

Adsorption of geosmin and 2-methylisoborneol onto granular activated carbon in water: isotherms, thermodynamics, kinetics, and influencing factors

Lingfei Ma, Fangyuan Peng, Haipu Li, Chaoyi Wang and Zhaoguang Yang

ABSTRACT

Adsorption was found to be an acceptable treatment option to remove geosmin (GSM) and 2-methylisoborneol (2-MIB). It is meaningful to investigate the adsorption capacity of granular activated carbon (GAC) for the two algal odorants in water, and the influences of natural organic material (NOM) and particle size. The adsorption process was studied with the four isotherm models (Langmuir, Freundlich, Temkin, and modified Freundlich), four kinetic models (pseudo first-order, pseudo second-order, Elovich, and intra-particle), and thermodynamics. The results showed that the adsorption of both compounds could be best described by the modified Freundlich isotherm and pseudo second-order model, and the obtained thermodynamic parameters (changes in heat of adsorption, entropy, and Gibbs free energy) revealed that the adsorption was endothermic and spontaneous. Downsizing the particle size of GAC was effective for improving the adsorption capacity and rate. The concentrations of the two odorants could be reduced from 500 ng L⁻¹ to less than 10 ng L⁻¹ with the presence of NOM (<20 mg L⁻¹ total organic carbon, TOC).

Key words | adsorbent, models, natural organic material, odors, removal

Lingfei Ma
Fangyuan Peng
Haipu Li (corresponding author)
Chaoyi Wang
Zhaoguang Yang
Center for Environment and Water Resources,
College of Chemistry and Chemical Engineering,
Central South University,
Changsha 410083,
China
E-mail: lhaipu@csu.edu.cn

INTRODUCTION

Geosmin (GSM) and 2-methylisoborneol (2-MIB) are two main nuisance odorants in drinking water and are often co-existing in surface water (Chen *et al.* 2010; Liu *et al.* 2016). Although non-toxic they can be detected by consumers at levels as low as 10 ng L⁻¹ (Graham *et al.* 2000; Matsui *et al.* 2009a). Conventional water treatment processes, such as coagulation and filtration, could not remove these odorants efficiently (Watson *et al.* 2007; Zamyadi *et al.* 2015), whereas advanced oxidation processes and adsorption were found to be effective and acceptable treatment options. Because activated carbon (AC) has advantageous characteristics (extended surface area, high adsorption capacity, microporous structure, and special surface reactivity) (Matsui *et al.* 2013), it has been applied in the adsorption to remove the odor compounds, and the adsorption treatment has become the simplest and the most widely applied method (Mall *et al.* 1996). It has been cited as one of the best available treatment options by the USEPA (EPA 2019). The two main types of AC used in water treatment are granular activated carbon (GAC) and powdered activated carbon (PAC). The adsorptive capacity of GAC makes it ideal for removing a

variety of contaminants from water. Therefore, locating a GAC treatment unit is a common option in water treatment plants (Nekoo & Fatemi 2013; Kose-Mutlu *et al.* 2017). However, there is still a lack of necessary information for the application of GAC to remove GSM and 2-MIB.

Adsorption is a complex process of transferring specific contaminants from a fluid phase to a solid phase. In order to successfully simulate and optimize the adsorption of a chosen AC, adsorption equilibrium isotherm, kinetics, and thermodynamics have to be studied. The results of the adsorption equilibrium isotherm will be used to evaluate the affinity or capacity of an adsorbent and select a suitable adsorbent and adsorbent dose (Yang & Al-Duri 2005). The study of adsorption kinetics will be used to obtain valuable information on the operation duration, the reaction pathways, and the mechanism of adsorption reactions (Alzaydien & Manasreh 2009). Combining the information from adsorption isotherm and kinetics studies also could enable the estimation of the economic feasibility of an adsorbent's commercial application for specific contaminants, whereas adsorption thermodynamics will provide the basis

for exploring the adsorption mechanism. Also, the particle size of GAC has been considered as an important factor affecting the adsorption kinetics and the contact time required for equilibration (Matsui *et al.* 2015). A previous paper revealed that adsorption capacity of AC substantially increased when carbon particle diameter was decreased for GSM and 2-MIB (Matsui *et al.* 2015). But the smaller particle may increase the difficulty of filtration, and it is not yet known what particle size of AC would be most suitable. Therefore, choosing the appropriate size of the GAC is important for water treatment. In water treatment processes, the effect of natural organic material (NOM) should be investigated since the concentration of NOM in natural water usually is much higher than the concentrations of the target compounds, which would lead to a large proportion of the adsorption volume within the AC not being available for the GSM and 2-MIB removals (Zoschke *et al.* 2011; Matsui *et al.* 2012).

The objectives of this paper were to investigate the adsorption capacity of GAC for 2-MIB and GSM based on the thermodynamics, adsorption isotherm, and kinetics, and to evaluate the impacts of key factors, including NOM and particle size, on the adsorption. The data acquired from this study should provide a scientific basis for controlling the pollution of 2-MIB and GSM in water by GAC adsorption.

