Prevention of bromate formation by adsorption phase ozonation using high silica zeolites


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Abstract
The objectives of this work are to propose a novel ozonation process in adsorption phase using high silica zeolites and elucidate its advantages for simultaneous achievement of prevention of bromate formation and sufficiently high ozonation performance. Bromate is formed from bromide during ozonation under conventional conditions and needs to be reduced at least below a regulated concentration because of its considerable carcinogenicity. The ozonation of 2-methylisoborneol (2-MIB), a model Taste and Odor (T&O) chemical, has been studied in our process. It was known that 2-MIB is adsorbed onto high silica zeolite and oxidized with ozone rapidly in micropores. An adsorbent, named US-Y, in which the SiO2/Al2O3 ratio is 70, was the best candidate in this study in terms of adsorption of 2-MIB, decomposition of 2-MIB and prevention of bromate formation. Actually, bromate formation was not detected, while about seventy five percent of 2-MIB was decomposed with extremely low ozone concentration of 0.07 ppm and short retention time of 0.2 min in the presence of US-Y. Its applicability for the treatment of natural water containing natural organic matters (NOMs) was also demonstrated.

Keywords Drinking water treatment; ozonation; 2-MIB; adsorption; bromate formation; high silica zeolite

Introduction
In drinking water treatments in Japan, taste and odour compounds (T&Os) such as 2-methylisoborneol (2-MIB) and geosmin are growing concerns, since these compounds have been included in water quality regulations from April 2004, in Japan. In order to remove or decompose these T&Os as well as precursors of trihaeomethanes (THMs), ozonation is commonly employed in advanced drinking water treatment processes.

In spite of advantages of current ozonation, problems encountered so far are as follows. First, high ozone dosage is needed for decomposition of T&Os to satisfy their concentration regulations which are supposed to be put into operation, because Natural Organic Matters (NOMs), which react with ozone much faster than T&Os, consume ozone quickly. This fact makes ozonation very energy-consuming and costly. Second, unexpected byproducts are usually generated during high dose ozonation in aqueous phase mentioned above. Main byproduct is bromate, which is confirmed to be harmful to human bodies (WHO, 1990). While activated carbon adsorption after ozonation is effective in removing organic byproducts such as aldehydes, it is difficult to remove by activated carbon adsorption in such a manner though it is initially successful (Asami et al., 1999; Bao et al., 1999; Kirisits et al., 2000, 2001; Siddiqui et al., 2002). Bromate is formed by ozone-oxidation of bromide in the water environment, and is going to be a sole regulated byproduct of ozonation in 2004 in
Japan. The new regulation in Japan is 10 ppb, and considerable numbers of ozonation treatment plants may not meet the regulation under conventional conditions. Novel ozonation methods that have high performance and reduce bromate formation simultaneously are needed.

There have been numerous numbers of researches on methodologies for reducing bromate formation so far. Changing reaction pathways by addition of acids or ammonia are confirmed to be effective for bromate reduction (Hoffmann et al., 2001; Pinkernell et al., 2001). However, adding such chemicals is unacceptable in drinking water treatment processes. Employing lower ozone concentration and shorter retention time are effective as well (Song et al., 1997). However, these methods result in insufficient performance of ozonation. Therefore, it seems necessary to develop a novel ozonation with less bromate formation and high ozonaiiton performance. We have been developing novel ozonation processes using newly developed adsorbents, high silica zeolites (Sakoda et al., 2002; Fujita et al., 2004a,b). In conventional ozonation process, 2-MIB is contained in raw water with various compounds such as bromide and natural organic matters (NOMs). Furthermore, 2-MIB concentration is extremely low, normally less than 1 ppb. Therefore, decomposition rate of 2-MIB is extremely low, so high ozone doze is required for sufficient decomposition of 2-MIB. That is why substantial bromate is formed during ozonation under conventional conditions.

In our method, we employed high silica zeolites, which are hydrophobic and porous adsorbents. Target organic compounds such as 2-MIB are usually hydrophobic, adsorbed onto high silica zeolites, and concentrated in the micropores. The concentration raises reaction rate of 2-MIB with ozone (Fujita et al., 2004b). Because of the increase in decomposition rate, sufficient decomposition will be possible with lower ozone concentration and shorter retention time. Lower ozone concentration and shorter retention time enable bromate reduction simultaneously.

While, natural water, that is, drinking water sources contains various Natural Organic Matters (NOMs) of high concentration (normally in ppm level). The NOMs have strong influence on ozone consumption and adsorption of minor organic contaminants such as 2-MIB (normally in ppb level) onto adsorbents. In other words, the major challenge in the treatments of 2-MIB is diminishing the adverse effects of NOMs. Therefore, we should clarify the applicability of our process for natural water prior to the practical use.

The objectives of this work are, to investigate the adsorption of 2-MIB onto high silica zeolites, to elucidate the decomposition of 2-MIB with preventing the formation of bromate ion on such adsorbents, and to demonstrate the applicability of our process for natural water solution.

