

Characteristics of deodorization for malodorants in aqueous solution by sonication

Young-Eok Yoo* and Yasuaki Maeda

**Department of Environmental Education, Daegu University, Gyeongsan 712-714, Korea*
Department of Applied Materials Science, Osaka Prefecture University, Osaka 599-8530, Japan

(Manuscript received 7 August, 2003 ; accepted 16 February, 2004)

A aqueous solution of malodorants (i.e., n-valeraldehyde, n-valeric acid, 2-methylisoborneol, and trimethylamine) was exposed to 200kHz ultrasound with a power of 6.0W/cm² per unit volume in a sonochemical reactor under room temperature and atmospheric pressure condition. The concentration of malodorants decreased with irradiation time, indicating pseudo-first-order kinetics. The removal efficiency of malodorants was about from 50% to 96% decomposed after 90 minutes sonication. At the deodorization, it was determined by triangle odor bag(TOB) method for odor sensory measurement, and it indicated that over 60% of relative odors were deodorized with degradation by the sonication.

Key Words : Triangle odor bag(TOB) method, ASTM, Ultrasound, Malodorants, Deodorization

1. Introduction

The problem according to an offensive odor is one of seven typical big pollutions, and there are recognitions that we have many difficulties in solving it. The reason is that odor did wide-spread damage to many people because it is a pollution which has an effect on the direct sense of smell and that we have difficulties in handling skill of getting rid of an offensive odor and in measuring method for a bad smell. There are some types of the measurement methods according to the sense of smell in odor substances. Air dilution methods are ones, which are carried out through static method, are as follows; odor bags method, odorless room method, syringe method defined in american society as testing material (ASTM). Dynamic method is well known for olfactometer (or/and sentometer). On the other hand as for an odor mention method according to the sense of smell like this, there is a measurement,

which indicates the intensity or an unpleasant sensation with the direct sense of smell like the method of odor intensity mention as well as a pleasant or unpleasant sensation.

Substance concentration, for example, needs to decrease by less than one tenth to fell that an odor of substance has become a half because odor intensity is in proportion to the logarithm of odor intensity. At present, the substances which are designated and restricted as malodorants are classified as twenty two sorts; sulfide compounds (like as hydrogen sulfide, dimethyl sulfide, dimethyl disulfide and methyl mercaptan), aliphatic fatty acids (like as propionic acid, n-butyric acid, n-valeric acid and isovaleric acid), nitrogen compounds (like as ammonia, trimethylamine), hydrocarbon compounds (like as styrene, toluene, and xylene), aldehydes (like as acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde and isovaleraldehyde), methyl isobutyl ketone, isobutyl alcohol, ethyl acetate, and either of them has a low odor thresholds, i.e., that value at which a stimulus just produces a sensation, or comes just within the limits of perception, of the sense of smell. The number of

Corresponding Author : Young-Eok Yoo, Department of Environmental Education, Daegu University, Gyeongsan 712-714, Korea
Phone : +82-53-850-6952
E-mail : youngeok@daegu.ac.kr

Table 1. Olfactory thresholds of some malodorants(ppm volume)

Malodorants	Thresholds			Odor
	Leonardos ^a	Hellman ^b	Japan ^c	
Ammonia	-	-	1.54	Urine odor
Methyl mercaptan	-	0.0021	0.00007	Rotten onion odor
Hydrogen sulfide	-	0.00047	0.00041	Smells of an addled egg
Dimethyl sulfide	-	-	0.001	Rotten cabbage odor
Dimethyl disulfide	-	-	0.0022	Rotten cabbage odor
Trimethyl amine	-	0.00021	0.000027	Smells of rotten fish
Acetaldehyde	-	0.21	0.00154	Stimulative grassy-odor
Propionaldehyde	-	0.009	0.00067	Stimulating sour odor
n-Butyraldehyde	-	-	0.009~0.08	Stimulating sour odor
Isobutyraldehyde	-	-	0.00055	Stimulating sour odor
n-Valeraldehyde	-	-	0.00041	Suffocating sour odor
Isovaleraldehyde	-	-	0.000069	Suffocating sour odor
Isobutylalcohol	-	-	0.011	Fermentative odor
Ethylacetate	-	-	0.027	Stimulative paint-thinner odor
Methyl isobutyl ketone	-	-	0.092	Stimulative paint-thinner odor
Toluene	2.14	1.74	0.31	Stimulative gasoline odor
Styrene	-	0.05	-	Smells of city gas
Xylene	-	0.08	0.06	Stimulative gasoline odor
Propionic acid	-	0.028	0.0057	Stimulative sour odor
n-Butyric acid	0.001	-	0.00019	Unpleasant sweaty-odor
n-Valeric acid	-	-	-	Unpleasant sweated socks odor
Isovaleric acid	-	-	0.000078	Unpleasant sweated socks odor

