Adsorption Characteristics of Granular Activated Carbon and SPME Indication of VOCs Breakthrough

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Abstract

Internal circulation cabinets equipped with granular activated carbon (GAC) to adsorb volatile organic compounds (VOCs) are extensively utilized to store bottles containing organic solvents in Taiwanese university, college, and hospital laboratories. This work evaluates the VOC adsorption capacity of GAC with various adsorption periods for 102–2652 ppm average inlet toluene concentrations at 27°C and relative humidity (RH) 72 ± 3%. Additionally, solid-phase micro-extraction (SPME) technology was employed for indicating the renew moment of GAC, and avoiding a breakthrough of toluene from adsorbents. Experimental results demonstrate that toluene adsorption capacity is linearly expressed as the natural logarithm of adsorption time ($\ln(t)$) at a constant temperature, and the equilibrium adsorption capacity (Q_e, g toluene/g GAC) for average 102–2652 ppm gaseous toluene was accurately simulated using the proposed models. The SPME fiber installed in the outlet air stream for adsorbing toluene exhausted through GAC effectively indicated the breakthrough of VOCs. The GAC-SPME operational instructions to indicate the replace time of adsorbent in the internal circulation cabinets are concluded in this study.

Keywords: Volatile organic compounds (VOCs); Emission; Solid-phase microextraction (SPME); Granular activated carbon (GAC).

INTRODUCTION

Many organic solvents are used in laboratories in Taiwanese universities colleges, and hospitals. Mobile cabinets with internal circulating adsorption system (Fig. 1) are commonly utilized for storing solvents. Adsorbents, molecular sieves and granular activated carbon (GAC), must be renewed periodically to prevent over-adsorption of volatile organic compounds (VOCs) by the adsorbent under breakthrough. The detailed adsorption characteristics of molecular sieves used by local manufacturers of storage cabinets have been examined by Cheng and

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(a) Schematic structure   **(b) Directions of circulating air streams**
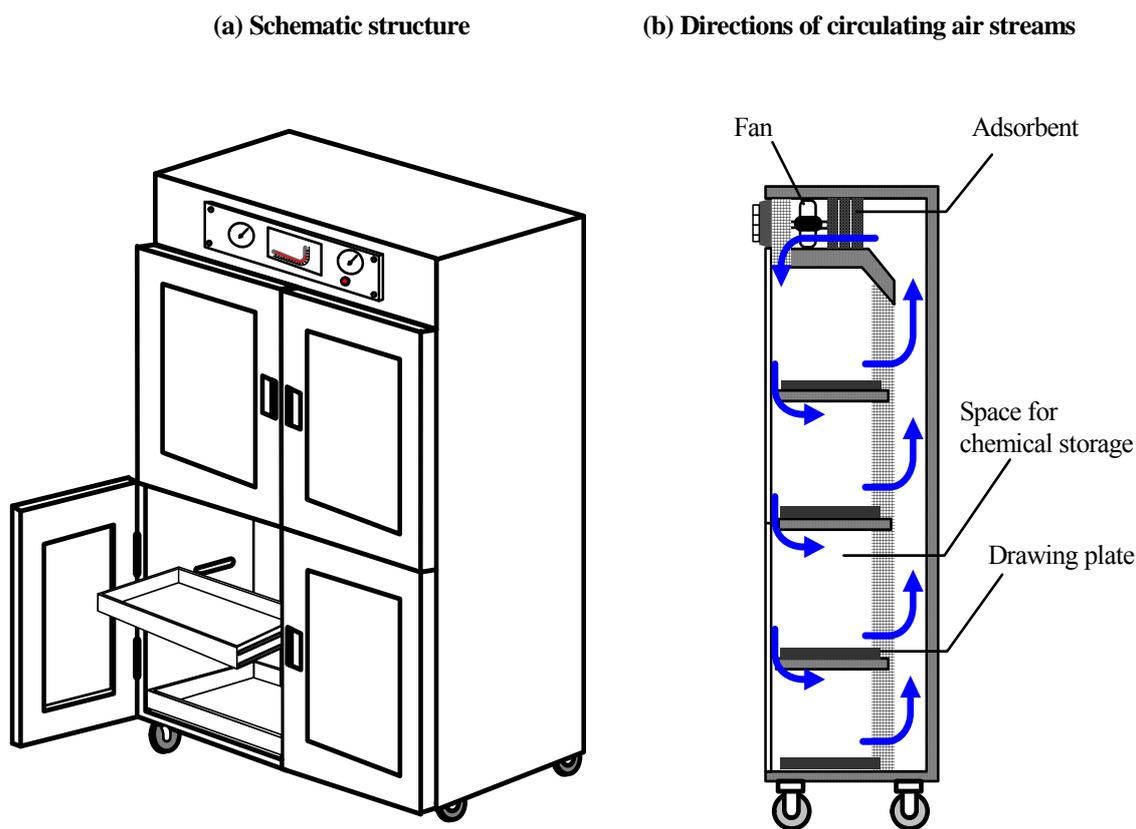
Fig. 1. Internal circulation adsorption storage cabinets.

