Prediction of powdered activated carbon doses for 2-MIB removal in drinking water treatment using a simplified HSDM approach

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HIGHLIGHTS

- We propose a simplified approach to quickly determine PAC dose for 2-MIB removal.
- After simplification, HSDM parameters were obtained by only one kinetic experiment.
- The Freundlich 1/n value for the approach was assumed to be in a range of 0.2–0.6.
- The simplified approach well predicts the data for 5 PACs in 3 source waters.
- The approach was further validated with the data collected from one full scale WTP.

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ABSTRACT

The addition of powdered activated carbon (PAC) is an effective measure to cope with seasonal taste and odor (T&O) problems caused by 2-methylisoborneol (2-MIB) and trans-1, 10-dimethyl-trans-9-decalol (geosmin) in drinking water. Some T&O problems are episodic in nature, and generally require rapid responses. This paper proposed a simplified approach for the application of the homogenous surface diffusion model (HSDM) to predict the appropriate PAC doses for the removal of 2-MIB. Equilibrium and kinetic experiments were performed for 2-MIB adsorption onto five PACs in three source waters. The simplified HSDM approach was compared with the experimental data, by assigning the Freundlich 1/n value in the range of 0.1–1.0 and obtaining the Freundlich equilibrium parameter K value through a 6-hr adsorption kinetic test. The model describes the kinetic adsorption data very well for all of the tested PACs in different source waters. The results were validated using the data obtained from one full scale water treatment plant, and the differences between the predicted and observed results were within 10% range. This simplified HSDM approach may be applied for the rapid determination of PAC doses for water treatment plants when faced with 2-MIB episodes in source waters.

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1. Introduction

Lake and reservoir source waters often experience periodic odor episodes (Suffet et al., 1996; Watson et al., 2008; Watson, 2003; 2004). Although this is typically an aesthetic issue, water companies often have to invest considerable amounts of money in response to customer complaints caused by the resulting taste and odor (T&O) problems (Suffet et al., 1996). 2-Methylisoborneol (2-MIB) and trans-1, 10-dimethyl-trans-9-decalol (geosmin), two secondary metabolites of some cyanobacteria and actinomycetes (Wilkins, 1996; Zaitlina and Watson, 2006; Wu and Duirk, 2013), are the most frequently encountered odorants in drinking water. These two compounds can impart an earthy/musty odor, may be perceived even at levels as low as 10 ng/L (Watson et al., 2000), and are not readily removed by conventional water treatment processes (Lin et al., 2002; Ho et al., 2007, 2012; Zamyadi et al., 2015). However, addition of powdered activated carbon (PAC) has been demonstrated to be an effective approach to dealing with the...
Adsorption of 2-MIB/geosmin onto PACs in natural water strongly depends on the properties of activated carbon used (Lalezary-Craig et al., 1988; Pendleton et al., 1997; Newcombe et al., 2002; Yu et al., 2007) and the compositions of natural organic material (NOM) in the water (Lalezary-Craig et al., 1988; Chen et al., 1997; Newcombe et al., 1997). The properties of PAC, including surface functional groups and pore structure have been considered as the factors influencing the adsorption capacity of trace organic compounds onto PACs (Lahaye, 1998; Radovic et al., 1997). More recently, micropore volume has been proposed to be an effective indicator to estimate the adsorption for 2-MIB/geosmin onto PAC (Newcombe et al., 2002; Nowack et al., 2004; Yu et al., 2007). NOM is known to suppress the adsorption capacity of targeted organic compounds onto PAC during adsorption processes (Newcombe et al., 1997). For water treatment scenarios, the concentrations of contaminants of interest such as 2-MIB/geosmin and atrazine are at ng/L to μg/L level, and are significantly lower than that of NOM, usually at mg/L level. Under this condition, the removal ratios of 2-MIB/geosmin by PAC in NOM-laden natural water under equilibrium condition was found to be independent of initial 2-MIB/geosmin concentration and only dependent on carbon dose (Gillogly et al., 1999; Graham et al., 2000). This relationship could be simulated with bi-solute ideal adsorbed solution theory (IAST) (Knapp et al., 1998; Graham et al., 2000), in which NOM and the targeted compound are considered as two solutes.