MATERIALS AND METHODS

Chemicals

GSM, 2-MIB, and the internal standard 2,3,6-trichloroanisole (2,3,6-TCA) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The stock solutions of 2-MIB, GSM, and 2,3,6-TCA (100 mg mL⁻¹) were prepared in methanol (HPLC grade) obtained from Sigma-Aldrich® (Saint Quentin Fallavier, France). All the standard solutions were stored at -20 °C in darkness. All the other solutions were prepared with deionized water obtained from a Milli-Q ultrapure water purification system (Millipore, USA). In order to get the humic acid stock solution, three grams of humic acid (Aladdin®, Shanghai, China) was dissolved in 0.1 M NaOH, and was mixed with a magnetic stirrer for 24 h. The suspension was filtered by a 0.45 µm membrane filter. The pH of the filtered solution was adjusted to 7.5 by adding 0.1 M NaOH. The solution was diluted to 1,000 mL in a measuring flask and was stored in the dark. Total organic carbon (TOC) was measured by a TOC analyzer (Shimadzu®, TOC-VCPN,

Japan), and the TOC of the stock humic acid solution was found to be 1,120 mg L⁻¹. This humic acid solution at experiment concentration (5, 10, or 20 mg L⁻¹) was obtained by diluting the stock solution before use.

Coconut shell-based GAC was purchased from Aladdin (Shanghai, China). GAC was ground and sieved to specific sizes, and GAC samples with different size were obtained, including <61, 61–74, 74–106, 106–150, 150–250, and 250–850 µm. All the GAC samples were ultrasonic rinsed with ultrapure water for 30 min, dried in an oven at 110 °C for 12 h, then cooled down to room temperature, and finally were stored in a desiccator prior to use.

Adsorption experiments

For the kinetic experiments, 40 mg GAC was introduced into 2 L solutions in a 3 L volumetric flask with GSM and 2-MIB. The initial concentration of each compound was 500 ng L⁻¹. Then the flask was placed on an orbital shaker with a rotation speed of 100 rpm at 25 °C. The samples were withdrawn from the flask at predetermined intervals. The concentrations of GSM and 2-MIB were determined using solid-phase microextraction coupled with gas chromatography–mass spectrometry (GC-MS).

For the adsorption isotherm, a 500 mL solution containing GSM and 2-MIB, each at concentration of 500 ng L⁻¹, was added into a 600 mL volumetric flask. A specified amount (0.2, 0.3, 0.5, 0.8, 1, 2, 5, and 10 mg L⁻¹) of GAC with particle size less than 61 µm was added, and then the flask was placed on an orbital shaker at 100 rpm for 24 h at control temperature. The flask was sealed with a glass stopper to avoid volatilization, and a blank (without GAC addition) was included with each experiment to evaluate the losses other than that through adsorption. The sample was filtered with a 0.45 µm membrane to remove the solid adsorbents, and the filter had been cleaned in advance by ultrapure water before use. The temperatures in the experiments were set at 293, 303, 313, and 323 K, respectively.

Analytical method

The concentrations of GSM and 2-MIB were analyzed using 65 µm PDMS/DVB solid-phase microextraction (SPME) (Supelco, USA) coupled with GC-MS (Agilent 7890A/5975C, USA) equipped with an HP-5MS column (30 m × 0.25 mm × 0.25 µm, Agilent, USA). High purity helium (99.999%, Rising Corp., China) was used as the carrier gas and kept at 1 mL min⁻¹ constant flow. The injection port was operated at splitless mode with temperature controlled

at 250 °C, and the oven temperature program was as follows: initially stayed at 40 °C for 3 min, heated at a rate of 15 °C min⁻¹ to 280 °C, and finally kept at 280 °C for 1 min. The MS ion source temperature was set at 230 °C. For the selected ion monitoring mode, m/z of 167, 195 and 210 for 2,3,6-TCA; m/z of 95 and 108 for 2-MIB; and m/z of 112 and 125 for GSM were monitored, respectively (McCallum et al. 1998).

Data analysis

To get an adsorption isotherm plot, a set of adsorption tests with varied GAC dose D (mg L⁻¹) under a fixed initial solute concentration C_0 (mg L⁻¹) should be conducted until the amount adsorbed per unit mass of carbon Q_t (ng mg⁻¹) reaches equilibrium; the maximum amount adsorbed per unit mass of carbon Q_e (ng mg⁻¹) is measured, and the concentration of adsorbate in solution correspondingly reduces from C_t (ng L⁻¹) to C_e (ng L⁻¹). The relationship can be expressed as follows:

$$Q_t = (C_0 - C_t) \frac{V}{m} = \frac{C_0 - C_t}{D} \quad (1)$$

$$Q_e = (C_0 - C_e) \frac{V}{m} = \frac{C_0 - C_e}{D} \quad (2)$$

where V (L) is the solution volume and m (mg) is the mass of adsorbent. Generally, the adsorbent that has a higher Q_e value at a specified equilibrium concentration will be preferred for a given application (Ho et al. 2002).