Experiments

Materials

High silica zeolites were porous materials with narrow pore size distribution, resulting in their molecular sieving function. These SiO₂/Al₂O₃ ratio means molar ratio of SiO₂ to Al₂O₃ in a crystal lattice and strongly relates to hydrophobicity. Four high silica zeolites, provided by Mitsubishi Heavy Industries, Ltd., Japan, were employed as adsorbents in this work. US-Y and ZSM-5 are typical high silica zeolites, and their pore sizes were close to 2-MIB molecular size. Since water dissolved ozone decomposes rapidly in the presence of hydroxy ions in water (Gurol et al., 1982), zeolite samples were rinsed well with a 2 N NH₄Cl solution before uses. The larger SiO₂/Al₂O₃ ratio is, the higher hydrophobicity is. This means that high silica zeolites are hydrophobic. Activated carbons are also hydrophobic and commonly used for adsorptive removal of organic pollutants in water treatments. However, activated
carbons react and are consumed by water-dissolved ozone (Fujita et al., 2004a). On the other hand, water-dissolved ozone is irreversibly adsorbed and desorbed onto/from high silica zeolites, and ozonation of co-adsorbed organics takes place in the adsorption phase (Fujita et al., 2004b).

2-Methylisoborneol (MIB), since it is one of the typical T&Os and the major concerns in Japan in drinking water treatment, was chosen as a model T&O chemical in this work. 2-MIB was purchased in crystal form from Wako Pure Chemical Industries, Japan. A stock solution of 70 ppb was prepared with glass-distilling purified water from a Milli-Q water purification system. Though the 2-MIB concentration in practical drinking water sources is usually lower than 1 ppb, a stock solution of 70 ppb was prepared and used in this work to clarify the fundamental adsorption and reaction taking place in the proposed process.

Natural water sample was obtained from a river, and kept at 4°C before using in experiments. Average dissolved organic carbon (DOC) concentration, pH, E260, and bromide ion concentration were 1.0 ppm, 7.1, 0.051 cm⁻¹, 0.1 ppm, respectively.

**Sample measurement**

The concentrations of 2-MIB were measured by a GC/MS system (GC-17B/QP-5000, Shimadzu, Japan) combined with solid phase extraction method (SPME). Ozone concentration was measured with the Indigo method. DOC was measured with a TOC analyzer (TOC-5000, Shimadzu, Japan). Bromate concentration was measured with Shimadzu LC-VP bromate analysis System (Shimadzu, Japan).

**Procedures**

*Batch adsorption experiment.* Adsorption of 2-MIB onto high silica zeolite in pure water was studied by a batch adsorption method. 2-MIB solutions and adsorbent were sealed in a 70 mL vial without a dead space for preventing 2-MIB from volatization. The vial was covered with aluminium foil to prevent the photodecomposition of 2-MIB, and shaken for 168 hours under 25°C. Thereafter, the 2-MIB concentration in the solution was measured to estimate the equilibrium adsorption.

Influence of NOMs in natural water on adsorption of 2-MIB onto US-Y zeolite was also examined by the same method. The 2-MIB solution was added to the natural water with a certain ratio, and poured into a 70 mL vial without a dead space. The concentration of 2-MIB in the solution was measured with elapsed time.

*Decomposition of 2-MIB in pure water.* 2-MIB decomposition rates were measured in the presence and absence of high silica zeolites in flow ozonation experiments. A schematic diagram of the experimental apparatus employed in this work is shown in Figure 1. First, 2-MIB solution was sealed in a glass syringe without void and fed into an adsorbent packed column by a syringe pump until whole adsorbent was equilibrated with influent 2-MIB concentration. After equilibrium reached, the effluent concentration, C (mg/L), was confirmed to be equal to the influent concentration, C₀ (mg/L). Then ozone and 2-MIB solutions were fed together. Gaseous ozone was produced by an ozone generator (POX-10, Fuji Electric Co., Ltd., Japan) and fed into 1 L of distilled water contained in a glass vessel, and its concentration was kept constant at a scheduled level. After introducing ozone solution, the effluent concentration of 2-MIB was measured with time elapsed until it become constant at Cₘ (mg/L) in a steady state. The remaining ratio of 2-MIB was defined as Cₘ/C₀. The defined remaining ratios were obtained for different adsorbents and different retention times.

Furthermore, decomposition of 2-MIB and bromate formation in pure water was simultaneously measured by employing lower dissolved ozone concentration of 0.07 mg/L.
and shorter retention time of 0.2 min using a high silica zeolite, US-Y. As shown in Figure 1, a bromide solution and a 2-MIB solution were fed into the column with ozone solution. Ozone, bromate, bromide, and 2-MIB concentrations were measured at the outlet of the column.

Applicability for natural water. Prior to the 2-MIB decomposition experiment in natural water, the ozone consumption by the adsorbed NOMs on zeolite (US-Y) was investigated. Natural water and ozone solution were fed simultaneously into a column packed with US-Y zeolite or glass beads using the apparatus shown in Figure 1. After the steady state was achieved, ozone concentration at effluent was measured. The ozone concentration at the head of column was fluctuated to clarify the ozone requirement to decompose the NOMs.