In water treatment plants, the typical contact times of PAC are in the order of 1 h, which is much less than the equilibrium time for PAC adsorption. Therefore, adsorption kinetics should be considered for PAC application. Although the observation of 2-MIB/geosmin removal ratio being independent of initial concentration has been extended to non-equilibrium conditions for PAC adsorption in natural water (Matsui et al., 2001, 2002, 2003; Zoschke et al., 2011), to determine an appropriate PAC dose, multiple experiments are needed for different PAC doses for a specific natural water. Homogeneous surface diffusion model (HSDM), developed based on the diffusion of adsorbed adsorbate molecules on the surface of internal pores within adsorbent particles (Crittenden and Weber, 1978), has been successfully employed to simulate the adsorption kinetics of a range of compounds, including 2-MIB/geosmin onto activated carbon (Sontheimer et al., 1988; Najm et al., 1991; Huang et al., 1996; Gillogly et al., 1998). The model makes it possible to predict the carbon doses required for drinking water treatment and has been tested in several studies (Najm et al., 1991; Huang et al., 1996; Gillogly et al., 1998, 1999; Graham et al., 2000). Gillogly et al. (1998) studied the adsorption of 2-MIB onto five PACs in Lake Michigan water, and demonstrated that the PAC doses required for any contact time of interest may be quickly determined with the HSDM. Similarly, Cook et al. (2001) successfully employed the HSDM to predict the PAC doses required to reduce 2-MIB and geosmin concentrations to below 10 ng/L in three of the four waters in Adelaide, South Australia. The only poorly predicted case was attributed to higher turbidity in the studied water, which made PAC incorporate into a larger, denser floc, leading to a reduced effective contact time of the adsorbent (Cook et al., 2001).

When applying the HSDM, the surface diffusion coefficient ($D_s$) and the two Freundlich isotherm constants ($K$ and $1/n$) need to be known in advance. Adsorption of 2-MIB and geosmin onto activated carbon is known to be influenced by the type of adsorbent and water matrix (Knapp et al., 1998; Summers et al., 2013). Therefore, for each source water/PAC combination, experiments are needed to obtain $D_s$, $K$, and $1/n$. At least one adsorption kinetic experiment is required for the determination of $D_s$, and three equilibrium experiments for $K$ and $1/n$ as demonstrated in previous studies (Gillogly et al., 1998; Cook et al., 2001). These adsorption tests may generally take several days to reach equilibrium, due primarily to the slow diffusion process of the adsorbates within the intraparticle pores (Gillogly et al., 1998). It is therefore desirable if the number of adsorption tests can be reduced and time required for the experiments can be shortened for a faster response. Huang (Huang et al., 1996) suggested that the three HSDM parameters, $D_s$, $K$ and $1/n$, could be extracted from fitting the data of three kinetic tests, which may significantly reduce the effort required for the equilibrium experiments. However, the model was only tested with one PAC and one source water. In addition, three parameters were adjustable in the model fitting, making the calculation more complicated.

Table 1 summarizes the values of $1/n$ for the adsorption of 2-MIB onto the PACs reported in the literature. As indicated, the values normally fall into the range of 0.1–1.0 and between 0.2 and 0.5 for almost all the cases in natural water. If assigning a $1/n$ value within the above range, the Freundlich $K$ may be estimated from the adsorption capacity data obtained from the plateau values at the end of the kinetic experiments. Then $D_s$ value is the only adjustable parameter in the model, and can be optimized through minimizing the differences between the data obtained in the kinetic test and those predicted by the model. In this study, the feasibility of this simplified approach for the use of HSDM for 2-MIB removal was tested with different PAC/source water combinations, and further verified using the field data collected from a full scale water treatment plant during a 2-MIB episode. The results of this study could provide a simple approach to quickly determine the appropriate carbon dose for controlling seasonal odor problems in waterworks.

