

Application Bulletin

A NEW WEAPON IN THE CHLORAMINE BATTLE

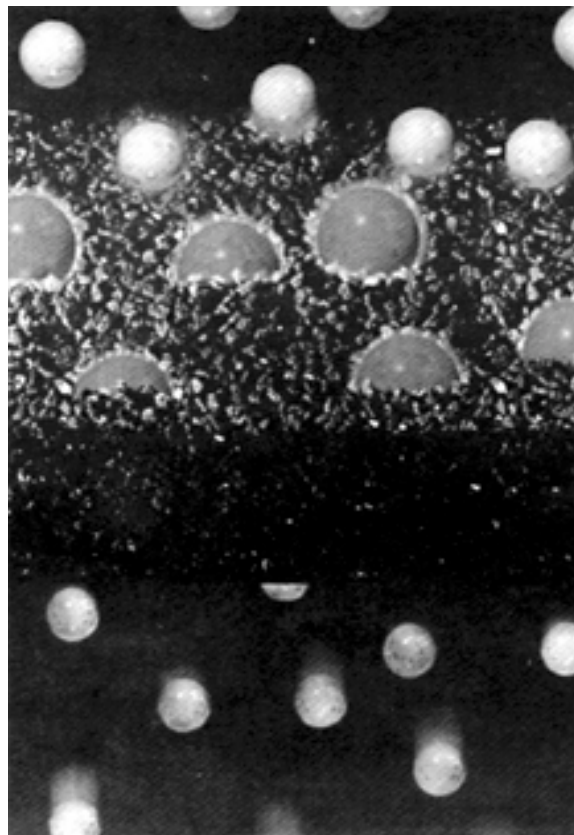
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Summary

With the growing use of chloramine as an alternative to chlorine disinfection and its by-products, the problem of chloramine removal also is getting attention. Standard activated carbon provides one solution but has limitations. A new method - using enhanced catalytic carbon - may provide dealers with an efficient option, one that lets dealers use smaller systems and extend carbon life.

Water treatment dealers struggling with the removal of chloramines can be sure of one thing - they're not alone. Many municipalities are switching to chloramination for disinfection; and, more than ever, dealers around the country are reporting the presence of chloramines in their local drinking water supplies. These residual chloramine concentrations - and their resulting taste and odor issues - are cause for concern among homeowners and commercial establishments alike.

Breakthroughs in the development of catalytic carbon have offered a more efficient and cost effective method of monochloramine decomposition. These revelations have proven to be more effective than the traditional activated carbons currently in use. And, as an added benefit, catalytic carbon decreases the contact time required and significantly extends the life of the carbon. Water treatment dealers find that, by taking advantage of catalytic carbon, they use smaller systems that provide enhanced performance at less cost.



The synergy of adsorption with enhanced catalytic capability.

How Do Chloramines Originate?

In areas where standard chlorinating practices are used, chloramines can be formed through the reaction of free chlorine and ammonia. In other locations, chloramines are intentionally introduced into the water by municipal treatment plants as an alternative disinfectant. This is done mainly for two reasons: First, chloramines control bacterial growth, both in the facility and the distribution system; and second, chloramine disinfection replaces chlorine disinfection and reduces the formation of trihalomethanes (THMs) that result when chlorine reacts with naturally occurring organic matter. However, chloramines must be removed from water used in hemodialysis, production of soft drinks and fisheries. In particular, they have been found to cause hemolytic anemia in patients undergoing kidney dialysis.¹

Chloramines exist in water in three forms - monochloramine, dichloramine and trichloramine (*see Table 1*). The particular chloramine that is produced depends upon the pH level of the water and the chlorine-to-nitrogen (Cl:N) ratios. At low pH levels (around 4) and high Cl:N ratios, the primary chloramine reaction product is trichloramine. At a pH level above 4 but less than 5 and a moderate Cl:N ratio, dichloramine formation will occur. Finally, when the pH levels exceeds 6, monochloramine formation will occur. Since the pH of most drinking water supplies is neutral or above - that is, 7 or higher - the overwhelming majority of chloramines in drinking water are monochloramines. Complicating matters is the fact that monochloramines are highly stable in nature, making them the most difficult type of chloramine to remove via activated carbon.