Tsai (2007). However, replace time and indication of VOCs breakthroughs the adsorbents have not been exactly described by storage cabinet manufacturers. This work, based on a study by Cheng and Tsai (2007), evaluated VOC adsorption capacity (Q) of GAC for average toluene concentrations of 102–2652 ppm at 27°C. Furthermore, solid-phase microextraction (SPME) technology was applied to identify the renewal time for GAC, and avoid toluene breakthrough from the adsorbent.

Pawliszyn, of the University of Waterloo, Canada, developed SPME in 1990 for sampling VOCs at concentrations in air, liquid, or soil phase. (Pawliszyn, 1997) Organic compounds are directly adsorbed and concentrated on the SPME fiber, coated with silicone compounds. The VOCs are then desorbed at the injection port of a gas chromatographer with a flame ionization detector (GC-FID) at a high temperature. The GCFID-SPME is a solvent-free sampling and analytic method that has been used recently for sampling organic pollutants in indoor atmospheres and in human blood, urine, and muscle. (Gorlo *et al.,* 1999; Koziel and Pawliszyn, 2001; Waidyanatha *et al.,* 2001) However, the operation procedures and parameters of GCFID-SPME (e.g., the sampling period for adsorbing VOCs, and desorption temperature and time for GC-FID) must be modified by users. The standardized procedures of diffusion adsorption sampling

with SPME fiber were described in the following section.

METHOD

Time dependence of VOC adsorption capacity for GAC and SPME fiber

The VOC adsorption capacity (Q, g VOC/g GAC) by an adsorbent increases as the concentration of VOC increase (C, ppm) (Yun *et al.*, 1998; Erdem-Şenatalar *et al.*, 2004; Cheng and Tsai, 2007). Additionally, Scahill *et al.* (2004) used the Nelson-Harder correlation to determine the breakthrough time variations (t_1 and t_2) of the different inlet contaminant concentrations (C_1 and C_2):

$$\frac{t_1}{t_2} = (\frac{C_1}{C_2})^n \tag{1}$$

where n is a constant. According to findings obtained by Scahill et al., the VOC adsorption capacity (Q) by an adsorbent is proportional to the natural logarithmic value of adsorption time (t).