The adsorption isotherm models and kinetic models were established using Origin 8.0. The models were evaluated by the coefficient of determination (R^2) and chi-square (χ^2). The chi-square is given as follows:

$$\chi^2 = \sum \frac{(Q_{e,ex} - Q_{e,cal})^2}{Q_{e,cal}} \quad (3)$$

where $Q_{e,ex}$ is the measured Q_e , and $Q_{e,cal}$ is the Q_e calculated with the models. All data were determined using the Origin 8.0.

RESULT AND DISCUSSION

Adsorption kinetics

Determining the adsorption rate and identifying the potential rate-controlling step are primary for practical operation. Thus, different kinds of kinetic models, namely pseudo first-order model, pseudo second-order model, intra-particle model, and Elovich model, were used to describe the adsorption kinetic behavior.

Figure 1 shows that the adsorbed amount of GSM and 2-MIB increased dramatically in the first 10 min, and then increased slowly from 10 min to 20 min. The change from 20 min to 30 min and even to 2 h was slight. The intra-particle kinetic model holds that the adsorption rate is controlled by diffusion, and if the line passes through the origin, the process rate is controlled only by internal diffusion

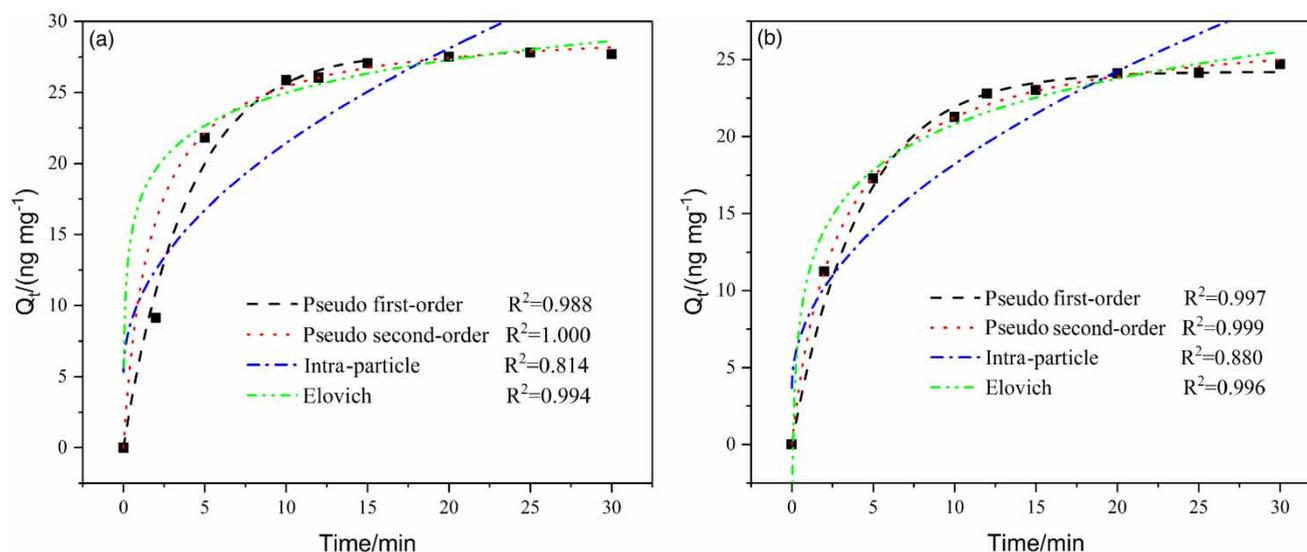


Figure 1 | Kinetic models for the adsorptions of GSM (a) and 2-MIB (b) onto granular activated carbon ($C_0 = 500$ ng L⁻¹, $m = 20$ mg L⁻¹ for GAC, $T = 25 \pm 1$ °C, GAC particle size <61 μm).

(Nassar 1999). In this study, the intra-particle kinetic model fitted the measured adsorption data poorly for 2-MIB and GSM with the low R^2 (0.880 and 0.814) and the high χ^2 (0.767 and 13.240), which indicated that internal diffusion is not the rate-controlling step in this adsorption process.

The pseudo first-order model is the empirical kinetic equation for one-site occupancy adsorption which simulates a rapid adsorption due to the absence of sorbate–sorbate interaction. The pseudo second-order model involves all the potential adsorption procedures, such as external film diffusion, surface adsorption, and intra-particle diffusion (Ho & McKay 1999). As shown in Table 1, the pseudo first-order and second-order kinetic models well fitted the measured adsorption data with the high R^2 (0.988 and 1.000 for GSM, 0.997 and 0.999 for 2-MIB). Q_e calculated with the pseudo second-order model (27.38 ng mg^{-1} and 29.81 ng mg^{-1} for 2-MIB and GSM respectively) were close to the measured data (30.25 ng mg^{-1} and 30.15 ng mg^{-1} for 2-MIB and GSM respectively), which indicated the sorbate–sorbate interaction was weak in the adsorption process and adsorption kinetics was mainly governed by the one-site occupancy surface adsorption. GSM had a higher adsorption rate than 2-MIB (27.7 min^{-1} vs 24.9 min^{-1}), and GAC possessed a larger adsorption capacity for GSM, which is probably ascribed to the molecular size since the GSM molecule is bigger than the 2-MIB one.

