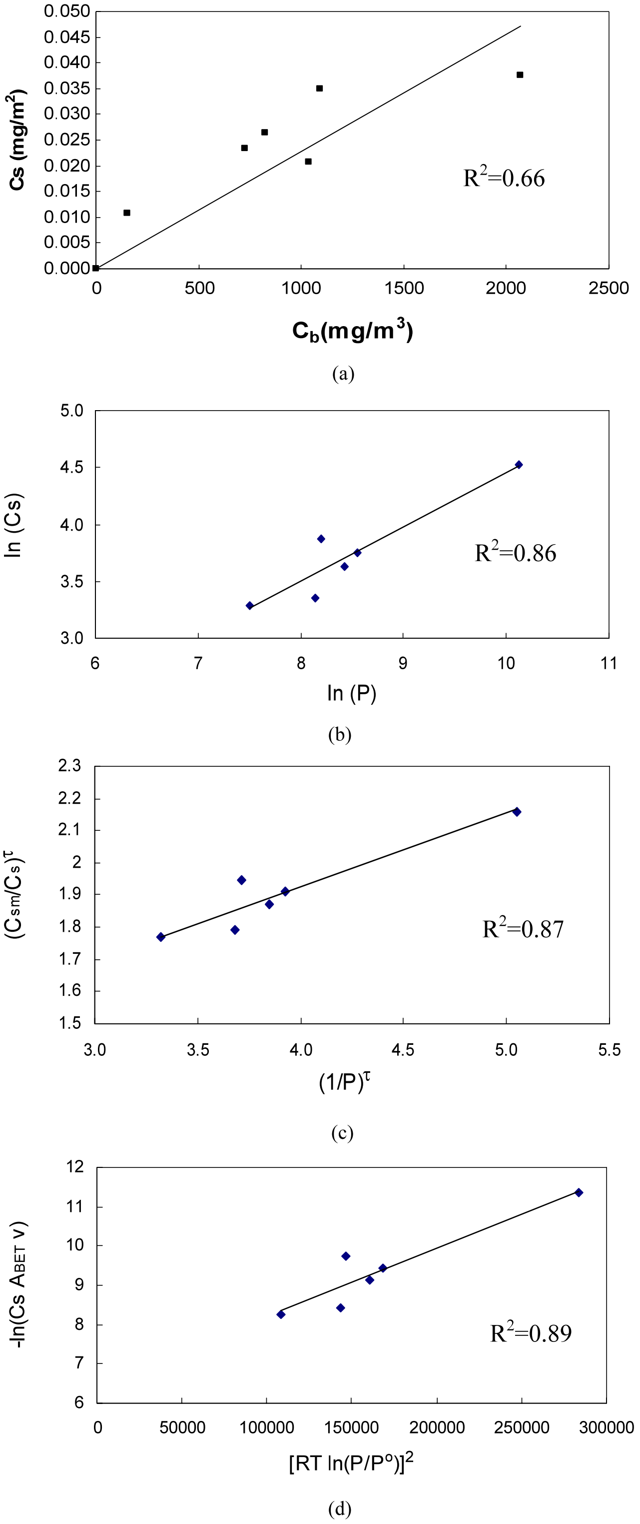


Fig. 5 Linear and nonlinear isotherms for toluene on silica alumina at 40°C (**a**) Henry, (**b**) Freundlich, (**c**) Toth, (**d**) Dubinin

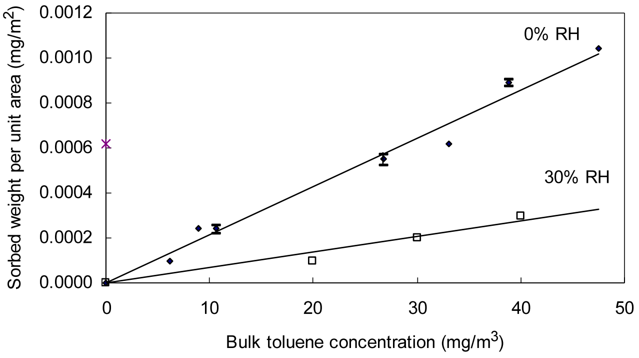


Fig. 6 Typical plot of sorbed weight per unit area versus bulk concentration of toluene on activated carbon granules at 25°C and relative humidities of 0% and 30%

Table 11 summarizes values of H obtained in the elevated relative humidity experiments. The Henry constant decreased monotonically with relative humidity over the range studied. In most cases, the H versus RH plots obtained at 25°C and 35°C converged at high relative humidities. Similar results were obtained by Brandani and Ruthven (2004) for the adsorption of CO_2 on zeolites.

