

Chlorine and Chloramine Removal with Activated Carbon

By Robert Potwora

Municipalities routinely began using chlorine to treat drinking water starting in 1908 with Jersey City, NJ. Its use has helped to virtually eliminate diseases like typhoid fever, cholera and dysentery in the US and other developed countries. Globally the World Health Organization (WHO) estimates that 3.4 million people in underdeveloped countries die every year from water-related diseases.

Use of chlorine in water can produce an undesirable taste; therefore, many consumers prefer to remove it. Disinfection byproducts (DBPs) may also unintentionally form when chlorine and other disinfectants react with natural organic matter that is in the water. To reduce DBP formation, many municipalities are switching to monochloramine.

Monochloramine treatment was first used in Ottawa, Ontario, Canada in 1916 and in Denver, CO in 1917. Use of monochloramine took a downturn during World War II due to ammonia shortages. Currently the US EPA estimates more than 30 percent of larger US municipalities use monochloramine.

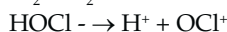
It's a common misperception that activated carbon removes chlorine and monochloramine from water by adsorption. Understanding how activated carbon removes chlorine and monochloramine from water is critical to the design and operation of such systems.

Chlorine formation and reactions

Use of chlorine is the most common method to disinfect public water supplies. Chlorine is a powerful germicide, killing many disease-causing microorganisms in drinking water, reducing them to almost non-detectable levels. Chlorine also eliminates bacteria, molds and algae that may grow in water supply systems.

US EPA's maximum residual disinfection levels (MRDLs) are four mg/L for chlorine; however, chlorine may cause problems that activated carbon can help resolve. The addition of chlorine to disinfect water is accomplished by one of three forms: chlorine gas (Cl₂), sodium hypochlorite solution (NaOCl) or dry calcium hypochlorite, Ca (OCl)₂.

The addition of any of these to water will produce hypochlorous acid (HOCl). This dissociates into hypochlorite ions (OCl⁻) to some degree. (The reaction is summarized below).



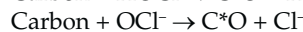
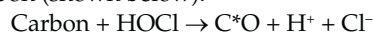
The ratio of hypochlorous acid and hypochlorite ion in water is dependent upon pH level and, to a much lesser degree, water temperature. The ratio of hypochlorous acid and hypochlorite ion at various water pH and temperature is shown in Table 1.

It is important to understand the ratio of hypochlorous

acid and hypochlorite ion in water. First, it has been estimated that hypochlorous acid is almost 100 times more effective for disinfection than hypochlorite ion. Secondly, activated carbons more readily remove hypochlorous acid compared to the hypochlorite ion.

Chlorine concentrations greater than 0.3 ppm in water can be tasted. Activated carbon is very effective in removing free chlorine from water. The removal mechanism employed by activated carbon for dechlorination is not the adsorption phenomena that occur for organic compound removal.

Dechlorination involves a chemical reaction of the activated carbon's surface being oxidized by chlorine. There are reactions when hypochlorous acid and hypochlorite ion react with activated carbon (shown below).



C*O represents the oxidized site of activated carbon after reacting with chlorine; the chlorine has been reduced to chloride ion (Cl⁻). These reactions occur very quickly.

Factors impacting dechlorination

When designing an activated carbon dechlorination system, several process factors must be considered. If the system is being designed for organic removal and dechlorination, design criteria for organic removal will override design criteria for dechlorination. Since organic adsorption onto activated carbon is a slower process than dechlorination, a system that has been properly designed for organic removal will work well for dechlorination.

When the design is strictly for dechlorination, consideration must be given to any dissolved organics that may be present in the water. These organics can reduce the capacity of carbon for dechlorination by occupying the available sites used for dechlorination.

Particle size of activated carbon is the most important factor impacting effective dechlorination. The smaller the activated carbon particles, the faster the dechlorination rate. A disadvantage of smaller particles is greater pressure drop within the media bed and, therefore, must be given careful consideration in the overall system design.

A 20x50 mesh size granular activated carbon (GAC) will be more effective than a 12x30 or 8x30 mesh GAC. Carbon block filters are made with fine mesh powder activated carbon with particle sizes predominantly between 50 and 325 mesh.

Carbon block filters, therefore, are very effective for dechlorination because of their very small activated carbon particle size. If a GAC dechlorination system was designed for 20x50 mesh GAC and it was replaced with 12x40 mesh GAC, it

Table 1. Percentages of HOCl and OCl⁻

pH	% HOCl	% OCl ⁻	% HOCl	% OCl ⁻
	32°F	32°F	68°F	68°F
4	100.0	0.0	100.0	0.0
5	100.0	0.0	97.7	2.3
6	98.2	1.8	96.8	3.2
7	83.3	16.7	75.2	24.8
8	32.2	67.8	23.2	76.8
9	4.5	95.5	2.9	97.1
10	0.5	99.5	0.3	99.7
11	0.05	99.95	0.03	99.97

would need about 25 to 50 percent more 12x40 mesh GAC. If that system was designed for 12x40 mesh GAC and it was replaced with 8x30 mesh GAC, about 100 percent more 8x30 mesh GAC would be needed.

