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Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons

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ABSTRACT

When treating water with activated carbon, natural organic matter (NOM) is not only a target for adsorptive removal but also an inhibitory substance that reduces the removal efficiency of trace compounds, such as 2-methylisoborneol (MIB), through adsorption competition. Recently, superfine (submicron-sized) activated carbon (SPAC) was developed by wet-milling commercially available powdered activated carbon (PAC) to a smaller particle size. It was reported that SPAC has a larger NOM adsorption capacity than PAC because NOM mainly adsorbs close to the external adsorbent particle surface (shell adsorption mechanism). Thus, SPAC with its larger specific external surface area can adsorb more NOM than PAC. The effect of higher NOM uptake on the adsorptive removal of MIB has, however, not been investigated. Results of this study show that adsorption competition between NOM and MIB did not increase when NOM uptake increased due to carbon size reduction; i.e., the increased NOM uptake by SPAC did not result in a decrease in MIB adsorption capacity beyond that obtained as a result of NOM adsorption by PAC. A simple estimation method for determining the adsorbed amount of competing NOM (NOM that reduces MIB adsorption) is presented based on the simplified equivalent background compound (EBC) method. Furthermore, the mechanism of adsorption competition is discussed based on results obtained with the simplified EBC method and the shell adsorption mechanism. Competing NOM, which likely comprises a small portion of NOM, adsorbs in internal pores of activated carbon particles as MIB does, thereby reducing the MIB adsorption capacity to a similar extent regardless of adsorbent particle size. SPAC application can be advantageous because enhanced NOM removal does not translate into less effective removal of MIB. Molecular size distribution data of NOM suggest that the competing NOM has a molecular weight similar to that of the target compound.

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1. Introduction

2-methylisoborneol (MIB) is an earthy-musty odor compound that causes frequent customer complaints because it deteriorates the organoleptic qualities of drinking water. A widely accepted means for removing MIB is the addition of powdered activated carbon (PAC) prior to solid–liquid separation. MIB is a hydrophobic compound (log $K_{ow} = 3.31$) with small molecular size (molecular weight = 168) and is therefore efficiently adsorbed on activated carbon if it is present as a single compound in pure water. However, MIB always coexists with natural organic matter (NOM) in drinking water sources. Because NOM also adsorbs on activated carbon, it reduces the MIB adsorption capacity by competing for adsorption sites (direct site competition) and/or by hindering diffusion of MIB into carbon pores (pore blockage/constriction). NOM is also targeted for removal by many utilities because it is a precursor material for disinfection byproducts. Therefore, activated carbons that are effective for the simultaneous removal of MIB and NOM are desirable.

NOM can dramatically reduce the adsorption capacity of a micropollutant, but a micropollutant does not affect the adsorption of NOM because the concentration of NOM (mg/L) is several orders of magnitude higher than the concentration of most micropollutants including odor compounds (MIB), pesticides, and PPCPs (pharmaceuticals and personal care products), which occur at ng/L to μg/L levels. The competitive effect, namely the magnitude of the decrease in micropollutant adsorption capacity, is dependent on the loading of NOM on the carbon (Kilduff et al., 1998; Kilduff and Karanfil, 2002). Direct competition is the dominant mechanism at low NOM loading while pore blockage/constriction becomes important at high NOM loading (Kilduff et al., 1998; Matsui et al., 2003; Ding et al., 2006). It was shown that NOM of low molecular weight (MW) exerts a strong competitive effect on micropollutant adsorption (Newcombe et al., 1997, 2002b; Hepplewhite et al., 2004; Kilduff et al., 1998; Matsui et al., 2002). Low MW NOM is adsorbed to a greater extent than higher MW NOM (Matsui et al., 1993, 1998; Kilduff et al., 1996; Newcombe et al., 2002a). The resulting higher loading of low MW NOM likely exerts a greater competitive effect on micropollutant adsorption. However, even at the same loading, low MW NOM reduces micropollutant adsorption to a greater degree than high MW NOM (Kilduff et al., 1998; Matsui et al., 2002), most likely because low MW NOM can access the same adsorption sites on which micropollutants adsorb.

Although adsorption competition mechanisms between NOM and micropollutants are complex, simple quantitative modeling approaches based on multi-component adsorption theory (i.e., ideal adsorption solution theory) have been proposed and verified. One approach describing the adsorption of a micropollutant from water containing NOM utilizes an equivalent background compound (EBC) to approximate NOM (Najm et al., 1991) whereas another employs fictive components (Frick and Sontheimer, 1983; Crittenden et al., 1985). Based on the EBC approach, a simple relationship was found and validated: the percentage of micropollutant removal that can be achieved with a given carbon dose in a batch adsorption system is independent of the initial concentration of the micropollutant (Knappe et al., 1998; Gillogly et al., 1998; Graham et al., 2000). This relationship holds when the micropollutant concentration is low compared to the NOM concentration. In addition, the relationship is valid at non-equilibrium conditions in both PAC and GAC adsorption processes (Matsui et al., 2001, 2002, 2003; Zoschke et al., 2011).

To help water treatment professionals choose effective activated carbons, many studies have been conducted to better understand the mechanism of competition and to mathematically model the competitive adsorption process. However, the increased knowledge seldom results in the production of activated carbons that minimize the carbon usage rate. Some studies report enhancing the effectiveness of activated carbon for MIB removal. In one such study, PACs were tailored by changing activation conditions such that the PAC obtained with the optimized activation protocol outperformed commercially available PAC (Tennant and Mazyck, 2003). Tailoring efforts were also conducted for virgin and spent granular activated carbons to enhance their effectiveness for MIB removal (Nowack et al., 2004; Mackenzie et al., 2005). On the other hand, our research group proposed the use of superfine activated carbon (SPAC) with a particle size finer than that of traditional PAC, from which SPAC is produced by wet-milling. The design concept of SPAC was originally to improve the adsorbate uptake rate. In fact, SPAC is far superior to PAC in removing geosmin and NOM, especially at short contact times (Matsui et al., 2005, 2007, 2009). It was also found that SPAC has a higher NOM adsorption capacity than the parent PAC (Matsui et al., 2004; Ando et al., 2010). The higher NOM adsorption capacity of SPAC can be explained by the shell adsorption mechanism (SAM), which postulates that NOM molecules do not completely penetrate the adsorbent particle. Instead, they preferentially adsorb near the exterior particle surface (Ando et al., 2010, 2011; Matsui et al., 2011). As a result, a larger fraction of adsorption sites is accessible to NOM on SPAC compared to PAC due to the higher external surface area of the former. In the presence of NOM, geosmin and MIB adsorption capacities of SPAC did not become smaller than those of PAC even though NOM adsorbed to a greater extent on SPAC than on PAC (Matsui et al., 2010). This result suggests that the adsorption competition is less severe for SPAC than for PAC. However, the competitive mechanism was not inferred.

In this paper, adsorption equilibrium data of MIB and NOM were collected for SPAC and PAC and analyzed with the EBC and SAM models to elucidate differences in the mechanism of adsorption competition between MIB and NOM on PAC and SPAC.

2. Methods

2.1. *Activated carbon*

Commercially available PAC (wood-based thermally activated carbon, Taikou-W, Futamura Chemical Industries Co., Gifu, Japan) was obtained in 2008 and 2010 and prepared as a slurry in ultrapure water. PAC was pulverized into SPAC with a wet