2. Material and methods

2.1. Materials

2-MIB. 2-MIB was purchased from Sigma-Aldrich Co., USA, at a concentration of 10 mg/mL in methanol. Stock solutions of 1 mg/L were prepared by diluting the methanol solution with ultra-pure water (resistivity $\geq 18$ m cm$^{-1}$).

Natural waters. Three natural waters collected from Taiwan (Fengshen Reservoir and Chengching Lake) and mainland China (Miyun Reservoir) were used in batch adsorption experiments. The pH was 7.5, 8.1 and 7.9, and the dissolved organic carbon was 2.8, 1.3 and 2.1 mg/L, respectively.

Powdered activated carbons. Five commercial powdered activated carbon (PACs) products were used in the adsorption experiments, including three coal-based ones: (WPH_PAC, Calgon Carbon Corp., USA; SX_PAC, Shaxi Xinhua Carbon Corp., China; NX_PAC, Ningxia Taixi Carbon Corp., China), a wood based one (TAC_PAC, Taiwan Active Carbon Industry Co.), and one used in Fengshen Water Treatment Plant (FS_PAC). Prior to batch experiments, the PAC samples were washed using ultra-pure water, dried overnight at 110 °C to remove excess water, and then cooled and stored in a desiccator. Physical characterization of the PACs was conducted using a surface analyzer (ASAP, 2010; Micromeritics, USA), and the data are shown in Table 2.

2.2. Equilibrium adsorption test

The bottle-point technique was used for the adsorption isotherm tests. Water samples containing 2-MIB were acquired by spiking the stock solution to the natural waters. PAC slurry was prepared by mixing 10 g oven-dried PAC in 1 L ultra-pure water before adding into the water samples. The carbon doses varied...
between 2 and 30 mg/L. The bottles were sealed and agitated on a rotary mixer for 4 days to reach adsorption equilibrium (Graham et al., 2000), and the solutions were filtered immediately using glass fiber membranes (Whatman GF/C, UK). The final 2-MIB concentrations were determined immediately by using headspace solid phase microextraction (SPME) combined with gas chromatography/mass spectrometry (GC/MS). The detection limit was 6 ng/L for 2-MIB.

### 2.3. Kinetic adsorption test

2-MIB was spiked into a 6-L glass container with natural water samples. After 15 min of mixing, the first sample was taken to determine the initial 2-MIB concentration. Following addition of PAC, water samples were taken at predetermined intervals over a period of 6 h, and filtered immediately using glass fiber membranes (Whatman GF/C, UK) for 2-MIB analysis.

### 2.4. Procedure to determine HSDM parameters

In HSDM, adsorbed adsorbate molecules are assumed to transport through diffusion on the pore surface within adsorbent particles. During the transport, a local equilibrium is assumed to be instantaneously established between the adsorbate in the pore fluid and that on the pore surface. For a spherical adsorbent particle, the HSDM can be expressed as Eq. (1) (Sontheimer et al., 1988):

$$\frac{dq}{dr} = D_t \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right)$$

Assuming no external film resistance for the mass transfer of adsorbate molecules, Eq. (1) can be numerically solved by setting the initial and boundary conditions as follows:

$$t = 0, \ q = 0$$

$$r = 0, \ \frac{\partial q}{\partial r} = 0$$

$$r = R_p, \ q = K (C)\frac{1}{n}$$

where \( r \) is the radial coordinate of the adsorbent, \( R_p \) is the radius of the adsorbent particle, \( D_t \) is the diffusion coefficient of the adsorbate on the surface of intraparticle pores, \( q \) is the solid-phase concentration of the adsorbate, \( q_s \) is the solid-phase concentration of the adsorbate at the surface of the particle \( (r = R_p) \), \( C_s \) is the fluid-phase concentration of the adsorbate in the bulk fluid, \( t \) is the adsorption time, and \( K \) and \( 1/n \) are Freundlich isotherm constants.

