

A Test of Relative Removal Properties of Various Offensive Odors by Zeolite

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ABSTRACT

The adsorptive removal properties of synthetic A4 zeolite were investigated against a total of 16 offensive odors consisting of reduced sulfur compounds (RSCs), nitrogenous compounds (NCs), volatile fatty acids (VFAs), and phenols/indoles (PnI). Removal of these odors was measured using a laboratory-scale impinger-based adsorption setup containing 25 g of the zeolite bed (flow rate of 100 mL min⁻¹). The highest and lowest breakthrough (%) values were shown for PnIs and RSCs, respectively, and the maximum and minimum adsorption capacity (μg g⁻¹) of the zeolite was observed for the RSCs (range of 0.77-3.4) and PnIs (0.06-0.104), respectively. As a result of sorptive removal by zeolite, a reduction in odor strength, measured as odor intensity (OI), was recorded from the minimum of approximately 0.7 OI units (indole [from 2.4 to 1.6]), skatole [2.2 to 1.4], and p-cresol [5.1 to 4.4]) to the maximum of approximately 4 OI units (methanethiol [11.4 to 7.5], n-valeric acid [10.4 to 6.5], i-butyric acid [7.9 to 4.4], and propionic acid [7.2 to 3.7]). Likewise, when removal was examined in terms of odor activity value (OAV), the extent of reduction was significant (i.e., 1000-fold) in the increasing order of amy acetate, i-butyric acid, phenol, propionic acid, and ammonia.

Key words: H₂S, Malodors, Zeolite beads, Odor control, Adsorption efficiency

1. INTRODUCTION

Public outcry over incessant odor pollution from various sources (industrial, municipal, and agricultural)

has increased over the past decades (Kim *et al.*, 2008; Dincer and Muezzinoglu, 2006; Rappert and Müller, 2005; Mukhtar *et al.*, 2004; Gostelow *et al.*, 2001). Scientific research has identified several aspects of agricultural practice as major sources of pungent pollutants that contaminate our atmosphere, including feeding and rearing livestock, as well as composting their waste (Akdeniz *et al.*, 2012; Hottenstein and Ana, 2008; Smet *et al.*, 1999). The environmental significance of numerous farmed animal sources has been documented; for example, beef (Spiehs *et al.*, 2013; Shabtay *et al.*, 2009) and dairy cattle (Parker, 2008; Hayes *et al.*, 2006), swine (Parker, 2011; Lim *et al.*, 2004), and poultry barns (Dunlop *et al.*, 2010; Hayes *et al.*, 2006; Carey *et al.*, 2004). Likewise, the production and use of animal feed (Hafner *et al.*, 2010; Montes *et al.*, 2010) and application of manure (Parker *et al.*, 2013) are also crucial factors in the release of malodors from agricultural activities into the air. The presence of common inorganic gases with characteristic foul smells (H₂S and NH₃) is well known (Panda *et al.*, 2012). In addition, detailed assessment of the air quality around livestock farms has revealed the presence of more pungent volatile organic compounds (VOCs), generally occurring at much lower (trace and ultra-trace) levels (Wing and Wolf, 2000). The presence of these odors has resulted in discontent among neighboring residents and has affected enjoyment of other human activities.

A number of approaches have been proposed and adopted to mitigate this environmental menace, such as source reduction by altering the dietary plans for animals (Archibeque *et al.*, 2006; Miller and Varel, 2001), use of bedded systems (Nicks *et al.*, 1997), and vegetable oil sprinkling (Takai, 2007). However, to achieve optimum production of livestock and ensure

economic feasibility without imposing detrimental health effects, post-production control of malodors should be a priority. In a report on air emissions from animal feeding operations (AFOs) by the National Research Council (NRC, 2003), malodorous compounds from such operations were described to have major environmental significance, especially at the local level. Hence, there is a strong need to develop proficient materials and techniques for simultaneous removal of various odorous pollutants.

Various technical approaches for odor control have been developed, including membrane processes (Micolli *et al.*, 2014; Nour *et al.*, 2014), conventional chemical absorption techniques (Abu-Khader, 2006), modern absorption approaches with ionic liquids (Smiglak *et al.*, 2007), and sorption processes using various adsorbents. Among these technologies, one of the most preferred choices has been adsorption, e.g., use of activated carbon (Zhang *et al.*, 2014), activated alumina (Saha and Deng, 2010), metal-organic frameworks (MOFs) (Glover *et al.*, 2011), or zeolite (pristine or ion-exchanged) (Jung *et al.*, 2014; Tang *et al.*, 2011; Mustafa *et al.*, 2010). The collection of malodors on dry and porous surfaces by adsorption has been exalted for its inherent excellence, especially when used in low-level pollution scenarios (Bottani and Tascón, 2011).

To learn more about the sorptive behavior of odors, we characterized the sorption properties of zeolite against diverse odor species. We selected zeolite by considering its characteristic physical (regular hierarchical pore structure) and chemical (definite and modifiable composition) merits that are attributed to its comparatively low regeneration energy cost in association with its enhanced kinetic selectivity (Zhao *et al.*, 2007). However, zeolite has some disadvantages, including a relatively low adsorption capacity for heavier air contaminants (based on molecular weights and kinetic diameters) compared to some carbonaceous sorbents such as activated carbon as a result of its definite micropore structure (unlike the hierarchical pore channels of other candidate materials), which restricts diffusivity (Lee *et al.*, 2012). Nevertheless, these negative features are mitigated by a moderately long and consistent adsorption rate (sieving effect) (Vellingiri *et al.*, 2016). Hence, zeolite is the best current candidate by balancing adsorption efficiency and energy regeneration cost in a more effective manner than other sorbents (Khalighi *et al.*, 2014).

This pilot study was carried out to assess the adsorptive removal characteristics (adsorption efficiency) of A4 zeolite against a mixture of 16 selected major pungent air pollutants. The choice of A4 zeolite was based on its merits such as high selectivity towards target

contaminants, low cost, and energy requirement (for regeneration) despite its relatively low specific surface area of $14.5 \text{ m}^2 \text{ g}^{-1}$. The results of adsorption experiments were further evaluated to describe the relationships between sorptive removal, breakthrough, and reduction of odor intensity for each odor. The overall results of our study provide valuable insights into the sorption processes of odors and subsequent chemical treatment of zeolite to improve its removal capacity and selectivity.

2. MATERIALS AND METHODS

2.1 Target Odors and Sorbent

In light of the diverse chemical functionalities among various odors, our target compounds were selected to represent four major groups: reduced sulfur compounds (RSCs), nitrogenous compounds (NCs), volatile fatty acids (VFAs), and phenols and indoles (PnI), as listed in Table 1. The adsorbent for this study (A4-type synthetic zeolite; mesh size approximately 1.40-2.36 mm) was purchased from Wako Pure Chemicals, Ltd., Japan. Brunauer-Emmett-Teller (BET) analysis after thermal pre-treatment at 473 K under N_2 flow estimated the specific surface area as $14.5 \text{ m}^2 \text{ g}^{-1}$, with average pore diameters of adsorption and desorption (4V/A) of 34.9 and 24 nm, respectively.