The Elovich kinetic model is an empirical model, which considers a series of reaction mechanisms, such as the diffusion of the solute in the liquid or interface and the activation

and deactivation of the surface. It is very suitable for systems with heterogeneous adsorbing surfaces and significant change in the activation energy during the reaction, such as the process on the interface of the soil and the sediment (Ahmad *et al.* 2014). The Elovich kinetic model also well fitted the adsorption data for GSM and 2-MIB with R^2 higher than 0.994 and χ^2 lower than 0.743, indicating that the adsorption is related to activation energy. So, it is necessary to investigate the adsorption thermodynamics.

Adsorption isotherms

Adsorption isotherm tests were conducted for GSM and 2-MIB. Measured and modeled single-solute adsorption isotherm data for GSM and 2-MIB are shown in Figure 2. The used models included Freundlich, Langmuir, Temkin, and modified Freundlich equations. The corresponding isotherm parameters obtained by nonlinear regression analysis are summarized in Table 2. When contact time was 24 h, adsorptions of GSM and 2-MIB were best described by the modified Freundlich isotherm, Freundlich isotherm model and Langmuir isotherm model.

The Langmuir adsorption model is the theoretical formula of adsorption based on homogeneous surfaces where a strong specific interaction between adsorbate and adsorbent only occurs on monolayer coverage; thus it fails to account for the surface roughness of the adsorbent (Song *et al.* 2013). The adsorption data for GSM and 2-MIB were fitted with Langmuir with the R^2 being 0.980 for GSM and 0.955 for 2-MIB and the χ^2 being 0.629 for GSM and 0.159 for 2-MIB, indicating that the adsorption mainly is monolayer coverage. The K_L value of the Langmuir adsorption model for GSM was higher than that of 2-MIB, suggesting that the adsorptive capacity of GAC for GSM is better than that for 2-MIB.

The Freundlich isotherm model is an empirical equation and particularly appropriate for hydrophobic adsorbates (Sotelo *et al.* 2002) in water. It is often appropriate to use the Freundlich model instead of the Langmuir adsorption model (Jaroniec 1975). The validity of the Freundlich model (R^2 being 0.988 and 0.957 for GSM and 2-MIB, respectively, and χ^2 being 0.087 and 0.016 for GSM and 2-MIB, respectively) and Langmuir model indicated that the adsorptions were controlled by one-site occupancy surface adsorption with monolayer coverage, and the effects of other factors were negligible. Similar findings on GAC adsorption for other taste and odor compounds were reported by Zhang *et al.* (2011) and An *et al.* (2012). The K_F parameter can roughly indicate the adsorption capacity and the parameter $1/n$ gives an indicator of the favorability

Table 1 | Kinetic parameters for adsorption of GSM and 2-MIB on GAC

Kinetic model	Equation	Parameter	GSM	2-MIB
Pseudo first-order	$Q_t = Q_e(1 - \exp(-K_1t))$	Q_e	27.9	24.0
		K_1	0.252	0.236
		R^2	0.988	0.997
		χ^2	1.82	0.314
Pseudo second-order	$Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e K_2 t}$	Q_e	29.8	27.4
		K_2	0.019	0.012
		R^2	1.00	0.999
		χ^2	0	0.002
Intra-particle	$Q_t = K_I t^{1/2} + a$	a	5.34	3.67
		K_I	5.09	4.59
		R^2	0.814	0.880
		χ^2	0.767	13.2
Elovich	$Q_t = b + K_e \ln t$	b	17.3	10.9
		K_e	3.32	4.287
		R^2	0.994	0.996
		χ^2	0.743	0.356

K_1 , first-order adsorption rate constant; K_2 , second-order adsorption rate constant; t , contact time; a and K_I , intra-particle diffusion rate constants; b and K_e , Elovich adsorption constants.

