

Water Conditioners:

Tannin Removal

Trial and Error for the Best Application

By Mike Keller

Summary: *The science of removing tannins from potable water is promulgated by purveyors of several water treatment technologies. In this case, each camp may be able to say their approach is best since there isn't one media that ensures complete removal. Rather than endorse one type of treatment, this article discusses tannins and their features.*

Tannins are the by-product of decay, primarily from vegetation. As plants vary from place to place, so too do the tannins' chemical structure. Thus, one type of media may be effective at their removal in one area, but ineffective down the road due to a change in the plant life. This is one factor that causes tannin removal to be difficult. Tannins generally fall within two categories—humic acids and fulvic acids.

This water treatment problem is typically found in shallow wells and surface water sources. Deeper wells will usually have little or no tannins since bio-organisms within the soil will feed upon the tannins. The soil and rock strata will also act as a filter, which helps to limit organic material from entering into deeper groundwater aquifers. Tannins aren't considered a health issue and aren't regulated in national primary drinking water standards. There's a chemical reaction between tannins and chlorine, which can form trihalomethanes (THMs), which are regulated and, as such, have a maximum contaminant level (MCL) assigned to them of 0.080 milligrams per liter (mg/L), or 80 parts per billion (ppb). There's also a secondary drinking water standard for color at 15 alpha units. A secondary drinking water standard isn't federally enforced since it's an aesthetic issue, but it can be enforced at the state or county level.

Resin history

Over the years, there have been several types of strong base anion (SBA) resins used to remove tannins from water. Prior to 1990, styrene-based macroporous SBA resins were used predominantly for this difficult application. These resins performed well in many areas; however, they would tend to fail after a short period of time in other areas. Many water treatment professionals avoided this application due to high failure rates in a given region. More

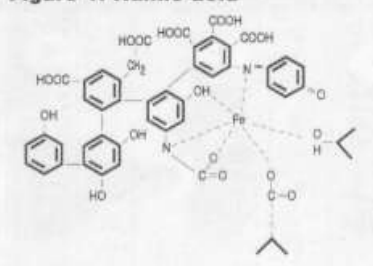
recently, acrylic resins have been used very successfully for tannin removal. Low cross-linked, high water retention, styrene-based resins have also gained acceptance in many locations.

Tannin resins need to have characteristics that allow pick-up and release of the large organic molecules. Strong-base anion resins with high porosity, high water retention and low cross-linking seem to work the best. Ion exchange resin will remove tannins through both an ion exchange process as well as an absorption process.

How the system works

Regenerations are performed with salt to strip the tannins from the resin. Typically, the resin is regenerated with 10 pounds (lbs.) NaCl (salt) per cubic foot. It's very important to regenerate the system frequently. When the tannin is exchanged onto the resin, it will tend to migrate into the middle of the bead. Once inside the resin bead, it's very difficult to remove. If the resin is regenerated every two to three days, the fouling potential can be kept to a minimum. Longer regeneration intervals will promote organic fouling and ultimately system failure.

Figure 1. Humic acid



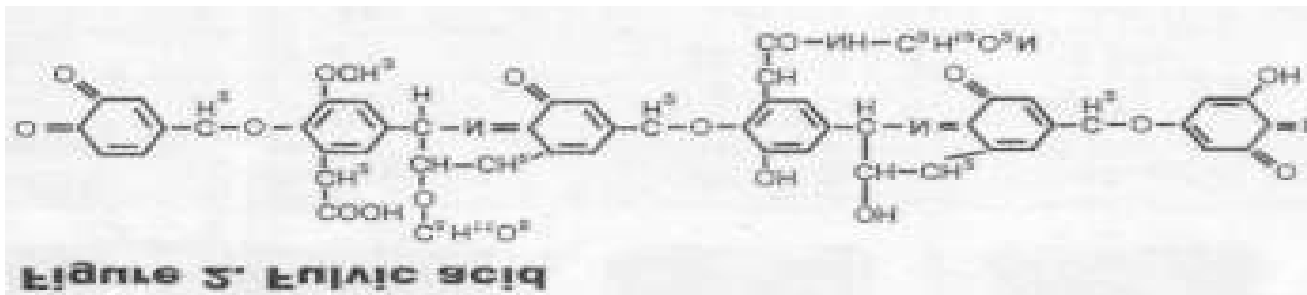
Tannin resins can be used in stand-alone systems or may be used in dual-bed applications. When utilizing a stand-alone system, it's set up is similar to a water softener with some minor changes. The backwash for a softener is usually set at 5 gallons per minute per square foot (gpm/sq. ft.). This translates to a 2.4-gpm flow control on a 9-inch (") tank. A tannin unit should backwash at a slower flow rate. In the same 9" tank, the flow control will be 1.2 gpm (2 gpm/sq. ft.). An upper basket or screen is also suggested as a safety feature to