$$Q \propto \ln(t) \tag{2}$$

According to the study by Ai (1998), under an unsteady-state (i.e. diffusion adsorption sampling for gaseous VOCs), the adsorption mass of VOC (Q_{SPME}) during adsorption time (t) by SPME fiber can be calculated using Eq. (3):
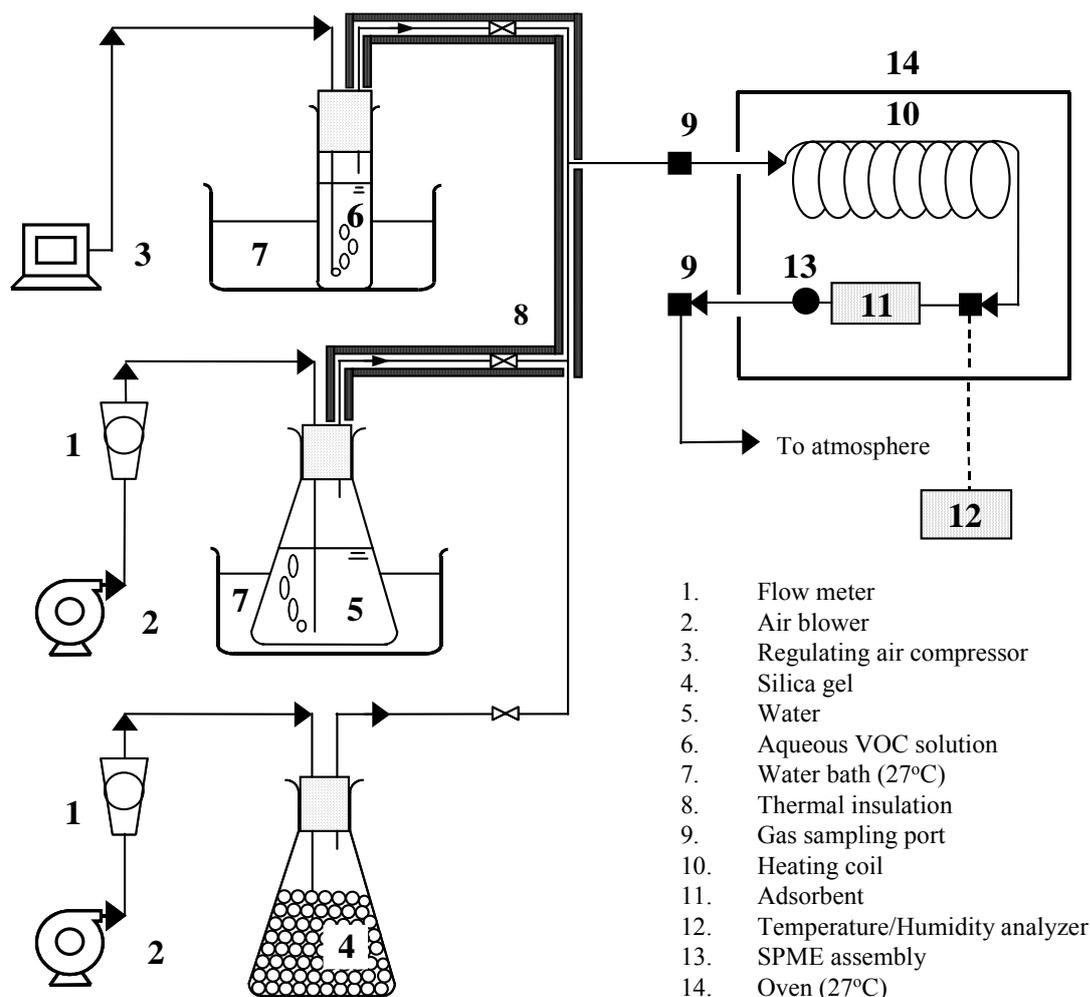
$$Q_{SPME} = Q_{SPME,0}[1 - \exp(-at)] \tag{3}$$

where $Q_{SPME,0}$ = VOC equilibrium adsorption mass by a SPME fiber under a constant temperature and gaseous VOC concentration; a = kinetic adsorption coefficient between the adsorbate (VOC) and SPME fiber. To modify Eq. (3), the excess VOC mass adsorbed by the SPME fiber can be expressed as

$$Q_{SPME,0} - Q_{SPME} = Q_{SPME,0}[\exp(-at)] \tag{4}$$

Both $Q_{SPME,0}$ and a in Eq. (4) can be found by the GCFID-SPME experiment using a gaseous sample of constant VOC concentration during varying adsorption periods (t) at a constant temperature.