^a G. Leonardos, J. Air. Poll. Cont. Assoc., 19, 94 (1969)

^b T. M Hellman, J, of the Air Pollution Control Association, 19, 24 (1969)

^c "Research Report on Odor and Deodorization", Public Works Research Institute, Ministry of Construction, Japan, p. 105(1979), p.45(1980)
Law on Prevention of Offensive Odor, the Control Concentration by the 72nd Notice of the Environment Agency, Japan(1993)

complaints against odor substance like this has increased as the manufacturing industry like painting (or coating) factory, fiber (or textile) factory or metal factory has become active and animal husbandry like hog raising or poultry raising and the odor-generating regions like a petrochemical plant industry have increased. According to data in Japan(i.e., an *environmental white paper of Japan*), the number of complaints against odor in Japan is about 3,500 cases in 1991, when it is totaled up for the first time and amounts to maximum over 20,000 cases in 1999. At the peak of that year it decreases to 18,000 and at last it shows no marked changes now.

However, we are concerned about the increase of damage with the increase in urban population these years because the odor-generating regions are

approaching a residential area. The number of complaints against odor accounts for about 20 percent of complaints related to environment in Korea neighboring Japan. According to data in Korea, (i.e., an *environmental white paper of Korea*), the number of making complaints shows a tendency to increase every year; 356 cases in 1985, 40,921 cases in 1998, 56,632 cases in 2002, and one of cases which did great damage was a phenol pollution case in *Nakton river* in 1991. It is the case that tap water gives out a foul smell as if onions are rotten, and that it is not available in cooking and drinking because the trichlorophenol is generated by reaction between chlorine from chlorine pasteurizing process and phenol which was illegally discharged into the river from an electronic products factory. This case

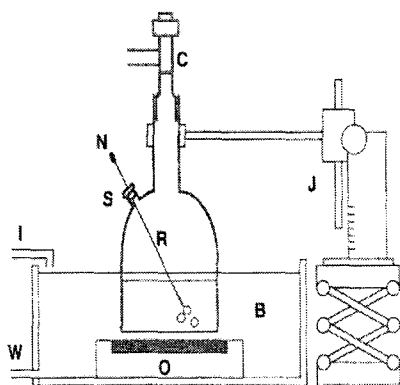


Fig. 1. Schematic diagram of the experimental apparatus for ultrasonic irradiation.

O: Oscillator(200kHz), R: Reactor(150ml), J: Jacker (for reactor fixation, 3.8mm from oscillator), N: Syringe needle(for gas purge), S: Septum, C: Stopcock, I: Cooling water inlet, B: Water bath(20°C)

becomes an issue as a social problem beyond pollution problems of a certain area.

There is a common knowledge as a deodorizing method for malodorants; chemical treating method like oxidizing method by ozone or infrared rays^{1,2)}, adsorption method by active carbon^{3,4)}, direct burning method⁵⁾, and biological treating method by a microscopic organism or bio-filter^{6,7)}. It is recently reported that odor substances are decomposed by a chemical action of ultrasonic waves^{8,9)}. The irradiation of ultrasonic waves from scores of kHz to several MHz frequency district to a aqueous solution would make a state of high temperature and high pressure locally owing to generation, growth and insulation compression collapse of delicate bubbles in a water solution. This phenomenon is called cavitations and is considered as the mother of a chemical action of ultrasonic waves.

This study aimed at a variety of chemical actions of ultrasonic waves and examined the possibility of application about the results of deodorization and the treatment of odor substances of various malodorants (c.f., Table 1) which have a low thresholds.