A number of studies of the effect of relative humidity (RH) on the adsorption of VOCs on activated carbon have been published in the literature. These articles illustrate the complexity of the phenomena involved in multicomponent adsorption. Werner (1985), for instance, studied the effect of RH in the range 5% to 85% on the adsorption of trichloroethylene (TCE) on activated carbon at 23 ± 2°C. Influent VOC concentrations ranged from 300–1300 mg/m^3. He observed that the weight of VOC adsorbed decreased with increasing humidity; the effect was most marked at high values of the latter and at low TCE influent concentrations. For example, at a VOC concentration of 300 mg/m^3, the quantities of TCE adsorbed were 0.285 and 0.257 g/g carbon at 5% and 25% RH, respectively. Much steeper declines were observed at higher humidities (0.180 and 0.027 g/g carbon at 50% and 85%). Werner noted that at least four factors influence the impact of humidity on VOC adsorption. This can make quantitative comparisons of different studies difficult. These factors are: (1) the manner in which the adsorbent is preconditioned; this can vary widely. (2) adsorbate concentration; the effect is most marked at low VOC influent concentrations. (3) type of adsorbate; hydrophobic compounds (such as those employed in the present study) are more adversely affected by RH than hydrophilic compounds. (4) type of adsorbent.

Cal et al. (1996) studied the removal of selected VOCs (acetone and benzene) from humidified air streams (0–90% RH) using activated carbon cloth (ACC). In the case of acetone (350 and 500 ppmv), relative humidity had little effect on the adsorption capacity of the ACC even at 90% RH. In contrast, with benzene at 500 ppmv, Cal et al. observed that there was little effect below 65% RH, the point at which capillary condensation of water vapor occurs in the pores of the ACC. However, at higher humidities, the adsorption

Table 10 Comparison between the present data and published fitting parameters for nonlinear isotherms

Toluene on activated carbon at 25°C		
	This work	Benkhedda et al. (2000)
Freundlich		
k_F	2.4E-4 mg/m^2 = (2.16 mol/kg)	2.43 mol/kg
n	8.2	8.38
Dubinin		
A	5.2E-5 (mol/J)^2	4.75E-5 (mol/J)^2
v_o	7.6E-3 (m^3/kg)	7.09E-3 (m^3/kg)
Toth		
τ	0.26	0.38
C_{sm}	0.65 mg/m^2 = (5.85 mol/kg)	6.92 mol/kg
k_T	1.6E-5 bar$^\tau$ = (1.6 Pa$^\tau$)	1.2 Pa$^\tau$
Trichloroethane on activated carbon at 30°C		
	This work	Yun and Choi (1998)
Dubinin		
A	2.1E-9 (mol/J)^2 = (21.8 kJ/mol)	19.5 kJ/mol
v_o	3.3 E-4 (m^3/kg) = (330 cm^3/kg)	370.8 cm^3/kg
Toth		
τ	0.31	0.3146
C_{sm}	0.43 mg/m^2 = (3.87 mol/kg)	4.2716 mol/kg
k_T	1.03E-3 bar = (0.103 Pa)	0.1033 Pa

Table 11 Henry constants (mm^3 air/mm^2 BET area) as a function of relative humidity

System	Relative Humidity				
	0%	5%	10%	20%	30%
Toluene/activated carbon at 25°C	0.0225	0.0187	0.0140	0.0106	0.0069
Toluene/activated carbon at 35°C	0.0104	0.0079	0.0061	0.0038	0.0028
1,1,1-trichloroethane/activated carbon at 25°C	0.0281	0.0199	0.0141	0.0085	0.0070
1,1,1-trichloroethane/activated carbon at 35°C	0.0174	0.0132	0.0113	0.0088	0.0075
Toluene/silica alumina at 25°C	0.0298	0.0194	0.0136	0.0111	0.0081
Toluene/silica alumina at 35°C	0.0289	0.0149	0.0120	0.0078	0.0046
1,1,1-trichloroethane/silica alumina at 25°C	0.0275	0.0169	0.0119	0.0087	0.0048
1,1,1-trichloroethane/silica alumina at 35°C	0.0170	0.0126	0.0085	0.0054	0.0032

capacity of the VOC decreased rapidly with increasing RH. Similar contrasting behavior between hydrophilic and hydrophobic VOCs has also been reported by other workers (e.g. Won et al. 2000; Tao et al. 2004).

