4-MCHM sorption to and desorption from granular activated carbon and raw 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 x 30 mesh particles exposed to 860 mg/L 4-MCHM solution for 24 hours). 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.

Keywords: 4-Methylcyclohexanemethanol, adsorption, desorption, granular activated carbon, GC-FID, volatilization

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; WVL, 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 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, 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, 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 hours) and sized by sieving in the laboratory. Three particle size classes were collected: 12 x 16 mesh (1.19 – 1.68 mm), 16 x 20 mesh (0.84 – 1.19 mm) and 20 x 30 mesh (0.59 x 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 Figures 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.

Table 1: Oxidizable content in GAC and coal samples.

Size Class (Mesh)	Oxidizable Content (mean $\pm$ standard deviation)	
	GAC	Coal
12x16	80.37 $\pm$ 1.25	67.83 $\pm$ 3.49
16x20	83.60 $\pm$ 1.21	70.30 $\pm$ 4.52
20x30	83.67 $\pm$ 0.80	72.03 $\pm$ 0.31

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 minutes. 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 1,000 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

122 solution and solid surfaces. After a period of 1 and 24 hours, 10 mL aliquots were taken from
123 each flask. The concentration of 4-MCHM in each aliquot was then measured.

124 Desorption experiments were also carried out using 20x30 mesh GAC and raw coal.
125 Again, 1-g subsamples (two of GAC and two of coal) were split from the previously sized
126 materials. Each subsample was exposed to 100 mL of near-saturated crude MCHM solution. The
127 solution was made by vigorously mixing 2 g of crude MCHM with 1 L of DI water for
128 approximately 5 minutes. Following mixing, some MCHM could still be observed on the
129 solution surface, indicating that the maximum solubility achievable within the mixing time had
130 been met. The insoluble MCHM layer was carefully pipetted off of the solution surface, and then
131 the solution (950 mg/L 4-MCHM) was transferred into clean flasks with GAC and coal
132 subsamples. The flasks were sealed and gently agitated, for either 1 or 24 hours. Then, each
133 subsample was rinsed 20 successive times with 30 mL of DI water in each rinse. Rinsing was
134 done via a careful pipette-and-refill protocol: the solution in the flask was removed using a
135 pipette to avoid removal of solids, and then fresh rinse water was added to the flask and gently
136 agitated for 5 minutes. On rinses 1, 2, 3, 5, 10, 15 and 20, a 10 mL aliquot of the rinse solution
137 was collected and the 4-MCHM concentration was measured in each of these.

138 139 2.3. GC Analysis

140 The volatility of 4-MCHM lends it to quantitation by GC. Here, GC with HS analysis
141 was used with an FID. HS analysis involves measurement of the gaseous portion of 4-MCHM
142 that diffuses into the head space in a capped vial. The GC method details are summarized in
143 Table S1 for quick reference, and a brief description follows.

Vials containing samples for 4-MCHM quantitation were heated to 80°C and agitated for 30 min by an HS2000 auto sampler. The sampler made injections with 0.2 mL head space into a Thermo Scientific Finnigan TRACE GC Ultra GC, with a DB-624 column (dimensions in Table S1 in SI). A temperature program was used to elute the MCHM in a timely manner by increasing the oven temperature from an initial 100 °C after 1 minute had passed at a rate of 20 °C/min to 140 °C, which was held for 3 minutes before the temperature was again increased at a rate of 40 °C/min until a final temperature of 220 °C was reached and maintained for 2 minutes. Both the *trans* and *cis* isomers of 4-MCHM eluted between 5 and 6 minutes using this method. The remaining 4 minutes of the method were used to ensure that minimal carryover occurred between runs; and two blanks were also employed between each run for this reason. It should be noted that no carryover was observed in any blanks between samples reported here.

