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

Adedeji A. Adelodun, Kowsalya Vellingiri1), Byong-Hun Jeon2), Jong-Min Oh3), Sandeep Kumar4) and Ki-Hyun Kim1),*

Department of Marine Science and Technology, School of Earth and Mineral Sciences, The Federal University of Technology, P.M.B. 704, Akure, Nigeria
1)Department of Civil and Environmental Engineering, Hanyang University, 222, Wangsimni-Ro, Seoul 04763, Republic of Korea
2)Department of Natural Resources and Environmental Engineering, Hanyang University, Seoul 04763, Republic of Korea
3)Department of Environmental Application Science, Kyung Hee University, Suwon, Republic of Korea
4)Department of Bio and Nano Technology, Guru Jambheshwar University of Science and Technology, Hisar, Haryana 125001, India
*Corresponding author. Tel: +82-2-2220-2325, E-mail: kkim61@hanyang.ac.kr

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: H\(_2\)S, 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 (H\(_2\)S and NH\(_3\)) 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 ultratrace) 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 odoriferous 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., 2012), 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 m² 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 N₂ flow estimated the specific surface area as 14.5 m² 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 NH₃ were supplied in cylinders by RIGAS, Korea. Using 99.999% N₂ as a diluent, 20 ppm standards of the RSCs were prepared. This mixing procedure was replicated to produce a specific concentration of NH₃ through dilution with N₂ 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 (CH₃SH).

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 [NH₃] to 16,500 [CH₃SH]). 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-
| 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 |
|-------|----------------|------------------------|-----------------------------|---------|-----------------|-----------------------------------|----------------------|-----------------|--------------------------------|
| 1     | RSCs           | Hydrogen sulfide       | H\(_2\)S                     | 7783-06-04 | H\(_2\)S         | 34.1                              | 3.081                | 0.9986         | 0.03 0.81                              |
| 2     | Methanethiol   | CH\(_3\)SH             | 74-93-1                     | C\(_3\)H\(_6\)S         | 48.1                          | 3.170                | 0.9986         | 0.07 0.39                              |
| 3     | Dimethyl sulfide | DMS                   | 75-18-3                     | C\(_2\)H\(_6\)S\(_2\)   | 62.1                          | 2.885                | 0.9992         | 0.03 1.33                              |
| 4     | Dimethyl disulfide | DMDS                 | 624-92-0                     | C\(_2\)H\(_6\)S\(_2\)   | 94.2                          | 4.089                | 0.9973         | 0.03 0.81                              |
| 5     | NCs            | Ammonia                | NH\(_3\)                     | 7664-41-7                  | NH\(_3\)          | 17.0                                | –                    | – – –                                   |
| 6     | Trimethylamine | TMA                    | 75-50-3                     | C\(_3\)H\(_6\)N         | 59.1                          | 511.361              | 0.9932         | 0.00 4.92                              |
| 7     | VFAs           | 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\(_3\)H\(_6\)O\(_2\)   | 88.1                          | 17.571               | 0.9995         | 0.76 3.07                               |
| 9     | i-Valeric acid | IVA                   | 503-74-2                     | C\(_3\)H\(_6\)O\(_2\)   | 102                          | 18.520               | 0.9986         | 0.86 3.66                               |
| 10    | n-Valeric acid | VLA                   | 109-52-4                     | C\(_3\)H\(_6\)O\(_2\)   | 102                          | 19.946               | 0.9983         | 1.19 4.06                               |
| 11    | Acetic acid    | ACA                   | 64-19-7                     | C\(_3\)H\(_6\)O\(_2\)   | 60.05                         | 6.115                | 0.9933         | 2.25 1.77                               |
| 12    | i-Butyric acid | IBA                   | 79-31-2                     | C\(_3\)H\(_6\)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                               |
| 14    | p-Cresol       | p-C                   | 106-44-5                     | C\(_6\)H\(_6\)O       | 108                          | 11.493               | 0.9901         | 1.30 4.17                               |
| 15    | Indole         | Indole                | ID                          | 120-72-9                    | C\(_6\)H\(_6\)N       | 117                              | 27.841               | 0.9987         | 0.98 0.23                               |
| 16    | Skatole        | Skatole               | SK                          | 83-34-1                     | C\(_6\)H\(_6\)N       | 131                              | 35.571               | 0.9991         | 0.61 2.36                               |