Qualitatively at least, the results obtained in this study are in general agreement with those published by Werner (1985) and Cal et al. (1996). Given that relatively low influent concentrations of hydrophobic VOCs were employed, the observed reduction in VOC adsorption with increasing RH would be anticipated, although perhaps not on the scale observed. However, as different VOCs and adsorbents were employed, this is hardly surprising.

Lodewyckx and Vansant (1999) studied the adsorption characteristics of seven organic compounds, which were insoluble or only slightly soluble in water. Their experiments were performed on three different types of activated carbon at a constant temperature of 23 ± 3°C and an RH range of 0–90%. Adsorption of water vapor in the absence of VOC was also studied. Their results showed that there was a loss of VOC adsorption capacity due mainly to the presence of

Table 12 Sorption rate constants for toluene and 1,1,1-trichloroethane at 25°C and 40°C on silica alumina and silica alumina impregnated with $KMnO_4$ (TGA dynamic experiments)

	Toluene				1,1,1-trichloroethane			
Temperature	25°C		40°C		25°C		40°C	
Adsorbent	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$
$k_a \times 10^6$ (m/h)	58	62	28.1	37.8	61	63	20	56
k_d (1/h)	1.9	0.44	1.2	0.51	2.6	0.66	1.3	0.82
H', mm	0.0305	0.141	0.0234	0.0741	0.0235	0.0955	0.0154	0.0683

Table 13 Sorption rate constants for toluene and 1,1,1-trichloroethane at 25°C and 35°C on activated carbon granules and pellets (TGA dynamic experiments)

	Toluene				1,1,1-trichloroethane			
Temperature	25°C		35°C		25°C		40°C	
Adsorbent	Activated carbon granules	Activated carbon pellets	Activated carbon granules	Activated carbon pellets	Activated carbon granules	Activated carbon pellets	Activated carbon granules	Activated carbon pellets
$k_a \times 10^6$ (m/h)	60	61	35	33	63	63	30	31
k_d (1/h)	2.73	2.65	3.21	3.14	2.1	2.1	1.69	1.77
H', mm	0.0220	0.0230	0.0109	0.0105	0.0300	0.0310	0.0177	0.0175

pre-adsorbed water on the filter. This highlights the need for effective storage of filters prior to use. Water vapor in the air stream was shown to reduce VOC adsorption capacity only at very high values of relative humidity.

In the present study, the Henry constant was found to decrease significantly (by around 70%) over the relatively narrow RH range of 0–30%. In the case of 1,1,1-trichloroethane (0–50 mg/m^3), the amount of VOC adsorbed on activated carbon decreased from an average value of 0.15 g/g at 0% RH to around 0.08 g/g at 30% RH. As noted above, Werner (1985) studied the adsorption of trichloroethylene on activated carbon at much higher VOC concentrations in the range 300–1300 mg/m^3. He observed that the effect of relative humidity was most marked at high values of the latter and increased as the bulk VOC concentration decreased. The present results are therefore consistent with his findings. At the low VOC concentrations employed in this study, the effects of RH were significant in the range 0–30%. In contrast, in Werner's (1985) study, significant reductions in VOC adsorption only occurred over the relative humidity range 50–85%.

4.1.2 Dynamic tests

Values of k_a and k_d were determined by applying (2) and (3) to the dynamic portions of the TGA plots in which the weight of the adsorbent changed with time. The results of these calculations are summarized in Tables 12 and 13, which also list derived values of the Henry constant $H' = k_a/k_d$. Comparison between the data presented in Tables 1 and 2 and in Tables 12 and 13 shows that there is good agreement between corresponding values of H and H'.

4.2 Test chamber experiments

Figure 7 shows the results obtained in the test chamber experiments using toluene and 1,1,1-trichloroethane at 25°C. Experiments were performed with no adsorbent present in the test chamber and in the presence of untreated and $KMnO_4$-impregnated silica alumina. The results were similar to those reported by Elkilani et al. (2003) for polyacrylonitrile carpet fibers. The VOC concentration in the air leaving the chamber was initially zero. It subsequently rose to a peak value before progressively declining again to zero. From the experiments in which no adsorbent was present in the chamber, (12) was solved to find $R_s(t)$ as a function of time. From these values, R_o and k_s were calculated from (13).

When adsorbent was present in the test chamber, the peak concentration shifted to the right and the maximum concentration was lower than that observed in the corresponding empty-chamber experiment. These observations can be explained by the initial adsorption of VOC as it evaporates into the bulk air. After the dish has emptied the progressive reduction of VOC concentration within the chamber brought about by mixing with fresh inlet air causes the adsorbent to desorb VOC in an attempt to maintain equilibrium.