Design of adsorption system

The adsorption apparatus (Fig. 2), adopted from the studies of Chou and Chiou (1997), and Cheng and Tsai (2007), was utilized to assess VOC adsorption capacity of GAC during the period of adsorption (t, min), and the feasibility of SPME identifying VOC breakthrough. This system was based on the air-stripping method using a low- flow-rate regulating air compressor (part 3 in Fig. 2), and VOCs transferred at 1–20 mL/min. The VOC tested was toluene. The other air blower (part 2 in Fig. 2) passed a saturated water stream (roughly 0.5 L/min) with a relative humidity (RH) of approximately 100%, mixed with dry air (roughly 1 L/min). The gaseous stream was maintained at 1.5 L/min during all tests. Influent toluene concentrations of 102–2652 ppm, were used to evaluate the

Fig. 2. Schematic experimental adsorption system.

1. Flow meter
2. Air blower
3. Regulating air compressor
4. Silica gel
5. Water
6. Aqueous VOC solution
7. Water bath (27°C)
8. Thermal insulation
9. Gas sampling port
10. Heating coil
11. Adsorbent
12. Temperature/Humidity analyzer
13. SPME assembly
14. Oven (27°C)

variation of adsorption capacity (Q) by GAC and SPME fiber with various VOC concentrations (C) and adsorption times (t). Notably, based on the practical detection in the storage space of the sealed cabinet, the VOC emission concentrations were typically near 100 ± 2.5 ppm, which was covered in the testing concentration range.

A gastight glass tube (part 11 in Fig. 2) was filled with approximately 10 g of GAC. The space velocity (v_S) of the VOC-rich air stream through the adsorbent zone was approximately 1.3 L/s, and the empty bed residual time (EBRT) was around 0.76 s. The adsorbent tube

was placed in an oven (part 14 in Fig. 2) at a constant temperature of 27°C. When the SPME indication tests for VOC breakthrough were conducted, the SPME assembly (part 13 in Fig. 2) was installed and connected to the gastight tube outlet. The VOC adsorption periods were 60 – 900 min. The RH value of stream carrying VOCs was measured using a humidity analyzer (testo 400, TESTO, Germany) (part 12 in Fig. 2). The RH of gas streams was maintained at 72 ± 3% during all tests. System operation at a constant RH and temperature prevented moisture and heat from affecting the VOC adsorption capacity.

Calculating VOC adsorption capacity

When the adsorption test was completed, the glass tube and GAC were placed in a high-temperature oven to desorb VOCs in a dry stream of 0.5 L/min at 250°C. The desorbed VOC-rich gas was collected using several 10 L Teflon gas sampling bags (SKC, USA). The desorption period took 2.5 hr, during which exceeding 99.99% of adsorbed VOCs were removed from GAC. All desorbed gases were taken using gastight syringes (Hamiltom, USA) and then analyzed using a GC-FID (6890N, Agilent, USA). The internal volume of the Teflon bags was determined by the buoyancy method using drained water. Multiplying the analyzed concentration by bag volume yielded VOC mass adsorbed by GAC. Summing all VOC masses in a desorption run and then dividing that sum by GAC mass yielded Q.

To determine the VOC mass adsorbed by SPME fiber, GCFID-SPME procedures were followed. Initially, the SPME fiber was pretreated for conditioning in the GCFID injection port at 250°C for 120 min. After the VOCs were adsorbed by SPME, the fiber was injected into GCFID and the VOCs were desorbed for analysis within 3 min. Finally, a 10-min post-treat for the fiber was implemented prior to the next adsorption test.

