

Competition among Mixed Adsorbates Affecting the Adsorption of Gaseous Methyl Ethyl Ketone by Hydrophobic Molecular Sieve

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Abstract

Internal circulation cabinets, equipped with adsorbents for emitted volatile organic compounds (VOCs), are extensively used to store organic solvents in Taiwanese university and hospital laboratories. This work evaluates how ketone and isopropanol (IPA) respectively influence the methyl ethyl ketone (MEK) adsorption capacity of a hydrophobic molecular sieve (MS) with a high Si/Al ratio of 1000, HiSiv 1000, manufactured by UOP LLC Corporation, USA. Experimental results for MEK at concentrations from 113 to 2815 ppm reveal that the MEK adsorption capacity is linearly expressed as the natural logarithm of adsorption time ($\ln(t)$) at the constant temperature 27°C and relative humidity $72 \pm 3\%$. The variations in the simulated MEK equilibrium adsorption capacity (Q_e , g MEK/g MS) and concentration (C , ppm) are closely fitted using a Langmuir isotherm. Lower VOC concentration ratios less than 0.17 for mixing acetone and IPA respectively with MEK rarely affect the MEK adsorption by HiSiv 1000. However, the effect of competitive adsorption, which evidently reduces the adsorption capacity of MEK, is related to the higher mixture concentration ratio (> 0.80) of IPA to MEK. The experimental results show that the hydrophobicity characteristics of MEK, acetone and IPA were responsible for variation in adsorption capacity of hydrophobic molecular sieve. Working parameters of adsorbent materials in the internal circulation cabinet have been also provided for preventing breakthrough of VOC adsorption by the molecular sieve.

Keywords: Adsorption; Molecular sieve; Competitive adsorption; Volatile organic compound (VOC); Organic solvent.

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INTRODUCTION

Many organic solvents have been used in laboratories of Taiwanese universities and hospitals. These volatile organics with low boiling points are typically stored in sealed storage cabinets to prevent the unhealthy effects of gaseous volatile organic compounds (VOCs) on workers. Mobile cabinets with internal circulating adsorption system (Fig. 1) are widely employed to store solvents in indoor area. The adsorbent, currently molecular sieves (MS) in Taiwan, must be periodically renewed to prevent the over-adsorption of VOCs by the adsorbent under breakthrough. However, the detailed adsorption characteristics of molecular sieves, used by local manufacturers of storage cabinets, have not been thoroughly examined, nor has the adsorption performance been well evaluated.

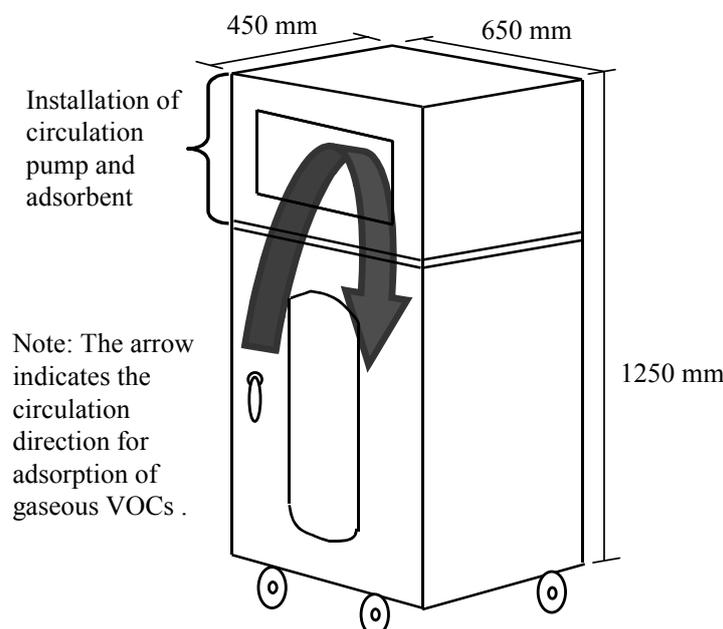


Fig. 1. Schematic internal circulation cabinet for storage of solvents.