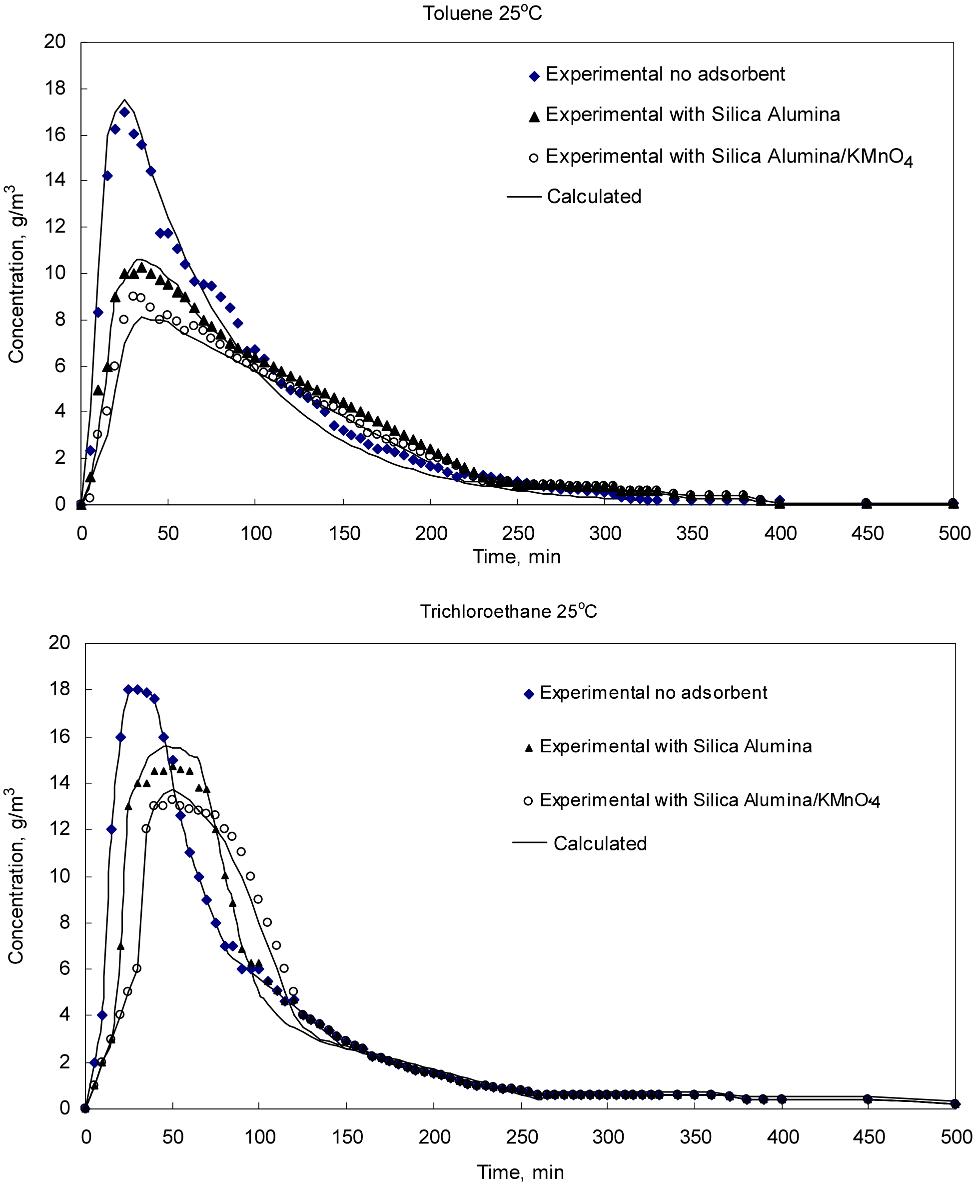


Fig. 7 Experimental and calculated VOC concentrations in the air leaving the test chamber as a function of time

One objective of the present work was to determine whether the unsteady-state adsorption model of the test chamber, (9)–(10), was applicable to a wider range of adsorbents than employed in the Elkilani et al. (2003) study. Table 14 shows the results for toluene and 1,1,1-trichloroethane adsorbed on untreated silica alumina and silica alumina impregnated with $KMnO_4$. Comparing the Henry constants given in Table 1 with those in Table 14 shows that there is again reasonable agreement (3–10%) between corresponding values of H and H''.

The solid curves in Fig. 7 serve as a comparison between the experimental values of VOC concentration and those calculated from the model, both with and without adsorbent in the test chamber. The average value of the normalized mean square error (NMSE) between the measured concentrations of both toluene and 1,1,1-trichloroethane in the test chamber and those estimated from the model was 0.023. This indicates that there was a good fit between the data and the model.