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Forms of Chloramine
Table 1

Species	Chemical Formula	Water Conditions Present
Monochloramine	NH ₂ Cl	pH 7 - 9
DiChloramine	NHCl ₂	pH 4 - 4.6*
TriChloramine	NCl ₃	pH < 4.4**

* Chloride / Nitrogen ratios between 5-to-1 and 7.6-to-1

** Chloride / Nitrogen ratios exceeding 7.6-to-1

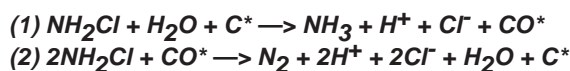
Activated Carbon Peroxide Numbers
Table 2

Activated Carbon	CAP* Number (Minutes)
Catalytically Enhanced Bituminous Coal-Based	8
Conventional Bituminous Coal-Based	40
Subbituminous Coal-Based	40
Lignite Coal-Based	80
Wood-Based	<120
Coconut-Based	>120

* Catalytic Activity Peroxide

Monochloramine Removal

Traditionally activated carbon has been used for chloramine removal. All activated carbons have some catalytic functionality and act as a catalyst to decompose monochloramine. The following two parallel reactions are believed to be the paths of decomposition:



In the decomposition of monochloramine, the first reaction predominates when the system begins operation. In doing so, the carbon surface (C*) reacts with monochloramine to reduce the monochloramine to ammonia and oxidize the carbon surface to form surface oxygen groups (CO*). It is these CO* groups that can mask the catalytic activity of an activated carbon. Fortunately, as the number of surface oxygen groups increases, the second reaction begins. If a sufficient number of original catalytic sites are not present, however, the second reaction does not take place with enough frequency to regenerate the sites, leaving the carbon "spent."

Catalytically Enhanced Carbon

Catalytic carbon is developed through an advanced process, starting as a bituminous coal-based granular activated carbon (GAC). By altering the electron structure, the GAC offers enhanced catalytic capability enabling it to cause chemical reactions to proceed without changing its own basic structure. With more catalytic sites available for electron transfer, it also promotes a wide range of chemical reactions where conventional carbons are not effective.

To varying degrees, the existence of catalytic properties in activated carbon has been widely reported.² The fundamental significance of catalytic carbon is that its catalytic activity can not only be controlled, it can also be significantly enhanced during manufacturing - without the use of chemical impregnates. By modifying the electronic properties of the carbon surface, the manufacturing process results in 10-to-100 times greater catalytic functionality as compared to standard activated carbons.

The catalytic activity of carbon can be measured by the rate at which a carbon decomposes hydrogen peroxide (H₂O₂). Carbons with more catalytic sites show higher catalytic activity and decompose hydrogen peroxide at a faster rate. Table 2 compares the catalytic activity "Peroxide Number" for several types of activated carbon. The number given is the time in minutes required to decompose a fixed amount of peroxide. As shown in Table 2, catalytically enhanced bituminous coal-based carbon requires a fifth of the time of conventional bituminous coal-based carbons, 1/10th the time of lignite-based carbons and less than 1/15th the time of wood- and coconut-based carbons.