Zhao *et al.* (1996) defined that the pore size of the microporous molecular sieve as under 20\AA . Giaya *et al.* (2000) and Erdem-Şenatalar *et al.* (2004) reported that increasing the SiO_2 to Al_2O_3 (Si/Al) ratio by dealumination would change the material from hydrophilic to hydrophobic. Experimentally, the adsorption capacities of chloroanilines on montmorillonite and kaolinite sieves depend on the hydrophilicity and lipophilicity of adsorbates; that is, the extent of adsorption on hydrophobic adsorbents increases with lipophilicity of adsorbates (Angioi, *et al.*, 2005; Polati, *et al.*, 2006). Additionally, the effects of moisture competition and high temperature desorption, which reduce the VOC adsorption capacities of adsorbents, have been extensively investigated (Keener and Zhou, 1990; Chou and Chiou, 1997; Lercher and Seshan, 1997; Yun, *et al.*, 1998; Gawryś *et al.*, 2001; Bilgiç and Aşkin, 2003; Manjare and Ghoshal, 2006).

Generally, various solvents (such as ketones and alcohols) are gathered together in an internal

circulation cabinet. This investigation evaluated the competitive adsorption of mixed gaseous methyl ethyl ketone (MEK), acetone and isopropanol (IPA) by a hydrophobic molecular sieve. The experimental data for MEK adsorption capacity (Q , g MEK/g MS), which is altered by mixed acetone and IPA, have been provided to local manufacturers to improve the application of adsorbent materials used in an internal circulation cabinet.

METHODOLOGY

Fundamental adsorption theory used in this study

The VOC adsorption capacity (Q , g VOC/g MS) by molecular sieve increases with the concentration of VOC (C , ppm) (Erdem-Şenatalar *et al.*, 2004; Yun, *et al.*, 1998). Additionally, Scahill *et al.* (2004) used the Nelson-Harder correlation to relate the breakthrough time variations (t_1 and t_2) of the different inlet contaminant concentration (C_1 and C_2):

$$\frac{t_1}{t_2} = \left(\frac{C_1}{C_2}\right)^n \quad (1)$$

where, n is a constant. According Scahill *et al.*'s findings, the VOC adsorption capacity by molecular sieve is proportional to the natural logarithmic value of adsorption time.

$$Q \propto \ln(t) \quad (2)$$

Since zeolite molecular sieves rely on strong physical forces rather than chemisorption, the shape of the isotherm for single component adsorbate is characterized by a Langmuir-type (Bhatia, 1989). Langmuir model are most frequently used to describe adsorption equilibrium on homogeneous solids, like HiSiv 1000 used herein (Himeno, *et al.*, 2007). The Langmuir (Eq. (3)) isotherm models are used to fit the experimental equilibrium capacity data (Q_e) with various inlet concentrations (C) for adsorption of a single VOC at a constant temperature (Chou and Chiou, 1997; Yun, *et al.*, 1998; Manjare and Ghoshal, 2006; Choudary, *et al.*, 2002; Yoo, *et al.*, 2005; O'Connor, 2006).

$$Q_e = \frac{abC}{1 + bC} \quad (3)$$

where a is mass of adsorbate required to saturate completely a unit mass of adsorbent; and b is the Langmuir adsorption constant (Reynolds and Richards, 1995; Lin *et al.*, 2006). Values of a and b are constants to be determined by performing a series of isothermal continuous-flow column tests (Benfield, *et al.*, 1982).

Rudziński *et al.* (1995) used the exponential formula, like the Freundlich equation, to simulate the competitive adsorption between methane and ethane in binary gas mixtures. The modified relationship used to find the competitive adsorption capacity of component A (Q_A), based on the work of Rudziński *et al.*, is:

$$\frac{Q_A}{Q_{A0}} \propto \left(\frac{C_B}{C_A}\right)^n \quad (4)$$

where Q_{A0} represents the adsorption capacity for the single component A. According to the competitive adsorption between concentrations of components A and B, if n is negative, the adsorption capacities of components A and B reduce each other, because Q_A and C_B are inversely proportional.

Design of adsorption system

The adsorption apparatus, presented in Fig. 2 and taken from Chou and Chiou's study (1997), was adopted to assess exactly the effect of mixed VOCs on the adsorption capacity of MEK by molecular sieves (Q , g MEK/g MS) during the period of adsorption (t , min). This system was based on the method of air-stripping using a low flow rate regulating air compressor (part 3 of Fig. 2), and transferred VOC (q_{VOC}) with a gaseous concentration of C_g^* at a constant rate (5 mL/min). The tested VOC was MEK. MEK separately mixed with various volume ratios of ketone and IPA was also tested by mixing liquid VOCs in the tube (part 6 of Fig. 2). The other air blower (part 2 of Fig. 2) passed a saturated water stream ($q_w = 0.3\text{--}0.8$ L/min) with a relative humidity (RH) about 100%, mixed with dry air ($q_d = 0.7\text{--}1.2$ L/min). The gaseous flow rates satisfied $q_{\text{VOC}} \ll (q_w + q_d)$. The ranges of VOC concentration (C) and RH were determined by setting q_{VOC} , q_w and q_d for a series of adsorption tests, using the following calculations.