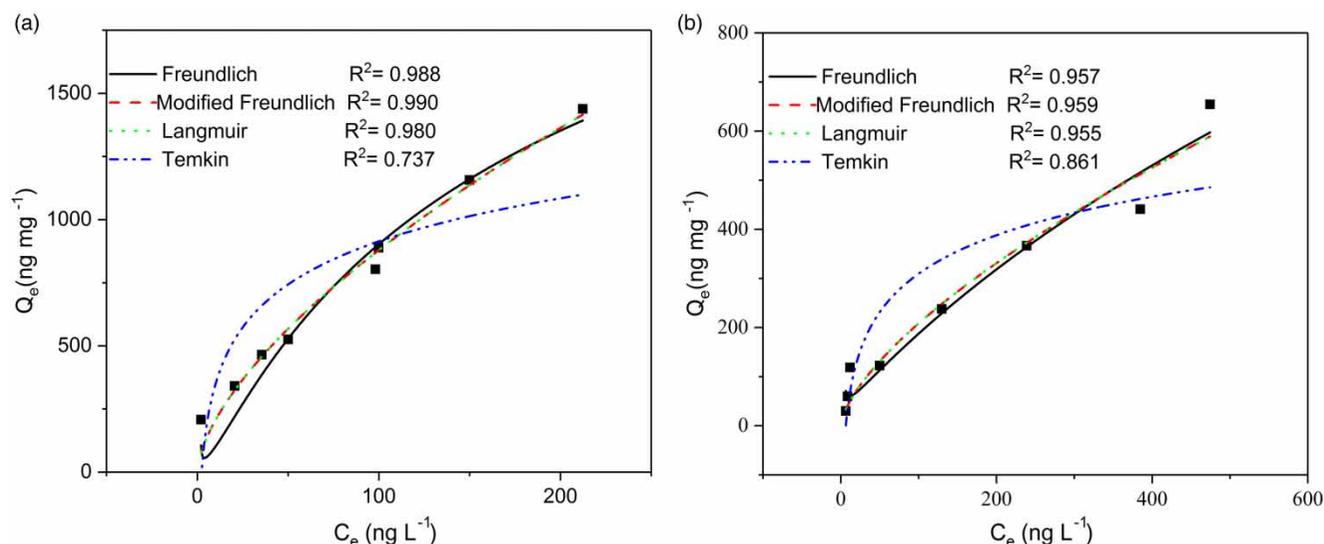


Figure 2 | Adsorption isotherm data for GSM (a) and 2-MIB (b) on GAC ($C_0 = 500 \text{ ng L}^{-1}$, 24 h contact time, $T = 25 \pm 1 \text{ }^\circ\text{C}$, GAC particle size $< 61 \text{ }\mu\text{m}$).

Table 2 | Constants of isotherm models at 24 h equilibrium time

Isotherm models	Equations	Parameters	GSM 500 (ng L^{-1})	2-MIB 500 (ng L^{-1})
Langmuir	$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$	Q_0 (ng mg^{-1})	833	1111
		K_L (L mg^{-1})	0.120	0.0053
		R^2	0.980	0.955
		χ^2	0.629	0.199
Freundlich	$Q_e = K_F C_e^{1/n}$	K_F ($\text{ng}^{(1-1/n)} \text{ L}^{1/n} \text{ g}^{-1}$)	116	11.40
		$1/n$	0.487	0.574
		R^2	0.988	0.957
		χ^2	0.087	0.016
Modified Freundlich	$Q_e = K'_F \left(\frac{C_e}{D}\right)^{1/n}$	K'_F ($\text{ng}^{1-1/n} \text{ mg}^{1/n-1}$)	130	60.7
		$1/n$	0.439	0.737
		R^2	0.990	0.959
		χ^2	0.004	0.007
Temkin	$Q_e = \ln(K_T C_e)^{B_T}$	K_T	0.005	0.182
		B_T	620	111
		R^2	0.737	0.861
		χ^2	1.07	0.0432

Q_0 and K_L , Langmuir constants related to the adsorption capacity and intensity of adsorption, respectively; K_F and $1/n$, Freundlich constants related to the adsorption capacity and energy of adsorption, respectively; K'_F , modified Freundlich constant related to the adsorption capacity; K_T and B_T , Temkin constants.

of adsorption. The value of $1/n$ usually ranges from 0.1 to 1, and the smaller value of $1/n$ implies the stronger interactions between the adsorbent and adsorbates (Tan et al. 2008). The values of $1/n$ for GSM and 2-MIB are comparable, but GSM had a higher K_F than 2-MIB, implying that GAC had a slightly higher adsorption capacity for GSM than for 2-MIB.

The modified Freundlich model is a special case of dosage-dependent heterogeneous surface adsorption with non-negligible intermolecular reactions, which is an appropriate explanation of adsorption behavior in diluted solution. The

modified Freundlich model well fitted the measured adsorption data with R^2 being 0.990 for GSM and 0.959 for 2-MIB, and χ^2 being 0.004 for GSM and 0.007 for 2-MIB, respectively. GSM had a higher K'_F than 2-MIB, representing that GAC had a slightly higher adsorption capacity for GSM than for 2-MIB. Smaller $1/n$ values were obtained for GSM than for 2-MIB, implying that GAC had a higher affinity with GSM than with 2-MIB, and the adsorption for 2-MIB was more readily affected by equilibrium concentration. The result agreed well with that obtained with the Freundlich model.

The Temkin isotherm is another two-parameter isotherm model established on the theoretical hypothesis that the decline of the heat is linear with the amount of adsorption, due to adsorbate with adsorbent interactions (Tan et al. 2007). The bad fitness indicates that the heat of adsorption is independent of the adsorption amount, and the adsorption may not be chemical adsorption.