Since dechlorination is a chemical reaction, the higher the water temperature, the faster the dechlorination rate. Winter water temperatures in northern climates can cause dechlorination rates to be reduced by as much as half as compared to summer water temperatures.

Although it is generally not feasible to adjust the pH of the water, it does have an impact upon the dechlorination rate. As discussed earlier, the pH level will affect the ratio of the hypochlorous acid and the hypochlorite ion.

Since the removal rate for hypochlorite ion is slower than that for hypochlorous acid, water at an extremely high pH will

require additional activated carbon for effective dechlorination. Going from a neutral pH of 7 to a pH of 9 or 10 will require 30 to 60 percent more GAC for effective dechlorination.

The expected service life of 12x40 and 8x30 mesh GAC at a water temperature of 70°F (21°C) and pH 7 is given in Figure 1. Flowrates through the GAC bed were 4 GPM/ft³ GAC, 2 GPM/ft³ GAC and 1 GPM/ft³ GAC. This corresponds to an empty bed contact time (EBCT) of 1.9, 3.7 and 7.5 minutes respectively.

EBCT calculation equation is:

$$\frac{\text{Volume of activated carbon (ft}^3\text{)}}{\text{Flow rate of the water (ft}^3\text{/minute)}}$$

The chart assumes no organic or bacteria interference and breakthrough at 0.1 ppm Cl₂.

A typical activated carbon cartridge breakthrough curve

Figure 1. Dechlorination with GAC

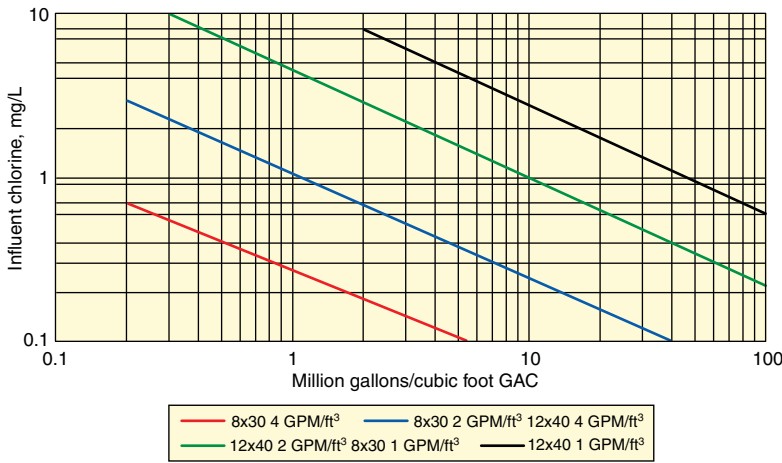


Figure 2. Dechlorination

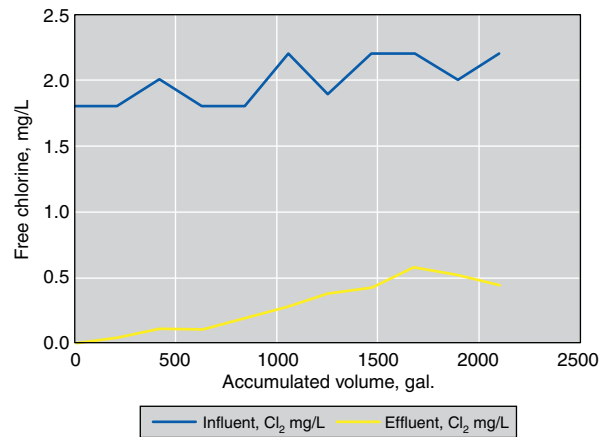


Table 2. Properties of surface-enhanced coconut shell GAC and bituminous coal GAC

Parameter	Surface-enhanced coconut shell-based	Surface-enhanced bituminous coal-based
Apparent density, g/cc	0.48	0.56
Apparent density, lb/ft ³	30	35
Iodine number, mg/g	> 1,100	825
CCl ₄ , %	60	—
Total ash, %	< 3	7
Hardness number	> 97	85

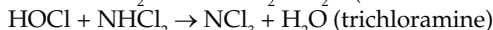
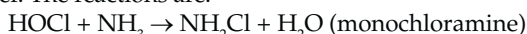
tested for dechlorination per NSF/ANSI 42 protocol is shown in Figure 2. The carbon cartridge contained 20x50 mesh coconut shell GAC. The flow rate was 0.5 GPM with an EBCT time of 0.14 minutes.

Chloramine formation and reactions

Using free chlorine to disinfect, however, can cause problems. Free chlorine can react with naturally occurring organics in the water, like humic and fulvic acids, to form total trihalomethanes (TTHMs) and haloacetic acids (HAAs).

