

수용액 중 Musty-Odorou Compound류의 분해에 따른 초음파의 응용

유영억 · 永田良雄 · 前田泰昭**

大邱大學校 中央器機센터 · 日本 大阪府立大學 尖端科學技術研究所*
日本 大阪府立大學 工學部 機能物質學科 環境物質講座**

Application of Ultrasound for the Decomposition of Musty-Odorou Compounds in Water

Young-Eok Yoo · Yoshio Nagata · Yasuaki Maeda**

Center for Laboratory Facilities, Taegu University, Kyungsan, Kyungpook 712-714, Korea
Research Institute for Advanced Science and Technology, University of Osaka Prefecture, Gakuen-cho1-2,
Sakai, Osaka 593, Japan.*
Department of Applied Materials Science, College of Engineering, University of Osaka Prefecture,
Gakuen-cho1-1, Sakai, Osaka 593, Japan.**

요 약

Musty-odorous compound(Geosmin, 2-Methylisoborneol) 水溶液 中에 超音波(200kHz, 6.0W/cm²)를 照射 시켜 照射時間에 따른 濃度 및 臭氣의 變化를 考察했다. 超音波 照射에 의해 이 물질들은 빠르게 分解되었고, 分解形態는 濃度에 대한 類似1次 反應을 나타내었다. 空氣 飽和 霧圍氣에서 이들의 初期 分解速度는 각각 2.5 10⁻³ Msec⁻¹(2-MIB), 3.2 10⁻³Msec⁻¹(Geosmin)로 나타났다. 超音波 照射 時 아르곤 등의 飽和가스(Envelope gas)의 影響은 아르곤(Ar) 산소(O₂) 공기(Air) 질소(N₂) 順序로 純粹한 아르곤(Ar) 霧圍氣에서 musty-odorous compound 類의 分解가 가장 빠르게 進行되었고 그 分解生成物로 CO, CO₂ 그리고 HCOOH, CH₃COOH 등의 低級 有機酸類가 檢出되었다. 또한 이들의 分解反應은 물의 超音波分解에 따라 生成된 hydroxyl radical에 의한 radical反應, cavitation bubble內에서의 高溫高壓에 의한 熱分解 및 直接燃燒反應으로 進行됨을 알 수 있었다.

I. Introduction

The chemical effects of free radicals such as hydrogen atoms and hydroxyl radicals are generalized upon the sonochemical researches.

These effects are known to happen in terms of reactions occurred inside, at the interface, or at some distance away from cavitating gas bubbles. In the interior of a collapsing bubble cavities where several thousands degree of temperature and hundreds of atmospheric press-

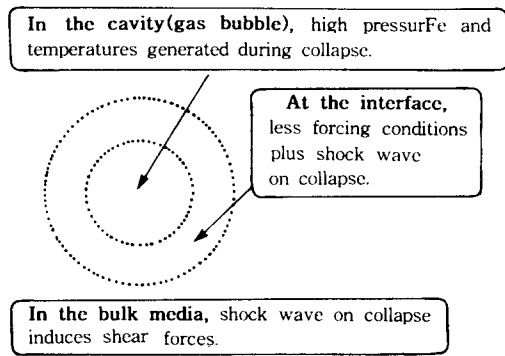


Fig. 1. Reaction sites of a collapsing bubble in homogeneous liquid.

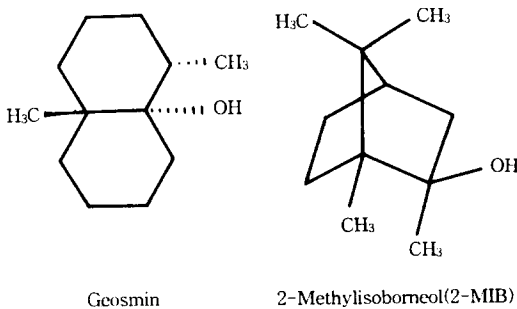


Fig. 2. Structures of musty-odorous compounds.

ure have been known to exist. In the interfacial region, temperatures about 2000k have been determined for the interfacial region, and pressures of hundreds have been calculated^{1,2)} The mechanical and chemical effects of collapsing bubble in homogeneous liquid will be explained in three distinct regions(c.f., Fig. 1). In recent years, some studies have been carried out by the use of ultrasound to the decomposition of a variety of chemical contaminants in aqueous solution, such as hydrogen sulfide³⁾, diverse phenols^{4,5)}, volatile fatty acids⁶⁾, chlorinated hydrocarbon^{7,8,9)} and CFCs^{10,11)}