Adsorption thermodynamics

Gibbs free-energy change (ΔG^0) of the adsorption processes can be determined by the classical Van 't Hoff equation:

$$\Delta G^0 = -RT \ln K_{ad} \quad (4)$$

where ΔG^0 is the free-energy change (kJ mol^{-1}), R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), and K_{ad} is the adsorption equilibrium constant determined above. Also, ΔG^0 can be calculated from Equation (5).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

where ΔS^0 is the change in entropy ($\text{kJ mol}^{-1} \text{ K}^{-1}$), and ΔH^0 is the change in heat of adsorption (kJ mol^{-1}) at a constant temperature. Combining Equations (4) and (5) leads to Equation (6):

$$\ln K_{ad} = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (6)$$

In Equation (6), ΔH^0 can be determined from the slope of the linear Van 't Hoff plot, i.e. $\ln K_{ad}$ versus $(1/T)$, using Equation (7):

$$\Delta H^0 = R \frac{d \ln K_{ad}}{d(1/T)} \quad (7)$$

This ΔH^0 corresponds to the isosteric heat of adsorption ($\Delta H_{st,0}$) with zero surface coverage (i.e. $Q_e = 0$). K_{ad} at $Q_e = 0$ was obtained from the intercept of the $\ln(Q_e/C_e)$ versus Q_e

plot at different temperatures (293, 303, 313, and 323 K). Figure 3 shows the Van 't Hoff plot, from which the values of ΔH^0 , ΔS^0 , and ΔG^0 were determined (Table 3).

It is observed from Table 4 that ΔH^0 and ΔS^0 are positive, and ΔG^0 is negative in both adsorption processes. The positive ΔH^0 value confirms the endothermic nature of the overall sorption process, and the positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in GSM and 2-MIB affinity to GAC. The negative ΔG^0 indicates the feasibility and spontaneity of the adsorption process.

Effect of GAC particle size

As shown in Figure 4, the smaller the particle is, the shorter the equilibration time needed, but the odorants could be removed almost completely if the contact time is sufficiently long (such as 24 h) regardless of the particle size of the GAC. Reduction of particle size from 250–850 μm to 150–250 μm or from 150–250 μm to 74–106 μm was effective in shortening the equilibrium times to 20 min, meaning that the removal rates were improved. But the removal rates

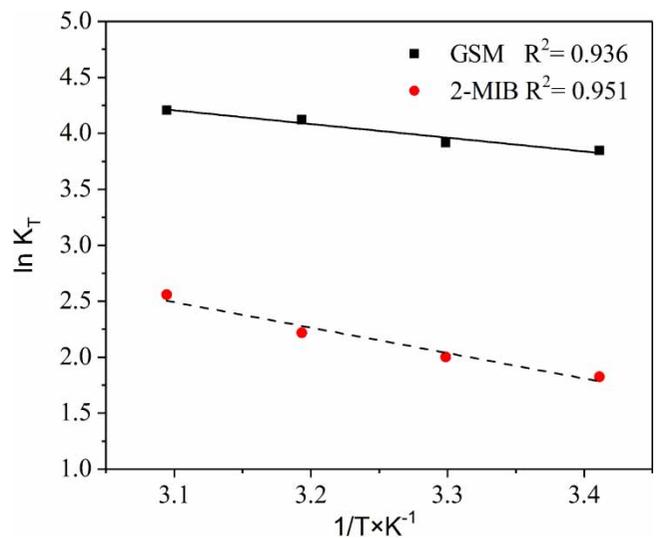


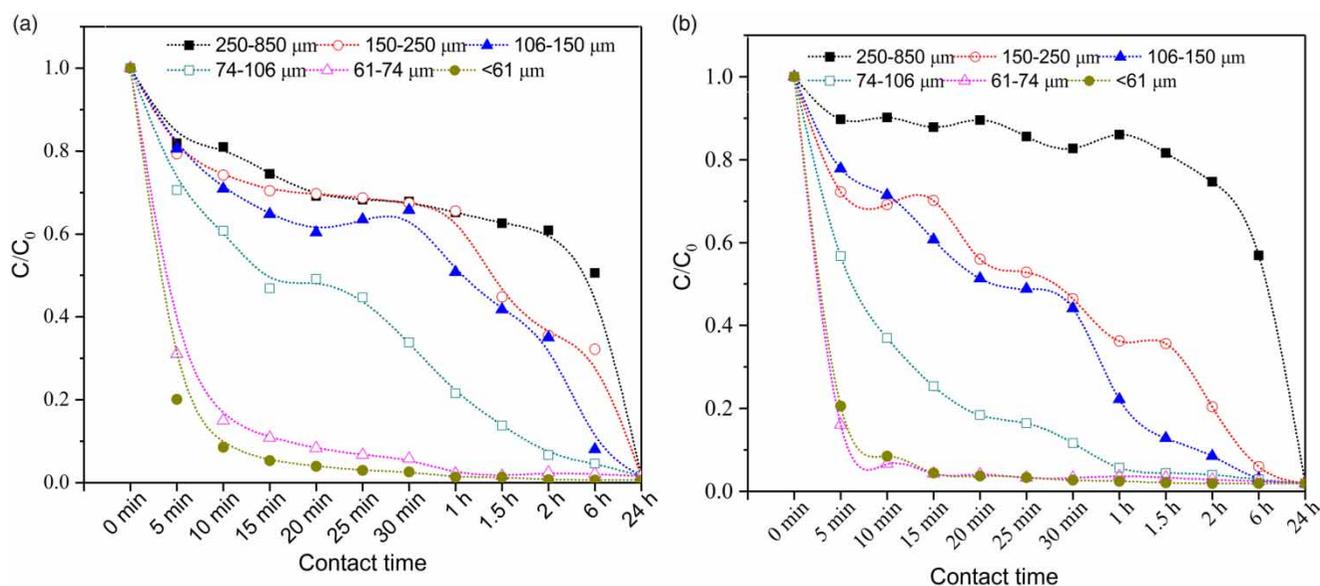
Figure 3 | Van 't Hoff plot for the determination of ΔH^0 , ΔS^0 , ΔG^0 ($C_0 = 500 \text{ ng L}^{-1}$ for 2-MIB and GSM, respectively, $m = 20 \text{ mg L}^{-1}$ for GAC).