$$\text{RH}(\%) = \frac{100 q_w}{q_w + q_d} \quad (5)$$

$$C = \frac{C_g^* q_{\text{VOC}}}{q_w + q_d} \quad (6)$$

The totally gaseous stream ($q_{\text{VOC}} + q_w + q_d$) was maintained at 1.5 L/min in all test runs. Influent MEK concentrations (C_i) typically ranged from low (113–416 ppm), through middle (759–1429 ppm) to high (2815–4564 ppm), to evaluate the variation of the adsorption capacity (Q) with various VOC concentration (C) and adsorption time (t).

A gastight glass tube (part 11 of Fig. 2) was filled with around 10 g of hydrophobic molecular sieve (HiSiv 1000, UOP LLC Company, Des Plains, IL, USA). The space velocity (v_s) of 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 13 of Fig. 2) at a constant temperature of 27°C. The VOC adsorption periods ranged from 20 to 720 min. The RH value of the VOC-carrying stream was measured using a humidity analyzer (testo 400, TESTO, Germany, part 12 of Fig. 2). The RH of the gas streams was maintained at $72 \pm 3\%$ in all test runs. Operation of the system at a constant RH and temperature prevented moisture and heat from affecting the VOC adsorption capacity.

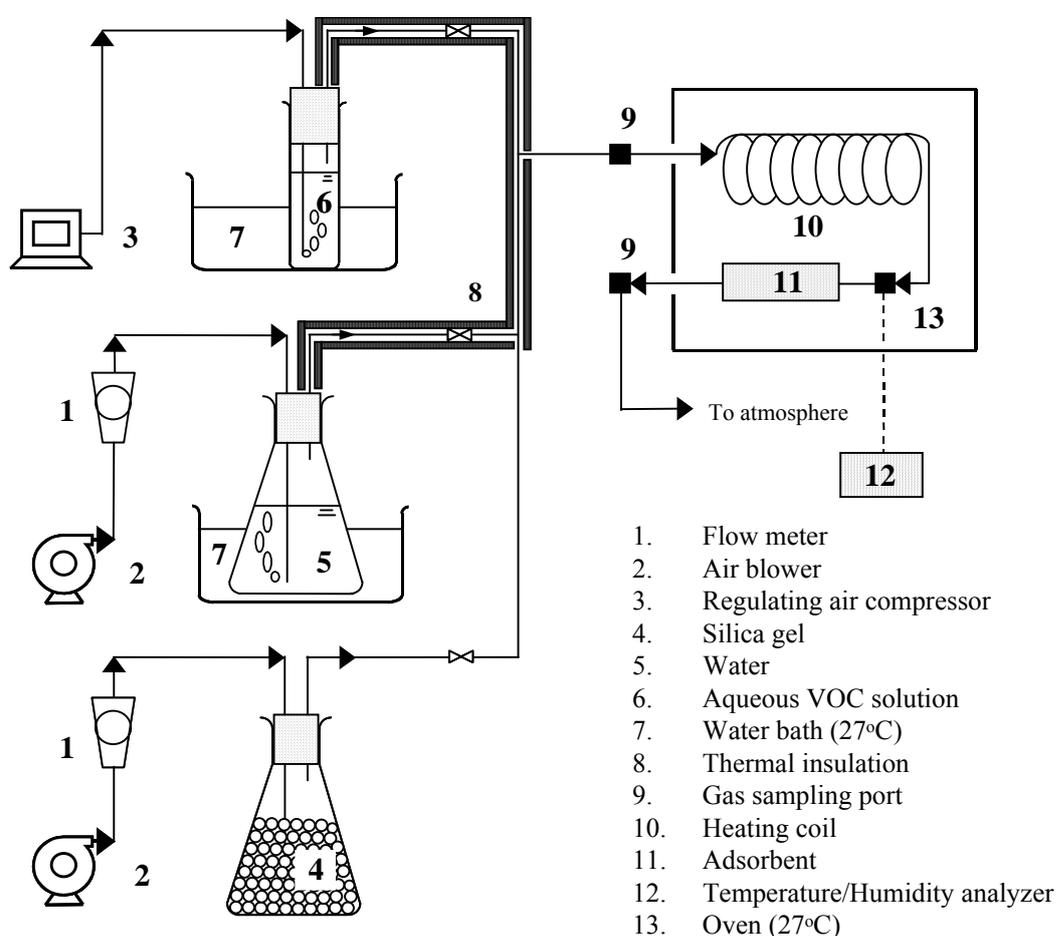


Fig. 2. Schematic experimental adsorption system.