The musty-odorous compounds(c.f., Fig. 2.) in drinking water have become aware of deterioration of the drinking water worldwide. These bicyclic structural musty-odorous compo-

unds have low threshold odor concentrations¹²⁾, specifically have been found in surface waters with earthy-musty odors in Europe and in Japan¹³⁾. For removing these compounds in water, adsorption methods using activated carbon^{14,15)}, zeolites^{16,17)}, adsorption decomposition methods by powdered active carbon¹⁸⁾ or an acclimatized biofilm reactor¹⁹⁾ have been investigated. On the other hand, the techniques of deodorization for odorous compounds by ultra-violet irradiation, condensation of offensive fumes, combustion, i.e., it is chemical combination of oxygen with combustible matter, wet-scrubbing by water spray and chemical cleaning were also used²⁰⁾.

However, the decomposition and deodorization of musty-odorous compounds by ultrasonic

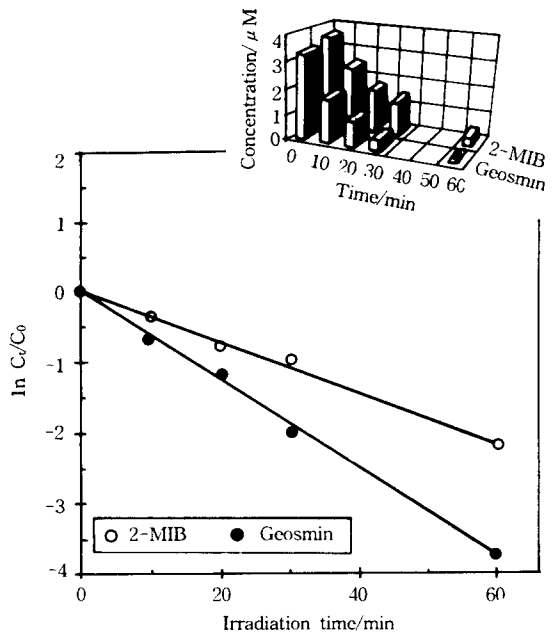


Fig. 3. Schematic diagram of the irradiation apparatus.

- | | |
|-------------------------|--------------------------|
| V : glass vessel | S : sample solution |
| O : oscillator | G : ultrasound generator |
| W : cooling water | E : cock or stopper |
| C : clamp | P : silicone septum |
| B : bulling gas | I : cooling water inlet |
| D : cooling water drain | |

irradiation have not been reported. In this study, we report the results of sonochemical decomposition and deodorization of musty-odoriferous compounds such as 2-Methylisoborneol(2-MIB) and Geosimin. We also discuss the products and mechanics of the decomposition by ultrasound.

II. Materials and Methods

1. Materials.

2-MIB, geosmin and tert-butyl alcohol(tert-BuOH) was obtained from Wako Pure Chemical Industries Co. Inc. All chemicals were of at least 99 % purity and were used without further purification. Bubbling gases as for argon, oxygen and nitrogen of four-nine grades were purchased from Osaka Sanso, and water was purified with Millipore system(MILLI-Q Labo).

2. Apparatus and Procedures.

A multiwave ultrasonic generator(KAIJO DENKI model 4021) and a barium titanate oscillator of 65 mm were used for ultrasonic irradiation and operated at 200kHz with an input intensity of 200W(c.f., Fig. 3.). A cylindrical glass vessel of 65 mm with total volume of 150mL was used for ultrasonic irradiation. The vessel has a side arm with a silicon rubber septum for gas bubbling, solute injection or sample extraction. The bottom of the vessel was planar and made as thin as possible 1.0mm thickness, because transmission of ultrasonic wave increases with decreasing thickness of the bottom glass. And the vessel was fitted at a constant position of a nodal plane of the ultrasound wave, i.e., $\lambda/2$; 3.8mm, upon the oscillator. During the irradiation the vessel was sealed, and the solution was bubbled by enveloping gases for 30 minutes, i.e., the

flow rate is 30mL/min before irradiation. The irradiation was stopped at desired time intervals, and the 2.0mL solution was extracted in a sealed 5.0mL bottle by a 10mL glass syringe for analysis. The initial sample gas of musty-odor was prepared by the dilution of irradiated 30L solution in a 1000mL vacuum glass bottle for odor sensory measurements, and it was diluted with high purity helium to the threshold odor number by the triangle plastic bag, i.e., the volume is 3000mL, method(i.e. it is a sort of odor sensory measurements, that is, a method that six panellers guess which is the odour-containing bag among three plastic bags : Only one of three bags is odour-contained gas and the others are odorless gas.).