\(^a\)Grouping based on the chemical properties/compositions of the compounds  
\(^b\)Retention factor  
\(^c\)Method 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).  
\(^d\)Relative standard error (RSE): Triplicate analyses of the calibration point.  
\(^e\)AS/TD/GC/SCD = Air server (UNITY I, 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 = Quadruple mass spectrometer.  
\(^f\)Sensor: NH\(_3\) sensor system (Ibrid mx6, USA)  
\(^g\)ST/TD/GC/Q-MS = ST = Sorbent tube, TD = Thermal desorption, GC = Gas chromatography, Q-MS = Quadruple mass spectrometer.
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 1-130 ng \( \mu L^{-1} \). This was followed by liquid calibration analysis in which 1 \( \mu L \) of each LWS was spiked into a 3-bed sorbent tube (ST) using a 10 \( \mu L \) 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 \( \mu m \), 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 impingine 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 PhI 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-\(\Sigma\) 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:

\[
\%SR = \frac{S - (L1 or L2)}{S} \times 100 \tag{1}
\]

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 [OU] 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

\[
OI = kC^n \tag{2}
\]

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:

\[
\log OI = n \log C + \log k \tag{3}
\]

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 (g) |
|-------|-------------|------------------------------|------------|
| (A)   |             |                              |            |
| 1     | B           | Blank impinger               |            |
| 2     | S           | Passing GWS \(^c\) without zeolite |            |
| (B)   |             |                              |            |
| 3     | L1          | First loading of GWS on zeolite | 25.0       |
| 4     | L2          | Second loading of GWS on zeolite | 25.0       |

\(^c\)The second sample was collected immediately after completion of the first sampling. 
\(^d\)The amount of zeolite used for the removal test was 25 g, with the exception of TMA (0.25 g).

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

| Order | Group | Sample code | Sampling type | Gaseous working sample (GWS) | Blank (B) | Standard (S) | Concentration (ppb) | Output | Mass sorbed per sorbent (μg g\(^{-1}\)) |
|-------|-------|-------------|---------------|-------------------------------|-----------|--------------|---------------------|--------|------------------------------------------|
|       |       |             |               |                               | ppb       | ng           | L1                  | L2     | L1 + L2                                  |
|       |       |             |               |                               | ng        |              | L1                  | L2     | L1 + L2                                  |
|       |       |             |               |                               | L1        | L2           | L1                  | L2     | L1 + L2                                  |
|       |       |             |               |                               | L1        | L2           | L1 + L2             | L1     | L2                                       |
| 1     |       | H\(_2\)S    | Blank impinger | 16,500                         | 23,080    | 0.004        | 18,888              | 26,324 | 16.7                                    |
| 2     | RSCs  | CH\(_3\)SH  | PEA bag       | 16,560                         | 32,581    | 0.07         | 21,585              | 42,466 | 12.7                                    |
| 3     |       | DMDS        | Blank impinger | 4,040                          | 10,260    | 0.03         | 3,780               | 9,601  | 2.76                                    |
| 4     |       | DMDS        | Blank impinger | 4,100                          | 15,794    | 0.02         | 3,537               | 13,626 | 16.9                                    |
| 5     | NCs   | NH\(_3\)    | Blank impinger | 29.9                           | 20.8      | 1.00         | 26.5                | 18.5   | 1.00                                    |
| 6     |       | TMA         | eTube          | 100                            | 242       | 0.003        | 116                 | 280    | 0.89                                    |
| 7     | VFAs  | PPA         | Blank impinger | 100                            | 302       | 0.22         | 73.8                | 224    | 0.42                                    |
| 8     |       | BTA         | Blank impinger | 108                            | 390       | 0.22         | 88.6                | 319    | 0.65                                    |
| 9     |       | IVA         | Blank impinger | 113                            | 473       | 0.21         | 94.0                | 393    | 1.24                                    |
| 10    |       | VLA         | Blank impinger | 114                            | 478       | 0.29         | 87.6                | 366    | 0.70                                    |
| 11    |       | ACA         | Blank impinger | 482                            | 2,566     | 0.94         | 374                 | 1,993  | 4.78                                    |
| 12    |       | IBA         | Blank impinger | 109                            | 394       | 0.36         | 91.7                | 331    | 0.77                                    |
| 13    | Phenol | PhAl        | Blank impinger | 106                            | 407       | 0.24         | 66.6                | 256    | 2.90                                    |
| 14    |       | p-C         | Blank impinger | 443                            | 1,960     | 0.30         | 320                 | 1,416  | 38.2                                    |
| 15    |       | ID          | Blank impinger | 213                            | 1,020     | 0.21         | 96.7                | 463    | 9.22                                    |
| 16    |       | SK          | Blank impinger | 117                            | 625       | 0.12         | 47.3                | 254    | 3.93                                    |