The *trans* isomer was seen to elute before the *cis* isomer. A sample chromatogram from a fresh MCHM solution (i.e., not having contacted either of the sorbent materials) is shown in Figure S3 in SI. The *trans* to *cis* ratio in fresh solutions used in this study was consistently $1.92 \pm 0.03:1$. This is slightly higher than the ratio found in previous studies, which reported 1.75:1 (Dietrich et al., 2015) or 1.77:1 (Foreman et al., 2014) in solutions of crude MCHM from similar chemical stocks. Notably, these studies used different analytical techniques (i.e., NMR or purge and trap GC-MS, respectively) and investigated MCHM concentrations that were higher than many of those investigated here.

A calibration curve was established using a stock solution of 100.00 mg/L crude MCHM (or 86.00 mg/L as 4-MCHM) in DI water, which was diluted to concentrations of 1.25, 6.25, 12.50, 25.00 and 50.00 (or 1.08, 5.38, 10.75, 21.50 and 43.00 as 4-MCHM). The curve exhibited very good linearity above the 5.38 mg/L 4-MCHM concentration (see Figure S4 in SI), which

can be taken as limit of quantitation for the HS with GC-FID method used here. At the lowest concentration, 4-MCHM was detectable but the FID response was lower than predicted by the linear calibration curve.

3. Results and Discussion

At the outset, it is important to note that the experimental methods and GC-FID with HS analysis were observed yield reproducible results. Reproducibility was implied by running random replicate tests (see Tables S2 and S3 in SI) as well as by analyzing replicate standard solutions on several occasions. Standards solutions with target 4-MCHM concentrations of 10.75, 43.00 and 86.00 mg/L were measured to be 10.71 ± 0.12 ($n = 5$), 43.26 ± 0.85 ($n = 6$) and 85.66 ($n = 2$, values of 88.03 and 83.28) mg/L, respectively. For the volatilization experiment, the initial test solution concentration was also effectively measured in triplicate (i.e., the $t = 0$ samples for the control, heated and stirred tests). The target 4-MCHM concentration of that solution was 48.16 mg/L, and the measured test solutions were determined to be 48.27 ± 0.11 mg/L.

3.1 Volatilization of 4-MCHM

The experiment to investigate volatilization of 4-MCHM from aqueous solution confirmed that the dissolved chemical does not readily come out of solution under stagnant conditions at room temperature (Table S4 in SI). In the control test, the 4-MCHM concentration after 1 hour was still 99.99% of the initial concentration. This is consistent with a very small Henry's Law constant (i.e., partial pressure in atmosphere to equilibrium concentration in solution) which has been estimated and reported elsewhere for 4-MCHM (Gallagher *et al.*, 2015). However, in tests where the solution was stirred or heated, the 1-hour concentration was

only 78.09 and 67.94% of the initial, respectively. These results illustrate the relative volatility of this chemical, and are in agreement with previous studies that found that constant agitation and elevated temperatures increase the rate at which volatilization occurs (Noble *et al.*, 2015).

3.2 4-MCHM Sorption to GAC and Coal

Though both sorbent materials were effective, the GAC sorbed substantially more 4-MCHM than the raw coal when comparing similar particle sizes and exposure times (Figures 1 and 2, and Figures S5 and S6 in SI). The highest uptake for both materials was observed for the smallest size class (20 x 30 mesh) and longer exposure time (24 hours). Under these conditions, the GAC loading was found to be 84.9 mg/g and the coal loading was 63.1 mg/g; however, these values likely do not represent the actual sorption capacity. From Figures 1 and 2, only the sorption isotherms exhibited by the larger coal particles (i.e., 12 x 60 mesh and 16 x 20 mesh) indicate the maximum achievable loading was approached (i.e., loading on a mass per mass basis began to level off as the residual concentration in the test solution increased). For the 20 x 30 mesh coal and all GAC particle sizes, the sorption isotherms appear to be nearly linear, which suggests that more 4-MCHM could have been loaded to these materials by test solutions with higher initial concentrations.

With respect to GAC, the highest loading observed here (84.9 mg/g) is double that reported in a prior study (i.e., about 39.3 mg/g) (Dietrich *et al.*, 2015). While that study does not provide the particle size range of the GAC tested, the particles were presumably larger than those in the 20 x 30 mesh sample used here. Regarding the loading to raw coal, no prior reports were found to which the results presented here could be reasonably compared. Recent studies surrounding use of MCHM in coal flotation, and partitioning of the chemical to process

wastewaters, have indeed shown that coal significantly sorbs 4-MCHM (He *et al.*, 2015; Noble *et al.*, 2015). But loading values were determined on coal particles from a processing facility, which would have been wetted and likely contacted with other processing chemicals prior to testing.