2.2 Acquisition and Preparation of Gaseous Working Standards

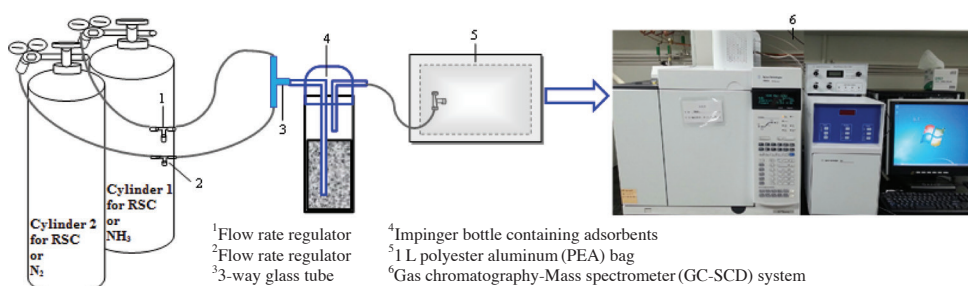
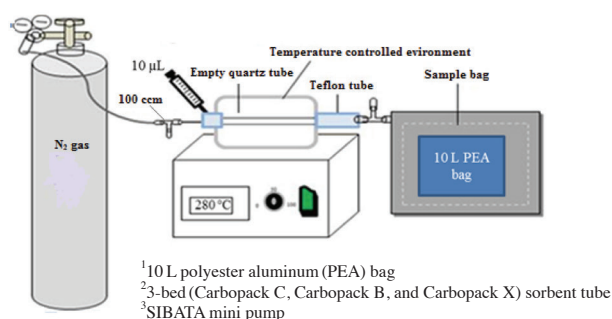
The primary standards (PS) for RSCs and NH_3 were supplied in cylinders by RIGAS, Korea. Using 99.999% N_2 as a diluent, 20 ppm standards of the RSCs were prepared. This mixing procedure was replicated to produce a specific concentration of NH_3 through dilution with N_2 at steady flow rates of 15 and 85 mL min^{-1} , respectively (sum, 100 mL min^{-1}) for the adsorption experiment (Fig. 1a). In both cases, the system was set up to deliver the standard gases from respective PS gas cylinders. The concentration level of each target was prepared at a few tens of ppb to ppm levels, which correspond to odor intensity (OI) levels of 2.23 (SK) to 11.4 (CH_3SH).

To determine the scope of odor removal by zeolite, the concentration levels of the target odors were arbitrarily selected to represent a wide range of concentrations with considerably high OI levels (within the range of 30 [NH_3] to 16,500 [CH_3SH]). The preparation of gaseous working standards (GWS) for semi-volatile compounds is problematic because of the high instability of the components in static conditions (e.g., high adsorptivity and low saturated vapor pressure) (Kim and Kim, 2012). Hence, most of these odors are intrin-

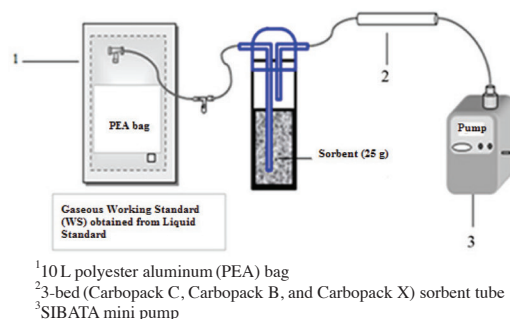
Table 1. Information on the target compounds investigated in this study.

Order	Group ^a	Chemical name	Chemical formula/ Sample ID	CAS No.	Chemical formula	Molecular weight (g mol ⁻¹)	Calibration RF ^b	Results R ²	QA		Instrumental analysis methods
									MDL ^c (ppb)	RSE ^d (%)	
1		Hydrogen sulfide	H ₂ S	7783-06-04	H ₂ S	34.1	3,081	0.9986	0.03	0.81	
2	RSCs	Methanethiol	CH ₃ SH	74-93-1	CH ₄ S	48.1	3,170	0.9986	0.07	0.39	
3		Dimethyl sulfide	DMS	75-18-3	C ₂ H ₆ S	62.1	2,885	0.9992	0.03	1.33	AS/TD/GC/SCD ^e
4		Dimethyl disulfide	DMDS	624-92-0	C ₂ H ₆ S ₂	94.2	4,089	0.9973	0.03	0.81	
5		Ammonia	NH ₃	7664-41-7	NH ₃	17.0	—	—	—	—	Sensor ^f
6	NCs	Trimethylamine	TMA	75-50-3	C ₃ H ₉ N	59.1	511,361	0.9932	0.00	4.92	ST/TD/GC/Q-MS ^g
7		Propionic acid	PPA	79-09-4	C ₃ H ₆ O ₂	74.1	5,803	0.9939	0.63	1.46	
8		n-Butyric acid	BTA	107-92-6	C ₄ H ₈ O ₂	88.1	17,571	0.9995	0.76	3.07	
9	VFAs	i-Valeric acid	IVA	503-74-2	C ₅ H ₁₀ O ₂	102	18,520	0.9986	0.86	3.66	ST/TD/GC/Q-MS ^g
10		n-Valeric acid	VLA	109-52-4	C ₅ H ₁₀ O ₂	102	19,946	0.9983	1.19	4.06	
11		Acetic acid	ACA	64-19-7	C ₂ H ₄ O ₂	60.05	6,115	0.9933	2.25	1.77	
12		i-Butyric acid	IBA	79-31-2	C ₄ H ₈ O ₂	88.1	7,151	0.9922	1.25	2.13	
13	Phenol	Phenol	PhAl	108-95-2	C ₆ H ₆ O	94.1	25,617	0.9982	0.90	0.74	ST/TD/GC/Q-MS ^g
14		p-Cresol	p-C	106-44-5	C ₇ H ₈ O	108	11,493	0.9901	1.30	4.17	
15	Indole	Indole	ID	120-72-9	C ₈ H ₇ N	117	27,841	0.9987	0.98	0.23	ST/TD/GC/Q-MS ^g
16		Skatole	SK	83-34-1	C ₉ H ₉ N	131	35,571	0.9991	0.61	2.36	

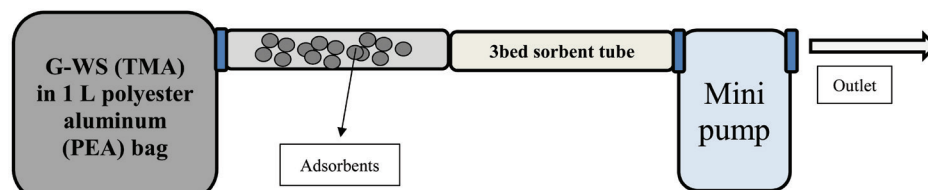
^aGrouping based on the chemical properties/compositions of the compounds^bRetention factor^cMethod detection limit (MDL): The product of the standard deviation of the seven replicates multiplied by the Student's t-value at the 99.9% confidence level (6 df, t = 3.14).^dRelative standard error (RSE): Triplicate analyses of the calibration point.^eAS/TD/GC/SCD = Air server (UNITY 1, Markes International, Ltd., UK), TD = Thermal desorber, GC = Gas chromatography (7890A, Agilent Technologies, USA), SCD = Sulfur chemiluminescence detector (355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA), ST = Sorbent tube, Q-MS = Quadrupole mass spectrometer.^fSensor: NH₃ sensor system (Ibrid mx6, USA)^gST/TD/GC/Q-MS: ST = Sorbent tube, TD = Thermal desorption, GC = Gas chromatography, Q-MS = Quadrupole mass spectrometer.

