Geosmin and 2-methylisoborneol adsorption on super-powdered activated carbon in the presence of natural organic matter

Y. Matsui, Y. Nakano, H. Hiroshi, N. Ando, T. Matsushita and K. Ohno

ABSTRACT

Geosmin and 2-methylisoborneol (2-MIB) are naturally occurring compounds responsible for musty-earthy-odors in surface water supplies. They are a severe problem confronting utilities worldwide. Adsorption by powdered activated carbon (PAC) is a widely used process to control this problem, but it has low efficiency, which engenders large budget spending for utilities services. Super-powdered activated carbon (S-PAC) is activated carbon with much finer particles than those of PAC. Experiments on geosmin and 2-MIB adsorptions on S-PAC and PAC were conducted. Geosmin and 2-MIB adsorption capacities on S-PAC were not smaller than those on PAC although natural organic matter, which adversely impacted the adsorption capacity of geosmin and 2-MIB, was more adsorbed on S-PAC than on PAC, meaning that the adsorption competition is less severe for S-PAC than for PAC.

Key words | competitive adsorption, humic substance, PAC, particle size, submicrometer, taste and odor

INTRODUCTION

Although taste and odor problems are not considered a direct threat to public health, they are perhaps the single greatest public relations issue confronting many water utilities because consumers generally rely on the taste of their water as the primary indicator of its safety (Wear 2006). Taste and odor are aesthetic qualities of drinking water. For that reason, their assessment depends on human perception. The human perception of taste and odor in drinking water depends on numerous factors, but tastes and odors are sometimes perceived at extremely low concentrations, typically for taste and odor problems caused by algae, mold, and bacteria. The major components within algae that give rise to tastes and odors are geosmin and 2-MIB. In Japan, geosmin and 2-MIB concentrations in tap water from drinking water suppliers are regulated by the drinking water quality standard to be less than 10ng/L, which are the lowest concentrations among all items.

The removal of geosmin and 2-MIB during water treatment is usually done by adsorption using activated carbon or oxidation by ozone. Among such methods, PAC is the simplest most widely applied method, but means that are more economical are anticipated (Newcombe & Cook 2002). The process of 2-MIB and geosmin adsorption onto PAC takes time, usually more than 1 h (Huang et al. 1996). Maximizing the contact time between PAC and water is critical, for efficiently utilize its adsorptive capacity of the PAC. Particle size reduction of PAC, which improves the adsorbate uptake rate, is another means for efficient utilization of its adsorptive capacity (Najm et al. 1990). Recently, activated carbon that is much finer than conventional PAC has become available: super-powdered activated carbon (S-PAC). In fact, S-PAC is far superior to PAC in removing geosmin and natural organic matter (NOM) (Matsui et al. 2004, 2007, 2009). However, the removal of 2-MIB, which has less affinity to activated
carbon than geosmin, has not yet been investigated. Moreover, characteristics of adsorptive removals of 2-MIB/geosmin by S-PAC, which adsorbs NOM more than PAC, remain unknown. In this paper, the adsorption equilibrium of 2-MIB/geosmin on S-PAC and PAC were investigated experimentally along with their adsorption in the presence of NOM.

**METHODS**

**Activated carbon**

Commercially available wood-based PAC (Taikou-W; Futamura Chemical Industries Co. Ltd., Gifu, Japan) was wet-ground to produce S-PAC using a wet bead mill (Metawater Co. Ltd.; Tokyo, Japan, Matsui et al. 2004). We used both the S-PAC and the as-received (i.e. normal) PAC. The S-PAC was stored in slurries (2.1 and 0.21%) with pure water at 4°C, as was the PAC (2.6 and 0.28%). The particle size distributions of S-PAC and PAC (Figure 1) were determined using laser-light scattering instruments (LMS-300; Seishin Co., Ltd., Tokyo, Japan).