2. Experimental Details

2.1. Materials and Apparatus

Reagent grade chemicals, *n*-valeric acid,

trimethylamine(TMA), *n*-valeraldehyde, and 2-methylisoborneol(2-MIB) were obtained from Wako Chemicals, and used as starting materials for deodorization by ultrasonic irradiation. All chemicals were used without further purification and water was purified with Millipore system (Milli-Q Labo). Fig. 1 shows the ultrasound irradiation set-up. The experimental apparatus ultrasonic irradiation were performed using a Kaijo Denki multiwave ultrasonic generator Model 4021, and a 65 mm diameter barium titanate oscillator, operated at 200kHz, with an input power of 200W. The reaction cell was immersed into the water bath, cooled by an external cooler to keep the temperature constant at 20°C. All the experiments were made in duplicate and the results presented in the paper are the average of two experiment.

2.2. Experimental Procedures

2.2.1. Preparation of sample solution and sonication

A cylindrical pyrex glass vessel of 50 mm inside diameter with a total volume of 150 ml was used for the sonication experiment(c.f., Fig.1). The vessel had a side arm with a silicon rubber septum for gas bubbling and sample injection and extraction without exposing the sample to air. The bottom of vessel was planar and made as thin as possible(1.0 mm) because transmission of ultrasonic waves increases with decreasing bottom thickness. The vessel was mounted at a constant position from the oscillator relative to a nodal plane of the sound wave (3.8 mm: half a length of the ultrasound wave). During the irradiation, the vessel was sealed and sonicated to desired time intervals.

2.2.2. Preparation of odor sample and odor sensory measurements

The initial gaseous odor sample was prepared by the dilution of irradiated solution (30 μl) in a vacuum glass bottle (1.0 L) for odor sensory measurements, and it was diluted with high purity helium to the threshold odor number by the triangle odor bag (3.0 L) method, i.e., it is a sort of odor sensory measurements, that is, a method that six panellers guess which is the odor-containing bag among three plastic odor bags: Only one of three bags is odor-contained air and the others are odorless air¹⁰⁾.

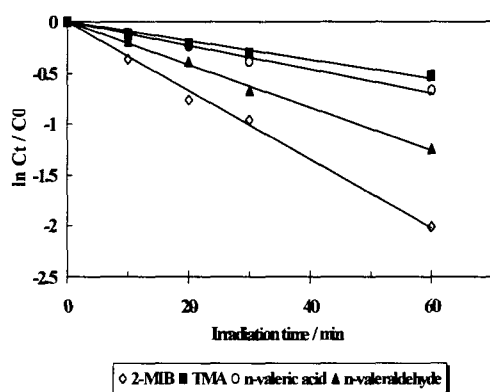


Fig. 2. Degradation of malodorants by ultrasonic irradiation under Air. The dots represent the logarithm of ratio actual(C_t) and initial(C_0) concentration.

3. Results and Discussion

3.1. Sonication of Odorous compound

Fig. 2. shows the change in concentration as a function of time during the degradation of odorous compound by ultrasonic irradiation. The initial concentration of all the solutes was $100 \mu\text{M}$. The pseudo-first-order rate constant for odorous compound degradation under the conditions of the present work, kt is defined in eq(1) as

$$\ln(C_t/C_0) = -kt \quad (1)$$

Where C_t is the odorous compound concentration (in aqueous solution) at time t , C_0 is the initial odorous compound concentration, and k is the apparent pseudo-first-order rate constant. At that time, the apparent rate constants k was calculated from eq(1), these results are presented in Table 2. The degradation rates ($\times 10^{-2} \text{min}^{-1}$) of these odorous compounds under an atmosphere of argon/air/nitrogen followed the order 2-MIB(3.91/3.37/3.41) > n-Valeraldehyde(2.51/2.08/-) > n-Valeric acid (1.34/1.16/-) > TMA (1.22/0.92/-). The degradation rates of odorous compounds under argon were faster than that under air and nitrogen, and that was increased with the increment of hydrophobicity, and its also increased with the increment of their hydroxyl radicals reaction. During the sonolysis of an aqueous solute solution, the dependence of nature of the saturating gas, such as the solubility in water and the thermal conductivity was observed in the same manner as our previous studies^{11,12}.

