WATER RESEARCH 68 (2015) 784–792

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

A rapid kinetic dye test to predict the adsorption of 2-methylisoborneol onto granular activated carbons and to identify the influence of pore volume distributions

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ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form
7 October 2014
Accepted 8 October 2014
Available online 17 October 2014

Keywords:
2-methylisoborneol
Activated carbon
Xylenol orange
RSSCTs
Coconut
Bituminous

ABSTRACT

The authors have developed a kinetic dye test protocol that aims to predict the competitive adsorption of 2-methylisoborneol (MIB) to granular activated carbons (GACs). The kinetic dye test takes about two hours to perform, and produces a quantitative result, fitted to a model to yield an Intraparticle Diffusion Constant (IDC) during the earlier times of dye sorption. The dye xylenol orange was probed into six coconut-based GACs and five bituminous-based GACs that hosted varied pore distributions. Correlations between xylenol orange IDCs and breakthrough of MIB at 4 ppt in rapid small-scale column tests (RSSCTs) were found with R^2s of 0.85 and 0.95 for coconut carbons that processed waters with total organic carbon (TOCs) of 1.9 and 2.2 ppm, respectively, and with an R^2 of 0.94 for bituminous carbons that processed waters with a TOC of 2.5 ppm. The author sought to study the influence of the pore sizes, which provide the adsorption sites and the diffusion conduits that are necessary for the removal of those compounds. For coconut carbons, a linear correlation was established between the xylenol orange IDCs and the volume of pores in the range of 23.4–31.8 Å widths ($R^2 = 0.98$). For bituminous carbons, best correlation was to pores ranging from 74 to 93 Å widths ($R^2 = 0.94$). The differences in adsorption between coconut carbons and bituminous carbons have been attributed to the inherently dissimilar graphene layering resulting from the parent materials and the activation processes. When fluorescein dye was employed in the kinetic dye tests, the correlations to RSSCT-MIB performance were not as high as when xylenol orange was used. Intriguingly, it was the same pore size ranges that exhibited the strongest correlation for MIB RSSCT's, xylenol orange kinetics, and fluoroscein kinetics. When methylene blue dye was used, sorption occurred so rapidly as to be out of the scope of the IDC model.

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http://dx.doi.org/10.1016/j.watres.2014.10.022
0043-1354/

1. Introduction

2-Methylisoborneol is an organic compound typically found in surface waters in the presence of natural organic matter (NOM). For municipalities, the removal of odorants such as MIB and geosmin is the primary reason that activated carbons are used. This is because odorants can undermine the confidence of consumers in their water supply (Zoschke et al, 2011). The odorants MIB and geosmin, which typically occur simultaneously in surface waters, have not exhibited harm to humans at the low concentrations that they appear in water; however, they impart an "earth-musty" odor that can be tasted by humans at concentrations as low as 5–15 ng/L (Rangel-Mendez et al, 2005; Mallevialle et al, 1987; Chen et al, 1997). Water customers perceive that if they can taste these odorants in their water, it must be harmful. Granular activated carbon columns provide a promising means of removing these odorants while also benefiting from being easily integrated into existing water treatment systems.

For potable water sources, the sorption of MIB into granular activated carbons is influenced by the natural organic matter (NOM) that is simultaneously sorbing. The sorbed NOM can create bottlenecks within the pores, and it can cause MIB to diffuse via a more tortuous path. Also, the NOM can sorb to sites that could otherwise be available to trace contaminants such as MIB and geosmin (Matsui et al, 2012). Newcombe et al. (1997) found that NOM of various sizes could adsorb in a variety of activated carbon pores from a range of 0–500 Å, with some of these odorants being able to adsorb to secondary micropores (8–20 Å).