(a) Experimental setup for the removal of RSCs and NH_3 .

(b) Gas standard generation system for VFAs and PnI.



(c) Experimental setup for sorptive removal of VFA and PnI.



(d) Experimental setup for sorptive removal of TMA.

Fig. 1. Schematics for sampling of target compounds. Commercially available standard gases were used for the removal expts of RSCs and ammonia, while all others (VFA and PnI) were tested by generating the standard gas in the laboratory. (a) Experimental setup for generation and removal of RSCs and NH_3 . (b) Experimental setup for TMA. (c) Experimental setup for VFAs, phenols, and indoles.

sically subject to large sorptive losses during sampling; for this reason, their GWS are generally not available. For the purpose of this work, the precursor standards for 10 targets consisting of VFA and PnI compounds (VFA, $n=6$; phenol, $n=2$; and indole, $n=2$) were procured as liquids (Sigma-Aldrich, USA: purities of 98-99.7%) and were used as individual PS. By diluting each in 100% methanol (J. T. Baker, USA), liquid working standards (LWS) were prepared to cover a concentration range of $1\text{-}130\text{ ng }\mu\text{L}^{-1}$. This was followed by liquid calibration analysis in which $1\text{ }\mu\text{L}$ of each LWS was spiked into a 3-bed sorbent tube (ST) using a $10\text{ }\mu\text{L}$ syringe (SGE Analytical Science, Australia), while supplying pure (99.999%) N_2 gas to the ST at 100 mL min^{-1} for 3 min (Kim and Kim, 2013). Each ST was then placed in the thermal desorption unit (TD), where

the loaded standards or adsorbed odors were thermally desorbed at 320°C for a period of 5 min. The desorbed compounds (GWS) were then pre-concentrated on a cold trap (a combination of Carbopack C and B) at 5°C and subjected to thermal desorption at 330°C for 5 min (Fig. 1b). All VFAs and PnI were separated on a CP-Wax column (film thickness: $0.25\text{ }\mu\text{m}$, diameter: 0.25 mm , length: 60 m ; Agilent, USA) for gas chromatography (GC)-based detection during calibration and adsorption (Supporting Information S1(C)). For the subsequent adsorption test, GWS were also generated manually in the laboratory (by vaporizing the corresponding LWS) and collected in a 10 L polyester aluminum (PEA) bag prior to use (Fig. 1c).

For trimethylamine (TMA), a 100 ppb GWS was prepared by diluting the PS with N_2 in a 1 L PEA bag, after

which the outlet of the PEA bag was connected to the inlet of the sorbent tube containing 250 mg of the adsorbent, held in place with the aid of glass wool support. The other end was connected to the inlet of the ST (Carbopack C, B, and X) (Fig. 1d). In turn, the outlet of the ST was connected to a mini pump, which was set at 100 mL min^{-1} for a period of 2.5 min so as to achieve suction of 250 mL of the GWS.

2.3 Standard Calibration for the Adsorption Experiments

To perform calibration of the odors and subsequent sorption experiments, two different experimental setups were used depending on the optimum sampling methods for different target compounds. In the case of RSCs and ammonia, standard gases passing through the impinger (capacity: 145 mL, length: 19 cm, and diameter: 3 cm) were collected into PEA bags. These bags were then analyzed to derive standard curves to quantify concentration levels of target gases between prior to and after their removal by zeolite. Alternatively, the standard gases for all other targets were collected and quantified using the sorbent tube with the aid of a vacuum pump sampling method. As such, all targets were collected and analyzed by either the bag sampling method or the sorbent tube method. Using the instrumental procedure developed for each respective target, calibration curves were drawn for each set of pollutants before the actual adsorption test by zeolite. The blank samples for each sampling method were also collected and measured by supplying ultrapure nitrogen (99.999%) into the impinge system (at a flow rate of 100 mL min^{-1} for 10 min).

2.4 Analysis of Odor Removal

For the quantitation of RSCs and NCs, samples collected before and after GWS loading were analyzed using a thermal desorption (TD) system (Table S1(A)). In the TD system, gas samples in PEA bags were pre-concentrated on a cryofocusing (cold) trap (combination of Carbopack B and silica gel) at -15°C and then thermally desorbed at 275°C (5 min keep time). These four sulfur compounds were then separated on a HP-1 column and finally detected by sulfur chemiluminescence (SCD) at 250°C . NH_3 was quantified using an NH_3 sensor (supporting document S1(B)). All adsorption tests were carried out at ambient temperature and pressure.

The adsorption experiment for VFA and PnI was performed by connecting the inlet of the 10 L PEA bag filled with GWS to the inlet of the impinger system. The outlet of the impinger system was connected to the inlet of the ST, and the outlet of the sorbent tube was connected to the mini pump (MP- Σ 30, SIBATA,

Japan). With the aid of the pump, GWS were drawn through the adsorbent bed at a flow rate of 100 mL min^{-1} for 10 min for each removal experiment (Fig. 1c). As shown in Table 2, the sorptive removal was investigated by consecutively loading two odor standard samples (GWS) with the aid of multiple experimental setups, as shown in Fig. 1. The impinger system was first fed ultrapure N_2 (99.999%) as a blank test (B) at a flow rate of 100 mL min^{-1} for 10 min.

Two consecutive adsorption tests (experimental codes L1 and L2) were carried out to evaluate the removal of each odor against 25 g of the synthetic A4 zeolite. For bag sampling, the procedure was repeated to collect the compounds eluted from the impinger outlet into a 1 L PEA bag (L1). The second eluent (L2) was collected into another 1 L PEA bag as described in Table 2 (i.e., L2 sampling was performed immediately after completion of L1; for each experiment, 1 L of GWS was forced through 25 g of the zeolite). In addition, collection of samples was performed using an ST sampler in the case of VFAs and NCs.

After the replicate analyses, the sorptive removal (% SR) of each target by the adsorbent was estimated using equation 1:

$$\%SR = \frac{S - (L1 \text{ or } L2)}{S} \times 100 \quad (1)$$

where S indicates the inlet concentration of GWS, while L1 and/or L2 are the outlet concentrations of malodor exiting the zeolite bed (Table 2). The breakthrough of each pollutant in a mixture was calculated based on ratio of adsorbed mass to loaded mass over the two consecutive runs (L1 and L2).

