Common Pitfalls of Ion Exchange for Organic Traps

By Michael Gottlieb. Published in Water Technology Magazine, 1999
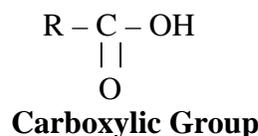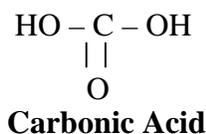
Summary: Organic traps are used primarily in two applications—color removal from drinking water and as protection for demineralizers to reduce fouling. The following article is not so much a "how to" piece on how to design such traps but rather a discussion of common problems and how to avoid them, with respect primarily to color removal. Fouling with organics is a separate issue not discussed here.

The suggestions discussed here are based, in most cases, on technology developed within the last five years and can help make better water for your customers.

Resins used in organic traps are strongly basic anion resins operated in the chloride cycle to reduce color in waters. The color-causing substances are naturally occurring organic matter, primarily tannic and humic acids. For this reason, the terms tannin removal, color removal and organic removal are often used interchangeably.

Many organic traps do not work properly, or work for a while and then crash miserably. This is primarily because of a less than optimum system design. Poor system design reflects a lack of understanding on the part of the people designing and installing the trap. Until recently, not much was known about the way that "naturally occurring" organic materials are removed by ion exchange resins. We now know (most of the reasons) why these units can fail and how to keep them running. Enough lab work has been done under controlled conditions to enable computer simulations of predicted performance for most water supplies. This article discusses the key points of the technology issues, the choices for organic trap resins, and the most common pitfalls. Since the primary effect of these resins—in most commercial installations—is to reduce color in water, that will be the primary focus.

Key principles of ion exchange organic traps

Only in the past six years has it been proven that when anion resins remove color-causing organics, they are exchanging inorganic anions for the colored anionic organic molecules. Over 90 percent of the natural organics found in potable water supplies are weak acids containing carboxylic acid groups. The dissociation of these molecules to form ions is similar in strength to carbonic acid.

When carbon dioxide dissolves in water, it forms carbonic acid according to the reaction:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3.$$

Carbonic acid then dissociates to form bicarbonate anions and hydrogen cations.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

The fraction of the CO_2 that is present as an anion increases with increasing pH.

The structural similarities of carbonic acid and the carboxylic groups is shown below

For the purpose of this discussion R represents the remainder of the organic molecule.

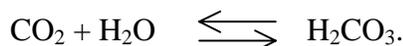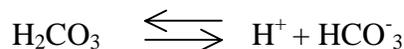|	
HO – C – OH | | O **Carbonic Acid**	R – C – OH | | O **Carboxylic Group**

Carbonic is the simplest of the organic acids. The naturally occurring organic acids, such as tannins, are made up of combinations of benzene and other chemical structures tied together to form single molecules. Each of the units may contain a carboxylic acid group. Like the carbonic acid, these may

not be fully dissociated at normal pH. Also, because of molecular structure, organic acids behave as multivalent ions. This is significant because it explains why high concentrations of salt can remove them from the resin. However, such a detailed discussion is beyond the scope of this article.

Organic trap resins exchange chlorides for all negatively charged anions in the inlet water, *even replacing the chlorides in the inlet water on an equivalent basis*. The ions that are removed then occupy the resin in layers according to their relative selectivity and the speed at which they exchange. Under ideal conditions, when the resin is exhausted, sulfate and the organic acids will be at the top, followed by nitrate, chloride and bicarbonates at the bottom.

During the initial part of the exhaustion cycle, the resin acts as a dealkalizer because it is removing bicarbonate (alkalinity). During this stage of the cycle, the effluent pH can drop to about 5.0, which often is one-to-two units lower than the untreated inlet water. The resin continues to load up with those ions having greater affinity than bicarbonate, at the expense of bicarbonate, which is displaced from the resin and appears in the effluent. As the bicarbonates leave the resin, the effluent pH rises and can even become

Regeneration Time Vs Elution Capacity

higher than the untreated inlet. As the run progresses, chlorides and then nitrates will be displaced by organics and sulfates. If the trap is operated long enough, the only species on the resin will be sulfates and organics.

Most tannins and other organic molecules have more than one carboxylic acid group. They also have relative affinities for anion resin similar to sulfates, but are much more slowly exchanged. The term "tannin"
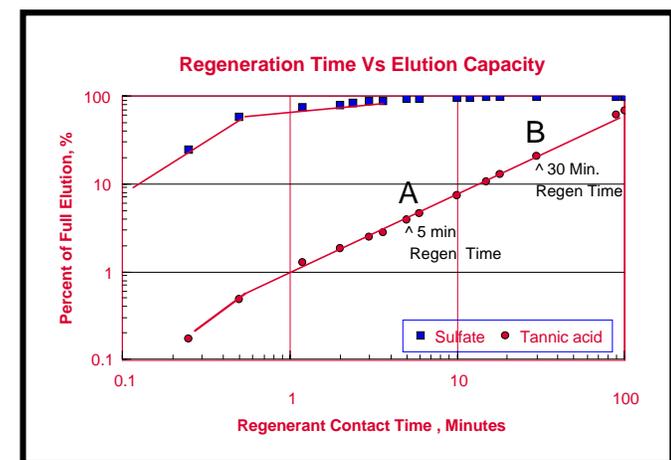
is descriptive and actually covers a large range of possible molecular weights and chemical structures. Sulfate fits roughly in the middle of the selectivity range exhibited by "tannins". About 50 percent of the tannins have a greater affinity than sulfate.

