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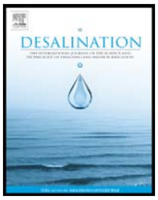

Granular activated carbon (GAC) adsorption of two algal odorants, dimethyl trisulfide and β-cyclocitral

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ABSTRACT

This study was to investigate granular activated carbon (GAC) adsorption of two algal odorants in water, dimethyl trisulfide and β-cyclocitral. Among the four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich), Freundlich isotherm showed the best fitting with the equilibrium data in terms of the coefficient of determination (R^2) and Chi-square (χ^2). Based on the parameters determined in the Freundlich isotherm equations for GAC adsorption of a single odorant, we successfully predicted the GAC adsorption behavior in a bisolute solution using the Ideal Solution Adsorption (IAS) model. In the kinetics study of the two odorants adsorption by GAC, pseudo first-order and pseudo second-order kinetic models both well fit the experimental data. The calculated Gibbs free-energy changes for GAC adsorption of dimethyl trisulfide and β-cyclocitral were −3.61 and −4.24 kJ/mol at 298 K, respectively. The pH effects on GAC adsorption of dimethyl trisulfide and β-cyclocitral were different. Alkaline condition (pH >10) favored GAC adsorption of dimethyl trisulfide, however, adsorption of the β-cyclocitral was not significantly influenced by pH (2–13). The presence of natural organic matter (NOM) hindered adsorption of dimethyl trisulfide and β-cyclocitral to different degrees. Low molecular weight NOM fractions (particularly <1000) showed the significant inhibiting effect in the GAC adsorption.

1. Introduction

Increasing attention has been paid to the occurrence of off-flavor chemicals in drinking water over the last few decades [1–3]. Although the causes of water taste and odor (T&O) are complicated, microorganisms, mainly algae and cyanobacteria, are known to be responsible for many episodes in water sources [4,5]. Among the odor-producing cyanobacteria, *Microcystis aeruginosa*, a producer of wooden-odor β-cyclocitral (2,2,6-trimethyl-1-cyclohexene-1-carboxaldehyde) [4,6,7], is frequently detected in many eutrophic lakes and reservoirs all over the world. β-cyclocitral, derived from the carotenoid degradation [8], has a sweet-tobacco, grape odor [9,10]. It is found at trace levels of 500 ng/L in water [7] and 15 ng/10^6 cell in *M. aeruginosa* [11]. On the other hand, dimethyl trisulfide, an important T&O-causing compound in China mainly responsible for the septic/swampy odor [12], has also been identified as a common odor-producing compound by *Microcystis*, particularly when *Microcystis* was decayed [13].

Control of T&O compounds in water sources is greatly difficult because most of these compounds are of natural origin and are closely related to the growth and metabolism of algae and bacteria in surface waters [14]. Currently, T&O problems can be minimized and even be avoided through utilization of advanced chemical oxidation in water treatment. For example, ozonation is effective in the removal of the off-flavors such as β-cyclocitral [15]. However, advanced chemical oxidation processes may be very costly or produce undesirable oxidation byproducts. Another commonly used method for T&O control is granular activated carbon (GAC) adsorption [16]. Most of the previous studies on GAC adsorption for T&O control focused on removal of two representative compounds with the earthy musty odor, geosmin and 2-methylisoborneol (2-MIB) [17–19]. However, adsorption of other important odorants such as dimethyl trisulfide and β-cyclocitral, two major excretion products of cyanobacteria and algae, has been largely ignored. In this study, our objective was to investigate equilibria, kinetics and thermodynamics of GAC adsorption of β-cyclocitral and dimethyl trisulfide in water. In addition, the effects of pH and natural organic matter (NOM) in the treatment were studied.

2. Materials and methods

2.1. Chemicals

Dimethyl trisulfide (98%), β-cyclocitral (90%), and the internal standard 2-isobutyl-3-methoxypyrazine (IB, 99%) were purchased from Sigma-Aldrich. The stock solutions of dimethyl trisulfide, β-

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cyclocitral and IB (1 g/L) were prepared in methanol (99%, Sigma). All the other solutions were prepared with deionized water obtained from Mill-Q Ultrapure Water Purification system.

2.2. Characteristics of GAC

GAC was purchased from Calgon Carbon Corp. Its characteristics were shown in Table 1. The specific surface area, pore volume and pore size of GAC were measured with the nitrogen adsorption isotherm by ASAP 2010 Micromeritics instrument and the Brunaer–Emmett–Teller (BET) method.

2.3. Fractionation of natural organic matters

The natural water from the Huangpu River of China was prefiltered through a 0.45 μm Millipore filter (dia.: 50 mm) prior to experiments. NOM was concentrated and fractionated into the nominal molecular weight fractions: <1000, <5000, <30,000 and >30,000 with ultrafiltration membranes (material: regenerated cellulose, dia.: 90 mm, Millipore Corp.). The fractions were diluted with Milli-Q water to a similar DOC level (ca. 3.9 mg/L).