**Water samples**

Hakucho and Suwannee humic acid waters were used as source waters containing NOM. The Hakucho water samples were collected from Lake Hakucho in Hokkaido, Japan, transported in polyethylene tanks, and stored at 4°C. The TOC and ultraviolet absorbance at 260 nm (UV260) served as parameters for bulk NOM quantification (TOC: Model 810; Sievers Instruments, Inc., Boulder, CO, USA; UV260: Model UV-240, Shimadzu Corp., Kyoto, Japan). The Suwannee humic acid water was prepared by dissolving Suwannee humic acid (International Humic Substance Society) in pure water (Milli-Q Advantage, Millipore Co.) after inorganic ions, which bring the ionic composition equal to that of water from Hakucho water. The molecular weight (MW) distributions of NOMs in the Hakucho water and Suwannee humic acid water were determined using liquid chromatography–organic carbon detection [HP1100 (Agilent Technologies, Inc., CA, USA); packed column GL-P252 (Hitachi, Ltd.); eluent: 0.02 M Na₂HPO₄ + 0.02 M KH₂PO₄]. Polystyrene sulfonate (MW 1800, 4600, and 8000) was used for calibration. The UV absorbance at 260 nm and TOC (Model 810 Turbo; GE Analytical Instruments) of the column effluent were measured continuously (see Table 1).

Single solute solutions of geosmin and 2-MIB were prepared respectively by diluting geosmin-MeOH liquid (Supelco, Sigma Aldrich Japan, Tokyo) and 2-MIB-MeOH liquid (Supelco, Sigma-Aldrich Japan, Tokyo) with pure water (Milli-Q Advantage, Millipore Corp., Billerica, MA, USA). Solutions of geosmin and 2-MIB in natural water were prepared respectively by diluting geosmin (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and 2-MIB (Wako Pure Chemical Industries, Ltd., Osaka, Japan) with pure water and natural water (Hakucho water or Suwannee humic acid water). All waters were filtered through a 0.2 µm pore size membrane before use. Geosmin and 2-MIB concentrations were adjusted to 100 ng/L. Geosmin and 2-MIB concentrations were analyzed using a Thermal Desorption System (TDS), a gas chromatography/mass spectrometer) (GC/MS), and the Stir Bar Sorptive Extraction (SBSE) method (Gerstel GmbH and Co. KG, Tokyo, Japan, and Agilent Technologies Japan, Tokyo) using deuterium-labeled geosmin (Hayashi Pure Chemical Ind., Ltd., Osaka, Japan) as an internal standard, or using a Purge and Trap Concentrator Coupled to the GC-MS (GCMS-QP2010 Plus; Shimadzu Corp., Kyoto, Japan; Aqua PT 5000 J, GL Sciences Inc., Tokyo, Japan).

**Table 1** | Properties of natural water samples

<table>
<thead>
<tr>
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<th>Hakucho water</th>
<th>Suwannee humic acid water</th>
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<tbody>
<tr>
<td>TOC</td>
<td>1.4 mg/L</td>
<td>1.6 mg/L</td>
</tr>
<tr>
<td>UV260</td>
<td>0.028 cm⁻¹</td>
<td>0.096 cm⁻¹</td>
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Figure 1 | Particle size distributions of S-PAC and PAC.
Batch adsorption tests

In adsorption equilibrium tests, aliquots (125 mL) from the 1 L solution containing each geosmin/2-MIB and PAC were transferred to 125-mL vials. Then the vials were agitated on a shaker for one week. In the preliminary experiment, it was confirmed that in one week geosmin/2-MIB adsorption equilibrium was reached and NOM adsorption equilibrium was almost reached.

After the water samples were filtered through a 0.2-μm membrane filter (DISMIC-25HP; Toyo Roshi Kaisha, Ltd., Tokyo), the water-phase of each geosmin/2-MIB concentration was measured using TDS-GC/MS and SBSE. The solid-phase of each geosmin/2-MIB concentration was calculated from the mass balance. They are shown against water-phase concentrations to obtain isotherm data. In the natural water system, the NOM concentration was evaluated by measuring the total organic carbon (TOC) concentration (Sievers 900 Laboratory TOC Analyzer; GE Analytical Instruments, Boulder, Colorado, USA).