The HSDM algorithm employed in this study was modified from the numerical BATCH code developed by Tien, (1994). The equations to link water and solid phases are listed below.

$$\frac{dC}{dt} = -m \frac{dq_{avg}}{dt}$$

$$q_{avg} = \frac{3}{R_p^2} \int_0^{R_p} r^2 q(r, t) dr$$

### Table 1

Summary of some of the reported Freundlich parameters for PAC adsorption of 2-MIB in waters.

<table>
<thead>
<tr>
<th>Water samples</th>
<th>TOC (mg/L)</th>
<th>Initial concentrations (ng/L)</th>
<th>Equilibrium concentration (ng/L)</th>
<th>K (ng/mg)(ng/L)</th>
<th>1/n</th>
<th>r²</th>
<th>PAC type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDW</td>
<td>–</td>
<td>7258</td>
<td>100–7000</td>
<td>18.33</td>
<td>0.643</td>
<td>0.99</td>
<td>Calgon WPH</td>
<td>Huang et al., 1996</td>
</tr>
<tr>
<td>DDW</td>
<td>–</td>
<td>38.9</td>
<td>0.5–20</td>
<td>20.65</td>
<td>0.439</td>
<td>0.99</td>
<td>Calgon WPH</td>
<td>Huang et al., 1996</td>
</tr>
<tr>
<td>NW</td>
<td>2.4±</td>
<td>9087</td>
<td>10–8000</td>
<td>21.6</td>
<td>0.328</td>
<td>0.98</td>
<td>Calgon WPH</td>
<td>Huang et al., 1996</td>
</tr>
<tr>
<td>NW</td>
<td>0.5</td>
<td>18.5</td>
<td>1–10</td>
<td>2.7</td>
<td>0.188</td>
<td>0.99</td>
<td>Calgon WPH</td>
<td>Huang et al., 1996</td>
</tr>
<tr>
<td>NW</td>
<td>1.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Watercard</td>
<td>Graham et al., 2000</td>
</tr>
<tr>
<td>NW</td>
<td>1.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Watercard</td>
<td>Graham et al., 2000</td>
</tr>
<tr>
<td>NW</td>
<td>1.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Watercard</td>
<td>Graham et al., 2000</td>
</tr>
<tr>
<td>NW</td>
<td>1.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Watercard</td>
<td>Graham et al., 2000</td>
</tr>
<tr>
<td>DDW</td>
<td>–</td>
<td>128</td>
<td>7–100</td>
<td>17.6</td>
<td>0.338</td>
<td>0.53</td>
<td>Calgon F200</td>
<td>Herzing et al., 1977</td>
</tr>
<tr>
<td>DDW</td>
<td>118</td>
<td>7–100</td>
<td>17.09</td>
<td>0.46</td>
<td>–</td>
<td>–</td>
<td>Nuchar Aqua</td>
<td>Lalezary-Craig et al., 1988</td>
</tr>
<tr>
<td>DDW</td>
<td>137</td>
<td>7–100</td>
<td>14.1</td>
<td>0.481</td>
<td>0.98</td>
<td>–</td>
<td>Calgon WPH</td>
<td>Lalezary-Craig et al., 1988</td>
</tr>
<tr>
<td>DDW</td>
<td>10</td>
<td>–</td>
<td>100–40,000</td>
<td>3.3</td>
<td>0.52</td>
<td>–</td>
<td>Nuchar Aqua</td>
<td>Lalezary-Craig et al., 1988</td>
</tr>
<tr>
<td>NW</td>
<td>10</td>
<td>–</td>
<td>100–20,000</td>
<td>1.75</td>
<td>0.79</td>
<td>–</td>
<td>Nuchar Aqua</td>
<td>Lalezary-Craig et al., 1988</td>
</tr>
<tr>
<td>NW</td>
<td>10</td>
<td>–</td>
<td>100–20,000</td>
<td>1.75</td>
<td>0.79</td>
<td>–</td>
<td>Nuchar Aqua</td>
<td>Lalezary-Craig et al., 1988</td>
</tr>
<tr>
<td>NW</td>
<td>3.5</td>
<td>1200</td>
<td>30–1000</td>
<td>15.8</td>
<td>0.33</td>
<td>0.96</td>
<td>Bituminous</td>
<td>Chen et al., 1997</td>
</tr>
<tr>
<td>NW</td>
<td>3.5</td>
<td>1200</td>
<td>100–1000</td>
<td>12.5</td>
<td>0.21</td>
<td>0.82</td>
<td>Lignite</td>
<td>Chen et al., 1997</td>
</tr>
</tbody>
</table>