Calculating VOC adsorption capacity

When the adsorption test was completed, the glass tube and molecular sieve 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 in 10 L Teflon gas sampling bags (SKC, USA). The desorption period took 2.5 hr, in which the 99.99% of adsorbed VOCs were removed from the molecular sieve within preliminary

desorption tests. For checking the performance of molecular sieve reuse and equilibrium adsorption achievement (Reynolds and Richards, 1995), the remained VOCs on molecular sieve after desorption procedures were examined less than 0.01% adsorption mass. The molecular sieve could be reused for the next experimental runs but not exceeding 5 runs. All desorbed gases were sampled using a gastight syringe (Hamilton, USA) and then analyzed using a GC-FID (6890N, Agilent, USA). The internal volume of the Teflon bags was determined by the method of buoyancy using draining water. Multiplying the analyzed concentration by the volume of the bag yielded the mass of VOC adsorbed by the molecular sieve. Summing all of the VOC masses in a desorption run and then dividing that sum by the mass of molecular sieve in grams yielded Q . The calibration curves for VOC analysis by GC-FID were interiorly replicated examination using samples of known concentrations once per week.

Experimental materials

The tested hydrophobic molecular sieve (HiSiv 1000) was produced by UOP LLC. HiSiv adsorbents are synthetically produced silicon-aluminum oxides that have an Si/Al ratio of from 10 to 1000. HiSiv 1000 differs from types A and X zeolites for its significantly higher proportion of Si/Al ratio in the molecular structure. Table 1 presents the typical characteristics of HiSiv 1000. UOP LLC states that HiSiv 1000 is preferred for adsorbing large molecules (0.6-0.8 nm), such as alcohols, aldehydes, ketones and ethers. Larger molecules such as multiple-ringed aromatic compounds are not adsorbed because they are too large for the pore openings. Notably, HiSiv 1000 is recommended as adsorbent under a humid condition of RH higher than 70%.

Target VOCs, MEK, acetone and IPA, were of analytic reagent grade. A water purification system (Millipore, RiOs-3/Milli-Q, France) provided water for all experiments.

Table 1. Typical Properties of HiSiv™ 1000.

Item	Unit	Value
Particle form	-	Extrudate
Particle size	m	0.004 (length) x 0.0015 (diameter)
Bulk density	kg/m ³	530
Void fraction	-	0.39
Surface area	m ² /kg	10 ⁶
Crush strength	kg	2.3
Specific heat	-	0.19 (25°C); 0.24 (175°C)
Thermal stability	°C	Up to 800 (dry air); up to 500 (moisture)

Note: Data cited from the information of products provided by UOP LLC.

RESULTS AND DISCUSSION

Variations of adsorption capacity with VOC concentrations

MEK adsorption tests were performed using the molecular sieve at an inlet concentration ranging from 113 to 4564 ppm, over periods of 60–600 min at 27°C. Fig. 3 shows the variations of MEK adsorption capacity (Q) with concentration (C) at various adsorption times, and Table 2 presents formulae (Eqs. (7)–(11)) in Fig. 3. Table 2 shows a proportional relationship between the natural logarithm of the adsorption time and adsorption capacity. In fact, the values of Q at $C = 2815$ ppm and 4564 ppm are close to each other, and the inlet concentration of MEK should be under 2815 ppm for an effective adsorption operation.