The trend of increased sorption with decreased particle size is expected since surface area, and thus availability of sorption sites, increases as particle diameter decreases. Increased sorption with exposure time is also expected – though the time significance was seen to be greater for the GAC than for the coal. To illustrate, comparing all 1 and 24 hour tests (i.e. test pairs having the same particle size and initial 4-MCHM concentration), sorption to the GAC increased by $26 \pm 9\%$ but sorption to the coal only increased by $4 \pm 6\%$. The relatively quick sorption to coal is consistent with recent findings by He *et al.* (2015). The observed difference in kinetics here may mean that key differences exist in the sorption mechanisms between the two materials – with one possible explanation being that GAC has higher porosity than coal, leading to increased surface diffusion and number of active sorption sites. As a result of reduced pore path length in GAC, inter-particle transport by the solution may be relatively fast in GAC as compared to coal. These characteristics, combined with the somewhat higher organic content of the GAC, may translate to a relatively lower activation energy of sorption for GAC, and thereby an increased rate and amount of 4-MCHM uptake (Steinberg, 1987; Pignatello, J.J., 1990; Pignatello and Xing, 1996; Adamson and Gast, 1997; Aktaş and Çeçen, 2007; Shih *et al.*, 2009).

Generally speaking, sorption to either material did not appear to be strongly preferential for one isomer versus the other. For the 1-hour tests with both materials and the 24 hour tests with coal, the *trans* to *cis* ratios in the residual solutions were near or only slightly higher (i.e., up to 2.12:1) than the 1.92:1 ratio observed in fresh solutions (see data in Tables S2 and S3 in SI).

238 This suggests that the isomers behave similarly in terms of their interaction with organic
 239 surfaces, as has been observed with other organic compounds having multiple isomers (Shih and
 240 Gschwend, 2009). For the 24-hour tests with GAC, the *trans* to *cis* ratio was typically observed
 241 to be slightly lower (i.e., down to 1.70:1) than the 1.92:1 ratio for fresh solutions. In two of the
 242 24-hour GAC tests, the 4-MCHM was almost completely sorbed (i.e., the residual concentration
 243 in the test solution was less than 12 mg/L) and the *trans* to *cis* ratio was relatively low (i.e.,
 244 1:46:1 or less). While the 4-MCHM concentration in these tests was approaching the limit of
 245 quantitation, other test and standard solutions with low total 4-MCHM still exhibited ratios at or
 246 near the 1:92:1. As such, these results may actually indicate that preferential isomer sorption can
 247 happen under some conditions – but further research is required to explore this more thoroughly.

248
 249 Figure 1. 4-MCHM loading to GAC and coal in 1-hour tests as a function of 4-MCHM
 250 concentration remaining in the test solution. Note that one data point in the GAC 16 x 20 size
 251 class test series appears to be an outlier and is not included in the trend-line.

Figure 2. 4-MCHM loading to GAC and coal in 1-hour tests as a function of 4-MCHM concentration remaining in the test solution

3.3 Desorption

In the desorption experiments, the effect of time was again observed. Materials exposed to the crude MCHM solution for 24 hours prior to rinsing desorbed more 4-MCHM during the rinsing than did materials that had only been exposed for 1 hour (Figure 3, and Table S5 and S6 in SI). This is probably because the materials exposed for longer were loaded with more of the chemical prior to rinsing.

