Catalytic Carbon for Chloramine Removal

By Vivekanand Gaur

Many water utilities across the U.S. are transitioning to chloramine for disinfection as an alternative to chlorine. This change is in response to stricter U.S. Environmental Protection Agency regulations on disinfection byproducts (DBPs), which are created when chlorine reacts with organics in water. Chloramine, a combination of chlorine and ammonia, is more stable and does not create DBPs.

Removing chloramine at the point of use, however, is more difficult than removing chlorine. Standard granular activated carbon (GAC) and carbon block products have limited capacity for chloramine reduction. Products known as “catalytic” or “surface-modified” activated carbon can provide a solution.

In general, the catalytic properties of carbon are measured by the rate at which carbon decomposes hydrogen peroxide. The resulting peroxide number, measured in minutes, estimates the carbon’s utility in any catalytic application, including chloramine reduction. Based on the comparative results obtained for different mesh size commercial carbons, the efficiency of chloramine reduction is discussed in the terms of peroxide decomposition capacity and further extended to the total life (volume) claims for corresponding GAC cartridge and carbon block.

**Reduction Mechanism**

Monochloramine is produced by adding ammonia to water containing free chlorine (HOCl or OCl, depending on the pH level) at the first stage of chlorination:

$$\text{NH}_2\text{(aq)} + \text{HOCl} \rightarrow \text{NH}_3\text{Cl} + \text{H}_2\text{O}$$

Hence, it has become an easy process for drinking water utilities to switch to chloramine by adding ammonia after the first stage of chlorination.

Activated carbon does not adsorb chloramine, but rather removes it through its ability to act as a catalyst for the chemical decomposition or conversion of chloramine to innocuous chloride in water. The theoretical reaction mechanism may be explained in the following steps:

Step 1: $$\text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{C}^* \rightarrow \text{NH}_3 + \text{H}^+ + \text{Cl}^- + \text{CO}^*$$

Step 2: $$\text{NH}_2\text{Cl} + \text{CO}^* \rightarrow \text{N}_2 + 2\text{H}^+ + 2\text{Cl}^- + \text{H}_2\text{O} + \text{C}^*$$

Catalytically active sites (C*) on the activated carbon decompose chloramine molecules into a carbon oxide intermediate (CO*), which further decomposes the molecules to chloride.

**Catalytic Carbon**

In general, basic activated carbon itself has some catalytic activity due to the presence of a small number of chemical functionalities present on the corners of its graphitic basal plane. To enhance the catalytic activity of carbon, the surface is modified by a chemical process in which the electronic structure of the carbon is altered in such a manner that the resulting carbon offers enhanced catalytic capability.

As a result, the catalytic carbon produced by this method is not only rich in chemisorption, but also physisorption capacity. A comparison of catalytic carbon’s properties before and after the modification process is demonstrated in Table 1.

**Measuring Catalytic Activity**

The catalytic activity of carbon may be measured by the rate at which a carbon decomposes hydrogen peroxide. In general, the peroxide number is represented in terms of the time, in minutes, required to decompose a fixed amount of peroxide. The peroxide number also can be represented in terms of capacity to decompose peroxide in a fixed time.

It is important to measure how fast the peroxide decomposition occurs. For comparison purposes, 1 gram of regular coconut shell-based activated carbon powder (100x325 mesh) shows approximately 20% capacity to decompose peroxide (from 30,000 ppm influent concentration), compared to more than 95% by corresponding catalytic carbon under an identical contact time of 10 minutes. Furthermore, it can be seen in Table 1 that the peroxide decomposition capacity increases significantly as the carbon particle size is decreased.

**Comparative Performance**

For comparing the chloramine reduction capacity of GAC, a column adsorption test method was used, wherein 10 grams of carbon were packed and an input of 3-ppm chloramine solution was passed through the column at a constant flow rate of 50 cc per minute.

The comparative results for regular 20x50-mesh GAC versus catalytic carbon GAC are shown in Figure 1. Breakthrough for standard GAC was observed within 10 minutes, whereas the breakthrough for the catalytic carbon occurred at 50 minutes. This increase in the chloramine reduction capacity is in line with the increase in the peroxide decomposition capacity from less than 5% to more than 50%.

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**Table 1. Comparative Properties of Standard & Catalytic Carbon**

<table>
<thead>
<tr>
<th>Sample Type &amp; Size (mesh)</th>
<th>Peroxide decomposition capacity (%) in 10 min. for 3% H₂O₂</th>
<th>Iodine Number (mg/g)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard GAC 20x50</td>
<td>1% – 5%</td>
<td>1,027</td>
<td>910</td>
<td>0.375</td>
</tr>
<tr>
<td>Catalytic GAC 20x50</td>
<td>&gt; 50%</td>
<td>1,072</td>
<td>1,110</td>
<td>0.467</td>
</tr>
<tr>
<td>Standard PAC 100x325</td>
<td>15% – 20%</td>
<td>1,036</td>
<td>1,127</td>
<td>0.515</td>
</tr>
<tr>
<td>Catalytic PAC 100x325</td>
<td>&gt; 95%</td>
<td>1,105</td>
<td>1,468</td>
<td>0.635</td>
</tr>
</tbody>
</table>
Powder activated carbon, both standard and catalytic, were used to make standard 10-in. blocks for the comparison of chloramine reduction capacity. Figure 2 shows the comparative adsorption profiles of chloraminated water filtered through carbon blocks at a flow rate of 2 liters per minute. Like the column performance data, the performance of catalytic carbon block was superior to standard carbon block. The chloramine reduction capacity of the catalytic carbon block increased in proportion to the peroxide decomposition of the corresponding carbon.

Conclusion
The surface modification of activated carbon by gas processing at high temperatures is one of the most effective techniques to develop the highest level of catalytic activity on carbon to reduce chloramine in water. This process results not only in higher chemisorption capacity, but it also significantly improves the physisorption characteristics, which in turn add to faster kinetics during catalytic conversion of chloramine.

The chloramine reduction capacity of any catalytic carbon can quickly be measured in terms of hydrogen peroxide decomposition. The higher the peroxide decomposition at a fixed time, the higher the catalytic activity and chloramine reduction capacity for that carbon sample. wqp

Vivekanand Gaur, Ph.D., is general manager of technology and R&D operations for Filtrex Technologies Pvt. Ltd. Gaur can be reached at vgaur@filtrex.co.in.

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**Figure 2. Comparative Performance Test for Carbon Block**

<table>
<thead>
<tr>
<th>Effluent Concentration</th>
<th>Volume Passed (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
</tr>
<tr>
<td>1.5</td>
<td>4000</td>
</tr>
<tr>
<td>1</td>
<td>6000</td>
</tr>
<tr>
<td>1</td>
<td>8000</td>
</tr>
<tr>
<td>0.5</td>
<td>10000</td>
</tr>
</tbody>
</table>

Regular Carbon Block  
Catalytic (EPC) Carbon Block

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