Experimental materials

The GAC, currently used in an internal circulation cabin, was manufactured by the China Carbon Company. The material of GAC was coconut shell, and it was of the cylinder type and had a diameter of 4 mm and a length of 10 mm, an iodine value of 1143 mg/g, an ash content 12.6%, BET surface area > 700 m^2/g, and a bulk density of 0.454 g/mL. Tested adsorbate, toluene (J.T. Baker), was of analytical reagent grade. The SPME assembly was provided by the SUPELCO (USA), and the fiber was coated with 100-μm polydimethylsiloxane (PDMS).

RESULTS AND DISCUSSION

Variations of GAC adsorption capacity with toluene concentrations

Toluene adsorption tests were conducted using GAC as the adsorbent at an inlet mean concentration of 102–2652 ppm, over periods of 60 – 900 min at 27°C. Fig. 3 presents variations of toluene adsorption capacity (Q) with concentrations (C) at various adsorption periods. The proportional relationship between the natural logarithm of the adsorption time [ln (t)] and toluene adsorption capacity (Q) is presented as the formulae (Eqs. (5)–(8)) in Table 1.
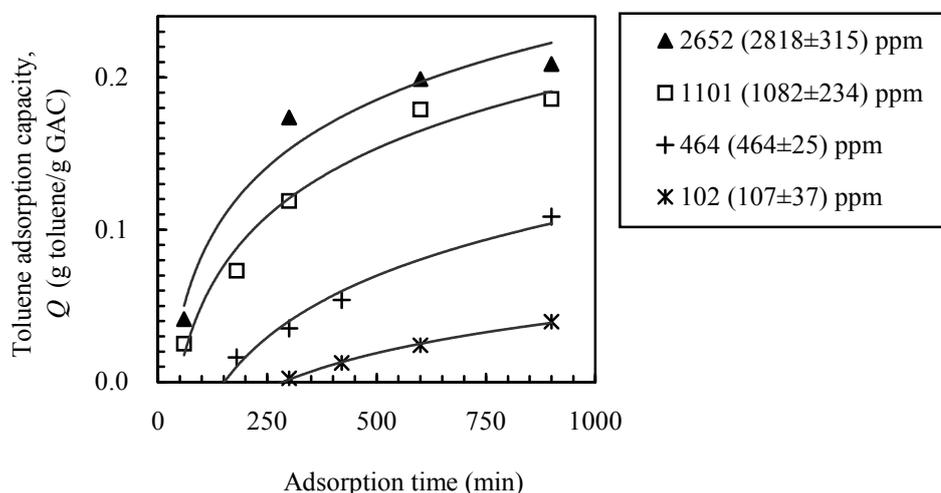
Toluene equilibrium adsorption capacities

The VOC adsorption curves (Fig. 3) have not yet reached equilibrium at the adsorption period of 900 min. Equations (5)–(8) were applied with various mean inlet concentration (102, 464, 1101, and 2652 ppm) using an extended adsorption period of 4000 min to determine equilibrium adsorption capacity Q_e (Table 2). The equilibrium adsorption times declined from 3900 min at C = 102 ppm to 2300 min for C = 2652 ppm. The equilibrium adsorption times in Table 2 reveal the valid

Table 1. Correlations of toluene adsorption capacity with time and concentrations.

Concentration (C, ppm)	Formula of adsorption capacity (Q, g toluene/g GAC) varying with adsorption time (t, min)	
2652 (2818 ± 315)	$Q = 0.0637 \ln (t) - 0.211, R^2 = 0.961$[a]	(5)
1101 (1082 ± 234)	$Q = 0.0639 \ln (t) - 0.244, R^2 = 0.974$[a]	(6)
464 (464 ± 25)	$Q = 0.0584 \ln (t) - 0.293, R^2 = 0.976$[a]	(7)
102 (107 ± 37)	$Q = 0.0338 \ln (t) - 0.191, R^2 = 0.997$[a]	(8)

Note: a. Values of R^2 denote the correction coefficients.

Fig. 3. Variations of toluene adsorption capacity with adsorption times and inlet concentrations.

adsorption periods for Eqs. (5) – (8) respectively. Table 3 presents the equilibrium adsorption capacity deviations between simulated and experimental results for $C = 97$ and 1025 ppm. Deviations ≤10% suggest that the approach of extending adsorption period to predict equilibrium adsorption capacity Q_e was satisfactory.