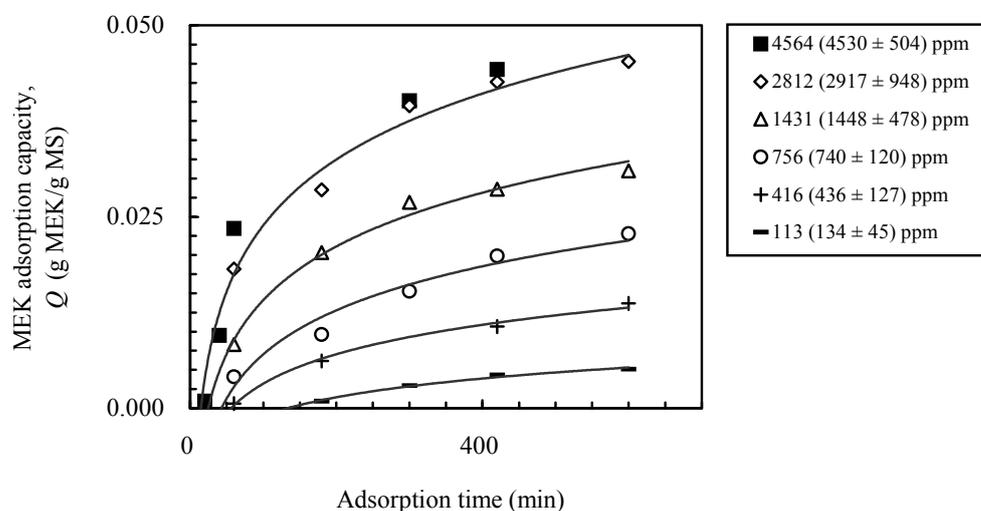


Fig. 3. Variations of MEK adsorption capacity with inlet concentration at various adsorption times.

Table 2. Correlations of MEK Adsorption Capacity With Time and Concentrations.

Concentration (C , ppm)	Formula of adsorption capacity (Q , g MEK/g MS) varying with adsorption time (t , min)	
2815 (2920 ± 947)	$Q = 0.0124 \ln(t) - 0.0333$, $R^2 = 0.975^a$	(7)
1429 (1446 ± 476)	$Q = 0.0101 \ln(t) - 0.0325$, $R^2 = 0.986^a$	(8)
759 (743 ± 116)	$Q = 0.0083 \ln(t) - 0.0312$, $R^2 = 0.959^a$	(9)
416 (437 ± 126)	$Q = 0.0055 \ln(t) - 0.0223$, $R^2 = 0.993^a$	(10)
113 (134 ± 45)	$Q = 0.0035 \ln(t) - 0.0173$, $R^2 = 0.986^a$	(11)

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

Determining the VOC equilibrium isotherms of adsorption

The VOC adsorption curves (Fig. 3) have not yet reached at equilibrium for the adsorption period of 600 min. Equations (7)–(11) were adopted with various mean values of inlet concentration (113, 416, 759, 1429 and 2815 ppm) using extended adsorption period of 3200 min to determine the equilibrium adsorption capacity Q_e (Table 3). The equilibrium adsorption times drop from 3200 min at $C = 113$ ppm to 2000 min for $C = 2815$ ppm.

Table 3. Estimation of Equilibrium MEK Adsorption Capacity (Q_e) With Time Using Adsorption Formula Eqs. (7)–(11).

Items	Ranges of MEK concentration (C , ppm)				
	2815 (2920 ± 947)	1429 (1446 ± 476)	759 (743 ± 116)	416 (437 ± 126)	113 (134 ± 45)
Equilibrium adsorption time (t , min)	2000	2200	2500	2600	3200
Equilibrium adsorption capacity (Q_e , g MEK/g MS)	0.0521	0.0442	0.0337	0.0245	0.0109
$(\Delta Q/Q)/\Delta t$ (1/min) ^a	9.93E-05	9.93E-05	9.65E-05	9.91E-05	9.84E-05

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

Fig. 4 presents the simulated equilibrium adsorption isotherms obtained using Langmuir formulae with the data of Q_e and C in Table 3. Notably, the reciprocal values of Q_e and C , $1/Q_e$ and $1/C$ in Fig. 4, must be adopted to find constants a and b in Eq. (3) (Benfield, *et al.*, 1982). Table 4 shows that the Langmuir formula, $Q_e = [0.000117C/(1+0.00216C)]$, as well as $a = 0.0542$ g MEK/g MS, and $b = 0.00216$ 1/ppm, more properly specifies the equilibrium MEK adsorption capacities by HiSiv 1000 for lower MEK concentrations under 27°C and RH = 72±3%. The highest simulation deviation (10.7%) for $C = 2815$ (2920 ± 947) ppm in Table 4 may be resulted from the more extreme deviations of inlet concentrations than lower MEK concentration ranges.

