Screening of powdered activated carbons to remove 2-methylisoborneol for drinking water

T. Watanabe, Y. Amano and M. Machida

ABSTRACT

A 95% confidence interval was estimated from 2-methylisoborneol (2-MIB) numbers, as an index of adsorption capacity described in this article, for 31 different powdered activated carbons (PACs) used for drinking water purification. The seven PACs selected in this study were chosen as five of them were within the 95% confidence interval and the other two PACs were not. The PACs were assessed based on previous studies, which represented the relationships between 2-MIB adsorption capacity and surface area, pore distribution, bulk oxygen content and surface oxygen functional groups. From the results, we assumed the 2-MIB adsorption mechanism and studied relationships between 2-MIB number and ash content of PAC or pH value of PAC slurry. It was shown that the 2-MIB number correlated with the ash content and the pH value. Easily measurable ash content and pH values would help a water supplier briefly screen PACs for removing 2-MIB at a water purification facility.

Key words | activated carbon, adsorption, drinking water, 2-methylisoborneol (2-MIB), odor compound

INTRODUCTION

Chlorine, coagulants and activated carbons are employed as purification materials in waterworks sites. Activated carbons especially play an important role to remove dissolved organic contaminants, such as typical odor compounds of 2-methylisoborneol (2-MIB) and geosmin, surfactants, phenols, trihalomethanes and their precursors, volatile organic compounds like trichloroethylene, trace amounts of harmful substances such as pesticides and other accidentally contaminated compounds in rivers and lakes (JWWA 2003). Recently, huge amounts of powdered activated carbons (PACs) have been used for adsorptive removal of 2-MIB and geosmin at water treatment plants.

Previous studies have already revealed many relationships between 2-MIB adsorption capacity and properties of activated carbons, which include pore size distribution, oxygen content and surface functional groups (Newcombe et al. 1997; Pendleton et al. 1997; Considine et al. 2001). These studies are available for the synthesis of activated carbon. However, in water purification facilities whether the activated carbon is useful or not must be determined as soon as orders are delivered.

The adsorption capacity of activated carbon can be affected by some specific oxygen functional groups on the carbon surface as observed by Pendleton et al. (1997) and Considine et al. (2001). This is because a stable water cluster can be formed around the acidic groups via hydrogen bond (Franz et al. 2000; Ania et al. 2007) and block the entrance of the pore mouth (Kato et al. 2008; Li et al. 2009). The specific oxygen functional groups are supposed to lower the pH value of the slurry of activated carbon. Similarly, the metal compound contained in activated carbon would form the stable water cluster and the ash content of activated carbon can be measured as an alternate method of metal quantitative analysis in activated carbon. Both pH value and ash content are detected easily and
could be useful as a brief screening for activated carbon in water purification facilities.

However, the relationships between 2-MIB adsorption capacity and pH value of PAC slurry or ash content has not been investigated as yet.

The purpose of this study is to examine the relationships between 2-MIB adsorption capacity and pH value of PAC slurry, ash content or the other properties of PACs based on previous studies (Newcombe et al. 1997; Pendleton et al. 1997; Considine et al. 2001). In addition, a brief method for screening PACs to remove 2-MIB is suggested based on the experimental results.

In this study, seven PACs were examined to elucidate the relationships between adsorption capacities of 2-MIB and the properties of PACs. Of the seven PACs selected, five were within a 95% confidence interval of the 2-MIB number as described in the section below and the other two PACs were not. The 95% confidence interval was estimated from 2-MIB numbers of the 31 different PACs that were used for the purification of tap water and have already been studied elsewhere (Watanabe et al. 2010). The seven PACs were analyzed to inspect pore distribution, ash content, elemental analysis, surface functional groups and pH value of PAC slurry.

MATERIALS AND METHODS

Since 2-MIB adsorption is known to be more sensitive to the nature of activated carbons than geosmin (Sugiura & Nishimura 1997), 2-MIB was employed to study adsorption onto PACs.

Thirty-one PACs used in the process of tap water production had already been investigated to obtain 2-MIB numbers. The 2-MIB numbers of these 31 PACs were used for statistical analysis and the 95% confidence interval was estimated as described in the section below (Watanabe et al. 2010). The examples belonging to the 95% confidence interval were confirmed as better performing the removal of 2-MIB in natural water (Watanabe et al. 2010). The seven PACs examined were divided into two groups: five belonging to the 95% confidence interval and the other two not. The five PACs (AC-3, AC-4, AC-5, AC-6 and AC-7) were basically selected randomly but a high amount of available samples were employed from the 31 PACs to represent a sufficient 2-MIB adsorption capacity. The two PACs (AC-1 and AC-2) were selected to represent PACs with insufficient 2-MIB adsorption capacity because of significantly weak adsorption capacity in environmental water (Watanabe et al. 2010).