NW: nature water; DDW: distilled deionized water; r²: correlation parameter of equilibrium adsorption curve; “—”: not reported.
where \( c \) = solute concentration in the bulk water phase, \( V \) is the volume of water in the reactor, and \( m \) is mass of PAC in the reactor.

Parameters for HSDM fitting include the initial concentration of 2-MIB (\( C_0, \text{ng/L} \)), average granule radius of PAC (\( R_b, \text{cm} \)), PAC dose (\( m, \text{mg/L} \)), reactor volume (\( V, \text{L} \)), surface diffusion coefficient (\( D_s, \text{cm}^2/\text{min} \)), contact time (\( DT, \text{min} \)), and Freundlich parameters (\( K, 1/\text{n} \)). In this study, \( D_s \) was determined by both the conventional and simplified approaches. For the conventional approach, \( K \) and 1/n were acquired through the equilibrium adsorption tests, and \( D_s \) was then determined by fitting the model with the experimental data. Eqs. (1)–(4) and Eqs. (5)–(6) were used to determine the mass of the targeted compound adsorbed and remained in the water at different time. Then, the best fitted \( D_s \) for the system was determined based on the minimum sum of error between the experimental and model concentrations. The equation (Eq. S(1)) and procedure to calculate the minimum sum of error are presented in the supplementary information. Fig. S1 shows an example of the calculation for the best fitted \( D_s \) at different assigned 1/n values, which was based on the minimum sum of error between the experimental data and model.

For the simplified approach, the procedure is similar to the conventional one, except that 1/n and K was first calculated. In the calculation, 1/n was assumed to be 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, and then K was determined from the Freundlich isotherm (\( q = K (C)^{1/n} \)) based on the equilibrium data obtained at the end of kinetic experiment at 6 h. Once 1/n and K were determined, the procedure of determining the best fitted \( D_s \) is similar to the conventional approach. Then the best fitted \( D_s \) could be used for the prediction of other adsorption data at different PAC dosages.

2.5. Validation

Fengshen water treatment plant, which experienced a 2-MIB episode during the study period, was chosen for validation with the HSDM prediction results. The water treatment process, sampling points and operational parameters are all shown in Fig. S2 (see Supplementary Data). During the odor event, a 2-MIB concentration of approximately 110 ng/L was detected in the source water, and FS_PAC was added to the water intake at a dose of 10 mg/L. Water samples were taken at different points every 2–4 h over a period of 48 h, filtered immediately using glass fiber membranes (Whatman GF/C, UK) and transported to the laboratory for 2-MIB analysis. In addition to the field sampling, laboratory jar tests (Model 7790-400, Phipps and Bird, Richmond, Virginia, USA) were also conducted to test 2-MIB removal. The experimental conditions, including coagulant dose, contact time and PAC dose, were the same as those in the field experiments. The investigated 2-MIB values for the field study and laboratory jar tests were then compared with those predicted by HSDM.

