



4-MCHM sorption to and desorption from granular activated carbon and raw coal



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HIGHLIGHTS

- GC-FID with head space analysis was used to determine 4-MCHM in water.
- Both granular activated carbon and raw coal can effectively sorb 4-MCHM.
- Desorption of 4-MCHM from activated carbon may be more significant than from coal.

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ABSTRACT

4-Methylcyclohexanemethanol (4-MCHM) is a saturated higher alicyclic primary alcohol that is used in the froth flotation process for cleaning coal. In early 2014, a large spill of crude chemical (containing primarily 4-MCHM) to the Elk River near Charleston, WV contaminated the local water supply. Carbon filters at the affected water treatment facility quickly became saturated, and the contaminated water was distributed to nearby homes and businesses. Sorption of 4-MCHM to granular activated carbon (GAC) was studied in the laboratory using head space (HS) analysis via gas chromatography with a flame ionization detector (GC-FID). Sorption to raw coal was also investigated, since this material may be of interest as a sorbent in the case of an on-site spill. As expected, sorption to both materials increased with decreased particle size and with increased exposure time; although exposure time proved to be much more important in the case of GAC than for coal. Under similar conditions, GAC sorbed more 4-MCHM than raw coal (e.g., 84.9 vs. 63.1 mg/g, respectively, for 20 × 30 mesh particles exposed to 860 mg/L 4-MCHM solution for 24 h). Desorption from both materials was additionally evaluated. Interestingly, desorption of 4-MCHM on a mass per mass basis was also higher for GAC than for raw coal. Overall, results indicated that GAC readily sorbs 4-MCHM but can also readily release a portion of the chemical, whereas coal sorbs somewhat less 4-MCHM but holds it tightly.

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1. Introduction

Crude MCHM, of which 4-MCHM is major component, is most commonly used as a frothing agent in the flotation process for cleaning fine coal (Noble et al., 2015). Just a couple of years ago, the chemical was not widely known, but on the morning of January 9, 2014, roughly 10,000 gallons of crude MCHM spilled from a storage tank sitting on the bank of the Elk River near Charleston, WV (Aluise, 2014). The spill resulted in contamination of the local water supply, and quickly spurred dialogue – and some action – at

multiple levels surrounding chemical regulation, emergency response and source water protection (Manuel, 2014; Rosen et al., 2014; WV, 2014; Scaggs et al., 2015).

4-MCHM is a saturated higher alicyclic primary alcohol with two isomers (Foreman et al., 2015). The chemical is classified as nonhazardous in terms of US transportation and storage requirements, though its material safety data sheet (MSDS) describes it as a skin, eye and respiratory irritant, and says that ingestion may cause nausea, vomiting or diarrhea (Eastman, 2011). It is near colorless and moderately volatile; and its strong odor is reminiscent of licorice and mint, and is detectable at extremely low (i.e., sub-ppb) concentrations (McGuire et al., 2014; Dietrich et al., 2015; Gallagher et al., 2015).

At the time of the Elk River spill, these few facts, and the lack of

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more detailed information regarding human and environmental risks, combined to cause widespread panic. The spill site is just upstream of the principal intake for a West Virginia American Water (WVAW) treatment and distribution center, which serves a population of more than 300,000. This facility continued to distribute water for hours after first receiving contaminated water from the intake (WVAW, 2014a). On the evening of the spill, WVAW concluded that its activated carbon filters could not effectively remove the MCHM from its water (Pritt, 2014), and a “do not use” order was issued to customers (WVAW, 2014a). The order remained in effect for over a week, during which time extensive flushing of the treatment facility, and plumbing systems in many affected residences and businesses, occurred. But, continued customer complaints and concerns related to odor and possible health effects of MCHM-contaminated water led WVAW to keep flushing its facility until late February 2014 (WVAW, 2014b; Whelton et al., 2015); and it eventually replaced the carbon media in the affected filters in June of that year (WVAW, 2014c).

Since the Elk River spill, much has been learned about the fundamental properties of 4-MCHM (Noble et al., 2015; Sain et al., 2015), analytical methods for its measurement (Dietrich et al., 2015), and its behavior in premise plumbing systems following contamination (Whelton et al., 2015). However, the performance of sorption media for removing the chemical from water or other environmental media has not been extensively studied yet. Here, we report on basic laboratory experiments to investigate 4-MCHM uptake and holding capacity of both granular activated carbon (GAC) and raw coal, which are of interest in different applications. GAC is commonly used as sorbent for dissolved organics in water treatment; while raw coal, being readily available onsite where crude MCHM is often used, might be employed to respond to a chemical spill (Simonović et al., 2009; Bayer et al., 2005; Cornelissen et al., 2005).