Table 2. Results of kinetic data for degradation of malodorants by ultrasonic irradiation

Malodorants	k^a		k_{OH}^b
	in Air	in Argon	
2-MIB	3.37	3.91	-
TMA	0.92	1.22	1.46
n-Valeric acid	1.16	1.34	2.90
n-Valeraldehyde	2.08	2.51	2.82

^a Pseudo-First-Order rate constant ($\times 10^{-2} \text{min}^{-1}$)

^b Rate constant of hydroxyl radical reaction ($\text{M}^1 \text{s}^{-1}$), taken from R. Atkinson, Chem. Rev., 86, 69(1985)

This implied that the maximum temperature inside the cavitation bubble, when acoustic cavitation bubbles were violently collapsed, depends on the ratio of the specific heat ($\gamma = C_p/C_v$) and the thermal conductivity of the saturating gas. In addition, the formation of reactive radical species ($\cdot\text{OH}$, $\cdot\text{OOH}$) would be enhanced because of the high temperature inside the collapsing cavitation bubble. Table 3 indicates the degradation rates of 2-MIB in aqueous solution saturated with various gases. The order of the degradation rate is as follows; argon > nitrogen \geq air. Specific heat ratio of the envelope gas used are Table 3, and results show that the degradation rate was increased with increasing γ value of the envelope gas.

Also the deodorization (c.f., Fig. 3) is conducted by triangle odor bag method for odor sensory measurement in sonication of odorous compounds. The deodorization was determined by odor threshold number with odor sensory measurement, and was indicated that over 60% of their relative odor intensity (ROI) were deodorized with decomposition of malodorants by ultrasonic irradiation under the air atmosphere.

3.2. Relationship between odor intensity and malodorants concentration by sonication

There are detection threshold value and recognition threshold value in olfactory sense threshold value. In this study, the method that six

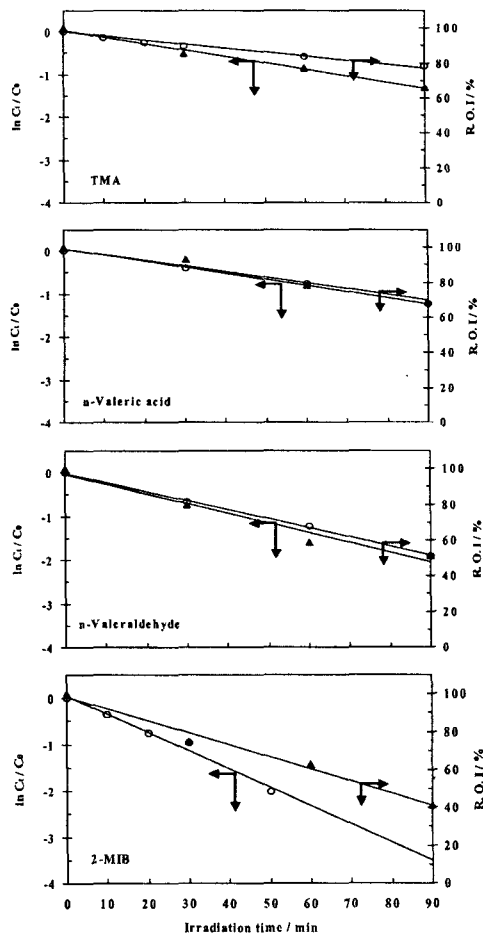


Fig. 3. Time-profiles of deodorization of malodorants by ultrasonic irradiation under Air.

○: Odor concentration,
▲: Relative odor intensity(R.O.I)

Table 5. Measured results of the malodorants with triangle odor bag method for the sample treated by ultrasonic irradiation

Malodorants	Relations, Y and X/Th	$k_{deodorization}^a$	$k_{degradation}^b$
2-MIB	$Y=0.47\ln(X)+0.04$	4.42	3.37
TMA	$Y=0.95\ln(X)-7.67$	2.40	0.92
n-Valeric acid	$Y=0.67\ln(X)-3.64$	2.04	1.16
n-Valeraldehyde	$Y=0.67\ln(X)-2.35$	3.46	2.08

^a Deodorization rate constant($\times 10^{-2} \text{min}^{-1}$)

^b Degradation rate constant($\times 10^{-2} \text{min}^{-1}$)