Applying SPME for indicating toluene breakthrough from adsorbent

Values of $Q_{SPME,0}$ and a in Eq. (4) was determined via a GCFID-SPME experiment using a gaseous sample of toluene at concentration of 13.34 ± 0.32 ppm with various adsorption times at a constant temperature. Notably, a toluene concentration of roughly 13 ppm was the mean value, which was detected practically at the GAC outlet during $C = 102$ ppm toluene adsorption experiments. The Q_{SPME} (GC analysis peak area count) increases as adsorption time

Table 2. Estimation of equilibrium toluene adsorption capacity (Q_e) with time using adsorption formula Eqs. (5)–(8).

Items	Ranges of toluene concentration (C, ppm)			
	2652 (2818±315)	1101 (1082±234)	464 (464±25)	102 (107±37)
Equilibrium adsorption time (t, min)	2300	2500	3300	3900
Equilibrium adsorption capacity (Q_e, g toluene/g GAC)	0.285	0.258	0.180	0.088
$(\Delta Q/Q)/\Delta t)$ (1/min)[a]	9.60E-05	9.79E-05	9.67E-05	9.61E-05

Note: a. Calculation based on an increment rate of adsorption capacity less than 0.01 per 100 min.

**Table 3.** Comparison of toluene adsorption capacities calculation from Eqs. (7), (8) and experimental data.

Toluene concentration (ppm)	Adsorption time (min)	Adsorption Capacities (g toluene/g GAC)		Deviation between simulation and experimental data ($|Q_1 - Q_2|/Q_2$, %)
		Q_1, calculation based on Eqs. (7) and (8)	Q_2, experimental	
97 (110 ± 29)[a]	3900	0.088	0.081	8.6
1025 (1069 ± 211)[a]	2500	0.258	0.266	3.0

Note: a. Toluene concentration among the valid ranges 107 ± 37 and 1082 ± 234 ppm for Eqs. (7) and (8).

increases, and parameters $Q_{SPME,0}$, t and a are determined as excess adsorption mass for SPME fiber like Eq. (4) in Fig. 4. The experimental Q_{SPME}, which varied with adsorption time (min) (Fig. 4), was fitted using Eq. (10).

Toluene peak area count analyzed by GC
$$= 1.996 \ln(t) - 1.91 \qquad (10)$$

To determine whether the SPME fiber can exactly identify adsorption time of GAC during 0–400 min, four additional GAC-SPME toluene adsorption tests (adsorption times = 30, 115, 210, and 360
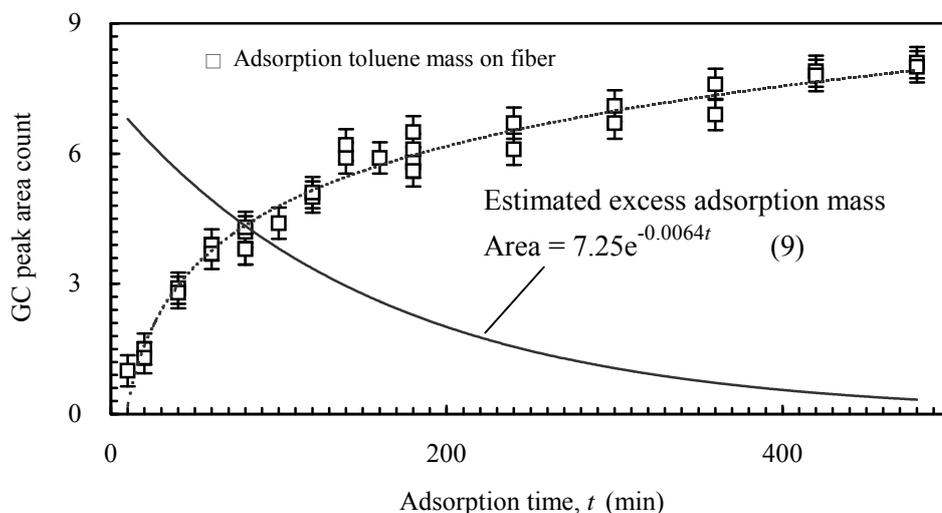
Fig. 4. SPME difussion adsorption of 13.34 ± 0.32 ppm gaseous toluene varying with adsorption time at 27°C by 100-µPDMS fiber.