The 7 PACs (AC-1, AC-2, AC-3, AC-4, AC-5, AC-6 and AC-7) were characterized by the bulk and surface properties of BET surface area, pore distribution, ash content, elemental composition, surface functional groups and pH value of PAC slurry as well as 2-MIB number. All chemicals supplied to the study were regent grade purchased from Kanto Chemical Co., Inc.

Furthermore, two treated PACs were prepared to confirm the relationship between 2-MIB number and pH values of PAC slurries and also other two treated PACs were prepared to confirm the relationship between 2-MIB number and ash content.

De-ashing treatment (DA) was performed for AC-1 and AC-2 to control the amount of ash content. AC-1 and AC-2 were used for the purpose because they had a high ash content. AC-2 was applied in spite of the effect of the other surface properties of AC-1 and AC-2 because high ash content PACs were less commonly available. For the removal of ash from PAC, CH₃COOH treatment was used because ash content could be removed while no alteration of the nature of the surface takes place (Blackburn & Kipling 1955). Mixtures of PACs with 10 and 20% CH₃COOH were each stirred for 5 h. After CH₃COOH treatment, the PACs were repeatedly washed by boiled de-ionized water. The PACs were then dried at 110 °C overnight. The PACs obtained in this DA process were named AC-1-DA10, AC-1-DA20, AC-2-DA10 and AC-2-DA20.

Out-gassing treatment (OG) was performed for AC-3 to control the amount of functional groups for the purpose of confirming the relationship between 2-MIB number and pH values of PAC slurries. AC-3 was right for the purpose because AC-3 has the highest amount of oxygen functional groups and the adsorption capacity was not affected by the other surface properties of AC-3.

AC-3 was heated under He flow with a flow rate of 150 mL/min for 10 and 20 min after the temperature reached 300 °C. After this process, the PACs were cooled...
to room temperature under He flow. These PACs were named AC-3OG10 and AC-3OG20, respectively.

Adsorption of 2-MIB onto activated carbon

Adsorption capacity of 2-MIB

The removal of 2-MIB from the test water was investigated at 25°C. Six 200 mL conical flasks with stopper including 50 mL of 800 ng/L 2-MIB standard solution were prepared and 0, 1, 2, 5, 10 and 20 mL of 200 mg/L PAC slurry were added to them. All solutions were diluted accurately to 200 mL with de-ionized water. The seven 200 mL solutions were agitated at 100 to 200 rpm for 1 h. After the mixed solutions were quietly placed for 30 min, the 2-MIB solution was separated from PACs by pressure filtration and 2-MIB was measured by the GC/MS system.

Determination of 2-MIB number

The adsorption characteristics were studied in terms of 2-MIB number (the amount of activated carbon required for 90% removal of 2-MIB, which indicates the ability of the activated carbon to remove 2-MIB), defined as the mass of adsorbent required to reduce the concentration of 2-MIB/L water from 200 to 20 ng/L (JWWA 2005). A lower 2-MIB number implies that it is more suitable for 2-MIB adsorption.

Properties of PACs

BET surface area and pore distribution

For the surface area measurements, 0.1 g of PAC was placed in a glass tube and outgassed in vacuum at 300°C for 90 min as a pretreatment with a Beckman Coulter Model SA-3100. Nitrogen adsorption and desorption isotherms at −196°C were measured for the outgassed PACs to calculate the BET specific surface area and pore distribution using the αs-plots method.

Ash content

Each 1 g of PACs after drying in an oven at 110°C was put into a ceramic plate and incinerated in air at 750°C for 2 h to completely combust the carbon. The ash content (%), \( Y_{ash} \), was determined by:

\[
Y_{ash} = \left( A/A_0 \right) \times 100, \tag{1}
\]

where \( A_0 \) and \( A \) are the amounts of dried carbon and ash after incineration, respectively.

Elemental composition

The elemental analysis was conducted with a Perkin-Elmer PE2400 CHN Elemental Analyzer. One milligram of PAC dried at 110°C for 1 h was enclosed in a tin capsule and incinerated at 980°C to convert the C, H and N elements to CO₂, H₂O and NOₓ, and the NOₓ was further reduced to N₂ to be measured quantitatively by a thermal conductive detector (TCD). Assuming that the incinerated materials in the PACs consisted of C, H, N and O elements, the oxygen content was determined by difference.