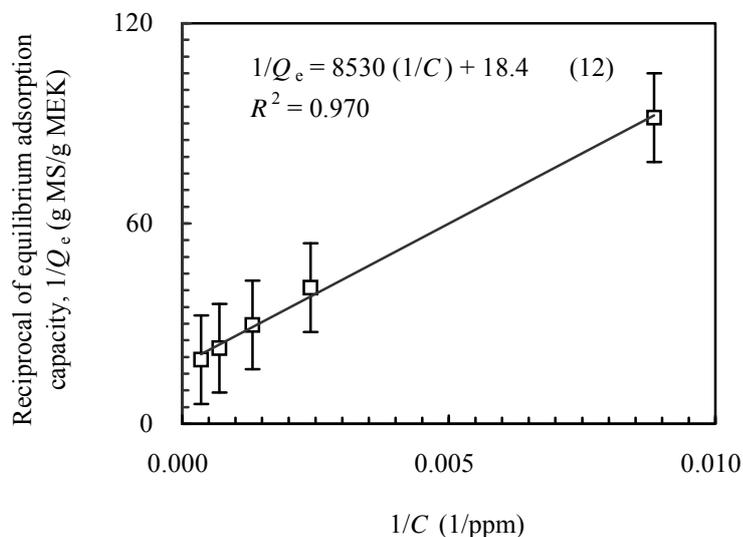


Fig. 4. MEK Langmuir adsorption isotherm.

Table 4. Comparison of MEK Adsorption Capacities Calculation from Eqs. (7)-(11) and the Proposed Langmuir Model.

MEK concentration (C, ppm)	Adsorption Capacities (Q_e , g MEK/g MS)		Deviation between calculation and model simulation ($ C_1 - C_2 /C_1$, %)
	C_1 , calculation from Eqs. (7)-(11) ^a	C_2 , based on Langmuir model Eq. (12)	
113 (134 ± 45)	0.0109	0.0106	2.7
416 (437 ± 126)	0.0245	0.0256	4.5
759 (743 ± 116)	0.0337	0.0336	0.3
1429 (1446 ± 476)	0.0442	0.0409	7.5
2815 (2920 ± 947)	0.0521	0.0465	10.7

Note: Based on the results in Table 3.

Breakthrough experiment of MEK adsorption by molecular sieve

Gaseous VOC breakthrough tests for molecular sieve adsorption have frequently been utilized to evaluate the equilibrium adsorption capacity (Q_e , g VOC/g MS) (Yoo, *et al.*, 2005; Lin, *et al.*, 2005; Manjare and Ghoshal, 2005). Breakthrough tests of MEK adsorption ($C = 1448$ (1471 ± 319) and 440 (483 ± 183) ppm) were performed herein to verify the feasibility of the simulated equilibrium capacity data in Table 3. The initial ($t = 0$ –100 min) and complete adsorption curves are shown as Fig. 5. According to the simulated equilibrium adsorption times of 2200 min for 1448 ppm and 2600 min for 440 ppm in Table 3, the experimental values of C_0/C_i at 2200 and 2600 min are satisfactorily 0.990 and 0.994 in Fig. 5, which are close to equilibrium adsorption condition of $C_0/C_i = 0.990$. If further calculating equilibrium adsorption capacity, using the formula $[(C_0 - C_i) \times (q_{VOC} + q_w + q_d) \times \Delta t]$ ($\Delta t =$ VOC detection period deviation), the simulation errors for calculation in Table 3 are 3.7% and 1.2% for the inlet MEK concentrations = 1448 and 440 ppm.