Table 3 | Thermodynamic parameters for the adsorption of GSM and 2-MIB onto GACs

Organic matters	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{kJ mol}^{-1} \text{ K}^{-1}$)	ΔG^0 (kJ mol^{-1})			
			293 K	303 K	313 K	323 K
GSM	10.2	0.00671	-9.44	-10.1	-10.8	-11.4
2-MIB	19.0	0.00794	-4.21	-5.00	-5.79	-6.58

Table 4 | Adsorption kinetic parameters ($m = 20 \text{ mg L}^{-1}$ for GAC, $T = 25 \pm 1 \text{ }^\circ\text{C}$)

Organic matters	TOC mg L^{-1}	$Q_{e,\text{exp}}$ ng mg^{-1}	Pseudo first-order				Pseudo second-order			
			$Q_{e,\text{exp}}$ ng mg^{-1}	K_1 min^{-1}	R^2	χ^2	$Q_{e,\text{exp}}$ ng mg^{-1}	K_2 $\text{g ng}^{-1} \text{ min}^{-1}$	R^2	χ^2
GSM	0	27.7	27.4	0.310	0.999	0.0633	29.8	0.0194	0.999	0.166
	5	26.4	26.0	0.34	0.999	0.124	27.3	0.0246	0.999	0.102
	10	27.17	26.6	0.325	0.995	0.364	25.6	0.0295	0.991	0.066
	20	26.04	25.6	0.231	0.997	0.209	26.9	0.0177	0.989	0.758
2-MIB	0	25.6	24.9	0.215	0.994	0.436	26.2	0.0162	0.997	0.199
	5	25.4	24.5	0.209	0.990	0.682	25.9	0.0154	0.999	0.0815
	10	25.6	24.5	0.164	0.987	0.865	26.18	0.0109	0.998	0.106
	20	25.3	24.3	0.143	0.986	0.931	25.99	0.00926	0.999	0.0844

**Figure 4** | Effect of GAC particle size on adsorption for GSM (a) and 2-MIB (b) ($C_0 = 500 \text{ ng L}^{-1}$ for 2-MIB (a) and GSM (b), respectively, $m = 20 \text{ mg L}^{-1}$ for GAC, $T = 25 \pm 1 \text{ }^\circ\text{C}$).

have no obvious difference in 6 h when particle size was reduced from 61–74 μm to <61 μm .

A conventional drinking water treatment plant consists of coagulation, sedimentation, filtration, and disinfection units (Angreni 2013). AC can be added in the source water, or the process waters after the coagulation or before the filtration. Adding AC to the source water, the contact time between AC and adsorbates would be sufficient. Thus, the various sizes of AC in this study could all be applied to this unit. After coagulation, the coagulation and sedimentation time was longer than 2 h (China 2006); thus the AC with the particle size smaller than 106 μm might be suitable. However, the flocculents added in the water tend to adsorb on the AC and cause an encapsulation effect (Cook et al. 2001). And the encapsulation greatly depends on the particle size of the AC (Matsui et al. 2009b). Thus the particle size

should be chosen sophisticatedly. Before the filtration, the contact time of filtration is less than 30 min (China 2006), while the smaller size AC easily penetrates the filter layer and increases effluent turbidity (Matsui et al. 2009b). Therefore, choosing a suitable AC size is important. In general, the optimal particle size of GAC needs to be combined with specific water treatment processes.

Effect of NOM

NOM is a complex mixture of organic compounds, primarily composed of fulvic acids, humic acids, hydrophilic acids, and carbohydrates. Humic acid is the main organic substance in soil and water at forestry protected watersheds, which can account for 50%–80% of the total organic matter (Davies & Ghabbour 2004). Several previous studies have