When determining the effectiveness of a carbon for adsorbing MIB in the presence of NOM, the pore volume distributions (PVDs) can be the controlling factor (Newcombe et al, 2002). Over short adsorption times, higher volumes of mesopores have been correlated to higher sorption rates of MIB in enhanced activated carbons (Rangel-Mendez and Cannon, 2005). Mesopores provide transport for smaller molecules (MIB) as well as storage for larger molecules such as NOM (Hsieh et al, 2000; Newcombe et al, 2002). Several authors have discussed the effects of surface chemistry and pore volume distributions on the sorption of MIB and similar trace compounds (Karanfil et al, 1999; Redding et al, 2009; Snyder et al, 2007; Tennant et al, 2007; Mackenzie et al, 2005; Yu et al, 2007).

Several research teams have attempted to predict MIB adsorption in the presence of NOM (Graham et al, 2000; Nowack et al, 2004; Rangel-Mendez et al, 2005; Yu et al, 2007; Summers et al, 2013). Also, several teams have compared pore volume distributions to dye adsorption (Krupa et al, 1996; Kasaoka et al, 1989). However, the authors herein are not aware of others who have quantitatively linked MIB bed life to specific pore volume distributions and dye sorption while considering bituminous and coconut carbons.

The objective of the research herein was to: (a) develop a rapid batch dye protocol for predicting the sorption of the trace contaminant MIB to select granular activated carbons, and (b) discern the pore sizes that correlated most prominently with the rate and extent of MIB and dye sorption. In developing these protocols the authors employed six coconut based activated carbons and five bituminous based activated carbons. These hosted a range of pore size distributions. With these carbons, the authors monitored MIB breakthrough during rapid small scale column tests (RSSCTs) while employing natural surface waters that had been spiked with 14C-MIB. Also, the authors devised an experimental kinetic dye test method, wherein the activated carbons were mixed in batch solutions that contained either xylenol orange, fluorescein, or methylene blue. To better quantify the results of the test method, the authors fit the experimental data from the kinetic dye test to the Intraparticle Diffusion Model (IPD) during the initial times (from 10 to 80 min). The amount of dye remaining at various (early) times was plotted by loading (mg/g) versus the square root of time in hours, fit to a linear regression forced through (0,0), and the slope of the line was characterized as the Intraparticle Diffusion Constant (IDC) (Wu et al, 2009; Serpen et al, 2007; Zhang et al, 2007). For each carbon, this IDC was compared to the RSSCT MIB breakthroughs and to the pore volumes.

The authors selected the IDC model on the basis of being an easily interpretable and applicable model to identifying diffusion properties of carbons from experimental dye test results. In addition to this, the differentiation between when dye is being uninhibited by pore availability and when pseudo equilibrium is being approached is evident when data points no longer conform to a linear regression through (0,0).

While this paper will not focus on the adsorption of geosmin, the kinetic dye test method could potentially be used for the appraisal of carbons for geosmin removal from surface waters. Geosmin typically occurs in concentrations similar to MIB in surface waters, has a similar molecular weight and structure to MIB, and the same water characteristics that would hinder MIB adsorption (such as the presence of NOM) would affect waters containing geosmin.

2. Materials and methods

2.1. Carbons and waters

The six coconut based activated carbons were provided by Siemens Water Technologies, and included commercially available carbon (C-1), enhanced carbons (C-2, C-3, C-4), and reactivated carbons (C-5R, C-6R). The bituminous carbons provided by Calgon Carbon Corporation were commercially available carbons (B-1, B-2, B-3) and a reactivated (B-5R) carbon, while B-4D (direct activated), was provided by Siemens. These selected activated carbons had all been activated in a similar manner, and they all hosted slurry pH's of 9.3–10.0 so that surface chemistry distinctions were minimized. Pertinent characteristics of these 11 activated carbons have been presented in Table 1. The potable water sources all came from Pennsylvania municipalities and hosted TOC contents of 1.9–2.5 mg/L.

2.2. Carbon preparation

Activated carbons were grinded and sieved to specific sizes and then washed to remove dust fines. For the batch kinetic dye tests, carbon samples were prepared to a mesh size of US