3. Analysis.

Sample solution, 1.0L was submitted to analysis using a Hewlett-Packard 5890, GC/FID gas chromatograph with a 15m \times 0.3mm i.d. \times 0.33m film thickness, and DB Ultra-1capillary column. The determination of organic acids products was performed by an IC100-A5 ion chromatograph analyzer with a Model-PRE, PCS 5-052 Yeuchrom's packed column for high performance, and gases such as carbon dioxide, and carbon monoxide were determined by a Hewlett-Packard 5890, GC/TCD gas chromatograph with a 3.0mm i.d. \times 2.0m molecular sieves(30/60 mesh) stainless-steel column for CO, a 2.0mm i.d. \times 2.0m porapak Q(30/60 mesh) stainless-steel column for CO₂. Total organic carbon(TOC) was measured by TC-500 Shimadzu's TOC analyzer.

III. Results and Discussion

1. Sonication of musty-odoriferous compound.

Fig. 4. shows the time-profiles of geosmin

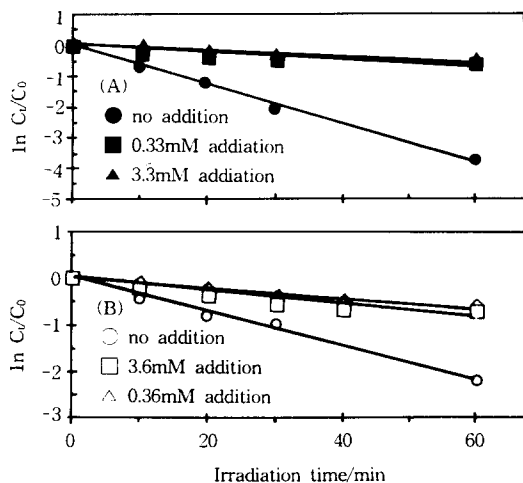


Fig. 4. Time-profiles of musty-odorous compounds by ultrasonic irradiation under air atmosphere.

[2-MIB]_i=3.6M, [Geosmin]_i=3.3M. C₀ is a initial concentration and C_t is a concentration at irradiation time t.

and 2-MIB during a sonication under the airatmosphere. Both geosmin and 2-MIB were exponentially decomposed with sonication time. Over 60 % of the reactants were decomposed within 30 minutes. The initial decomposition rate for geosmin, the concentration is 3.3M, was $3.2 \times 10^{-3} \text{Msec}^{-1}$ and that for 2-MIB, i.e., the concentration is 3.6M, was $2.5 \times 10^{-3} \text{Msec}^{-1}$, and the rate did not differ so much from other.

2. Cavitation effects of envelope gases.

Acoustic cavitation refers to the formation and collapse of small gas or vapor-filled cavities (bubbles) in liquids exposed to ultrasound. In aqueous solution, water vapor is pyrolyzed to OH radicals and hydrogen atoms in collapsing cavities²¹⁾. It is known that the efficiency of acoustic cavitation is dependent upon the dissolved gas. Table 1 indicates the decay rates of musty-odourous compounds, i.e., the concentration

Table 1. Comparison of initial decomposition rate constants of musty-odorous compounds under atmospheric gases.

Atmosphere gas	k ^a		C _p /C _v ^b
	Geosmin ^c	2-MIB ^d	
Argon	6.5±0.53	5.8±0.13	1.670
Oxygen	5.7±0.52	5.0±0.69	1.396
Air	4.4±0.43	3.7±0.25	1.402
Nitrogen	3.5±0.32	2.9±0.42	1.401

^a Decomposition rate constant($\times 10^{-3} \mu \text{Ms}^{-1}$)

^b J.Hilsenrath et al., "Tables of thermal properties of gases" NBS Circular, 564(1955). At 1atm, 300K.