Surface functional groups

The surface functional groups on the carbon surface were determined based on the Boehm titration method (Boehm & Knoezinger 1985). Five hundred milligram of the PACs and 15 mL of NaHCO₃ (0.1 mol/L), Na₂CO₃ (0.05 mol/L) or NaOH (0.1 mol/L) solution were each mixed in conical flasks. These were agitated by 100 rpm for 5 days at 25°C and 5 mL aliquot of the solution for each sample was back titrated with HCl (0.1 mol/L). NaHCO₃ neutralizes only carboxylic groups on the carbon surface, Na₂CO₃ does carboxylic and lactonic groups and NaOH reacts with carboxylic, lactonic and hydroxyl groups. Accordingly, the difference between the groups neutralized by NaHCO₃ and Na₂CO₃ become lactones, and the difference between those neutralized by Na₂CO₃ and NaOH are hydroxyls. The same procedure was carried out for the mixtures of 0.5 g of the carbons and 15 mL of HCl (0.1 mol/L) solution to determine the basic sites of the carbon surface. After an excess amount of NaOH (0.1 mol/L) solution was added to the remaining HCl solution, the NaOH solution was back titrated with HCl (0.1 mol/L) solution again. Neutralization points were detected using methyl red solution as an indicator for weak base titrated with strong acid, and
phenolphthalein solution for strong acid and strong base combination (Kato et al. 2008).

**pH value of slurry of activated carbon**

We prepared the slurry, i.e., 0.1 g of PAC was added to 50 mL de-ionized water and treated by ultrasonic bath for 1 h. Then, the pH value of the slurry was measured with a portable pH meter (Model D-51 Horiba).

**RESULTS AND DISCUSSION**

**Adsorption capacity of PACs for 2-MIB**

Table 1 shows the statistical analysis results of 2-MIB numbers for 31 different activated carbons used for drinking water purification. The 95% upper confidence limit ($\mu + 2\sigma$) was estimated to be 5.0. Seven PACs were selected in this study: five PACs within and two PACs without the upper confidence limit.

Table 2 shows the 2-MIB number obtained for the seven PACs, which represents the PAC amount required to reduce the 2-MIB from 200 to 20 ng/L. AC-1 and AC-2 exhibited poor capabilities of 2-MIB adsorption in the seven PACs.

Table 2 shows the 2-MIB numbers of AC-1 and AC-2 to be 5.9 and 8.9, respectively, which were beyond the 95% upper confidence limit of 5.0 (Table 1). This result revealed that the two PACs clearly exhibited lower capacities compared to the other five PACs and were not sufficient for water purification. In the present study, the seven PACs including AC-1 and AC-2 were characterized to elucidate the difference in the properties and find suitable parameters correlated with 2-MIB adsorption capacity.

**Properties of PACs**

**BET specific surface area**

Textural properties of surface area and pore distribution for the seven PACs are represented in Table 3. BET specific surface area of the PACs ranged from 930 to 1,150 m²/g, except for AC-2 which was 620 m²/g. The meso- and macropore areas of the seven PACs were within a narrow range between 210 and 320 m²/g for all PACs, while the micropore areas were in the broad range from 400 to 850 m²/g. Though the meso- and macropores do not provide strong adsorption sites compared with micropores, they play an important role in the capillary condensation of adsorbates so as to efficiently introduce the adsorbates into the micropores. It is generally known that the adsorbates are restricted to diffuse in the micropores. This is the reason that the adsorption is stronger