prevent resin loss. When hardness levels in the water exceed 15 grains, softening should occur prior to the tannin unit. This will help prevent calcium carbonate precipitation in the tannin unit. The water should also be pretreated if iron is present in the raw water.

Dual-bed units are frequently used to reduce the amount of space required for a complete system as well as system cost. Dual beds utilize both cation softening resin and tannin resin in the same unit. This type of design has performed satisfactorily in many areas; however, during regeneration the salt will displace calcium from the cation and potentially the alkalinity from the anion resin, which can promote calcium carbonate precipitation. The precipitation can be seen as a milky white floc in the resin bed or coming from the drain line during backwash. It will also form scale in the drain line. Pressure drop, low capacity due to poor regeneration, and a milky white substance in the backwash drain water are indicators of precipitation. It should also be noted that the anion resin has a lower density than cation softening resin. When the dual bed is backwashed, the cation will settle to the bottom of the tank and the anion will settle on top of the cation resin. The anion resin will be exposed to the raw water first. This increases the potential for anion resin fouling as well as chemical degradation from substances like chlorine. The only way to avoid calcium carbonate precipitation—and related fouling—is to soften the water in a separate unit prior to the tannin removal unit. Cleaning procedures will be discussed later.

Operational characteristics

Tannin resins typically operate in the chloride (CD form). They'll remove tannins as well as other negatively charged ions (sulfate, nitrate, alkalinity, etc.) in water and replace them with chloride. Chloride levels will increase in the treated water. The increase will be approximately equivalent to the total dissolved solids (TDS) of the raw water. This elevation will only last until the resin's capacity for alkalinity has been exhausted and then the chlorides will start to decrease. Since alkalinity is being removed, the pH of the treated water will drop. The anion resin has a limited amount of capacity for alkalinity and should only decrease pH for a short period of time. The extent of the pH drop is based upon the amount of alkalinity and carbon dioxide (CO₂) in the water; however, one can look at the TDS and expect a greater drop in pH



with low TDS water. If the water has a TDS of 100 parts per million (ppm)—or mg/L—the pH drop can be significant; while water with a TDS of 400 ppm will have a pH drop of much less.

Tannin resin is frequently associated with a fishy odor. The odor comes from the amine used to functionalize (the ion exchange site) the anion resin. The amine can come off the resin as a by-product of manufacturing during the service cycle. The odor threshold of this chemical is less than 50 ppb, or micrograms per liter (ug/L). Although the release of the amine isn't a health issue, it's aesthetically displeasing. The fishy odor is more common when the water is chlorinated and has a high pH (greater than 8). This is often the case when chloramines are used as a disinfectant. Chloramines are formed when chlorine and ammonia are mixed, causing an oxidative environment with a high pH. Oxidants should be removed prior to the tannin removal unit. The removal of these compounds will reduce the potential for the fishy odor as well as increase the life expectancy of the resin. Oxidizing agents will also attack and break down the skeletal structure of the resin. Since tannin resins are usually lightly cross-linked, they'll break down quickly in the presence of substances like chlorine.