Decomposition of 2-MIB and simultaneous bromate formation in natural water was then investigated using the same apparatus. Natural water with artificially added 2-MIB was fed into the column with a certain concentration of ozone solution. After the steady state was achieved, concentrations of 2-MIB and bromate ion at effluent was measured.

Results and discussion

Adsorption of 2-MIB onto high silica zeolites

Adsorption isotherm of 2-MIB on high silica zeolites are shown in Figure 2, indicating that 2-MIB was not adsorbed at all onto ZSM-5. The result showed that simply molecular size of 2-MIB, 5.5–5.8, is larger than micropore size of ZSM-5, 5–5.5. On the other hand, 2-MIB was adsorbed onto various US-Y zeolites with SiO₂/Al₂O₃ = 5.4–70. The adsorption isotherms were linear, and the adsorption equilibrium constant, β, was defined by Eq. (1), meeting shapes of the isotherms.

\[ \beta \frac{q}{C} = 1 \]

where, \( q \) is the amount adsorbed (µg/mg-adsorbent) and \( C \) is equilibrium concentration (µg/L).

The time course of the concentration of 2-MIB in natural water containing solution was depicted in Figure 3. In early period, 2-MIB concentration in natural water containing solution was decreased as well as that of pure water. Then, the concentration in natural water containing solution was increased with time elapsed, and finally, the concentration was reached the initial concentration. This result indicated that 2-MIB compete its adsorption onto US-Y with NOMs. High diffusion rate of 2-MIB due to its small molecular size allows its rapid adsorption. Thereafter, NOMs replace the 2-MIB with its high adsorption affinity for US-Y.
**Enhancement of 2-MIB decomposition rate by adsorbents**

The 2-MIB decomposition rates by ozone with and without high silica zeolites are compared in Figure 4. Figure 4 shows that the decomposition rate was highly enhanced in the presence of US-Y zeolites. In the presence of US-Y zeolites, 1/100 lower dissolved ozone concentration of 0.07 mg/L than that without high silica zeolites still could decompose 2-MIB approximately 10 times faster. Furthermore, the larger SiO₂/Al₂O₃ ratio was, the faster 2-MIB decomposition rate was. It can be concluded that adsorption of 2-MIB onto high silica zeolites causes significant enhancement of 2-MIB decomposition rates.

**Prevention of bromate formation**

2-MIB remaining ratio and effluent bromate formation were compared in the presence and absence of adsorbents in Figure 5. In the absence of adsorbent with a retention time of 4 min, only 20% decomposition was achieved at ozone concentration of 7 ppm, and effluent bromate concentration was higher than a new regulation level, 10 ppb. On the other hand, in the presence of adsorbents, 1/100 lower dissolved ozone concentration and 1/20 shorter retention time made sufficient 2-MIB decomposition and prevention of bromate formation possible simultaneously. The process proposed in this work is very promising as a novel ozonation process significantly reducing bromate formation.

**Applicability for natural water**

The effluent 2-MIB concentration as a function of retention time in the column was depicted in Figure 6. 2-MIB was not decomposed at all when the ozone concentration at the head of the column was set as 0.80 mg/L, indicating that this feeding concentration is not sufficient to decompose 2-MIB in this system. In the case where the inflow ozone concentration was 4.18 mg/L, the rapid degradation of 2-MIB was observed when the retention time was more than 10 second. Suggested NOMs and 2-MIB profiles in the US-Y packed column under steady state is depicted in Figure 7. The upper side of the column was adsorbed by NOMs, which has high affinity for US-Y. This adsorbed NOMs was decomposed with ozone, and the adsorption site was regenerated with the flow. Therefore, 2-MIB become adsorbed onto US-Y, and also decomposed with ozone when chemical stoichiometrically sufficient ozone was fed. The bromate formation in this system is shown in Figure 8. A little formation of bromate was observed when 4.18 mg/L of ozone was fed, however the concentration was below the level of the Japanese new regulation (10 μg/L). This result indicated that our novel process has high applicability for drinking water treatment.
**Figure 3** Time course of 2-MIB concentration in batch adsorption experiment

**Figure 4** Enhancement of 2-MIB decomposition by adsorbent

**Figure 5** Sufficient 2-MIB decomposition and bromate formation reduction by adsorbents

**Figure 6** 2-MIB concentration as a function of retention time
Conclusion
The adsorption capacity of zeolite for 2-MIB was depend on its micropore structure and chemical property. Especially, the adsorption capacity of 2-MIB was increased with the SiO$_2$/Al$_2$O$_3$ ratio of US-Y. The decomposition rate of 2-MIB in adsorption phase significantly increases depending on the adsorption capacity. The decomposition of 2-MIB with preventing the formation of bromate was demonstrated with our proposed novel ozonation process using US-Y even in the treatment of natural water.

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References