During the first portion of the cycle, while the entire resin bed is in the chloride form, the entire bed is available for exchange. As the resin exhausts into the organic and sulfate form, there is more competition for exchange sites. The exchange for organics is less favorable, and only a portion of the resin bed is available for removing organics.

Because the rate of exchange for organics is so slow, only the surface exchange sites on the resin beads are immediately available. Resins that possess large surface areas and/or high moisture contents are able to move exchanged organics from the surface to sites deeper within the resin beads at a faster rate, which frees up the surface sites more rapidly, making the removal more complete.

The presence of bicarbonates, in the feedwater increases the operating capacity and improves quality. This is because alkalinity raise the pH of the resin, which increases the degree of ionization of the weakly acidic organics which in turn increases their availability to exchange. If the influent water has been treated for low pH, the resin initially will counteract the benefit by removing the added alkalinity; but bypassing or treating both influent and effluent are possible ways of operating in such situations. For multiple cycles, we have to remove the loaded organic matter and make the resin ready for the next cycle. In the long run, the resin can only remove as much organic matter during the service cycle as is removed from the resin during the regeneration step. If the removal is substantially less than the loading, the resin will foul with the organics.

The key factor in removing organics from an anion resin is *brine contact time* (relative to time in service). Salt dose and frequency of regeneration are also significant factors. Increasing salt dose and frequency of regeneration also the absolute brine contact time. Just as effective is extra contact time created by a soak step after brining, but before the displacement and rinse step.

Divalent ions such as sulfate and multivalent ions such as tannin lose most of their affinity for the resins at the higher brine concentrations used during the regeneration step. However, the exchange rate of tannins is on average 50-to-100 times slower to regenerate than sulfates. If 16 hours were allowed for regenerant contact time, the regeneration would proceed for tannins (at similar dose levels) as effectively as the regeneration of sulfate. In reality, the regeneration time of many organic trap resins is as little as 5 minutes and rarely more than 30 minutes. While this is more than enough time for the inorganic ions, such as sulfate, it reduces the organic removal to a small fraction of its potential.

The relative contact time between the regeneration step and the service cycle is another way of stating the regenerant contact time. Increasing the frequency of regeneration increases the relative contact time for removing the organics from the resin. The salt dose could be cut proportionately with little impact, providing the absolute contact time remains the same at each regeneration.

There are several techniques to get more organics off the resin during the regeneration step. One way to increase contact time while dealing with the limitations of standard equipment (softener) designs is to reduce the salt concentration and extend the brine volume. This can work in combined softener/trap systems, especially when combined with increased regeneration frequency. Organic acids are only partially ionized, particularly at neutral and low pHs. This limits the ability of the regenerant to displace them. The addition of a small amount of alkaline material to the regenerant brine raises the pH of the regenerant solution, which increases the solubility and mobility of the organics - thus, enhancing their removal. It is not uncommon to see more than twice as much tannin eluted - or washed out - when soda ash is added to the salt regenerant. Likewise, increasing the regenerant temperature increases both the rate of exchange and the solubility of the organics but the benefit is not as great as adding soda ash to the salt.

Part II – Resin Choices

All common organic trap resins are strongly basic anion exchangers. They can be gel, macroporous, styrenic, acrylic, Type 1 or Type 2.

For a given resin type, the gel phase moisture content of the resin is the single most important attribute. Increasing gel phase moisture always increases the ability of the resin to be regenerated, and improves its performance on a regenerable basis.

Acrylic Anion Exchange Resins
On most waters, the acrylic polymer backbone is known to have superior organic loading characteristics, compared to styrenic resins of equivalent moisture content and capacity. However, acrylic resins can and do load beyond their regenerable limit and become clogged. Unable to be regenerated, the fouled resin has to be discarded. This can be overcome by restricting the service cycle length so as not to exceed the operating capacity of the resin, as defined by the resin's regeneration characteristics.

Styrenic Anion Resins
Styrenic resins do not have as open a polymer structure as have acrylic resins and therefore will always perform poorly compared to an acrylic resin of equal gel phase porosity and surface area. However, styrenic resins are good, provided that moisture and surface area are increased to compensate for the tighter polymer structure.

Macroporous Anion Exchange Resins
Macroporous resins are gel-type resins with large, discreet pores. The larger the surface area exposed to the solution, the more exchange sites are available to remove the slow moving organics. Macroporosity adds surface area, but most macroporous resins have higher "crosslinker" levels, which means lower gel-phase porosity and lower gel-phase moisture. This counteracts the benefit of greater surface area. Some macroporous resins do not perform as well as their gel counterparts for this reason.