^c [Geosmin]_i=33.0 μM, ^d [2-MIB]_i=36.2 μM

is 33M(Geosmin) and 36M(2-MIB), in aqueous solutions saturated with various gaseous envelope. The order of the initial decomposition rate is as follows; argon > oxygen air > nitrogen. These results indicate that the decomposition rate was increased with increasing of specific heat ratio, = C_p/C_v, of the envelope gas used. At the higher value(C_p/C_v) of bubbling gas, the target compounds are more likely to occur in the hot solvent layer surrounding the gas bubbles or/and in the bulk solution. The temperature in a collapsing cavity was defined²²⁾ as $T_f = T_i [P_f (-1) / P_i]$ where T_f and P_f are final temperature and pressure, and T_i and P_i are initial temperature and pressure in cavities, respectively. T_f is higher under argon than the other gases because of the higher value of argon than that of the other gases, therefore, the rate of OH radical formation would be faster under argon than under the other gases, and thermal decomposition of geosmin would also effectively occur if this compound exists in this region or it's surroundings of high temperature. Consequently, this may be because the cavitation effect is larger under higher value gas than lower value gas, and this result can be suggested by the following observations that the reaction is thermal

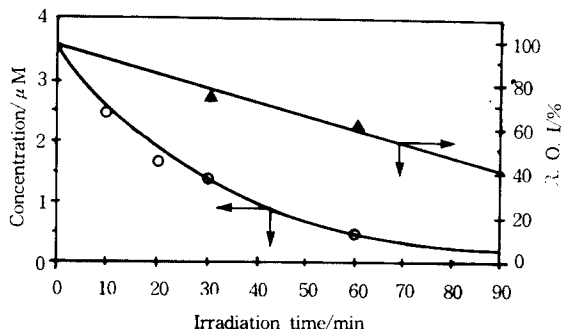


Fig. 5. Scavenging effects by t-BuOH addition on the decomposition of Geosmin (A) and 2-MIB (B) under air atmosphere. $[2\text{-MIB}]_i = 3.6\text{M}$, $[\text{Geosmin}]_i = 3.3\text{M}$.

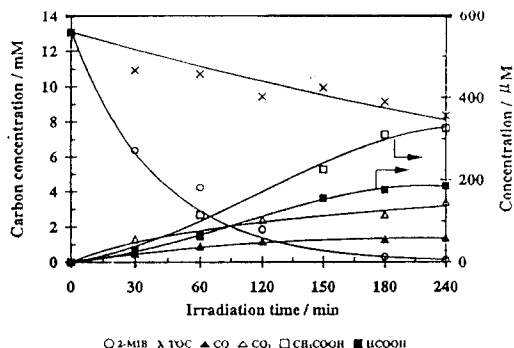


Fig. 7. Deodorization of 2-MIB by ultrasonic irradiation under air atmosphere.

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

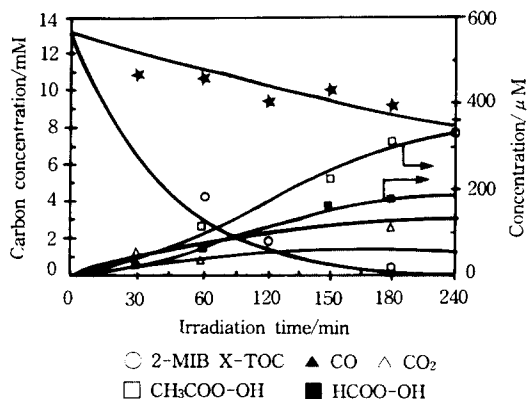


Fig. 6. 2-MIB decomposition and product formation during sonication under air atmosphere. The concentrations of 2-MIB and TOC were indicated as carbon concentration. $[2\text{-MIB}]_i = 1.2\text{mM}$

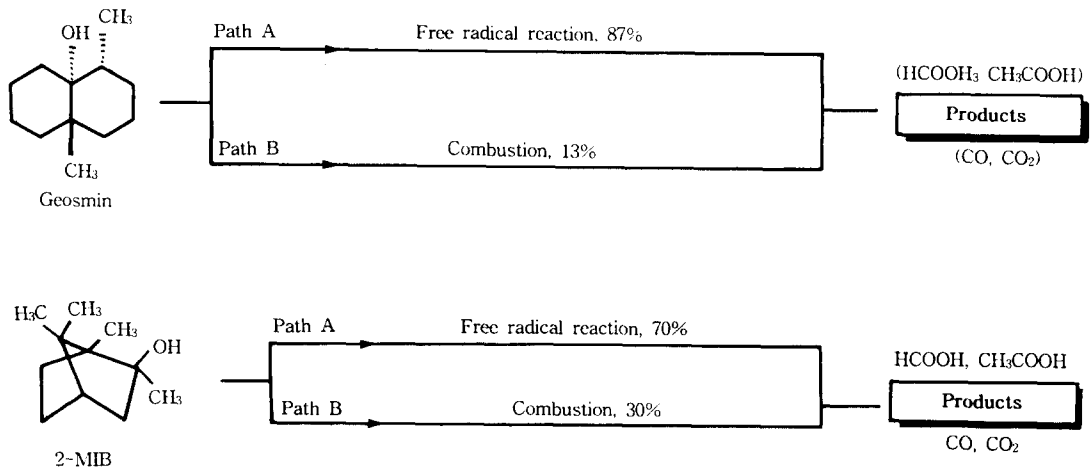
decomposition or/and combustion in cavitation bubble.