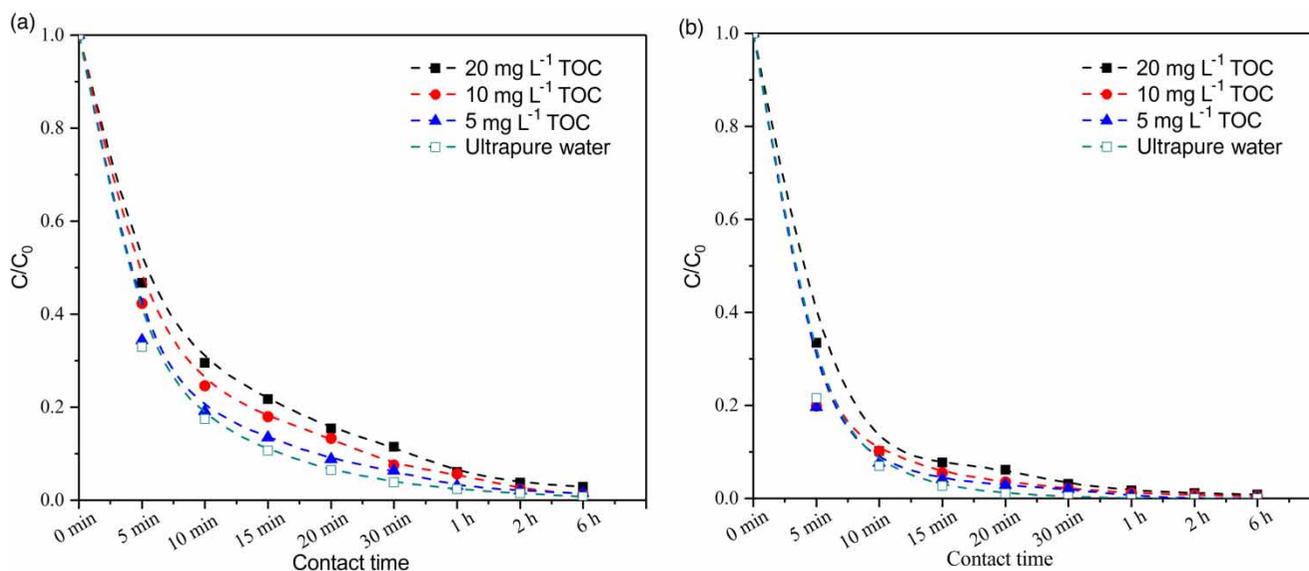


Figure 5 | Effect of initial TOC of the aqueous solution on the removal of GSM and 2-MIB by GAC ($C_0 = 500 \text{ ng L}^{-1}$ for 2-MIB (a) and GSM (b), respectively, $m = 20 \text{ mg L}^{-1}$ for GAC, $T = 25 \pm 1 \text{ }^\circ\text{C}$).

shown that the presence of NOM could cause a significant reduction of the target organic pollutants adsorbed by the AC (Moore *et al.* 2010; Zhang *et al.* 2011; Zoschke *et al.* 2011). In this study, the effect of humic acid in the background matrix on the adsorption process was considered.

Figure 5 shows that the removal ratios for both GSM and 2-MIB with the initial concentration of 500 ng L^{-1} could reach above 98% after 2 h in these solutions with different concentrations of TOC, and the residue concentrations could be decreased to 10 ng L^{-1} for 2-MIB and 4 ng L^{-1} for GSM.

The adsorption kinetics for GSM and 2-MIB still exhibited pseudo first-order or pseudo second-order kinetic behaviors ($R^2 = 0.98\text{--}0.99$), as shown in Table 4. The values of K_1 and K_2 for GSM adsorption were comparable for TOC concentrations of 0, 5, and 10 mg L^{-1} in water, while they showed a slight decrease at 20 mg L^{-1} TOC. As for 2-MIB, the values of K_1 and K_2 adsorption showed a slight decrease with TOC increasing from 0 to 20 mg L^{-1} . These results indicated that the inhibitory action of NOM was not significant with the TOC increasing in the present experiments, which was in accordance with the findings of other studies (Hepplewhite *et al.* 2004; Zoschke *et al.* 2011). It was generally considered that the larger NOM molecules could block pores of AC, or the smaller NOM molecules directly competed for adsorption sites with those low molecular weight compounds such as 2-MIB (Kilduff *et al.* 1998). The competitive mechanism was important for the effect of NOM on microcontaminant adsorption (Newcombe *et al.* 2002). However, in the present study,

the insignificant impact of NOM suggested that GSM and 2-MIB are more competitive than NOM for adsorption.

CONCLUSIONS

The adsorption kinetics and isotherm of GSM and 2-MIB could be best described by the pseudo second-order model and modified Freundlich isotherm. Other kinetic models also provide valuable pieces of information on the reaction pathways and the mechanism of adsorption reactions. The calculated thermodynamic parameters (ΔH^0 , ΔS^0 , and ΔG^0) revealed that the adsorption of the two compounds was endothermic, there was increased randomness at the solid/solution interface and the adsorption process was spontaneous.

The effect of particle size of GAC for removal of GSM and 2-MIB was studied and the results showed that downsizing the particles of GAC was effective in shortening the necessary contact times both for GSM and 2-MIB. When the particle size of GAC (20 mg L^{-1}) was less than $61 \mu\text{m}$, the equilibrium could be reached within 2 h, and the concentrations of the two odorants would be reduced from 500 ng L^{-1} to 10 ng L^{-1} for 2-MIB and to 4 ng L^{-1} for GSM with the presence of NOM ($<20 \text{ mg L}^{-1}$ TOC).

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