To explain the results with respect to odor concentration, the odor intensity (OI, measured in odor units $[\text{OU}] \text{ m}^{-3}$) of all samples (GWS, L1, and L2) was calculated before and after treatment. Note that, according to Stevens (1960), psychophysical phenomena such as odor strength follow a power law. Apparent odor strength is believed to increase as a power function of the stimulus (odor). Hence, Steven's law can be expressed as

$$\text{OI} = kC^n \quad (2)$$

where C = odor concentration in mg m^{-3} , k = stimulus-dependent constant (Dravnieks *et al.*, 1986), and n = characteristic constant of each odor. To extrapolate the n value, logarithmic transformation of the equation was used as follows:

$$\log \text{OI} = n \log C + \log k \quad (3)$$

The relationship between perceived psychological intensity and odor concentration was later modeled by the Weber-Fechner law (modified from the Steven's law) as

Table 2(a). Information on sample codes used for determination of removal efficiency of zeolite in this study.

Order	Sample code	Description	Weight ^b (g)
(A) Passage of gas samples without zeolite			
1	B	Blank impinger	—
2	S	Passing GWS ^c without zeolite	—
(B) Passage of gas samples with zeolite			
3	L1	First loading of GWS on zeolite	25.0
4	L2	Second loading of GWS on zeolite	25.0

^aThe second sample was collected immediately after completion of the first sampling

^bThe amount of zeolite used for the removal test was 25 g, with the exception of TMA (0.25 g)

^cGWS, Gaseous working standard

Table 2(b). Information on input and output gas sample samples and removal capacity data.

Order	^a Group	Sample ID	Sampling type	Input ^b				Output						
				Gaseous working sample (GWS)		Blank (B)	Standard (S)	Concentration (ppb)		^c C _{out} /C _{in} (%)		^d Mass sorbed per sorbent (µg g ⁻¹)		
				ppb	ng			ppb	ng	L1	L2	L1	L2	L1
1	H ₂ S	16,500	23,080	0.004	18,888	26,324	16.7	47.1	0.08	0.25	0.34	1.052	1.050	2.102
2	CH ₃ SH	16,560	32,581	0.07	21,585	42,466	12.7	17.1	0.06	0.08	0.14	1.698	1.697	3.395
3	DMS	4,040	10,260	0.03	3,780	9,601	2.76	0.94	0.07	0.02	0.10	0.384	0.384	0.768
4	DMS	4,100	15,794	0.02	3,537	13,626	16.9	5.28	0.48	0.15	0.63	0.542	0.544	1.087
5	NH ₃	29.9	20.8	1.00	26.5	18.5	1.00	1.00	3.77	3.77	7.55	0.001	0.001	0.001
6	TMA	100	242	0.003	116	280	0.89	0.55	0.76	0.47	1.24	1.112	1.116	2.228
7	PPA	100	302	0.22	73.8	224	0.42	0.22	0.57	0.30	0.86	0.009	0.009	0.018
8	BTA	108	390	0.22	88.6	319	0.65	0.26	0.73	0.30	1.02	0.013	0.013	0.025
9	IVA	113	473	0.21	94.0	393	1.24	0.43	1.32	0.46	1.77	0.016	0.016	0.031
10	VFA	114	478	0.29	87.6	366	0.70	0.33	0.80	0.38	1.17	0.015	0.015	0.029
11	ACA	482	2,566	0.94	374	1,993	4.78	2.37	1.28	0.63	1.91	0.079	0.079	0.158
12	IBA	109	394	0.36	91.7	331	0.77	0.36	0.84	0.39	1.23	0.013	0.013	0.026
13	PhAl	106	407	0.24	66.6	256	2.90	1.00	4.36	1.50	5.86	0.010	0.010	0.020
14	p-C	443	1,960	0.30	320	1,416	38.2	16.9	11.9	5.28	17.2	0.050	0.054	0.104
15	ID	213	1,020	0.21	96.7	463	9.22	4.7	9.53	4.86	14.4	0.017	0.018	0.034
16	SK	117	625	0.12	47.3	254	3.93	2.15	8.30	4.55	12.8	0.009	0.010	0.019

^aGrouping is based on the chemical properties/compositions of the compounds

^bFlow rate: 100 mL min⁻¹

^c%C_{out}/C_{in}: The percentage concentration ratio (%BT) of exciting gas (L1 or L2) to input gas (S)

^dAdsorption capacity

^eTube: Three-bed sorbent tube containing Carbo-pack C + Carbo-pack B + Carbo-pack x (50 mg each)

Table 2(c). Extrapolated data on odor intensity (OI) and odor activity value (OAV) of input and output odor concentrations.

Order	Group	Odor ID	^a OI Equation	Concentration (ppb)			OI ^b (OU m ⁻³)			^c Odor Threshold (ppb)	^d OAV		
				S	L1	L2	S	L1	L2		S	L1	L2
1	RSCs	H ₂ S	0.950 logC + 4.14	18,888	16.7	47.1	8.20	5.30	5.73	0.41	46068	40.7	114
2		CH ₃ SH	1.250 logC + 5.99	21,585	12.7	17.1	11.4	7.37	7.53	0.07	308350	181	245
3		DMS	0.784 logC + 4.06	3,780	2.76	0.94	6.87	4.41	4.04	3.00	1260	0.92	0.31
4		DMDS	0.985 logC + 4.51	3,537	16.9	5.28	8.01	5.72	5.72	2.20	1607	7.68	2.40
5	NCs	NH ₃	1.670 logC + 2.38	26.5	1.00	1.00	4.76	2.38	2.38	1,500	0.02	0.0007	0.0007
6		TMA	0.901 logC + 4.56	116	0.89	0.55	6.42	4.51	4.51	0.032	3622	27.7	17.2
7	VFAs	PPA	1.380 logC + 4.60	73.8	0.42	0.22	7.18	4.08	3.68	5.70	12.9	0.074	0.04
8		BTA	1.290 logC + 6.37	88.6	0.65	0.26	8.88	6.13	5.61	0.19	466	3.41	1.36
9		IVA	1.090 logC + 5.65	94.0	1.24	0.43	7.80	5.75	5.25	0.078	1205	15.9	5.51
10		VLA	1.580 logC + 7.29	87.6	0.70	0.33	10.4	7.04	6.54	0.037	2368	18.8	8.99
11		ACA	—	374	4.78	2.37	—	—	—	6.00	62.4	0.79	0.39
12		IBA	1.430 logC + 5.08	91.7	0.77	0.36	7.89	4.92	4.44	1.50	61.2	0.51	0.24
13	Phenol	PhAl	1.420 logC + 3.74	66.6	2.90	1.00	6.33	4.40	3.74	5.60	11.8	0.52	0.18
14		p-C	0.604 logC + 3.64	320	38.2	16.9	5.15	4.60	4.38	0.054	5930	707	313
15	Indole	ID	0.631 logC + 1.17	96.7	9.22	4.70	2.42	1.78	1.59	0.30	322	30.7	15.7
16		SK	0.631 logC + 1.17	47.3	3.93	2.15	2.23	1.54	1.38	0.0056	8454	702	384

^aOdor intensity as defined by the Weber-Fechner law ($I = a \log C + b$), where C is the odor concentration

^bUnits of OI = Odor unit/cubic meters

^cStandard threshold limit determine by detecting the difference from odor-free background

^dOdor activity value: i.e., Odor threshold (ppb)/Concentration (ppb)

$$OI = a \log(C) + b \quad (4)$$

where a is the Weber-Fechner coefficient, and b is the intercept constant (Jiang *et al.*, 2006). In this study, this formula was used to assess OI values of S, L1, and L2. Through the calculation of OI, the extent of reduction in odor intensity due to the zeolite was assessed. Also, by comparing the threshold values of the odors to the final odor concentrations (L2), we derived a dimensionless expression of odor strength termed the odor activity value (OAV), which was obtained as a ratio of odor concentration to its threshold value. Regardless of the magnitude of reduction in odor concentration, if $OAV > 1$, the adsorption was deemed “not environmentally relevant,” and vice versa. With respect to each target, the lower was the value of OAV, the more efficient was the adsorption performance of the A4 zeolite in decreasing the odor concentration.