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Statistical analysis of 2-MIB number for the activated carbons</th>
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<tbody>
<tr>
<td>Number of samples (N)</td>
<td>31</td>
</tr>
<tr>
<td>Maximum value</td>
<td>6.0</td>
</tr>
<tr>
<td>Minimum value</td>
<td>1.0</td>
</tr>
<tr>
<td>Sample mean ($\mu$)</td>
<td>2.77</td>
</tr>
<tr>
<td>Sample standard deviation ($\sigma$)</td>
<td>1.12</td>
</tr>
<tr>
<td>Upper confidence limit ($\mu + 2\sigma$)</td>
<td>5.0</td>
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<tr>
<th>Table 2</th>
<th>2-MIB number for the 7 PACs, OG PACs and DA PACs determined by the Japan Water Works Association (JWWA) K113 method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>2-MIB number</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
</tr>
<tr>
<td>AC-1</td>
<td>5.9</td>
</tr>
<tr>
<td>AC-2</td>
<td>8.9</td>
</tr>
<tr>
<td>AC-3</td>
<td>4.5</td>
</tr>
<tr>
<td>AC-4</td>
<td>3.6</td>
</tr>
<tr>
<td>AC-5</td>
<td>3.4</td>
</tr>
<tr>
<td>AC-6</td>
<td>3.4</td>
</tr>
<tr>
<td>AC-7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Specific surface area and pore distribution of the activated carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered activated carbon</td>
<td>BET specific surface area, m²/g</td>
</tr>
<tr>
<td>AC-1</td>
<td>980</td>
</tr>
<tr>
<td>AC-2</td>
<td>620</td>
</tr>
<tr>
<td>AC-3</td>
<td>1,010</td>
</tr>
<tr>
<td>AC-4</td>
<td>1,150</td>
</tr>
<tr>
<td>AC-5</td>
<td>930</td>
</tr>
<tr>
<td>AC-6</td>
<td>940</td>
</tr>
<tr>
<td>AC-7</td>
<td>960</td>
</tr>
</tbody>
</table>
with a reduction in the interaction potential between adsorbates and surface of the adsorbent as the pore diameter is decreased (Kondo et al. 2003). Tennant & Mazyck (2007) pointed out that the whole pore volume of PAC had a good linear relationship with the adsorption capacity of 2-MIB. In contrast, Yu et al. (2007) reported that the micropore was principally correlated to the adsorption amount of 2-MIB and meso- and macropore distribution hardly affected 2-MIB adsorption. The contradiction between Tennant & Mazyck (2007) and Yu et al. (2007) was caused by a disregard of the balance of meso- and macropore introduction efficiency and micropore interaction potential efficiency. Since the variation of meso- and macropore area was relatively small in the present study, the influence of the pore on the 2-MIB adsorption capacities would be small. Figure 1 shows the relationship between 2-MIB number and micropore specific surface area. Considering micropore surface area, the lower adsorption capacity of 2-MIB for AC-2 might be caused mainly by the lower micropore surface area; the adsorption sites for 2-MIB might not be sufficient on the AC-2 surface.

Ash content and elemental composition

Results of ash content and elemental analysis are displayed in Table 4. The ash content ranged from 5.7 to 8.1% except 17.3 and 25.8% for AC-1 and AC-2, respectively. Ash is an impurity of activated carbon and is composed of metal oxides that are hydrophilic on the surface whereas carbon surface are known as hydrophobic in general (Blackburn & Kipling 1955). Hence, the lower 2-MIB adsorption capacity of AC-1 and AC-2 also might be attributed to some extent, to the higher ash content, though significant influence of ash in the carbons on the adsorption of 2-MIB has not been reported in the literature.

To further investigate the effect of ash on 2-MIB removal, the considerable correlation between 2-MIB number and ash content is shown in Figure 2. The 2-MIB numbers of AC-5 and AC-6 were lower and that of AC-3 was higher against ash content. The reason for this could be attributed to the fact that AC-5 and AC-6 had less amount of total acidic groups and AC-3 had a considerable amount of total acidic groups, as described further below.

Oxygen content

Variation of carbon, hydrogen and nitrogen content was supposed not to significantly influence the 2-MIB adsorption capacity of the seven PACs because of the similar content for these elements in this study. On the other hand, oxygen content, especially surface acidic oxygen functional groups, has been recognized to greatly affect the adsorption capacity of aromatic compounds in aqueous solutions (Machida et al. 2006;
Sato et al. (2007). Pendleton et al. (1997) found a correlation between oxygen content of PAC and hydrophilic nature, and pointed out that hydrophilic PAC decreased the hydration enthalpy, resulting in stable adsorption of water preventing the hydrophobic 2-MIB from exchanging with a water molecule. In the five PACs other than AC-1 and AC-2 in Table 2, the 2-MIB number for AC-3 was greater than the other four PACs, reflecting relatively high oxygen content of 10.8% as indicated in Table 4 despite sufficient surface area. By contrast, the 2-MIB number of AC-4 was 3.6, lower than that of AC-3 by almost 1.0, even though oxygen content of 11.2% for AC-4 was greater than 10.8% for AC-3.

**Effect of surface functional groups**

Yu et al. (2007) indicated that ether and carbonyl groups on the carbon surface had no influence on the adsorption of 2-MIB. By contrast, Considine et al. (2001) indicated that oxygen content correlated with 2-MIB adsorption. This contradiction was associated with the reason of the difference in 2-MIB adsorption. The difference in 2-MIB adsorption between AC-3 and AC-4 could be attributed to some specific oxygen functional groups on the carbon surface rather than bulk oxygen content as observed by the adsorption of nitrobenzene (Kato et al. 2008). The surface acidic functional groups and basic sites obtained by Boehm titration are tabulated in Table 5.