3. Results and discussion

3.1. HSDM fitting using the conventional approach

2-MIB adsorption isotherms for four PACs (WPH_PAC, TAC_PAC, SX_PAC, NX_PAC) were performed in both deionized and natural waters. Fig. 1 shows the results for WPH_PAC in the Fengshen Reservoir water samples. In comparison with deionized water, the adsorption capacity for 2-MIB in natural water was markedly reduced, which should be mainly caused by the competitive adsorption from natural organic matter (NOM) in the source water (Herzing et al., 1977; Lalezary-Craig et al., 1988; Graham et al., 2000). The Freundlich isotherm constants (\( K \) and 1/n) of the four PACs determined from the individual equilibrium adsorption tests are listed in Table 3. The 1/n values varied between 0.2 and 0.4, which was within the range reported in previous studies (Table 1).

The 6-h kinetic experiments were conducted for different PACs under different initial 2-MIB concentrations, with the results for WPH_PAC and TAC_PAC in Fengshen Reservoir water shown in Fig. S3. As shown in the figures, the adsorption mainly occurred in the first few hours. For WPH_PAC, the first and second hour 2-MIB removals were 38% and 48%, respectively, at a PAC dose of 10 mg/L, and 68% and 78% at a dose of 20 mg/L. Similar results were also observed for TAC_PAC. For both PAC systems, the 2-MIB removal percentage data were found to be very similar for those with the

<table>
<thead>
<tr>
<th>PAC</th>
<th>Water</th>
<th>Initial concentration (ng/L)</th>
<th>( K (\text{ng/mg}/\text{L}/\text{ng})^{1/n} )</th>
<th>1/n</th>
<th>( R^2 )</th>
<th>( D_s (\text{cm}^2/\text{min}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPH_PAC</td>
<td>DW</td>
<td>100–300</td>
<td>34.84</td>
<td>0.21</td>
<td>0.63</td>
<td>1.2 \times 10^{-8}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>228</td>
<td>4.08</td>
<td>0.32</td>
<td>0.98</td>
<td>1.3 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>167</td>
<td>4.23</td>
<td>0.27</td>
<td>0.97</td>
<td>1.1 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>48</td>
<td>1.48</td>
<td>0.35</td>
<td>0.97</td>
<td>9.0 \times 10^{-10}</td>
</tr>
<tr>
<td>TAC_PAC</td>
<td>DW</td>
<td>100–500</td>
<td>46.97</td>
<td>0.22</td>
<td>0.54</td>
<td>2.9 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>404</td>
<td>5.45</td>
<td>0.39</td>
<td>0.96</td>
<td>1.9 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>119</td>
<td>5.32</td>
<td>0.20</td>
<td>0.99</td>
<td>1.6 \times 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>NW-FS</td>
<td>78</td>
<td>3.44</td>
<td>0.21</td>
<td>0.94</td>
<td>1.9 \times 10^{-9}</td>
</tr>
<tr>
<td>SX_PAC</td>
<td>NW-MY</td>
<td>100</td>
<td>2.31</td>
<td>0.36</td>
<td>0.96</td>
<td>3.2 \times 10^{-10}</td>
</tr>
<tr>
<td>NX_PAC</td>
<td>NW-MY</td>
<td>100</td>
<td>1.46</td>
<td>0.33</td>
<td>0.95</td>
<td>2.5 \times 10^{-10}</td>
</tr>
</tbody>
</table>

DW: deionized water.
NW-FS: natural water from Fengshen Reservoir.
NW-MY: natural water from Miyun Reservoir.
same PAC dosages (20 mg/L) but with different initial 2-MIB concentrations. This observation of 2-MIB removal percentage being independent of the initial 2-MIB concentrations has also been reported in previous studies (Gillogly et al., 1998; Knappe et al., 1998; Graham et al., 2000). Because of this property, when simulating the adsorption kinetics, the isotherms obtained at a specific initial concentration may be extrapolated to any other initial 2-MIB concentrations for the same PAC/natural water system, if the 2-MIB removal is expressed in percentage. Therefore, the adsorption kinetic data sets (Fig. S3) obtained for WPH_PAC and TAC_PAC in Fengshen Reservoir water were further tested for the HSDM.