Cleaning procedures

Soda ash has been used in combination with the salt to help keep the resin bed cleaner. This cleaning can also be performed on a periodic basis. A half to 1 lb. of soda ash can be added to the brine well. The soda ash raises the pH of the brine and will cause the resin bead to swell. Tannins will be more easily removed from the resin due to the swelling and the fact that they are more soluble at high pH. With some of the resin in the bicarbonate form, the pH drop during the service cycle will be less dramatic. A potential side effect of this treatment can be the fishy odor. If the soda ash is going to contact cation softening resin, the softening resin should be regenerated with salt and a reducing agent prior to the soda ash/salt treatment. This treatment can be effective primarily on stand-alone systems, so contact your resin supplier for suggestions on fouled dual bed units.

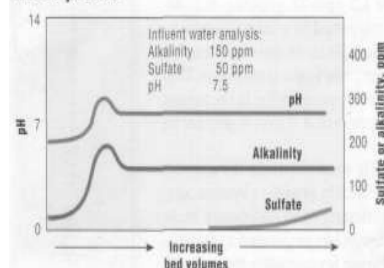
Organic fouling that occurs in industrial applications can be treated with a brine/caustic clean-up procedure.

Separate solutions of salt/NaCl (10 percent) and caustic/ NaOH (2 percent) are passed through the anion resin bed. The salt causes the tannin resin to shrink to its smallest size while the caustic causes it to swell to its largest size. This shrinking and swelling will help remove the tannins from the inner matrix of the resin bead. This procedure shouldn't be used in residential applications due to the corrosive nature of NaOH (NOTE: Caustic shouldn't contact exhausted cation resin. It must be fully regenerated to the sodium form).

There's one last procedure that can be used on organically fouled tannin resin. The use of bleach should be employed only as a last resort. Please remember oxidants will attack and break down ion exchange resin. Four ounces (110 milliliters) of standard household bleach (5.25 percent), without any additives, is placed in the brine well. Start to regenerate the tannin resin. When a chlorine odor can be detected in the waste brine, shut the system down for two hours. Then, continue the regeneration to completion. Put the system through a second standard salt regeneration before putting the system back into service. This procedure is very hard on the resin and should only be used when every other cleaning procedure has failed. If the resin fails to remove tannins after this cleaning process, the resin should be replaced or an alternative media or treatment method should be found.

Iron is the primary metal that may cause fouling of tannin resin. It can be

Figure 3. Tannin removal—Service cycle water profile



stripped from the resin bed with a reducing agent such as sodium hydro-sulfite or sodium bisulfite. Mild solutions of citric and phosphoric acid are also excellent cleaners as long as

the water treatment system and associated plumbing are compatible. Follow the manufacturers guidelines for treatment. The unit should be regenerated a second time with salt only when using an acid. Calcium carbonate precipitation that might occur can be dissolved with a mild acid like citric or phosphoric acid. Please follow the same guidelines as above.

Other ways to remove tannins

Oxidizing agents such as chlorine are effective at chemically breaking down tannins. A simple jar test will show the concentration and retention time required in oxidizing the tannins. An activated carbon unit following the retention tank will remove the oxidants and potentially any organics that remain. THMs may also form and be removed by the carbon. Carbon, while it can remove some organics, has relatively limited capacity for them and is not regenerable—so it really isn't feasible in household use as a sole treatment technology. Consult your carbon manufacturer for appropriate products.

Reverse osmosis (RO) is another effective method of removing tannins. Since tannins are a high-molecular weight organic, they'll be rejected effectively; however, tannins will tend to foul the membrane in the system. It's also expensive to treat the whole house by RO. Check with your RO manufacturer for details.

Conclusion

Tannins are one of those water treatment challenges that have no 100 percent guaranteed method for removal. There are several media that can be very-effective in this application and, with some trial and error, you can find the media best suited to your area. With any new application or media, put several systems in for extended trial to verify the technology. Once the trials have validated the product or treatment in a given area, proceed accordingly.

About the author

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