2.4. Chemical analysis

Concentrations of β-cyclocitral, dimethyl trisulfide and IB were analyzed using liquid–liquid extraction coupled with GC/MS. Gas chromatograph and mass spectrum SHIMADZU QP2010S equipped with an autosampler (AOC-1) was utilized for component separation and detection. A RTX-5MS capillary column 30 m × 25 mm × 25 μm was installed. The carrier gas was high purity helium (>99.999%, Chunyu Corp., China) at the pressure of 90 kPa. The injection port was operated at splitless mode with temperature controlled at 180 °C, and the oven temperature programme was as follows: initially at 40 °C for 3 min, heated at a rate of 8 °C/min to 120 °C, then heated at a rate of 15 °C/min to a final temperature of 250 °C, and finally kept at 250 °C for 2 min. The MS ion source temperature was set at 200 °C. For the selected ion monitoring (SIM) mode, *m/z* of 166, 124 for IB, *m/z* of 126, 79 for dimethyl trisulfide, and *m/z* of 137,152 for β-cyclocitral were monitored. NOM was quantified by measurement of dissolved organic carbon (DOC) using a TOC analyzer (TOC-V_{CPH}, SHIMADZU, Japan). Zeta analyzer (Zetasizer Nano, Malvern Instruments Ltd., UK) was used to determine zeta potential of the GAC surface. Solution pH was measured using a pH meter (PHS-3G, Leici Corp., China).

2.5. Procedure

Equilibrium and kinetic experiments were carried out in 250 mL stoppered glass vials at 25 °C in a batch mode. 200 mL dimethyl trisulfide or β-cyclocitral containing solution with an initial concentration (C_0) of 0.1–1 mg/L was dispended to the glass vials. The solution pH was adjusted to a desirable value (2–13) with 100 mM HCl and 100 mM NaOH solutions. Then, 4–40 mg of GAC was added. All the vials were installed in a temperature-controlled orbital shaker (HYG-A, China) at a constant rotation speed of 200 rpm. A typical equilibrium test was run for 48 h, which was adequate to reach the adsorption for both dimethyl trisulfide and β-cyclocitral. In a typical kinetics test, 5 mL sample was collected in a designated time for the sample analysis.

Thermodynamics experiments were carried out in 10 mL colorimetric cylinders with 5 mL sample at 15, 25, 35 and 45 °C, respectively. One gram NaCl (solid, analytical pure) and 5 μL internal standard IB were added to the solution. The water sample was extracted with 1 mL hexane (HPLC grade, Sigma) using the oscillator for 3 min. The organic phase was dried with anhydrous sodium sulfate and transferred to autosampling vials. 1 μL of the organic solution was injected to the GC/MS system. The standard curve with the target concentrations between 10 and 1000 μg/L was obtained directly by liquid–liquid extraction method. The coefficients of determination, R^2, for dimethyl trisulfide and β-cyclocitral were 0.9892 and 0.9970, respectively.

Table 1
The characteristics of GAC.

Specific surface area (m^2/g)			Pore volume (cm^3/g)			Pore size (nm)	
BET	Micro[a]	BJH[b]	Total[c]	Micro[a]	BJH[b]	Ave[d]	BJH[b]
925	912	299	0.457	0.433	0.177	1.97	2.36

[a] Micro: *t*-plot micropore.
[b] BJH: cumulative pores between 1.7 and 300 nm from BJH adsorption branch.
[c] Single point adsorption total pore volume at $P/P_0 > 0.99$ (corresponding to less than 200 nm pores).
[d] Adsorption average pore width (4 V/A by BET).

2.6. Data analysis

The experimental data were fitted using different equilibrium models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R)) and kinetic models (pseudo first-order and pseudo second-order). The amount of organics adsorbed per unit adsorbent mass was calculated as follows:

$$q = (C_0 - C_t)\frac{V}{m} \tag{1}$$

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{2}$$

where q is the amount adsorbed (mg/g), C_0 is the initial organics concentration in water (mg/L), C_t is the concentration at time t (mg/L), V is the solution volume (L), m is the mass of the adsorbent (g), C_e is the equilibrium concentration of odorants (mg/L) and q_e is the amount adsorbed of odorants at equilibrium (mg/g).

Adsorption equilibrium models were established using the KaleidaGraph software. The models were evaluated by the coefficient of determination (R^2) and Chi-square (χ^2). The Chi-square is calculated as follows [20]:

$$\chi^2 = \sum \frac{\left(q_{e,\mathrm{ex}} - q_{e,\mathrm{calc}}\right)^2}{q_{e,\mathrm{calc}}} \tag{3}$$

where $q_{e,\mathrm{ex}}$ (mg/g) is the measured amount adsorbed; and $q_{e,\mathrm{calc}}$ (mg/g) is the modeled amount adsorbed.

Two empirical kinetic models (pseudo first- and second-order) were used to describe the adsorption kinetic behaviors. In the pseudo first-order kinetic equation, the amount adsorbed of odorants is given as [16]:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{4}$$

where q_t (mg/g) is the amount adsorbed of odorants at time t, q_e (mg/g) is the amount adsorbed of odorants at equilibrium, and k_1 (h^{-1}) is the pseudo first-order rate constant.

The pseudo second-order kinetic model can be expressed as:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5}$$

where k_2 (g/(mg·h)) is the pseudo second-order rate constant. In the two kinetic models, k_1, k_2, and q_e were determined using the KaleidaGraph software.