Fig. 2 and S4 show the HSDM model fits and predictions for WPH_PAC and TAC_PAC in Fengshen Reservoir water, respectively. In the model simulation, the kinetic data at 20 mg/L PAC dose was first fitted with the model, by adjusting the diffusion coefficient $D_s$. Then the best fitted $D_s$ was used for the prediction of other adsorption data at different PAC dosages. It is noted that the Freundlich isotherm parameters used in the simulation is obtained from three isotherm tests with different initial 2-MIB concentrations (Fig. 1 and Table 3). As indicated in Fig. 2 and S4, the models follow the experimental data very well, even though the isotherms used were obtained from different initial concentrations. The results further support the observation that for the same PAC/natural water system, the isotherm obtained at a specific initial concentration can be used to simulate adsorption kinetics for 2-MIB with different initial concentrations.

Table 3 also lists the best fitted diffusion coefficient $D_s$ for each PAC under different 2-MIB concentrations. The $D_s$ values for WPH_PAC and TAC_PAC at different initial concentrations varied in a narrow range (0.9 $\times$ 10$^{-9}$–1.3 $\times$ 10$^{-9}$ cm$^2$/min and 1.6 $\times$ 10$^{-9}$–1.9 $\times$ 10$^{-9}$ cm$^2$/min, respectively), showing that the concentrations of 2-MIB did not impact the $D_s$ value significantly, as hypothesized by previous studies (Chen et al., 1997; Graham et al., 2000). Compared with WPH_PAC, higher mesopore volumes existed in TAC_PAC (Table 2), which may explain why the $D_s$ values of TAC_PAC were higher (Chen et al., 1997).

### 3.2. HSDM fitting using the simplified approach

As demonstrated in Sec. 3.1, the HSDM could predict the PAC dose by conducting one set of equilibrium adsorption tests and one kinetic test. However, in general equilibrium adsorption tests require at least 72 h, which is too long for a quick response to an odor episode. We thus tried to establish a simplified approach by conducting only one kinetic adsorption test. Cook et al. (2001) and Gillogly et al. (1998) suggested that 4 h of kinetic experiments can provide sufficient information for modeling the adsorption kinetics of 2-MIB onto PAC. Therefore, 4 or 6 h of kinetic experiments were conducted in this study.

As shown in Tables 1 and 3, the 1/n values mainly fell into the range of 0.1–1.0. 1/n was thus first assigned in the range of 0.1–1.0, and the corresponding K value was acquired according to the Freundlich equation by feeding the kinetic adsorption data from 0 to 6 h. The data of WPH_PAC in Fengshen water (Fig. S2) was first tested for the approach. Fig. 3 and S1 show the fitted and predicted results for the different assigned 1/n values. It can be seen that acceptable fitting results could be achieved when the 1/n value was in the range of 0.2–0.6. A similar degree of fitting was also obtained for TAC_PAC and FS_PAC in Fengshen Reservoir water in the same 1/n range (Fig. S5). According to Fig. 3 and S1, the best fitting was achieved at a 1/n value of 0.2–0.4. The case of 1/n = 0.4 and the corresponding K and $D_s$ values using the 6-hr plateau data with a 2-MIB initial concentration of 167 ng/L were 1.82 and 1.5 $\times$ 10$^{-9}$ cm$^2$ min$^{-1}$, respectively, as shown in Table 4. Comparing Table 4 with Table 3, it is clear that similar $D_s$ values were obtained for the same PAC. Good fitting and prediction results were also obtained for WPH_PAC and SX_PAC in Chengching and Miyun Reservoir waters, as shown in Fig. S5.