RESULTS AND DISCUSSION

Geosmin and 2-MIB adsorption capacities of S-PAC and PAC

As presented in Figure 2, no large difference in geosmin adsorption capacity was observed between S-PAC and PAC although there was a tendency observed that adsorption capacity on S-PAC was slightly higher than on PAC. For 2-MIB, adsorption capacities were not clearly different between S-PAC and PAC, as shown in Figure 3. In contrast, for NOM, a higher adsorption capacity of S-PAC than on PAC was reported for natural organic matter (Matsui et al. 2004). The reason for the higher NOM adsorption capacity on S-PAC was not clear, but the effect of carbon particle size on the adsorption capacity differed depending on the adsorbates. Adsorption equilibrium data of Figure 2 also show that the geosmin adsorption capacity was smaller in natural water than in pure water. This resulted from adsorption competition between NOM and geosmin, where NOM reduced the adsorption capacity of geosmin. The extents of geosmin adsorption capacity reductions were similar between S-PAC and PAC. The geosmin adsorption capacity was also almost the same for S-PAC and PAC in the presence of NOM. Figure 4 shows adsorption isotherms of NOM in the presence of geosmin for S-PAC and PAC in terms of TOC. For both Hakuo water and Suwannee humic acid water, S-PAC showed higher NOM adsorption capacity than PAC, indicating that S-PAC adsorbed NOM more than PAC at a given dose. The geosmin adsorption capacity in natural water did not, however, differ between S-PAC and PAC. The geosmin adsorption capacity on S-PAC was decreased by the competitive effects of NOM, but the competitive effects are the same degree between S-PAC and PAC although S-PAC adsorbed the larger amount of NOM than PAC. In other words, the large amount of NOM adsorbed onto S-PAC exerted the same
degree of competition to geosmin adsorption as the small amount of NOM adsorbed onto PAC. A similar result was obtained for 2-MIB, as portrayed Figures 3 and 4. Therefore, the adsorption competition effect of NOM is expected to differ between S-PAC and PAC, and the adsorption competition effect is less severe on S-PAC than on PAC. The size reduction of carbon particle could be advantageous for removing both the NOM and the geosmin and 2-MIB by avoiding the adsorption competition effect.

Geosmin and 2-MIB adsorption in Hakucho and Suwannee humic acid waters

The initial TOC of Suwannee humic acid water (TOC, 1.6 mg/L) was higher than that of Hakucho water (TOC, 1.4 mg/L) in the adsorption experiments. It was therefore expected that the adsorption competition was more severe in Suwannee humic acid water than in Hakucho water. However, results show that the amounts of geosmin adsorbed onto S-PAC and PAC in the Hakucho water were about half of those in the Suwannee humic acid water, as presented in Figure 5. Therefore, NOM existing in the Hakucho water tends more to compete in adsorption with geosmin than NOM existing in the Suwannee humic water. One reason related to this different adsorption competition effect is the difference of the molecular weight distributions of NOMs in the Hakucho water and Suwannee humic acid water. The molecular weight of NOM contained in Hakucho water was lower than that of the Suwannee humic acid water, as depicted in Figure 6. Accordingly, Hakucho water probably has a greater tendency to compete in adsorption with low molecular weight compound of geosmin than Suwannee humic acid water. Moreover, Figure 4 presents that TOC adsorption capacity in the Hakucho water was greater than in the Suwannee humic acid water. These results indicate that natural water whose NOM adsorbs more on S-PAC and PAC might decrease the geosmin adsorption capacity more.

Comparison between the geosmin adsorption capacity and 2-MIB adsorption capacities

As shown in Figure 2, the geosmin adsorption capacity was decreased by one-fifth through adsorption competition by NOM of Hakucho water. However, according to Figure 3, the 2-MIB adsorption capacity was decreased more. It was decreased by one-tenth by the NOM. These results demonstrate that 2-MIB has a greater tendency to receive adsorption competition from NOM than geosmin. Geosmin has slightly lower MW than 2-MIB (geosmin 220 and
2-MIB 206 Da), which might cause geosmin to have less severe adsorption competition from NOM, which has large MW, because adsorbates of similar MW would have high competition. Overall, the NOM competition effect observed for 2-MIB and geosmin on S-PAC and PAC is not straightforward and remains to be resolved.

CONCLUSIONS

(1) Geosmin adsorption capacities on S-PAC and PAC were not very different: the capacity on S-PAC was slightly higher than on PAC. Carbon particle size reduction did not largely change the geosmin adsorption.

(2) Although S-PAC adsorbed NOM more than PAC, the adsorption capacity of geosmin in natural water did not largely differ between S-PAC and PAC. Increased NOM adsorption through carbon particle size reduction did not influence the geosmin adsorption capacity.

(3) Adsorption competition with geosmin was severer in natural water including NOM of the lower molecular weight.

(4) Findings described in conclusions (1)–(3) for geosmin were also obtained for 2-MIB.

(5) 2-MIB shows a greater tendency to have adsorption competition with NOM than geosmin does.

ACKNOWLEDGEMENTS

This study was supported by Grant-in-Aid for Scientific Research A(21246083) from the Ministry of Education, Culture, Sports, Science and Technology of the Government of Japan, by a research grant from the Ministry of Health, Labour and Welfare, and by Metawater Co., Tokyo, Japan.

REFERENCES