The total acidic groups for AC-1, AC-3 and AC-4 were greater than those for the other PACs. Since the pKₐ values of carboxylic, lactonic and phenolic groups are smaller than other C-O complexes on the carbon surface, these groups tend to easily release the proton to the aqueous solution and have polarity. Therefore, the resultant surface acidic functional groups become hydrophilic sites leading to the stable water cluster formation around the acidic groups via hydrogen bond (Franz et al. 2000; Ania et al. 2007). The water cluster covers the entrance of the pore mouth and prevents compounds from entering inside (Kato et al. 2008; Li et al. 2009). Therefore, 2-MIB could not get inside the PAC particles, even if a small amount of carboxylic, lactonic and phenolic groups are present on the surface.

Figures 3 and 4 show the plots of 2-MIB number against the bulk oxygen content and the amount of total acidic groups, respectively. Both figures show that 2-MIB numbers on AC-1 and AC-2 had considerably higher values than the others. This would be the reason that AC-1 was strongly affected by ash content and AC-2 was strongly affected by both micropore shortage and ash content.

Figure 3 shows that the 2-MIB number did not correlate with bulk oxygen content. However, Figure 4
shows that the 2-MIB number clearly correlates with total acidic groups except the plots of AC-1 and AC-2. AC-1 and AC-2 were eliminated from the plots for the linear approximation in Figure 4, because of the reasons above mentioned. It was also clear that the ash content was only an affecting factor of 2-MIB adsorption on AC-1, because AC-1 had almost the same conditions of specific surface area and amount of total acidic groups compared with the samples used for the linear approximation. Additionally, AC-4’s highest specific surface area (Table 3) explains that AC-4 is slightly below the linear approximation in Figure 4.

Consequently, the total amounts of carboxylic, lactonic and phenolic groups on the PACs are considered to significantly affect 2-MIB removal from the aqueous solutions. Furthermore, the 2-MIB adsorption capacity is influenced by acidic functional groups rather than bulk oxygen content.

**pH values of slurry solution of activated carbons**

The variation of total acidic groups is associated with pH change of the slurry solution of activated carbons. The pH values of PAC slurries are also tabulated in Table 5. Figure 5 shows the relationship between total acidic groups and pH values. The pH values are supposed to be reflected principally by the acidic functional groups. However, AC-4 is strongly different from linear approximation. This could be attributed to the high rate of phenolic group amount shown in Table 5 because pKₐ of

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**Figure 3** | Relationship between 2-MIB number and percentage of oxidant content rate.

**Figure 4** | Relationship between 2-MIB number and amount of total acidic group values.

**Figure 5** | Relationship between total acidic groups and pH values of PAC slurries.

**Figure 6** | Relationship between 2-MIB number and pH values of PAC slurries.
the phenolic group is higher than those of the carboxylic and lactonic groups. The pH values did not correctly reflect the amount of total acidic groups. However, pH value measurement for PAC slurries proved useful as an alternative indicator though each amount of the acidic groups would influence the pH values to some extent. Furthermore, it is supposed that the 2-MIB number correlates with the pH value of PAC slurries (Figure 6). The linear approximation shows that the 2-MIB number correlated with pH value except for AC-1 and AC-2, for the reason described above.

**Application for brief screening of activated carbon**

The measurements of ash content and pH value of PAC slurry are quite easy and their combination can be practically applied for the first screening of the PACs which are supplied to water purification facility. For example, PACs exhibiting ash content more than 10–15% and pH value less than 9.0 at the same time, or whichever extreme over the threshold value, may be distinguished from appropriate PACs for 2-MIB removal.

**CONCLUSIONS**

Based on the analysis of 2-MIB number as well as characterization of bulk and surface nature for PACs, the following suggestions may be drawn for screening PACs to remove 2-MIB in aqueous solution effectively at a water purification facility.

1. The specific surface area, surface functional groups and ash content were found to affect the 2-MIB removal, from the results obtained in this study.
2. The results of Boehm titration indicated that surface carboxylic, lactonic and phenolic groups of PACs significantly influenced the 2-MIB removal rather than bulk oxygen content, which could also be supported and observed by other similar aqueous systems reported in the literature.
3. The pH value of PAC slurry was proved useful as an alternative indicator for the amount of the surface acidic functional groups on the carbon.
4. Easily measurable pH value of PAC slurry and ash content can be utilized in practice for brief screening methods of PACs to remove 2-MIB in aqueous solution at a water purification facility.

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