To further verify the applicability of the simplified approach, another set of 2-MIB kinetic data extracted from a previous study (Gillogly et al., 1998) was also tested. Fig. 4 shows the models fit and predict the experimental data very well, again using the same range of 1/n (0.2–0.6). Although the values of K, 1/n and $D_s$ are obtained under the conditions of model simplification, the models predict all the experimental data reasonably well, suggesting that the simplified approach is feasible. Considering the tested results for different sources of data, activated carbons, and source water, it is reasonable to conclude that the simplified HSDM approach is able to describe the kinetic data for adsorption of 2-MIB onto PAC.
Fig. 3. HSDM fit and prediction for 2-MIB adsorption by WPH_PAC at different $1/n$ assumed values in Fengshen Reservoir water (initial 2-MIB concentration = 167 ng/L).

Table 4
Best fitting kinetic adsorption data for four powdered activated carbons.

<table>
<thead>
<tr>
<th>PAC</th>
<th>Water</th>
<th>Initial concentration (ng/L)</th>
<th>$K$ (ng/(mg)(L/ng)$^{1/n}$)</th>
<th>$1/n$</th>
<th>$D_s$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPH_PAC</td>
<td>NW-PS</td>
<td>167</td>
<td>1.82</td>
<td>0.40</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>TAC_PAC</td>
<td>NW-PS</td>
<td>119</td>
<td>1.07</td>
<td>0.40</td>
<td>$2.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>SX_PAC</td>
<td>NW-MY</td>
<td>100</td>
<td>1.10</td>
<td>0.50</td>
<td>$8.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>NX_PAC</td>
<td>NW-MY</td>
<td>100</td>
<td>0.98</td>
<td>0.50</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
3.3. Validation of the simplified approach using full scale water treatment plant data

In May 2002, a 2-MIB episode with a concentration of 68–80 ng/L occurred in Fengshen Reservoir water. To remove 2-MIB, approximately 10 mg/L FS_PAC was added in the water treatment plant. As shown in Fig. 5, approximately 55% 2-MIB removal was attained after sedimentation.
Based on the data obtained from one kinetic experiment for FS_PAC in Fengshen Reservoir water (Fig. S3), the simplified HSDM approach was conducted to predict the adsorption data. By best fitting the experimental kinetic data with a 1/n value of 0.3, a $D_{eq}$ value of $9.5 \times 10^{-6} \text{cm}^2\text{min}^{-1}$ was obtained. The predicted result at a PAC dosage of 10 mg/L is compared with the full scale plant result in Fig. S2. As also shown in Fig. 5, the results at different treatment steps were within 10%, which is reasonable for the application of PAC.

The concentration of 9.5 mg/L is compared with the full scale plant result in Fig. S3. As also shown in Fig. 5, the results at different treatment steps were within 10%, which is reasonable for the application of PAC. Based on the data obtained from one kinetic experiment for FS_PAC in Fengshen Reservoir water (Fig. S3), the simplified HSDM approach was conducted to predict the adsorption data.

It is noted that a PAC dose of 10 mg/L was not sufficient for the control of the 2-MIB episode in this case, since the odor threshold concentration of 2-MIB is approximately 10 ng/L (Watson et al., 2008). Based on HSDM prediction results, at least 15–25 mg/L PAC should be added to remove 80%–90% 2-MIB, which would guarantee that no obvious 2-MIB odor is perceived in the finished water. It is thus possible to determine the PAC doses for the removal of 2-MIB from source water using the simplified HSDM without resorting to the time-consuming equilibrium adsorption tests.

4. Conclusions

In this study, the PAC prediction using HSDM for 2-MIB removal was simplified by assuming that the Freundlich 1/n value was within a range between 0.2 and 0.6. With this assumption, it is possible to predict PAC doses using the HSDM by conducting only one set of 4-h kinetic adsorption experiments. This simplified HSDM approach was performed successively for different types of PAC applied in different source waters, and validated with the data from one full scale WTP. This simplification of the HSDM makes it possible to respond rapidly to variations in the concentration of 2-MIB in source water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.05.010.

References