2. Experimental materials and methods

2.1. Materials

A sample of crude MCHM was donated by a chemical vendor. It consisted of primarily 4-MCHM (i.e., approximately 86% based on reports by others using the same chemical stock (Gallagher et al., 2015)), but no effort was made to identify other compounds in the sample. It was stored in a five gallon bucket initially, and then a subsample was taken after vigorously stirring the contents of the bucket. The subsample was used for all experiments reported here and stored in BD Vacutainers[®], kept out of sunlight and in a temperature controlled lab space.

GAC was obtained from CABOT Norit Americas Inc. CABOT lists this particular GAC as HYDRODARCO[®] 3000. It is an acid washed carbon designed for water treatment applications (i.e., expected to have high adsorption rate and capacity for organics) (Rivera-Utrilla et al., 2011). The GAC is produced from lignite that has undergone high temperature steam activation. Upon receipt, the GAC was dried (at 80 °C for 24 h) and sized by sieving in the laboratory. Three particle size classes were collected: 12 × 16 mesh (1.19–1.68 mm), 16 × 20 mesh (0.84–1.19 mm) and 20 × 30 mesh (0.59 × 0.84 mm). At this point, the GAC was stored in sealed plastic bags to prevent moisture uptake and oxidation; all experiments were completed within 4 weeks.

A raw coal sample was acquired from a mine in central WV, which was operating in the Upper and Lower Cedar Grove seams. The coal was run-of-mine (i.e., unprocessed) material, and was stored in a five gallon bucket for several weeks before it was crushed using laboratory jaw and roll crushers, and then dried and sized similarly to the GAC. The coal was stored in sealed plastic bags

to minimize oxidation; then all experiments were completed within five weeks.

Following preparation of the GAC and coal samples, proximate analysis was performed on both materials to determine their oxidizable (i.e., organic) mass fraction. Higher organic fraction should presumably increase organic sorption capacity of these materials (Leboeuf and Weber, 2000; Delle Site, 2001; Huang et al., 2003). The analysis was performed using a Leco TGA701 Thermogravimetric Analyzer. Table 1 reports the organic percent of material in each size class on a dry weight basis (i.e. after moisture and volatile removal). Results represent analysis of triplicate samples. A scanning electron microscope (SEM) using a backscatter electron detector (BSD) was also used to image samples of both materials (e.g., see Figs. S1 and S2 in the supplemental information). Both the proximate and SEM analyses showed that the GAC had a somewhat higher oxidizable mass fraction than the coal.

2.2. Volatilization, sorption and desorption experiments

An initial experiment was carried out to observe the extent to which 4-MCHM is lost due to volatilization under several conditions. Three Erlenmeyer flasks were each filled with a 100 mL of a crude MCHM solution having a concentration of 56 mg/L (or 48 mg/L as 4-MCHM). This solution was made by dissolving the crude MCHM in deionized (DI) water, and the concentration of 4-MCHM was confirmed by gas chromatography with flame ionization detector (GC-FID) using a head space (HS) method as described below. All three flasks were left uncovered; the first was left on the benchtop as a control (room temperature of 23 °C), the second was heated to 50 °C on a hot plate, and the third was vigorously stirred using a magnetic stir bar at room temperature. Aliquots of 10 mL were taken from each flask after a period of 0, 15, 30, and 60 min. These were collected in separate 22 mL vials appropriate for the HS analysis.

Next, 4-MCHM sorption and desorption experiments were carried out with both materials. Several test conditions were replicated to confirm reproducibility of results (described below). For the sorption experiments, four representative 1-g subsamples were split from each of the sized GAC and coal samples (i.e., 24 subsamples in total). These were placed in separate flasks. To each flask, 100 mL of a crude MCHM solution was added such that four solution concentrations were tested on each material type and size. The four test concentrations were: 125, 250, 500 and 1000 mg/L (or 108, 215, 430, and 860 mg/L as 4-MCHM). All of these are notably below the expected maximum solubility in DI water at room temperature (Dietrich et al., 2015; He et al., 2015).

During the sorption experiments, flasks were sealed to minimize losses due to volatilization. They were agitated gently on a shaker table to promote interaction between the solution and solid surfaces. After a period of 1 and 24 h, 10 mL aliquots were taken from each flask. The concentration of 4-MCHM in each aliquot was then measured.

Desorption experiments were also carried out using 20 × 30 mesh GAC and raw coal. Again, 1-g subsamples (two of GAC

Table 1
Oxidizable content in GAC and coal samples.

Size class (Mesh)	Oxidizable content (mean % ± standard deviation)	
	GAC	Coal
12 × 16	80.37 ± 1.25	67.83 ± 3.49
16 × 20	83.60 ± 1.21	70.30 ± 4.52
20 × 30	83.67 ± 0.80	72.03 ± 0.31

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