min) were implemented under an inlet toluene concentration of approximately 102 ± 2.0 ppm (381 ± 7.5 mg/m^3 at 27°C), which was the exact detection concentration in a cabinet for storing bottles of toluene. The SPME fiber adsorbed toluene exhausted from GAC. The toluene mass feeding was calculated as 381 mg/m^3 × 1.5 L/min × t min × 10^{-3} m^3/L × 10^{-3} g/mg = (0.000571t) g. Generally, the mass of exhausted toluene through GAC is proportional to that adsorbed by the SPME fiber. Thus, the relationship between toluene mass feeding for GAC of 10 grams, and those adsorbed individually by GAC (Eq. (8)) and by the SPME fiber (Eq. (10)) can be combined as

$$0.000571t - 10 [0.0338 \ln (t) - 0.191]$$
$$= k [1.996 \ln (t) - 1.91] \qquad (11)$$

where k is the toluene mass proportional

coefficient between the mass exhausted from GAC and that adsorbed by the SPME fiber.
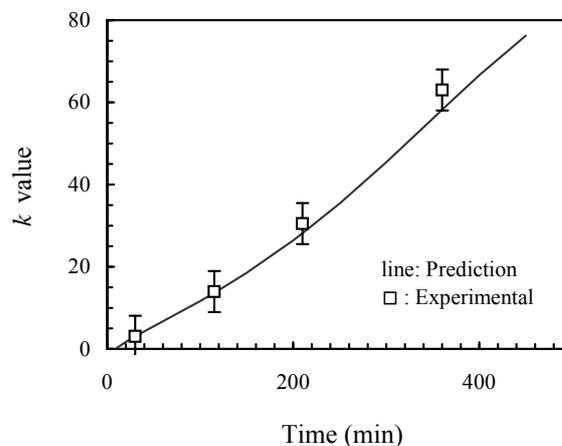
Fig. 5 Prediction and experimental results of toluene adsorption mass by GAC-SPME test.

Fig. 5 presents the simulation curve of varying k values with time using Eq. (10), and experimental values obtained from four GCFID-SPME tests. Moreover, deviations between predicted and experimental k values

were satisfactory at 4.4 ± 3.3%. Based on the distribution of *k* values increasing as adsorption times increase in Fig. 5, it is reasonable that in the GCFID-SPME test of short adsorption time (30 min), the toluene exhausted from GAC was lower than that of long adsorption time (360 min).

RECOMMENDED INSTRUCTIONS FOR USING SPME INDICATION

The GCFID-SPME was determined to be an effective approach, indicating toluene breakthrough from an adsorbent, GAC in this study. The practical instructions for using SPME fiber to indicate GAC adsorption time are as follows.

(a) Detect the concentration of VOC emissions in the storage space of internal circulation cabinet. For instance, the accumulated emission concentration was roughly 102 ± 2.5 ppm; this was the actual concentration detected in a sealed cabinet with about 20 bottles of 1-L toluene.

(b) Eq. (8) was applied to predict the toluene equilibrium adsorption time of 3900 min (see Table 2).

(c) Install a pre-conditioned SPME fiber of 100-μm PDMS in the outlet of a cabinet Fig.5 adsorbent chamber for adsorbing VOCs in the exhausted stream.

(d) Remove the SPME fiber and inject it into the GC-FID to analyze the peak area count of toluene. Equation (10) was applied to determine adsorption time (*t*).