3. RESULTS AND DISCUSSION

3.1 Sorptive Removal of Odors by Zeolite

In an attempt to estimate the removal capacity of synthetic zeolite for diverse odors, the GWS of these targets were pulled through a sorbent bed of zeolite in a continuous flow. The stream of gases exiting the zeolite bed was collected sequentially during each of

two consecutive runs so as to assess the replicate pattern of their removal.

First, the observed differences between estimated and actual concentrations of target odors can be accounted for by the high sorptive loss that took place upon gas/vapor contact with the impinger walls (Kim and Kim, 2012). The concentrations of odors measured during standard calibration (S) and after the two consecutive removal runs (L1 and L2) are plotted in Fig. 2(a). The values are presented in logarithmic form because of the large range between the inlet and outlet concentrations. The results shown here indicate that the synthetic zeolite acted as an effective adsorbent against all selected targets, as the concentrations in L1 are considerably reduced relative to results acquired without passing through the sorbent bed. Upon the second sampling of the exiting gas (L2), only two members of the RSC group (H₂S and CH₃SH) anomalously evinced a sudden increase in concentration relative to the first sampling (L1). It is worth bearing in mind that this group represents the lowest molecular weights with comparatively large GWS volume used compared to other groups, which could have contributed to this anomaly. Overall, VFAs showed the lowest residual concentrations. In contrast, RSCs (H₂S and CH₃SH specifically) showed the highest removal, with the most significant reduction for DMSO (from 3,780 to 0.94 ppb).

In the estimation of % SR (equation 1), RSCs were

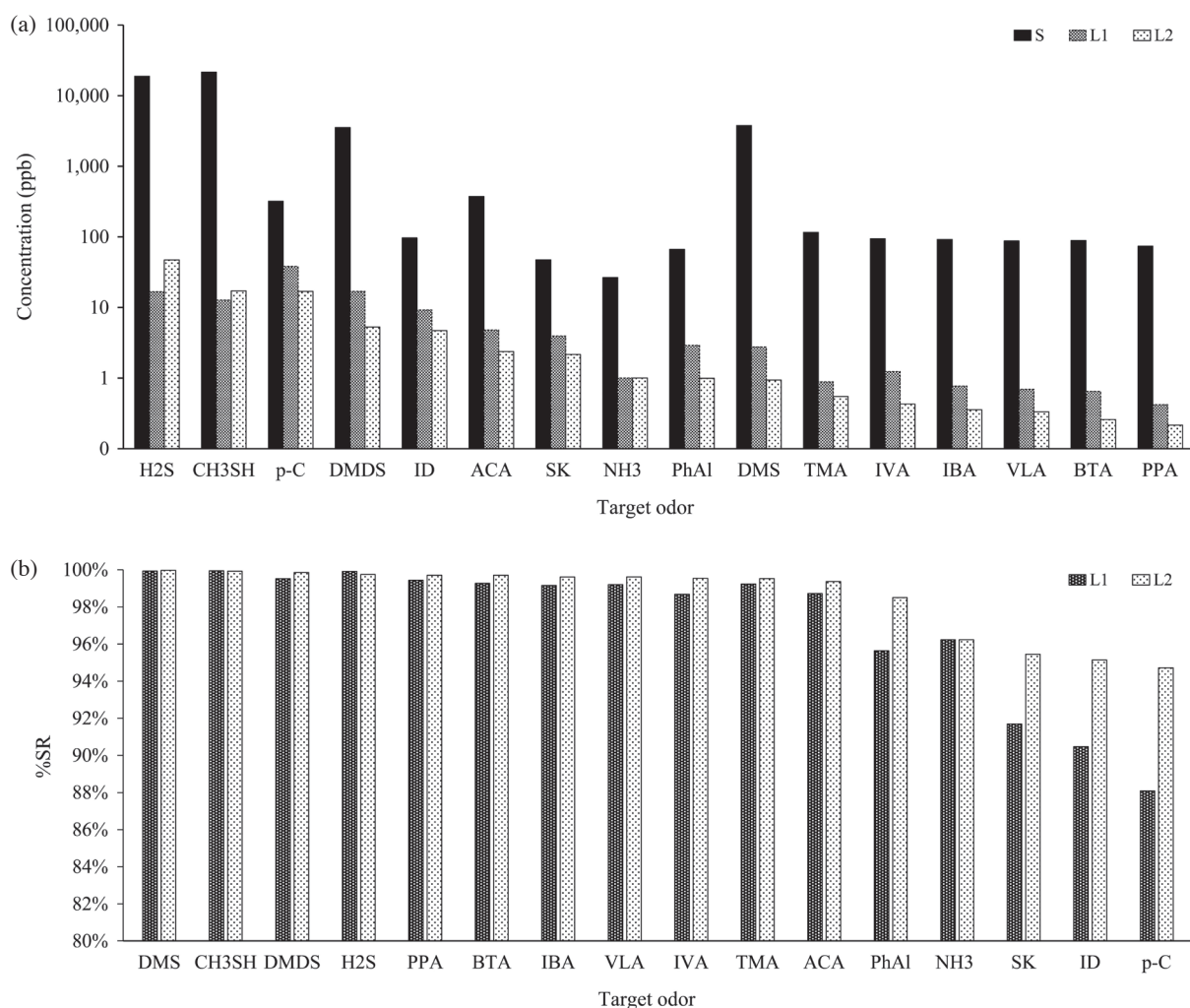


Fig. 2. Comparison of (a) estimated concentration of odors prior to and after adsorption by zeolite and (b) % sorptive removal (SR) of target odors.

most efficiently removed, recording a mean % SR of 99.9% over the successive samplings (Fig. 2(b)). The second highest removal capacities were noted for VFAs and TMA. With regard to the target malodors in these groups (trimethylamine, propionic acid, n-butyric acid, i-valeric acid, n-valeric acid, amy acetate, and i-butyric acid), the adsorbent showed a small but noticeable increase in % SR (range of 99.2-99.7). However, it exhibited a much more obvious increase in % SR (with a range of 88.1-98.5 between L1 and L2) for all four PnI compounds. This pattern was seen most clearly for the indoles among all target gases. Despite recording the lowest value among some important species (RSCs, NCs, and VFAs), the % SR for NH₃ was uniform between L1 and L2. Our observations thus indicate that the adsorbent efficiently removed most of the malodorous compounds loaded under our experimental settings,

with most effective sorptive removal of the RSCs. The removal efficiency trend of zeolite was in the descending order of RSCs > TMA > VFAs > NH₃ > PnI.