Table 4. Calculation in the olfactory sense methods of odor intensity and odor concentration

	DN ^a	30	100	300	1000	3000	10000	X ^b	Exclusion ^c
	log DN	1.48	2.00	2.48	3.00	3.48	4.00		
P a n e l l i s t	A	○ ^d	○	× ^e				2.24	*
	B	○	○	○	×			2.74	
	C	○	○	○	×			2.74	
	D	○	○	○	○	○	×	3.74	*
	E	○	○	×				2.24	
	F	○	○	○	○	×		3.24	

^a Dilution number

^b Odor intensity value

For example panelist A,

$$X_a = (\log a_1 + \log a_2) / 2$$

X_a: odor intensity value of panelist A

a₁: the dilution number of correct answer

a₂: the dilution number of wrong answer

$$X_a = (\log 100 + \log 300) / 2 = 2.24$$

$$X_{\text{average}} = (2.74 + 2.74 + 2.24 + 3.24) / 4 = 2.74$$

Odor intensity = 2.74

Odor concentration = 102.74

^c The highest and lowest values of log DN are excluded on calculation

^d Correct answer, ^e Wrong answer

panellers smell the sample bags several times to the point can not recognize the odor as dilution clean air is near by the inspection threshold value. The sonicated sample was used to investigation odor concentration and odor intensity by this method (c.f., Table 4, 5), i.e., it is inspection threshold value method. Usually, there is a proportional relation between the concentration and intensity of odor in Weber-Fechners Law. In this study utilized the Weber-Fechners low that is applied widely for researches of odor olfactory sense method¹³). From formula(2), odor concentration X, odor intensity Y when odor concentration X is threshold, odor intensity Y is zero. If threshold replaced Th, formula (2) will be formula (3).

$$Y = k \log X + A \tag{2}$$

$$Y = k \log (X / Th) \tag{3}$$

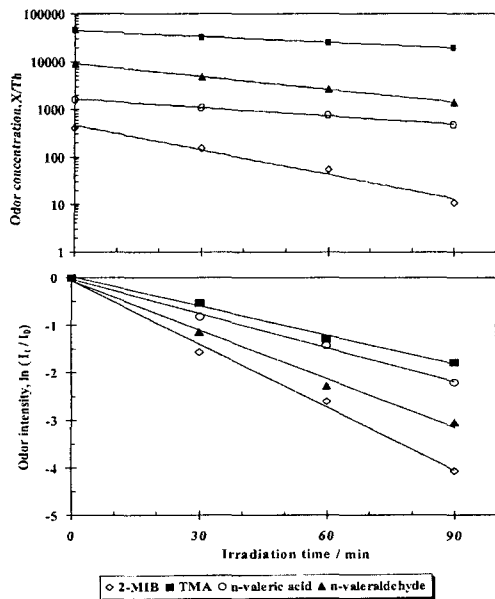


Fig. 4. Change of the odor concentration(top) and the odor intensity(bottom) of malodorants by ultrasonic irradiation under Air. I_0 is a initial odor intensity, and I_t is a odor intensity at irradiation time t .

Here, k , $A (= k \log Th)$ is constant that is decided from kinds of odors. This X/Th is called dilution threshold number^{14,15}, and if it replaced Dt , formula (3) will be formula (4).

$$Y = k \log Dt \quad (4)$$

From this formula, its able to get k by least squares method. As shown the time-profiles of intensity of odor on Fig. 4, there is a good relationship between the logarithm of odor concentration and odor intensity. Also, the removal rate of odor is shown on Table 6. 2-MIB deodorization rates constant is $4.42 \times 10^{-2} \text{min}^{-1}$, n-Valeraldehyde for $3.46 \times 10^{-2} \text{min}^{-1}$, n-Valeric acid for $2.40 \times 10^{-2} \text{min}^{-1}$, TMA for $2.04 \times 10^{-2} \text{min}^{-1}$. Form this order; if the degradation rate is faster deodorization rate is fast, too.