\(^a\)Grouping is based on the chemical properties/compositions of the compounds. 
\(^b\)Flow rate: 100 mL min\(^{-1}\) 
\(^c\)\(\text{C}_{\text{out}}/\text{C}_{\text{in}}\): The percentage concentration ratio (%BT) of exciting gas (L1 or L2) to input gas (S).
\(^d\)Adsorption capacity. 
\(^e\)Tube: Three-bed sorbent tube containing Carbopack C + Carbopack B + Carbopack × (50 mg each)
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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
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 Cout/Cin). 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 =
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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 (R² ≈ 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 (μg 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 0.77-3.4 μg g⁻¹) and PnI (0.06-0.104 μg g⁻¹), respectively. On the other hand, the sorbent showed the highest and lowest % BT values toward PnI and RSC, respectively. It is also interesting to note that the BT values of TMA and VFAs were in a moderate range of 0.86-1.91%, whereas NH₃ recorded a fairly high BT of 7.55%. This observation shows the intrinsic preference of the zeolite to adsorb TMA and VFA relative to NH₃. Overall, the results of this comparative study indicate that zeolite has the lowest adsorption capacity against NH₃, 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 (~300,000), followed by H₂S (~46,000). In contrast, the lowest value was seen for NH₃ (~2×10⁻²), 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 H₂S (~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., Log10) 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 (R² = 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 RSCs > TMA > VFAs > NH₃ > 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 NH₃;
- 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, CH\textsubscript{3}SH: Methanethiol, C\textsubscript{in}: Concentration in, C\textsubscript{out}: Concentration out, DMDS: Dimethyl disulfide, DMS: Dimethyl sulfide, GC: Gas chromatography, GWS: Gaseous working standards, H\textsubscript{2}S: 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, NH\textsubscript{3}: Ammonia, NRC: National Research Council, OA V: Odor activity value, OI: Odor intensity, p-C: p-Cresol, PEA: Propionic acid, ppb: Parts per billion, ppm: Parts per million, PS: Primary standard, R\textsuperscript{2}: 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
- Initial temp. (hold time): 80°C (5 min)
- Heating rate: 20°C min⁻¹
- Max. temp. (hold time): 200°C (5 min)
- Total time: 16 min
- Gas type: N₂ (> 99.999%)

2) Detector settings
- Plasma temp.: 800°C
- Detector temp.: 250°C
- H₂ flow rate: 40 mL min⁻¹
- Air flow rate: 60 mL min⁻¹

Air server/Thermal desorber (UNITY I, Markes International, Ltd., UK)
Cold trap sorbent: Carbopack B + Silica gel (volume ratio = 1.5 : 2.5)

Split ratio: 7 : 1
Split flow rate: 10 mL min⁻¹
Trap hold time: 5 min

(B) Operational conditions of NH₃ sensor system

Ibrid mx6 (USA)
1) Sampling (direct measurement)
- Flow rate: 333 mL min⁻¹
- Interval time: 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
- Operation temp.: 40°C (5 min)
- Heating rate: 24°C min⁻¹
- Max. oven temp. (hold time): 220°C (18 min)
- Total time: 32 min
- Gas type: He (> 99.999%)

2) Detector settings
- Ionization mode: EI (70 eV)
- Ion source temp.: 230°C
- Interface temp.: 230°C
- TIC scan range: 35-600 m z⁻¹
- Scan speed: 1250 sec⁻¹
- Initial gas flow: 1.85

3) Carrier gas settings
- Gas type: He (> 99.999%)
- Constant gas pressure: 25 psi

Thermal desorber (UNITY II, Markes International, Ltd., UK)
Cold trap sorbent: Quartz wool + Carbopack C + Carbopack B (volume ratio = 1 : 1 : 1)

Split ratio: 0.185
Split flow rate: 10 mL min⁻¹
Trap hold time: 5 min

Sampling (sorbent) tube
Absorbent: Carbopack C + Carbopack B + Carbopack × (70, 50, and 50 mg)

Desorption time: 7 min
Desorption flow rate: 100 mL min⁻¹
Desorption temp.: 320°C
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.