Trihalomethane Removal with Activated Carbon

By Robert J. Potwora

rihalomethanes (THMs) have been found to be the most widespread organic contaminants in drinking water. Trihalomethanes are part of a group of organic chemicals that contain one carbon atom, one hydrogen atom and three halogen atoms. The most common of these halogen atoms responsible for trihalomethane formation in water are bromine and chlorine. Figure 1 gives the chemical formulae of the four most common trihalomethanes which are formed during chlorination. These are chloroform (trichloromethane), bromodichloromethane, dibromochloromethane and bromoform (tribromomethane).

THMs are formed by the reaction of free chlorine with natural organic matter (NOM), man-made organic matter or bromide. The NOM responsible for THMs consists of humic and fulvic acids produced by decaying organic matter. Chloroform is typically found at higher concentrations in potable water than any other THM.

Regulatory info

Consumption of water with THMs has possible links to central nervous system damage, miscarriages and various cancers. A Nova Scotia, Canada study found a statistically significant incidence of stillbirth at THM levels greater than 100 parts per billion (ppb).

Regulations for the control of THMs in drinking water were first promulgated by the U.S. Environmental Protection Agency (U.S. EPA) in 1979. The maximum contaminant level (MCL) was set at 100 ppb for total trihalomethanes (TTHMs) for systems serving at least 10,000 people. The U.S. EPA revised this rule when it issued the Stage 1 Disinfectants/Disinfection By-Products Rule (D/ DBP) in 1998. The D/DBP rule reduced the MCL for TTHMs to 80 ppb. This new lower standard had to be met by the end of 2002 for systems serving over 10,000 people and by the end of 2004 for systems serving fewer than 10,000 people. Some states and industries such as bottlers have limits as low as 10 ppb TTHMs.

Treatment options

Waters that contain high amounts of NOM may be treated with granular activated carbon (GAC) prior to chlorination. The GAC adsorbs some of NOM (humic and fulvic acids), thereby reducing the amount of TTHMs formed upon chlorination.

When designing systems with water that has been previously chlorinated, GAC is used to remove the TTHMs directly. One method employed to deter-

Figure 1. Chemical formulas of the four	
most common trihalomethanes	

Chloroform	Dibromochloromethane
Cl	Cl
l.	I
Cl - C - Cl	Br – C - Br
l. I	I
Н	Н
Bromodichloromethane	Bromoform
Cl	Br
l.	I
Br - C - Cl	Br – C – Br
1	I
Н	Н

mine how long GAC will last removing TTHMs is to perform a carbon isotherm test on the specific water. Exact details on how to perform the test are available in ASTM International test method D 5919, Determination of Adsorptive Capacity of Activated Carbon by a Micro-Isotherm Technique for Adsorbates at ppb Concentrations. The test results are plotted according to the empirical Freundlich equation. As shown in Figure 2, the residual concentration of the THM in solution is plotted on the x axis and the amount of THM

adsorbed per unit weight of activated carbon is plotted on the y axis.

Activated carbon has different adsorptive ca-

Formula 2

 $\frac{0.10}{2.0}$ = 0.050 g/L x 8.34 = 0.417 pounds of carbon per 1,000 gallons of water

Formula 1

 $\frac{C_o}{x}$ = GAC usage rate, g/L

pacities for each individual THM. As seen from Figure 2, the more brominated the THM, the higher the adsorption capacity of the activated carbon. GAC has the highest capacity for bromoform and least with chloroform.

Using the isotherms in Figure 2, one may calculate a theoretical usage rate to determine how long the GAC will last for a specific THM. Let's assume a water has 0.10 mg/L (100 ppb) chloroform. Using the formula below (see Formula 1) and

the chloroform isotherm in Figure 2 the carbon usage rate is calculated.

 C_{o} is the initial chloroform concentration which is 0.10 mg/L. Using the chloroform isotherm in Figure 2, locate the 0.10 value on the x axis and draw a vertical line until it intersects the chloroform isotherm. At the point of intersection, draw a horizontal line to the y axis. This x/m value of 2.0 mg of chloroform per gram of carbon represents the equilibrium loading of chloroform

on the carbon. Using these values in the formula, the theoretical carbon usage rate is obtained.

In this illustration (see Formula 2), granular activated carbon would be consumed at a rate of 0.417 pounds for every 1,000 gallons of water treated. The isotherm curve was conducted under ideal conditions, lacking any background organics that may be present in any given stream. Therefore, the results obtained give the minimum carbon usage rate. Conducting the carbon adsorption iso-

therm on the actual water to be treated per the ASTM test method would yield more precise performance prediction. The actual water will contain background

organics, which may reduce the capacity of the activated carbon for THMs.

The isotherms from Figure





2 were conducted on bituminous coalbased activated carbon. Figure 3 contains two chloroform isotherms using bituminous coal-based and coconut shell-based activated carbons. At a chloroform concentration of 0.10 mg/L, the coconut shell-based carbon has an adsorption capacity of 2.8 mg of chloroform per gram of carbon. The bituminous coal-based carbon has an adsorption capacity of 2.0 mg of chloroform per gram of carbon, a reduction in adsorptive capacity of 30 percent.

The coconut shell-based activated carbons have a higher percentage of micropores (< 20 angstrom units) compared to bituminous coalbased carbons. Therefore, coconut shell-based carbons are preferred for adsorption of low molecular weight, smaller organics like THMs. Bituminous coal-based carbons have a higher percentage of mesopores (20-50 angstrom units) and macropores (> 50 angstrom units), making them preferred for adsorption of higher molecular weight, larger organics like humic and fulvic acids.

with THMs. EBCT is calculated by dividing the volume of the activated carbon bed by the volumetric flowrate. Therefore, a one cubic foot carbon bed treating one gallon (0.1337 cubic feet) per minute would achieve an EBCT of (1 / 0.1337) 7.5 minutes.

Typically 12 x 40 mesh size (majority of the carbon passes through a 12mesh screen but is retained on a 40-mesh screen) activated carbon is used to achieve a good balance between pressure drop and performance. In residential point of use (POU) and point of entry (POE) systems, where pressure drop is less of a concern, 20 x 50 mesh size acti-

System design

When designing a granular activated carbon system, dynamic factors must be taken into account to achieve the desired performance and fully utilize the capacity of the carbon. For municipal and industrial systems, a minimum empty bed contact time (EBCT) of seven minutes is preferred. Longer times up to 15 minutes EBCT are beneficial to more fully saturate the GAC

Figure 3. Chloroform adsorption isotherms



vated carbon may be utilized. With the smaller 20 x 50 mesh size activated carbons, EBCTs of three to five minutes (2.5- 1.5 gpm/ft^3 of GAC) may be utilized.

In waters with high levels of NOM, it's beneficial to use two carbon vessels in series. The first vessel would contain a bituminous-based carbon, which would reduce the level of higher molecular weight NOM and adsorb some of the THMs. The second vessel would contain a coconut shell-based carbon to adsorb the remaining THMs.

Conclusion

Chlorination of water produces undesirable disinfection by-products like THMs. Granular activated carbon is an excellent technology to reduce THM levels in POU/POE applications. With proper media selection and system design, THM can be controlled effectively.

About the author

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