4. Conclusions

The deodorization system using ultrasound irradiation processes was applied to the deodorization of typical malodorants such as 2-MIB, n-Valeraldehyde, n-Valeric acid, TMA. The main results are summarized as follows:

Table 6. Relationship between odor concentration (X/Th) and odor intensity(Y) for malodorants

Malodorants	Odor concentration(X)		Odor intensity(logX)	
	BS ^a	AS ^b	BS	AS
2-MIB	977	17	2.99	1.23
TMA	410	52	2.60	1.72
n-Valeric acid	309	23	2.49	1.36
n-Valeraldehyde	309	52	2.49	1.15

^a Befor sonication

^b After sonication

First, this treatment method of ultrasound irradiation is very simple and comfortable for deodorization and decomposition of malodorants to compare to other treatments developed presently. Also it is very economical method for the price which is very cheap to operate.

Second, this treatment has ability to deodorize and decompose for malodorants over 50~96% in short treatment time. As the change for intensity of odor its able to see to deodorize approximately 60%. Also it is very practical method for the price that is very cheap to operate.

Finally, this treatment has high possibility for deodorization malodorants, so that it can be expected highly as a new treatment method in near future.

Acknowledgements

This study was supported financially by the Daegu University, (Project Number : 20012510).

References

- 1) Beltrán, F. J., J. M. Encinar and J. F. García-Araya, 1993, Oxidation by Ozone and Chlorine Dioxide of two Distillery Wastewater Contaminants, *Wat. Res.*, 27, 1023-1032.
- 2) Lai, M. S., J. N. Jensen and A. S. Weber, 1995, Oxidation of simazine: Ozone, ultraviolet, and combined ozone/ultraviolet oxidation, *Water*

- Environment Research, 67, 340-346.
- 3) Ellis, J. and W. Korth, 1993, Removal of Geosmin and Methylisoborneol from Drink Water by Adsorption on Ultrastable Zeolite-Y, *Wat. Res.*, 27, 535-539.
 - 4) Yoo, Y. E., N. Takenaka, H. Bandbox, Y. Nagata, J. Morioka and Y. Maeda, 1996, *J. Odor Research and Eng.*, 27, 3, 143-149.
 - 5) Blake, P. G., H. H. Davies and G. E. Jackson, 1971, Dehydration Mechanism in the Thermal Decomposition of Gaseous Formic Acid, *J. Chem. Soc., B*, 1923-1925.
 - 6) Omori, T. and M. Alexander, 1987, Bacterial Dehalogenation of Halogenated Alkanes and Fatty Acids, *Appl. Environ. Microbiol.*, 35, 867-871.
 - 7) Rahmani, H., J. L. Rols, B. Capdeville, J. C. Cornier and A. Deguin, Nitrite Removal by a Fixed Culture in a Submerged Granular Biofilter, 1995, *Wat. Res.*, 29, 1745-1753.
 - 8) Yoo, Y. E., N. Takenaka, H. Bandow, Y. Nagata and Y. Maeda, 1995, Decomposition of geosmin in aqueous solution by sonication, *Chem. Lett.*, 961-962pp.
 - 9) Kotronarou, A., G. Mills and M. R. Hoffmann, 1992, Oxidation of Hydrogen Sulfide in Aqueous Solution by Ultrasonic Irradiation, *Environ. Sci. Technol.*, 26, 2420-2428.
 - 10) Research Report of Odor by the Method of Sensory Measurement, 1982, Department of Air Preservation of the Environment Agency, Japan, 63-68pp.
 - 11) Yim, B. B., Y. E. Yoo, Y. Nagata and Y. Maeda, 2001, Ultrasonic Enhancement of the Hydrolysis of Diethyl 1, 2-Benzenedicarboxylate, *Chem. Lett.*, 9, 938-939.
 - 12) Yim, B. B., Y. E. Yoo and Y. Maeda, 2003, Sonolysis of alkylphenols in aqueous solution with Fe(II) and Fe(III), *Chemosphere*, 50, 1015-1023.
 - 13) Summer, W., 1971, *Odor Pollution of Air*, Leonard Hill, London, 26-27pp.
 - 14) Yamakawa, M., K. Nishita and T. Honda, 1979, Technique and Apparatus for Quantitative Measurement of Odor Emission, *J. Japan Soc. Air Pollut.*, 14, 1-11.
 - 15) Gostelow, P., S. A. Parsons and R. M. Stuetz, 2001, Odour Measurements for Sewage Treatment Works, *Wat. Res.*, 35, 579-597.