(e) Repeat steps (c) to (d), and add

adsorption times for each SPME fiber. When total time reaches 3900 min, the GAC must be renewed.

Notably, if unexpected VOC emissions are at high concentration (i.e. solvent bottles are ruptured or poorly sealed), the excessive VOCs can impact the SPME adsorption time, as the VOC concentration is outside the range of 107 ± 37 ppm in Eq. (8). The VOC adsorption performance of the adsorbent and SPME fiber must be checked carefully.

CONCLUSIONS

In this study, a series of adsorption experiments (temperature = 27°C, RH = 72 ± 3%) were performed for GAC, which was used as the adsorbent in an internal circulation cabinet for storing organic solvents in the laboratories of universities, colleges and hospitals in Taiwan. Experimental results show that the toluene adsorption capacity, Q (g toluene/g GAC), can be simulated as the natural logarithm of adsorption time for average toluene concentrations ranging from 102 to 2652 ppm (Eqs. (5)-(8)).

Additionally, the SPME fiber installed in the outlet air stream for adsorbing toluene exhausted through GAC effectively indicated the breakthrough of VOCs. The GAC-SPME operational instructions to indicate the replace time of GAC in the cabinets are provided for users. If the advanced indication technology of VOCs breakthrough the GAC can be developed, like the color indication of SPME coating materials during VOC adsorptions, the internal circulation cabinet will be widely

extended, especially the laboratories which a GC-FID is unavailable.

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REFERENCES

Ai, J. (1998). Solid-Phase Microextraction in Headspace analysis. Dynamics in non-steady-state Mass Transfer. *Anal. Chem.* 70: 4822–4826.

Cheng, W.H. and Tsai, S.C. (2007). Competition Among Mixed Adsorbates Affecting the Adsorption of Gaseous Methyl Ethyl Ketone by Hydrophobic Molecular Sieve. *Aerosol Air Qual. Res.* 7: 205–220.

Chou, M.S. and Chiou, J.H. (1997). Modeling Effects of Moisture on Adsorption Capacity of Activated Carbon for VOCs. *J. Environ. Eng.* 123: 437–443.

Erdem-Şenatalar, A., Bergendahl, J.A. and Giaya, A. (2004). Adsorption of Methyl Tertiary Butyl Ether on Hydrophobic molecular sieves. *Environ. Eng. Sci.* 21: 722–729.

Gorlo, D., Zygmunt, B., Dudek, M., Jaszek, A., Pilarczyk. M. and Namieśnik, J. (1999). Application of Solid-Phase Microextraction to Monitoring Indoor Air Quality. *Fresenius J Anal. Chem.* 363: 696–699.

Koziel, J.A. and Pawliszyn, J. (2001). Air Sampling and Analysis of Volatile Organic Compounds with Solid Phase Microextraction, *J. Air Waste Manage. Assoc.* 51: 173–184.

Pawliszyn. J. (1997). Solid Phase Microextratcion, Theory and Practice. Wiley-VCH, Inc.

Scahill, J., Wolfrum, E.J., Michener, W.E., Bergmann, M., Blake, D.M. and Watt, A.S. (2004). A New Method for the Rapid Determination of Volatile Organic Compound Breakthrough Times for A Sorbent at Concentrations Relevant to Indoor Air Quality. *J. Air Waste Manage. Assoc.* 54: 105–110.

Waidyanatha, S., Rothman, N., Fustinoni, S., Smith, M.T., Hayes, R.B., Bechtold, W., Dosemeci, M., Guilan, L., Yin, S. and Rappaport, S.M. (2001). Urinary Benzene as A Biomarker of Exposure Among Occupationally Exposed and Unexposed Subjects. *Carcinog.* 22: 279–286.

Yun, J.H., Choi, D.K. and Kim, S.H. (1998). Adsorption of Organic Solvent Vapors on Hydrophobic Y-type Zeolite. *AIChE J.* 44: 1344–1350.