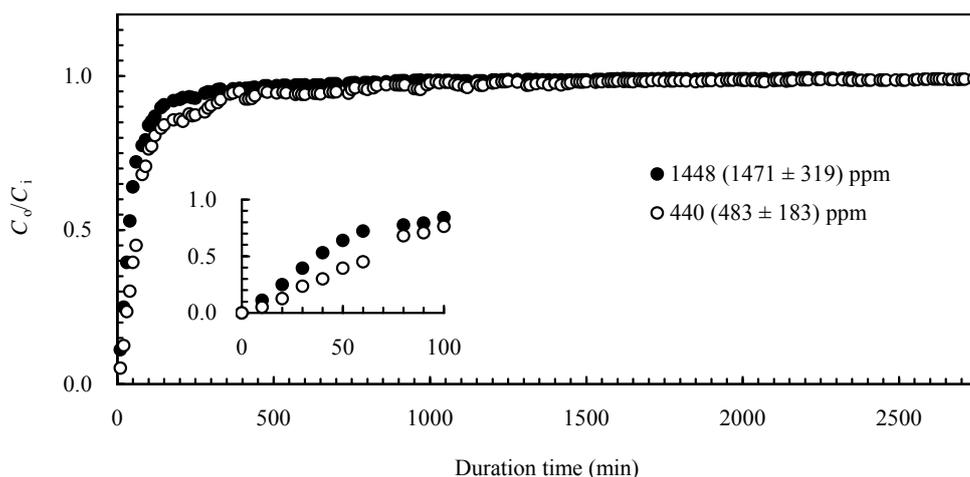


Fig. 5. Breakthrough curves of MEK adsorption.

Effect of mixture of VOCs on adsorption capacity

Based on Rudziński *et al.*'s competitive adsorption theory (1995) (Eq. (4)), Fig. 6 presents the effects of mixed VOCs on the adsorption capacity of MEK for a series of 300 min adsorption experiments of various acetone/MEK and IPA/MEK concentration ratios. The inverse proportionality between the adsorption capacity ratios of binary-component to single-component (Q/Q_0) and the concentration ratio is fully demonstrated for $n < 0$.

Table 5 compares the critical concentration ratios, at which mixed acetone and IPA evidently restrained the MEK adsorption capacities. When the acetone/MEK and IPA/MEK concentration ratios

are under 0.17 ($\frac{137}{844}=0.162$ and $\frac{134}{832}=0.161$), then the MEK adsorption capacities are close to those obtained using Eq. (9). The MEK adsorption capacities gradually drop below the simulated value as the acetone/MEK and IPA/MEK concentration ratios increase. Notably, when the IPA/MEK concentration ratio approached 0.80 ($\frac{670}{842}=0.796$), competitive adsorption of mixed IPA occurs at an actual adsorption capacity of as low as 79.4% of estimated value. However, the strong adsorption competition between mixed adsorbates does not dominate in a mixture of acetone and MEK, even when the concentrations of MEK and acetone were close to each other (730 ppm vs. 795 ppm).

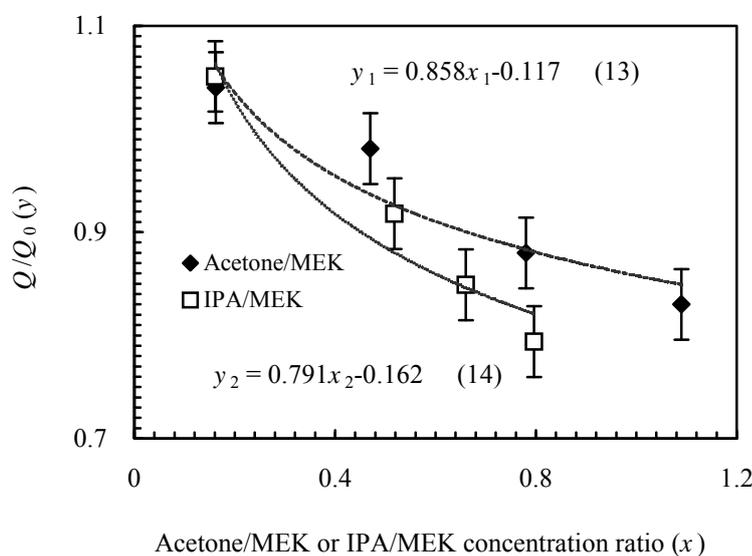


Fig. 6. Comparison of concentration competition effect of acetone and IPA for MEK adsorption by molecular sieve.

Table 5. Comparison of Estimated and Experimental Adsorption Capacity by Molecular Sieve for Mixed VOCs.

Operation parameter	Experiment series			
	Acetone/MEK	IPA/MEK	Acetone/MEK	IPA/MEK
MEK concentration (ppm)	844 (816±81)	826 (802±74)	730 (735±75)	832 (802±102)
Acetone concentration (ppm)	137 (143±34)	388 (377±71)	795 (803±24)	-
IPA concentration (ppm)	-	-	-	134 (134±20)
Experimental MEK adsorption capacity (g MEK/g MS)	0.01685	0.01583	0.01568	0.01697
Estimated MEK adsorption capacity ^a (g MEK/g MS)			0.01614	
Estimation deviation from experimental adsorption capacity (%)	4.4	-1.9	-2.9	5.1
				-4.0
				-20.7

Note:

a. Estimation using Eq. (9) and adsorption time 300 min.