4.3 Empirical correlations

Multi-variable linear regression was employed to derive empirical equations relating the Henry constant to the following variables: temperature (°C) T, percent relative humidity RH, and VOC. In order to include them in the derived correlations, the VOCs were designated by the parameter I_{voc}. Toluene was denoted by $I_{voc} = 1$ and 1,1,1-trichloroethane by $I_{voc} = 0$. The rational for this approach was that, for any given adsorbent, the Henry constants for toluene obtained at a given temperature and relative humidity were generally either consistently higher or consistently lower than those

Table 14 Sorption rate constants and emission rates for toluene and 1,1,1-trichloroethane at 25°C and 40°C on silica alumina and silica alumina impregnated with $KMnO_4$ (Test chamber experiments)

	Toluene				1,1,1 Trichloroethane			
Temperature	25°C		40°C		25°C		40°C	
Adsorbent	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$	Silica alumina	Silica alumina/ $KMnO_4$
k_s (1/h)	2.51	2.51	0.822	0.822	3.144	3.144	1.83	1.83
R_o (mg/m^2.h)	1.29	1.29	1.382	1.382	0.950	0.950	2.60	2.60
$k'_a \times 10^6$ (m/h)	68.1	64	29.5	44	63	66	15	50
k'_d (1/h)	2.2	0.47	1.223	0.58	2.51	0.64	1.32	0.85
H'', mm	0.0309	0.135	0.0241	0.076	0.0251	0.103	0.0113	0.059

for trichloroethane (see Tables 1 and 2). The following correlations were obtained for the individual adsorbents were obtained:

For silica alumina (NMSE = 0.00017):

$$\ln H = -21.0 + \frac{3122}{T + 273} + 6.9RH^{0.075} + 0.266I_{voc} \quad (14)$$

For silica alumina/$KMnO_4$ (NMSE = 0.0005):

$$\ln H = -1.64 + \frac{3562}{T + 273} + 0.762I_{voc} \quad (15)$$

There is no relative humidity term in (15) because this parameter was not varied in the case of silica alumina/$KMnO_4$.

For activated carbon granules and pellets (NMSE = 0.0176):

$$\ln H = -16.94 + \frac{1921}{T + 273} + 7.44RH^{0.075} - 0.313I_{voc} \quad (16)$$

A similar attempt was made to include the type of adsorbent in the above correlations. As may be seen in Tables 1 and 2, the Henry constants for silica alumina/$KMnO_4$ were consistently higher than those for silica alumina and activated carbon. The values of the latter were of comparable magnitude. A second parameter I_{ads} was therefore designated as unity for silica alumina/$KMnO_4$ and as zero for the other adsorbents. The resulting correlation exhibited considerable scatter and consequently this approach was judged to be unsuccessful in these circumstances.

5 Conclusions

The effects of ambient temperature and relative humidity in the ranges 25°C to 40°C and 0% to 30%, respectively, on the adsorption of toluene and 1,1,1-trichloroethane on selected adsorbents were studied. Measurements of the adsorbed weight of these VOCs on silica alumina, silica alumina impregnated with $KMnO_4$, granulated activated carbon, and activated carbon pellets were performed in a thermogravimetric analyzer (TGA). Although nonlinear isotherms (Freundlich, Toth and Dubinin) provided a somewhat better fit when silica alumina and impregnated silica alumina were employed as adsorbents, Henry's law was deemed to be generally satisfactory and had the advantage that only a single fitting parameter was required. The Henry constant H decreased with both increasing temperature and humidity. The highest values of H were consistently observed with silica alumina activated by $KMnO_4$. Preliminary correlations were derived relating the Henry constant to the experimental parameters varied in this study. There was good agreement between Henry constants calculated from the equilibrium data and those estimated from adsorption and desorption kinetic constants obtained in the TGA experiments. Measurements conducted in a 50.3-cm long × 45.0-cm wide by 14.8-cm high test chamber also yielded comparable values of H. These results therefore added further weight to the present authors' preliminary findings (Elkilani et al. 2003) that adsorption data obtained using small samples of adsorbent in the laboratory can be successfully scaled-up and used in combination with the theory described in this work to model indoor air quality in much larger chambers.

Acknowledgements This work was supported by Kuwait University Research Administration Grant No. EC 02/00 and by the College of Graduate Studies, Kuwait University. Thanks are due to Mr. Avor Krishnan for carrying out some of the experimental work.

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