3.2 Estimation of Sorptive Breakthrough

The breakthrough (BT) values for the odors were derived as the ratio of adsorbed mass to loaded mass over the two consecutive runs for adsorption (i.e., total adsorbed mass/total loaded mass). The estimated BT values (%) for each odor are listed in Table 2(b) and depicted in Fig. 3 for comparison. The BT behavior of different odors was then assessed with reference to 5% BT (or C_{out}/C_{in}). The results were evaluated based on the concept that the lower was the % BT value, the higher was the adsorption capacity. When considered by group, the RSCs demonstrated the lowest mean BT % of 0.1% (H₂S = 0.34, CH₃SH = 0.14, DMS =

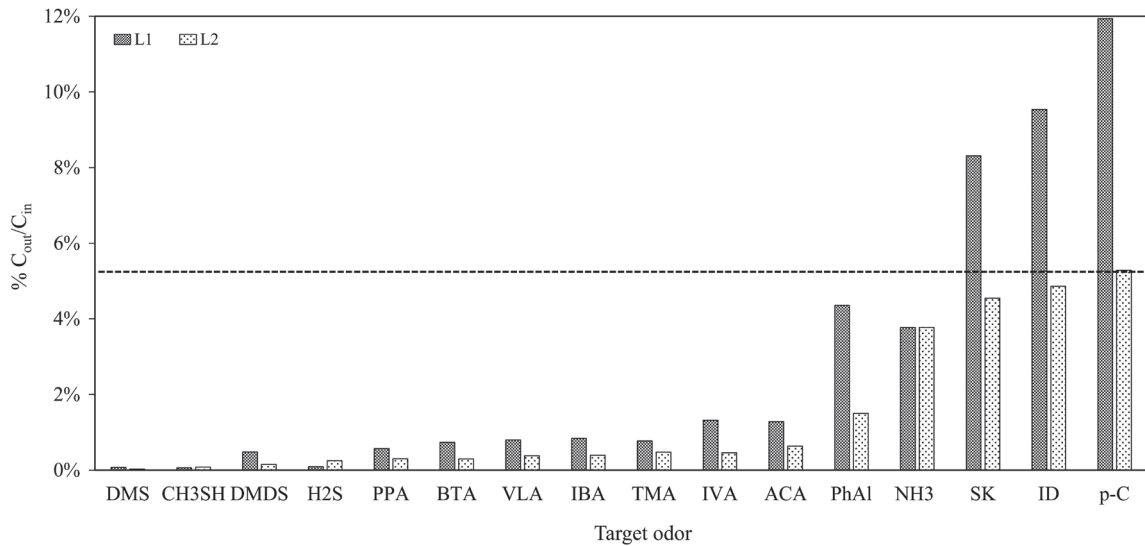


Fig. 3. Comparison of C_{out}/C_{in} values of the target odors.

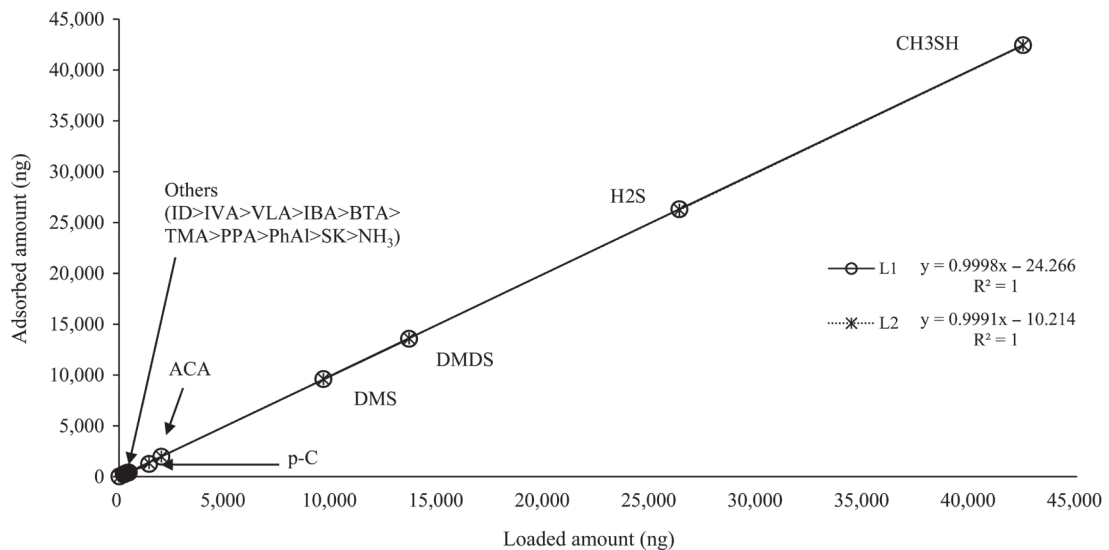


Fig. 4. Relationship between loaded mass and sorbed mass of odors on zeolite.

0.10, and DMDS=0.63%). The VFAs (6 compounds) showed a mean BT % of 1.32%, followed by phenol at 5.86%. On the other hand, NH₃ was found to adsorb at relatively high quantities with a constant rate of 3.77%. The maximum BT was noted for SK and p-C (excluding phenol) at 12.8% and 17.2%, respectively. These results indicate maximum sorptive removal from RSCs and VFAs (Fig. 3).

To investigate differences or commonalities in the trends of sorptive removal among the odors (and between the two analyses), statistical assessment was performed by generating a combined BT plot of loaded

against adsorbed amounts for individual L1 and L2 runs. Here, a plot of the mass loaded (S) against mass adsorbed of the odors (i.e., S - [L1 or L2]) after each sampling (L1 and L2) is shown in Fig. 4. Despite the wide range of initially supplied odor concentrations, good consistency was seen in the adsorbent response to the 16 compounds, with excellent linearity between loaded and adsorbed masses ($R^2 \approx 1$). This relationship was generally comparable to the relative order of sorptive removal with moderate alterations; for example, the maximum amount of sorption was found for CH₃SH, whereas the lowest BT was found for DMS (Table 2).

3.3 Adsorption Capacity of Zeolite against Target Odors

Adsorption capacity is an important factor when assessing the performance of a sorbent toward the sorbate. Hence, in this study, the sorptive removal patterns were analyzed by comparing the relationship between the total adsorption capacity of zeolite ($\mu\text{g g}^{-1}$) and cumulative BT value (a function of the sorbent's affinity for each target malodor) (Fig. S1, Supplementary Material [SM]). The highest and lowest affinities of zeolite were seen for RSCs (range $0.77\text{--}3.4 \mu\text{g g}^{-1}$) and PnI ($0.06\text{--}0.104 \mu\text{g g}^{-1}$), respectively. On the other hand, the sorbent showed the highest and lowest %BT values toward PnIs and RSC, respectively. It is also interesting to note that the BT values of TMA and VFAs were in a moderate range of $0.86\text{--}1.91\%$, whereas NH_3 recorded a fairly high BT of 7.55% . This observation shows the intrinsic preference of the zeolite to adsorb TMA and VFA relative to NH_3 . Overall, the results of this comparative study indicate that zeolite has the lowest adsorption capacity against NH_3 , whereas it shows the highest sorption toward RSCs, especially DMS (Table 2b). Our data also provide adequate evidence of the non-existence of a linear relationship between the sorbent's adsorption capacity and retention efficiency against each odor. Such findings will help overcome the shortcomings of the sorbent bed in response to diverse odor species for removal.