Besides the electrostatic force between the adsorbent and adsorptive sites of molecular sieves, which is primarily due to the cations within the crystal lattice structure of molecular sieves, the affinity between adsorbates and adsorbent for mixed VOCs is essential. The *n*-octanol-water partitioning constant (K_{ow}) is a universal parameter used in determining the affinity of organic compounds to the lipophilic/hydrophilic surface. A VOC with a higher K_{ow} is more easily adsorbed by the hydrophobic adsorbents on their adsorption sites. Angioi *et al.* (2005) and Polati *et al.* (2006) proposed the lipophilicity/hydrophobicity theory, based on the examination of the adsorption capacities of chloroanilines on montmorillonite and kaolinite sieves. According to the K_{ow} values in the Syracuse Research Corporation PhysProp's database, K_{ow} of MEK, acetone and IPA are 1.95, 0.575 and 1.12, respectively (2006). Among target VOCs, MEK is the most hydrophobic, and has the strongest affinity for hydrophobic HiSiv 1000. Table 5 reveals that when the acetone/MEK and IPA/MEK concentration ratios are under 0.17, both acetone and IPA result in limited competitive adsorption of MEK; however, as the acetone/MEK and IPA/MEK concentration ratios increase, IPA reduces the adsorption capacity of MEK more than does acetone. Given this concentration competition, hydrophobicity or K_{ow} values of hydrocarbons should be further considered if VOCs of different K_{ow} are presented in a sealed cabinet with hydrophobic molecular sieve adsorbents.

Working parameters for the internal circulation cabinet

To prevent the over-adsorption of VOC by HiSiv 1000, the operation parameters are recommended as follows. The accumulated emission concentration was approximately 100 ppm, based on the actual detection in a sealed cabinet, where storing about 20 bottles of 1-L and 3 bottles of 2-L bottles of MEK, acetone and alcohols. Using Eq. (11) in Table 2 with a 90% equilibrium adsorption ($0.0109 \times 0.9 = 0.00981$ g MEK/g MS) (see Table 3), the calculated adsorption time is 2312 min. If five times of taking out chemicals from this cabinet, a 2-min preliminary compulsory operation of circulation pump for cleaning the inner air is recommended before workers open the sealed door. The total adsorption period for renewing the adsorbent is estimated as 46.2 weeks [2312 min/(2 min \times 5 1/day \times 5 days/week)], which means the molecular sieve effectively adsorbs gaseous MEK, acetone and alcohols within this period. Notably, the design for the volume of adsorption bed and circulation pump must be based on the criteria, $v_s = 1.3$ 1/s, and EBRT = 0.76 s. If an unexpected VOC emission of high concentration (i.e. incompletely sealed or rupture of solvent bottles), the VOC adsorption performance of adsorbent must be checked. Additionally, the concentration competitive effect on adsorption capacities of molecular sieve for hydrocarbons with different K_{ow} values should be considered.

CONCLUSIONS

A series of adsorption tests (adsorption temperature = 27°C, RH = 72 ± 3%) were performed on the hydrophobic molecular sieve, which was used as the adsorbent in an internal circulation cabinet for storing organic solvents. Experimental results show that the MEK adsorption capacity, Q (g MEK/g MS), can be simulated as the natural logarithm of adsorption time for MEK concentrations from 113 to 2815 ppm (Eqs. (7)-(11)). This work also established the Langmuir model, which yields the MEK adsorption isotherm between the equilibrium adsorption capacity, Q_e , and the VOC concentration, C (ppm), at $Q_e = [0.000117C/(1+0.00216C)]$.

A lower concentration ratio (< 0.17) of mixed acetone and IPA with MEK rarely affects the MEK adsorption of hydrophobic HiSiv 1000. However, competitive adsorption, which reduces the adsorption capacity of MEK, results from the higher concentration ratio (> 0.80) of IPA to MEK. However, the higher concentration ratio of acetone to MEK does not cause dominant competitive adsorption. The hydrophobicity of hydrocarbons, specified by k_{ow} , should be further considered when various hydrophilic/hydrophobic VOCs are gathered in an internal circulating adsorption system cabinet with molecular sieve adsorbents. If the k_{ow} values of VOCs approach those of the other components, then competitive adsorption is occurring for the mixed adsorbates in the cabinet. It is recommended that specific internal circulating cabinet should be used for the hydrocarbon solvent of a single group to prevent the competitive adsorption.

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