The chemical effects of tert -BuOH are generalized as a scavenger of OH radicals above the sonochemical researches. As shown in Fig. 5, the decomposition of geosmin and 2-MIB was not completely suppressed, i.e., it was suppressed about 70% by the addition of tert -BuOH, which is known as a scavenger of OH

radicals. These results could also make one's appearance that the principal part of the decomposition reaction is pyrolysis types in the cavitation bubbles and free radical reaction in bulk liquid phase, i.e., the result suggests that decomposition of about 70% proceeds via radical reaction and that of about 30% thermal reaction.

3. Decomposition products and TOC change.

The decomposition of volatile fatty acids⁶⁾, aliphatic aldehydes²³⁾ in aqueous solution by sonication has been reported and the main product is observed to be carbon dioxide, but some partially oxidized products such as carbon monoxide and traces of CH₄, formic acid and acetic acid were also detected. Fig. 6. shows the decomposition plots of 2-MIB, a decreasing curves of TOC and a formation of products by ultrasonic irradiation under air atmosphere. The decomposition of 2-MIB is rapid about 99% cleaved after 120 minutes sonication. The main products of these systems were inorganic carbon forms as CO, CO₂, and small amounts of CH₃COOH, HCOOH was also found as a



Scheme 1. Decomposition pathway of musty-odorous compounds by ultrasonic irradiation.

product of sonolysis of 2-MIB. However, even if TOC was almost not decreased, i.e., that was cleaved about 28 %, the decreasing of TOC was agreed with a total amount of formation of carbon dioxide and carbon monoxide. These results can be suggested that almost all of 2-MIB being organic acid forms as HCOOH, CH₃COOH, etc. in aqueous solutions by ultrasonic irradiation, and the decomposition pathway of musty-odorous compounds was shown in Scheme 1.

4. Removal of odor.

Fig. 7. shows the deodorization curves of 2-MIB by ultrasonic irradiation. It was determined by threshold odor number with the triangle plastic bag method for odor sensory measurement, and was indicated that over 50% of their relative odors were deodorized with decay of odorous compounds by the ultrasonic irradiation under the air atmosphere.

IV. Conclusions

The results obtained in the present experiments

suggest that the main pathway of sonication of musty-odorous compounds is a pyrolysis in cavitation bubbles where the most thoroughgoing and rapid decomposition in sonochemical processes would take place. Musty-odorous compounds are hydrophobic and have high vapor pressure, so they can easily enter into the cavitation bubbles. Thus 2-MIB and Geosmin were found to be readily decomposed by sonication with high efficiency to inorganics, and decomposition method is a favorable and effective one for the removal of musty-odorous compounds.

According to the results, there are a few outcomes as following facts :

1. This sonolytical treatment by ultrasonic irradiation is very simple and comfortable for decomposition and deodorization to compare to other treatments developed presently, and also it is very cheap to operate.
2. This treatment has high possibility for deodorization of odorants, so that it can be expected highly as an alternative treatment method in the near future.