Trihalomethanes in water are generally composed of chloroform and, to a lesser extent, bromodichloromethane, dibromochloromethane and bromoform. To minimize TTHM and HAA formation, many municipalities have switched to alternate disinfection methods, the most common being monochloramine.

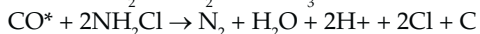
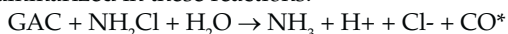
Chloramines are formed by adding ammonia to chlorinated water. The reactions are:



The chloramine formed is dependent upon water pH. At pH less than 4.4 trichloramine is formed. Between pH 4.4 – 6.0, dichloramine is formed. At pH above 7, monochloramine is the most prevalent.

Since most municipalities have a pH greater than 7, monochloramine is the only chloramine to be concerned about. Monochloramine may impact taste and odor, but to a lesser extent than chlorine. It is toxic to tropical fish and may cause anemia in patients being treated with kidney dialysis.

Removal by activated carbon, therefore, is becoming more common. How monochloramine is removed by activated carbon is summarized in these reactions.



CO* represents a surface oxide on the GAC

The preferred reaction is the second one because nitrogen and chloride are the end products. With a new bed of traditional GAC, the first reaction occurs to some degree with ammonia being formed. Over time with traditional GAC, the second reaction will occur.

GAC systems designed for free-chlorine removal may need to be retrofitted for monochloramine removal. The reaction rate for monochloramine removal is considerably slower than removing free chlorine using traditional GAC.

At least two to four times more EBCT will be required for monochloramine removal with traditional GAC. Regulatory authorities and some standards may require 10 minutes EBCT when removing monochloramine from water for kidney dialysis.

Information on treating water for hemodialysis may be found in ANSI/AAMI Standard RD 62:2006, "Water Treatment Equipment for Hemodialysis Applications."

Surface enhanced activated carbons

To compensate for poor performance of traditional GAC for monochloramine removal, manufacturers have developed surface-enhanced activated carbons. These activated carbons have surface reaction sites enhanced during the manufacturing process. They are superior for monochloramine removal compared to traditional GAC. For surface-enhanced GAC, an EBCT of three minutes will be sufficient to remove monochloramine from water. A coconut shell-based, surface-enhanced GAC can be compared to a bituminous coal-based, surface-enhanced activated carbon (Table 2).

In addition to excellent monochloramine removal with surface-enhanced coconut shell-based GAC, its higher iodine number means it has superior volatile organic chemical (VOC) capacity. It also has lower ash content and higher hardness, resulting in less dust.

A quick bench-scale test is used to evaluate how well different types of activated carbons perform for monochloramine removal. In a beaker containing 400 mL water and four-ppm monochloramine, 0.2 grams of pulverized activated carbon is added.

With constant stirring, reduction in

Figure 3. Removal of monochloramine

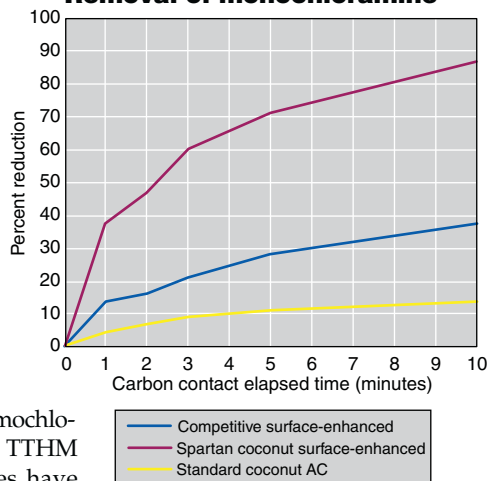


Table 3. Monochloramine removal guidelines

GPM	2.5	5.0	7.5	10.0
ft ³ surface-enhanced GAC	1.0	2.0	3.9	4.0
ft ³ traditional GAC	3.3	6.7	10.0	13.4

monochloramine is monitored over time. Different types of surface-enhanced activated carbons can be compared with a traditional activated carbon (Figure 3). The surface-enhanced, coconut shell-based activated carbon proved superior.

Based upon field studies for surface enhanced GAC, a minimum EBCT of three minutes is recommended. For traditional GAC, a minimum EBCT of 10 minutes is recommended. Using the recommended EBCT for each type of GAC, the volume of GAC required for various flow rates may be compared (Table 3). Surface-enhanced GAC costs more, but based upon the lower volume requirements, it is cost effective compared to traditional GAC.

About the author

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About the company

♦ Carbon Resources, based in Oceanside, CA, is a quality supplier of activated carbon products and services that is backed by technical support and individualized customer service. The Carbon Resources management team has over 85 years of experience in the activated carbon industry and offers an unmatched line of the most diverse activated carbon products on the market. The Sabre-series®, Spartan-series® (the surface-enhanced coconut shell-based activated carbon used in Table 2), Guardian Adsorber-series® and newly introduced Sentry-series® activated carbon products are widely recognized in the industry. For more information, please visit www.carbonresources.com.