Other Resin Choices
Other less commonly used choices for organic traps include Type II anion resins and weakly basic anion resins. Type II resins generally have too low of moisture to be effective in organic traps. Weakly basic resins work only under acidic conditions and are generally not suitable for use in potable water.

Part III – The Pitfalls

Resin Selection
Failure to understand the features that make a resin a good organic trap candidate, can result in an unsuccessful installation. Whatever the preference of manufacturer or polymer backbone, the higher the moisture content, the better the resin will perform.

Resin Volume
The most common pitfall is the failure to use a sufficient quantity of resin. Unless there is very little organic color in the water, or the users' expectations are quite modest, it is often necessary to maintain the flow rate through an organic trap at less than 2 gpm/ft^3. Leakage of organic acids increases dramatically when the flow through the resin is increased.

Flow Rate
When organic traps fail in their first cycle, it's usually because the flow rate is too high for the amount of resin used. The tannins are the slowest ions to be exchanged and need more contact time to be properly removed. The solution is simple: slow down the flow rate. For starters, slow the flow rate to one that achieves acceptable quality. At this benchmark flow rate, the resin is already on the verge of organic breakthrough and the capacity will be very limited. At the benchmark flow rate, the entire resin is required to give enough time for the organics to be removed. Cutting the benchmark flow in half will give about 50 percent of the resin's total capacity for sulfates plus organics.

Inadequate Brine Contact Time
During regeneration, the organics are exchanged off the resin using a solution of sodium chloride (NaCl). The bring concentration must be increased sufficiently to overcome the high affinity of the organic and sulfate molecules and drive them out of the resin beads. The slow exchange rate of organic ions complicates the regeneration process of organic removal contact resins. If the time is not adequate, the amount of organics loaded during the service cycle will be greater then the amount removed during the regeneration cycle. When this happens, there is a build-up of organics on the resin and eventually the resin will fail.

Most traps are not sufficiently regenerated to keep the organic concentration on the resin from building up, nor is the brine cycle extended to the maximum pos-

sible time, nor is the pH of the brine elevated. Increased regenerant contact time and or the addition of alkaline salts to the regenerant can greatly extend the life and performance of these traps.

Low/pH/Scaling
The exchange of chlorides for other inorganic ions causes the pH to be reduced during the first part of the run, and a scaling potential to occur during the latter part of the run. This phenomenon is frequently overlooked, and can cause both red water problems from excessive rusting and possible fouling of the resin with scale.

Biofouling
Biofouling occurs when the organic laden resin contacts water that is not chlorinated, or when there is sufficient organic matter to react with chlorine in the upper portion of the bed, leaving the lower portion of the bed unprotected. Biogrowths are very common in organic traps. The organic trap resins using the acrylic polymer backbone are most susceptible to problems with biofouling. Biofilms form a coating on the surface of the resin beads, block the exchange of organic ions, and cause the trap to crash and fail. Increasing the frequency of regeneration, use of hot water washes and use of sterilizing agents approved for potable water applications can all help overcome this problem. However, both equipment and resin limitations need to be addressed before such procedures are attempted.

Odor Throw
Strong base anion resins, at pH greater than 7 – 8, impart a fishy odor to the water. This can happen if excessive alkalinity is added to the brine, and can also happen toward the end of the run when the resin begins dumping alkalinity. The fish odor chemical is not toxic, but is a nuisance. The greatest potential odor problem resins are: Acrylic > Type 1 standard gel > Type 1 very porous gel > Type 2. There are also regeneration techniques to minimize odor throw, including the addition of small amounts of weak acid (citric or acetic) to the brine tank.

Conclusion
The design of organic traps has often been a hit or miss proposition. *The goal in this article has not been to show "how to build" an organic trap. Rather it has been to explain why these systems*

don't always work and how to avoid or minimize problems—practical approaches for non-technical people.

For example, the flow rate used in traps is a wide range of numbers (from as little as 0.5 gpm/ft^3 to as high as 40 gpm/ft^3). In the one case, very highly colored water is treated for 95 percent or more reduction. In the second, highly colored water is treated by throwing a small amount of tannin resin on top of the softener resin—which doesn't always work. It is not always practical for the local water treatment dealer to get enough information about the water to predict the amount of resin needed. A small demo system at the customer site is essentially identical in construction to the demo softener units that many sales people use, and is an excellent way to determine the amount of resin required as well as to help make the sale.

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With 30 years industry experience, Michael Gottlieb is founder and president of ResinTech Inc., an ion exchange resin supplier and manufacturer in Cherry Hill, N.J. In 1980, he was honored with the President's Achievement Award from Sybron Chemicals (formerly Ionac) for spearheading the growth of Ionac's ion exchange business. A member of the *WC&P* Technical Review Committee, Gottlieb's affiliations include the WQA, the American Institute of Chemical Engineers and the American Society of Testing and Materials (ASTM). He also is a member of the AWWA and has authored a chapter on ion exchange for its Water Treatment Plant Design Handbook. Gottlieb holds a bachelor's degree in chemical engineering from the New Jersey Institute of Technology. He can be reached at:
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