Catalytic Carbons Help Remove Chloramine

They succeed where other carbons may fail.

By Steven D. Spotts

Where chlorine creates high levels of trihalomethanes (THMs), chloramine can be an alternative for disinfecting drinking water. Removing it at the point of use (POU), however, can be more difficult than removing chlorine. When your job requires chloramine removal, you may consider using catalytic activated carbons.

Chloramine is more stable than free chlorine and is thus a much weaker oxidant. As a result, it forms less THMs. Typical chloramine residual throughout municipal distribution systems is 1 to 3 parts per million (ppm). It’s estimated that 13 percent of municipalities use chloramine as a disinfectant. This percentage is increasing as municipalities are faced with tougher standards.

Chloramine can also be created in water through the reaction of ammonia and residual free chlorine. Ammonia is most common in surface water and is produced by pesticide runoff and animal wastes. It’s estimated that 5 to 10 percent of water supplies contains 1 to 3 ppm chloramine from this source.

In potable water, chloramine can exist as monochloramine, dichloramine and trichloramine. Monochloramine (NH₂Cl) is produced in water where the pH is between 7 and 9. Because the pH of most water delivered through public water systems ranges from 6 to 9, monochloramine is the predominant species used for disinfecting.

Because of its highly stable nature, monochloramine is also the most difficult type of chloramine to remove using activated carbon. Dichloramine (NHC₁₂), a much less stable compound, is predominant in water when the pH is 4.4 to 6 or at chloride-to-nitrogen ratios between 5 to 1 and 7.6 to 1. Activated carbon readily removes dichloramine from water.

Trichloramine (NCl₃), or nitrogen trichloride, occurs only at pH levels of less than 4.4 or at chloride-to-nitrogen ratios exceeding 7.6 to 1. Because it exists only in a low-pH environment, it isn’t usually a concern for water treatment professionals.

Potable water with residual chloramine is considered to be a problem or potential problem to many industries, as well as a taste and odor concern to many home owners and commercial establishments.

Laboratory studies show that many conventional activated carbon products made from a variety of starting materials have some affinity for monochloramine removal.

Because the chloramine conversion reaction is catalytic in nature, however, activated carbons that exhibit enhanced catalytic activity are more efficient (see graph). In theory, monochloramine removal is a two-step reaction:
(1) \[ \text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{C}^* \rightarrow \text{NH}_3 + \text{H}^+ \text{Cl}^- + \text{CO}^* \]

(2) \[ 2\text{NH}_2\text{Cl} + \text{CO}^* \rightarrow \text{N}_2 + 2\text{H}^+ + 2\text{Cl}^- + \text{H}_2\text{O} + \text{C}^* \]

where \( C^* \) and \( \text{CO}^* \) represent surface carbons and surface carbon oxides, respectively, which are active sites for the monochloramine reaction.

It’s theorized that chloramine removal is enhanced with catalytic activated carbons because of their high number of catalyst sites compared to conventional carbons.

For both conventional and catalytic carbons, the rate of chloramine removal is initially faster than at steady state because surface carbon oxides eventually supplant the carbon active sites and results in a slower removal rate. The period during which this happens is known as the induction period.

The chloramine removal efficiencies of catalytic carbons cut required contact time, extend bed life and enable you to use smaller equipment. Each of these advantages translates into cost savings for the end user without sacrificing any of the carbon’s capabilities.

Particle size affects catalytic carbons similar to the way it affects conventional activated carbons. Although it influences the rate and extent of monochloramine removal, this isn’t as significant as it is in dechlorinating applications.

Smaller particle size translates to greater bed life for a given treatment objective and empty bed contact time (EBCT), but as particle size decreases pressure drop considerations increase, resulting in diminishing capacity improvements.

In general, increasing contact time significantly improves monochloramine removal capacity as well as the achievable effluent level for all carbons. However, the increased activity of catalytic carbons makes it possible to use shorter contact times or smaller equipment. Thus, for existing systems where conventional carbon has problems removing chloramine, catalytic carbons will show marked improvement and cost savings.

This concept is particularly important in POU applications where contact times are on the order of 10 to 30 seconds. In addition, increasing EBCT has a stronger effect on the efficiency of monochloramine removal by catalytic activated carbons than it does on conventional carbons.

For example, using the same test conditions and carbons described in the graphs, changing the EBCT from 10 seconds to 25 seconds improved the performance of the catalytic carbon threefold. The conventional carbon improved by only 30 percent. Likewise, increasing EBCT to 50 seconds led to an even more dramatic performance improvement for catalytic carbons compared to conventional carbons.

Because of the improved removal efficiencies of catalytic carbons, bed life can be extended two to four times longer than can be achieved with conventional activated carbons. These efficiencies may be further improved through use of extruded or molded block technologies which capitalize on improved adsorption kinetics through use of smaller particle sizes.
Conventional carbon shown features a Peroxide Number (PN) of 60 minutes and an Iodine Number (IN) of 953. Catalytic carbon shown features a PN of 12 minutes and an IN of 930. Both carbons are 20 x 50 U.S. mesh bituminous coal-based products. In both cases, 50 cubic centimeters of carbon were tested with deionized, chlorine-demand-free water at 20°C. Influent contained 3 to 4 parts per million (ppm) chloramine and 24 ppm alkalinity as CaCO₃. Empty bed contact times were 50 seconds and pH was 8.5. The chloramine treatment objective was 0.1 ppm.

Catalytic carbons can’t remove monochloramine indefinitely. Adsorbed contaminants tend to occlude catalytic sites, eventually reducing chloramine removal efficiencies to the point where thermal reactivation or replacement is necessary. Yet because most municipal water is relatively low in organic contaminants, organic competition for adsorption or reaction sites shouldn’t be a significant concern.

Catalytic carbon can remove chloramine from water more efficiently than conventional activated carbon. Because catalytic carbons have considerably faster reaction kinetics for conversion of chloramine, your customers can realize cost savings through reduced empty bed contact time, extended bed life or by using smaller equipment. In some chloramine removal applications, catalytic activated carbons may be used where conventional carbons were ineffective.

Steve Spotts is marketing manager for the commercial business group at Calgon Carbon Corp., Pittsburgh, PA.