3.4 Estimated Odor Intensity and Odor Activity Value

The concepts of OI and OAV can be used meaningfully to assess the strength of odor emissions from various sources. As our study was performed to test sorptive removal of different odors, the extent of odor reduction induced by the zeolite bed was also assessed by differences in odor unit values before and after adsorption.

Using the logarithmic expression of the Weber-Fechner's law (equation 4), the OI values for S, L1, and L2 were derived. A plot of OI (in decreasing order of magnitude with respect to L2) is depicted in Fig. S2(a). It is apparent that the extent of adsorption on the zeolite was not directly reflected by the reduction of OI. Adsorption by zeolite showed the highest reduction of OI (from S to L2: a mean of approximately 4 OI units) for several odors such as methanethiol (11.4 to 7.53), valeric acid (10.4 to 6.54), i-butyric acid (7.88 to 4.44), and propionic acid (7.18 to 3.68). In contrast, the smallest reductions (change in OI unit of approximately 0.7) were recorded for indole (2.42 to 1.59), skatole (2.23 to 1.38), and p-cresol (5.15 to 4.38).

As comparison is made between two contrasting conditions based on OI units, the results can also be

assessed in terms of the OAV concept. This is a dimensionless value obtained as the ratio of exiting concentration to the odor's threshold concentration, as presented in Table 2(c). The OAV of the initial standard concentrations (S) used for the adsorption test recorded the highest value for methanethiol ($\sim 300,000$), followed by H_2S ($\sim 46,000$). In contrast, the lowest value was seen for NH_3 ($\sim 2 \times 10^{-2}$), with the remainder of the compounds falling within the range of ~ 12 (phenol and propionic acid) to $60,000$ (p-cresol) (Table 2(c)). Upon removal by zeolite, all OAVs were significantly reduced by 1000-fold. However, at the high extreme, skatole (~ 400), p-cresol (~ 320), methanethiol (~ 245), and H_2S (~ 115) showed OAVs of environmental concern. A comparative plot is also presented in Fig. S2(b) based on the decreasing values of the final (L2) OAVs of the odors. This plot was graphed on a logarithmic scale because of the large difference between the actual values of the fed (S) and exiting odor concentrations (L1 and L2). Odors such as dimethyl sulfide, i-butyric acid, phenol, propionic acid, and ammonia clearly showed no significant OAVs of environmental concern, especially after adsorption. Overall, the zeolite was able to significantly reduce odor in terms of OAV to a value less than 1 (i.e., Log_{10}) in an ascending order of i-valeric acid, amy acetate, dimethyl disulfide, and n-butyric acid.

4. CONCLUSION

This study investigated the sorption patterns of 16 malodorous compounds. Synthetic A4-type zeolite was used for the simultaneous removal of these gaseous compounds in a laboratory-scale test, and removal efficiency and breakthrough were estimated for two consecutive samples obtained after passing the feed gas over the zeolite placed in an impinger (or a sorbent tube). Based on our observations, the following conclusions can be drawn:

- In general, the sorbent was effective for removing all of the test target compounds, albeit with different affinity values and kinetics;
- Perfect agreement ($R^2 = 1$) was observed in the breakthrough assessments among the samples (S) and between the samplings (L1 or L2) at a 1% feed volume (100 mL);
- The observed % SR trend was $\text{RSCs} > \text{TMA} > \text{VFs} > \text{NH}_3 > \text{PnI}$ over the analyzed range;
- A correlation between % BT and adsorption amount showed that the adsorption preference of zeolite was highest toward RSCs, moderate for ACA, and lowest for NH_3 ;

- With the proper calibration based on the above inferences, a pristine adsorbent can be engineered for individual or collective removal of the selected offensive odors.

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Abbreviations ACA: Acetic acid, AFO: Animal feeding operation, B: Blank test, BT: Breakthrough, BTA: n-Butyric acid, CH₃SH: Methanethiol, C_{in}: Concentration in, C_{out}: Concentration out, DMDS: Dimethyl disulfide, DMS: Dimethyl sulfide, GC: Gas chromatography, GWS: Gaseous working standards, H₂S: Hydrogen sulfide, IBA: i-Butyric acid, IN: Indole, IVA: i-Valeric acid, L1: First effluent, L2: Second effluent, LWS: Liquid working standards, MOF: Metal-organic framework, NC: Nitrogenous compound, NH₃: Ammonia, NRC: National Research Council, OAV: Odor activity value, OI: Odor intensity, p-C: p-Cresol, PEA: Polyester aluminum, PhAl: Phenol, PnI: Phenols/indoles, PPA: Propionic acid, ppb: Parts per billion, ppm: Parts per million, PS: Primary standard, R²: Regression coefficient, RSC: Reduced sulfur compound, S: Initial concentration of gaseous working standard, SCD: Sulfur chemiluminescence detector, SK: Skatole, SR: Sorptive removal, ST: 3-Bed sorption tube, TD: Thermal desorption, TMA: Trimethyl amine, VFA: Volatile fatty acids, VLA: n-Valeric acid, VOC: Volatile organic compound.

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Table S1. Instrumental setup and operational conditions for the analysis of target compounds.

(A) Operational conditions of AS/TD/SCD			
GC (7890A, Agilent Technologies, USA)			
SCD (355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA)			
Column: HP-1 (length: 60 m, diameter: 0.32 mm, film thickness: 5 μm)			
1) Oven settings		2) Detector settings	
Initial temp. (hold time):	80°C (5 min)	Plasma temp:	800°C
Heating rate:	20°C min ⁻¹	Detector temp.:	250°C
Max. temp. (hold time):	200°C (5 min)	H ₂ flow rate:	40 mL min ⁻¹
Total time:	16 min	Air flow rate:	60 mL min ⁻¹
Gas type:	N ₂ (>99.999%)		
Air server/Thermal desorber (UNITY I, Markes International, Ltd., UK)			
Cold trap sorbent: Carboxpack B + Silica gel (volume ratio = 1.5 : 2.5)			
Split ratio:	7 : 1	Adsorption temp.:	-15°C
Split flow rate:	10 mL min ⁻¹	Desorption temp.:	275°C
Trap hold time:	5 min	Flow path temp.:	80°C
(B) Operational conditions of NH ₃ sensor system			
Ibrid mx6 (USA)			
1) Sampling (direct measurement)		Interval time	
Flow rate:	333 mL min ⁻¹		5 min
(C) Operational conditions of ST/TD/GC/MS system			
GC (SHIMADZU GC-2010, JAPAN)/MS (SHIMADZU GCMS-QP2010, JAPAN)			
Column: CP Wax (length: 30 m, diameter: 0.25 mm, film thickness: 2.5 μm)			
1) Oven settings		2) Detector settings	
Operation temp.:	40°C (5 min)	Ionization mode:	EI (70 eV)
Heating rate:	24°C min ⁻¹	Ion source temp.:	230°C
Max. oven temp. (hold time):	220°C (18 min)	Interface temp.:	230°C
Total time:	32 min	TIC scan range:	35-600 m z ⁻¹
		Scan speed:	1250 sec ⁻¹
3) Carrier gas settings		Initial gas flow:	
Gas type:	He (>99.999%)		1.85
Constant gas pressure:	25 psi		
Thermal desorber (UNITY II, Markes International, Ltd., UK)			
Cold trap sorbent: Quartz wool + Carboxpack C + Carboxpack B (volume ratio = 1 : 1 : 1)			
Split ratio:	0.185	Adsorption temp.:	5°C
Split flow rate:	10 mL min ⁻¹	Desorption temp.:	330°C
Trap hold time:	5 min	Flow path temp.:	180°C
Sampling (sorbent) tube			
Absorbent: Carboxpack C + Carboxpack B + Carboxpack \times (70, 50, and 50 mg)			
Desorption time:	7 min	Desorption temp.:	320°C
Desorption flow rate:	100 mL min ⁻¹		