References

- Suslick, K. S., Hammerton, D. A., and Cline, R. E. Jr. : The Sonochemical Hot Spot, *J. Am. Chem. Soc.*, 108, 5641-5645, 1986.
- Shutilov, V. A. : *Fundamental Physics of Ultrasound* ; Gordon & Breach Science Publishers : New York, 1988.
- Kotronarou, A., Mills, G., and Hoffmann, M. R. : Oxidation of Hydrogen Sulfide in Aqueous Solution by Ultrasonic Irradiation, *Environ. Sci. Technol.*, 26, 2420-2428, 1992.
- Serpone, N., Terzian, R., Hidaka, H., and Perizzeri, E. : Ultrasonic Induced Dehalogenation and Oxidation of 2-, 3-, and 4-Chlorophenol in Air-Equilibrium Aqueous Media, *J. Phys. Chem.*, 98, 2634-2639, 1994.
- Hua, I., Hochemer, R. H., and Hoffman, M. R. : Sonochemical Degradation of p-Nitrophenol in a Parallel-Plate Near-Field Acoustical Processor, *Environ. Sci. Technol.*, 29, 2790-2796, 1995.
- Yoo, Y. E., Takenaka, N., Bandow, H., Nagata, Y., and Maeda, Y. : Characteristics of Volatile Fatty Acids Degradation in Aqueous Solution by the Action of Ultrasound, *Wat. Res.*, 31, 6, 1532-1535, 1997.
- Yoo, Y. E., Takenaka, N., Bandow, H., Nagata, Y., and Maeda, Y. : Decomposition of Geosmin in Aqueous Solution by Sonication, *Chem. Lett.* 961-962, 1995.
- Nagata, Y., Hirai, K., Bandow, H., and Maeda, Y. : Decomposition of Hydroxylbenzoic Acids in Water by Ultrasonic Irradiation, *Environ. Sci. Technol.*, 30, 1133-1137, 1996.
- Cheung, H. M., Bhatnagar, M., and Jansen, G. : Sonochemical Destruction of Chlorinated Hydrocarbons in Dilute Aqueous Solution, *Environ. Sci. Technol.*, 25, 1510-1512, 1991.
- Cheung, H. M., and Kurup, S. : Sonochemical Destruction of CFC11 and CFC113 in Dilute Aqueous Solution, *Environ. Sci. Technol.*, 28, 1619-1622, 1994.
- Hirai, K., Nagata, Y., and Maeda, Y. : Decomposition of Chlorofluorocarbons and Hydrofluorocarbons in water by Water by Ultrasonic Irradiation, *Ultrasonics Sonochemistry*, S205-S207, 1996.
- Jenkins, D. : Effect of Organic Compound Taste, Odor, Color, and Chelation. *Proc. 15th Wtr. Quality Conf., Snoeyink V. L. Organic Matter in Water Supplies : Occurrence, Significance and Control*; Engrg. Publications; Univ. of Illinois; Urbana, Ill., 1973.
- Herring, D. R., Snoeyink, V. L., Wood, N. F. : Activated Carbon Adsorption of the Odorous Compounds 2-Methylisoborneol and Geosmin, *J. Am. Wat. Wk. Ass.* 69, 223, 1977.
- Craig, S. L., Pirbazari, M., Dale, M. S., Tanaka, T., McGuire, and M. J. : Optimizing the Removal of Geosmin and 2-MIB by Powdered Activated Carbon, *J. Am. Wat. Wks. Ass.* 80, 73-76, 1988.
- Tanaka, A., Fuchigami, K. : Biodegradation of a Musty Odour Component 2-Methylisoborneol and Geosmin, *Wat. Res.*, 30, 759-761, 1996.
- Ellis, J., Korth, W. : Removal of Geosmin and Methylisoborneol from Water by Adsorption on Ultrastable Zeolite-Y, *Wat. Res.*, 27, 535-537, 1993.
- Derouane, E. G. *Guidelines for Mastering the Properties of Molecular sieve*; Plenum Press : New York, 1990.
- De Jonge, R. J., Van Andel, J. G. : Biodegradation of Powdered Activated Carbon (PAC) Loaded with Aromatic Compounds, *Wat. Res.*, 30, 875-878, 1996.
- Jacobsen, B.N.;Arvin, E. Biodegradation

- Kinetics and Fate Modelling of Pentachloro-phenol in Bioaugmented Activated Sludge Reactors, *Wat. Res.*, 30, 1184-1986, 1996.
20. Hepner, I. L. *Odour Pollution of Air : Causes and Control* ; Leonard Hill : London, 1971.
21. Apfel, R. E. *Ultrasonics*:Academic Press : New York, 1990.
22. Kotronarou, A., Mills, G., and Hoffman, M. R. : Ultrasonic Irradiation of p-Nitrophenol in Aqueous Solution, *J. Phys. Chem.*, 95, 3630-3634, 1991
23. Yoo, Y. E., Howang, K. T., and Maeda, Y. : Sonochemical Destruction of Aliphatic Aldehydes in an Aqueous Solution, *Kor. J. Env. Hlth. Soc.*,23, 4, 39-44, 1997.