Interestingly, results from these experiments also revealed that GAC tended to desorb more 4-MCHM than did coal of similar particle size. Anecdotally, this may provide some explanation for the prolonged release of chemical from the WVAW filters affected by the Elk River spill. Conversely, 4-MCHM is not generally found in significant concentrations in process waters associated with fine coal preparation where the chemical is used as a flotation reagent

(Noble *et al.* 2015; He *et al.* 2015). Taken together with the sorption results, it appears that following loading and then contact with clean water the GAC and coal actually tended to *hold* relatively similar amounts of 4-MCHM on a mass per mass basis. To explain: From Figure 3 it can be determined that the 24-hour exposed coal only lost about 0.86 mg/g of 4-MCHM total – i.e., about 21.5 mg/L desorbed in the first 30 mL of rinse water and 7.7 mg/L desorbed into the second 30 mL of rinse water. The 24-hour exposed GAC, on the other hand, lost approximately 12.6 mg/g of MCHM over 20 rinses (desorption estimated from the trend line for rinses where 4-MCHM was not measured); and this material was still desorbing on the last rinse. Assuming that the coal and GAC samples used in these tests had similar 4-MCHM loading as the 20 x 30 mesh samples exposed for 24 hours in the sorption experiments (i.e., 63.1 and 84.9 mg/g), the final 4-MCHM held by coal and GAC would be about 62.3 and 72.2 mg/g, respectively. And with continued rinsing, the GAC would be expected to lose an additional 4 mg/g or so given the trend for the first 20 rinses. This analysis provides further evidence that sorption mechanisms may be somewhat different between the two materials.

Notably, the *trans* to *cis* ratio in the rinse solutions from the coal was again found to be similar to the 1.92:1 ratio seen in fresh solutions – even when the total 4-MCHM concentration was as low as 7 mg/L. In the rinse solutions from the GAC, the ratio was also similar to that in fresh solutions – except for when the 4-MCHM concentration was very low. In the test with GAC that had been exposed for 1 hour, the solutions from rinse 5 had 4-MCHM of 6.55 mg/L and the *trans* to *cis* ratio was 1.55:1; in successive rinse solutions (i.e., 10, 15 and 20), the 4-MCHM concentration was below the limit of quantitation (though still detectable) and so a *trans* to *cis* ratio was not calculated.

Figure 3: Desorption of 4-MCHM with successive rinsing in fresh DI water from 20 x 30 mesh GAC and raw coal materials that had been exposed for 1 hour to a near-saturated crude MCHM solution. Trend line is shown only for the GAC results, which were above the limit of detection by the GC-FID method within all 20 rinses. For rinse numbers 10, 15 and 20, the GAC results did fall below the limit of quantitation, but estimated values based on the method calibration curve are include to illustrate the general data trend. For coal, only the first rinse solution showed 4-MCHM above the method detection limit.

Figure 4: Desorption of 4-MCHM with successive rinsing in fresh DI water from 20 x 30 mesh GAC and raw coal materials that had been exposed for 24 hours to a near-saturated crude MCHM solution. Trend line is shown only for the GAC results, which were above the limits of detection and quantitation by the GC-FID method within all 20 rinses. For coal, only solutions from rinses 1 and 2 showed 4-MCHM above the method detection limit.

4. Conclusions

Though only a limited range of experimental conditions were investigated here, some important observations were made regarding sorption of 4-MCHM (from a crude MCHM chemical stock) to GAC and raw coal particles. Both materials can effectively sorb the chemical, but capacity and sorption kinetics vary – indicating that fundamental sorption mechanisms may vary also. For similar particle sizes, GAC sorbs more 4-MCHM than does coal; and sorption increases appreciably on GAC, but not coal, with increased exposure time (i.e., 24 hours versus 1 hour). Additionally, 4-MCHM-loaded GAC tends to desorb much more of the chemical than does loaded coal.

In general, a near 2:1 ratio between the *trans* and *cis* isomers of 4-MCHM was observed in both fresh solutions and test solutions that had been contacted with GAC or coal. This indicates that, for these materials and the conditions studied, sorption and desorption of 4-MCHM is not preferential with respect to the isomer. Additionally, HS analysis via GC-FID proved to provide reproducible results for measuring 4-MCHM concentrations in water.

Further research might be carried out to more definitively determine sorption mechanisms and kinetics for sorbents of interest. For example, experiments with varying 4-MCHM concentrations in flow through columns with sorbent media may provide additional insight related to chemical uptake and holding by studying breakthrough.

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