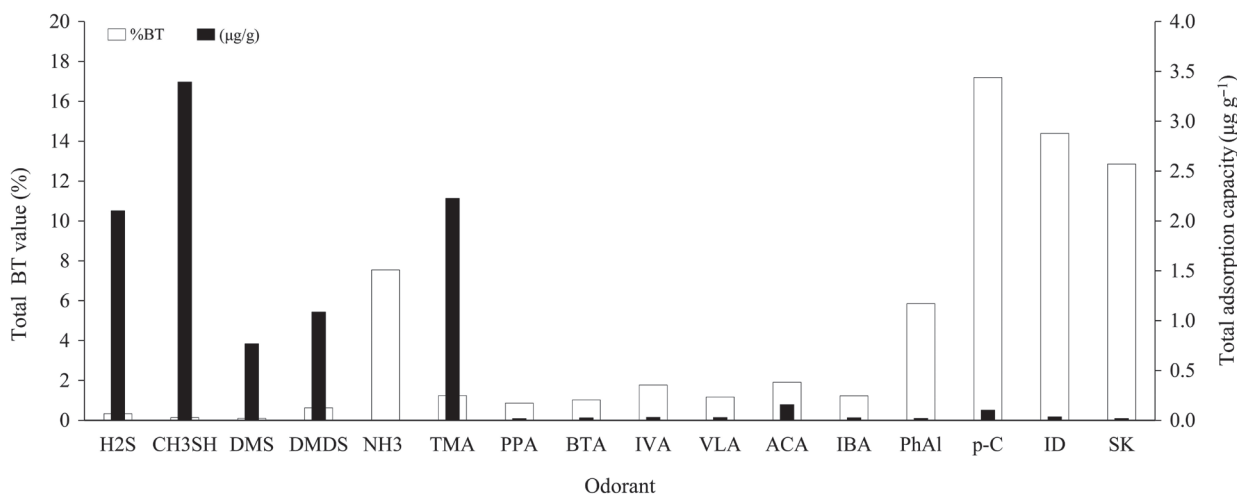


Fig. S1. Relationship between cumulative breakthrough (BT) and total adsorption capacity.

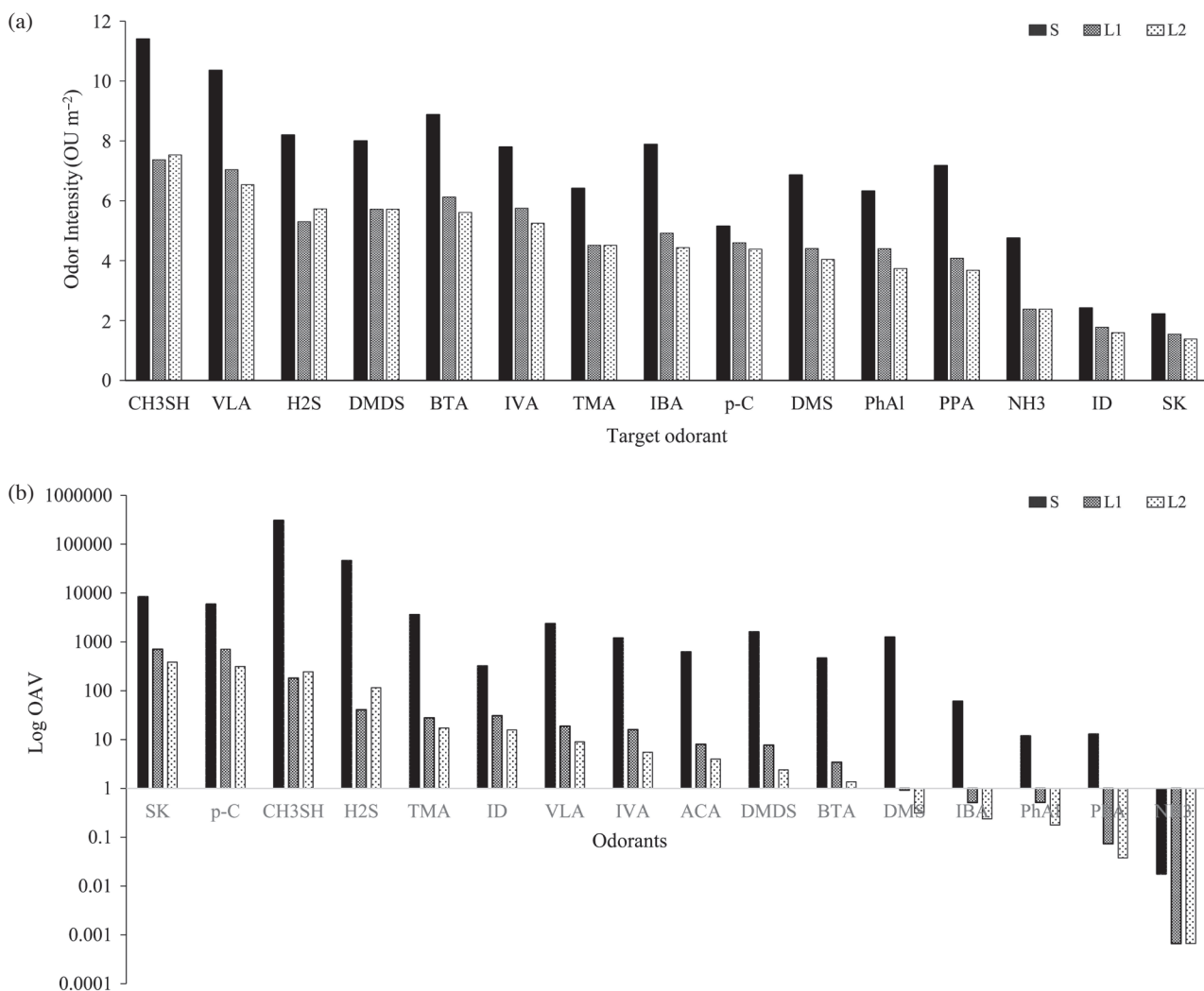


Fig. S2. Comparison of (a) odor intensity and (b) odor activity value (OAV) of the investigated odorants.