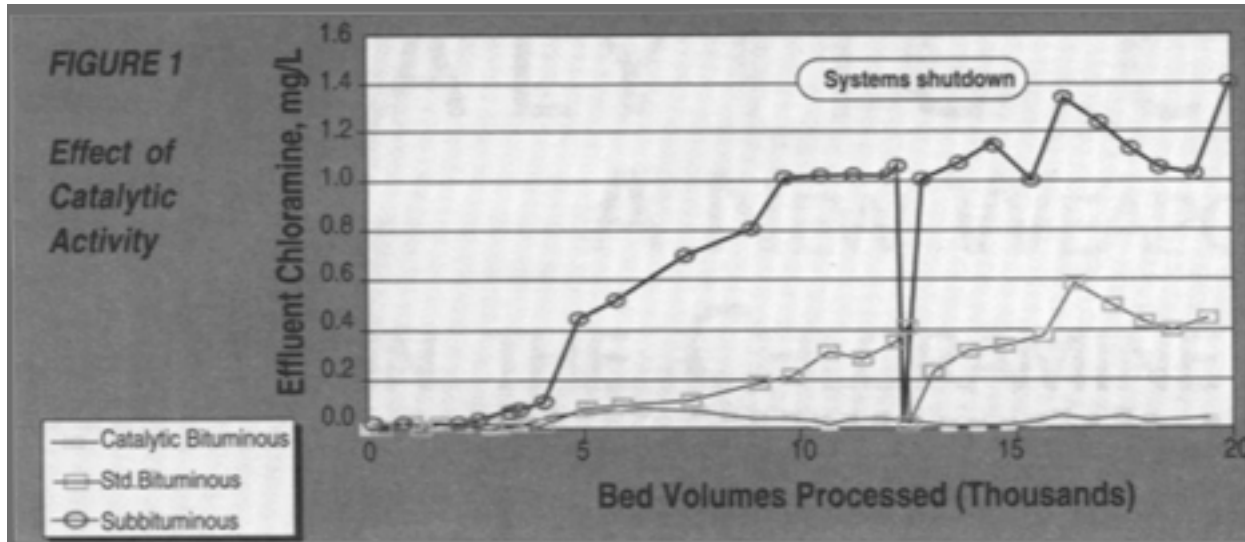
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The effect of the increased catalytic activity on chloramine destruction is dramatic.

Actual test results in Figure 1 show the chloramine breakthrough for three carbons in a two-minute empty bed contact time (EBCT) reactor system. EBCT is the volume of the carbon divided by the volumetric flow rate. Although Figure 1 only illustrates the results up to 20,000 bed volumes, the system actually continued through five months of operation, treating 88,000 bed volumes without ever exceeding a 0.1 mg/L treatment objective. It was then shut down.



System Design Considerations

As with any activated carbon system, proper system design is required to achieve the full benefits of a catalytic carbon system. Activated carbon particle size, EBCT and temperature of the influent stream all affect the performance of catalytically enhanced carbons in removing monochloramine.

A decrease in particle size will improve the rate and extent of monochloramine removal, although the effect is not as dramatic as that which is experienced in standard dechlorinating applications. Reducing the mesh size from 20 x 50 to 30 x 70 increases the bed volumes treated from 11,000 to 28,000 (at 30 seconds EBCT and 2 mg/L influent monochloramine concentration).

Increased contact times can dramatically improve the performance of the system. Increasing the EBCT from 10-to-30 seconds allowed 11,000 bed volumes to be treated as compared to 250 bed volumes (both systems utilized a 20 x 50 mesh catalytic carbon and 2 mg/L influent mono-chloramine concentration). A combination of reduced particle size and increased contact time can be used to give even more dramatic performance increases.

Because the destruction of monochloramine is a catalytic reaction, increasing the temperature of the water speeds up the reaction and extends the life of the carbon. Raising the temperature of the water from 14°C to 22°C increases the bed volumes treated from 1,500 to 4,000 (at 30 seconds EBCT and 5 mg/L influent monochloramine concentration).



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Conclusion

The development of catalytically enhanced carbon offers exciting, new opportunities for water dealers contending with chloramines. Replacing traditional activated carbon with catalytic carbon significantly improves the performance of water treatment systems, while at the same time increasing the volume of water that can be treated before experiencing chloramine breakthrough. Catalytic carbon makes it possible to use smaller systems that provide enhanced performance at less cost. For effective drinking water treatment, catalytic carbon offers dealers a much-needed alternative.

References

1. Komorita, J.D., and V.L. Snoeyink, "Technical Note: Monochloramine Removal From Water by Activated Carbon," *Journal AWWA*, January 1985, pp. 62-64.
2. Spotts, Steve, and Andy McClure, "Catalytic/Adsorptive Carbon Creates a Media 'Breakthrough,'" *WC&P*, June 1995, p. 26.

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