NUTS & BOLTS

The Ins and Outs of Dechlorination

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If you plan on using a municipal water supply for growing fish you will require a dechlorination step in your water treatment process. Most municipal water systems use chlorine or chloramine (a combination of chlorine and ammonia) to render the water safe for human consumption. While relatively harmless to humans in minute amounts, chlorine can be deadly to fish. In order to understand how to dechlorinate water, there must first be an understanding of how and why chlorine is used as a disinfecting agent.

Typical activated charcoal filter used to remove chlorine and other chemical contaminants.

Chlorine is water soluble gas (7160 mg/L at 20°C and 1atm) that hydrolyzes rapidly to form hypochlorous acid (HOCl). This reaction forms the basis for the application of chlorine as a disinfectant and oxidant as follows:

$$Cl_2 + H_20 \longrightarrow HOCl + H^+ + Cl^-$$

The by-product, hypochlorous acid(HOCl) ionizes to produce the hypochlorite (OCl-) ion. The rate of dissociation from hypochlorous acid to the hypochlorite ion is pH- and temperature dependent. The reaction is as follows:

$$HOCl \text{ —} H^+ + OCl^-$$

Hypochlorous acid and hypochlorite ions are referred to as *free available chlorine* (FAC). When chlorine is added to water, it will first react with any reducing agents, including any ammonia that may be present. Hypochlorous acid reacts with ammonia to form chloramines as follows:

$HOCL + NH_3 \_ H_2O + NH_2Cl$ (monochloramine)
$HOCL + NH_2Cl \_ H_2O + NHCl_2$ (dichloramine)
$HOCL + NHCl_2 \_ H_2O + NCl_3$ (trichloramine)

The formation of chloramines is also dependent on pH and temperature, as well as on the concentration of ammonia. With the added presence of these chloramines, the available chlorine is referred to as combined available chlorine (CAC). When these reactions are complete, residual chlorine will accumulate, either in the form of FAC or CAC. *Total residual chlorine* refers to the sum of the free and combined forms of residual chlorine. As a disinfectant, the FAC component is more effective than the CAC – this is because chloramines are considered to have only a moderate biocidal activity against bacteria and a low biocidal activity against viruses and cysts. However, as an additive, chloramine has become much more popular than chlorine in public water supplies because, unlike straight chlorine, it does not produce trihalomethanes which are toxic to humans.

Now that we understand the basics of chlorination, why and how must we DEchlorinate if we propose to use the water to grow fish? The first

Method	Advantages	Disadvantages
Chemical	• effective and safe (non-toxic)	• releases ammonia
Treatment	• inexpensive • can remove both chlorine and chloramines	• consumes oxygen
Heavy Aeration	• passively removes chlorine gas from water supply • aids in aeration process at the same time	• ineffective at low chlorine concentrations • does not remove chloramines
Charcoal	• can remove chlorine and chloramines • removes other contaminants and organics • can be used to polish incoming water	• requires backwashing • charcoal requires periodic reactivation or replacement • not practical for treatment for large flow rates • can provide a bacteria breeding ground
UV Irradiation	• can remove both chlorine and chloramine • provides additional disinfection for incoming water supply	• requires dosages much higher than usually required for aquaculture, especially for chloramine removal • not practical for high volume flows

question – why? – is most easily answered. We must dechlorinate because residual chlorine is toxic to aquaculture species at concentrations as low as 0.05 ppm for FAC and 0.2 ppm for CAC. The second question – how?– is more of a challenge, and is the topic of discussion for the remainder of this article.

The removal of chlorine from water for aquaculture is commonly achieved through one (or a combination) of four methods; chemical treatment, heavy aeration, activated carbon filters or UV irradiation. Each method has advantages and disadvantages that may dictate their suitability for a particular application.

The first method of dechlorination is chemical treatment with reducing agents. The most commonly used reducing agent in aquaculture systems is sodium thiosulphate ($Na_2S_20_3$). When mixed with chlorine-containing water, sodium thiosulphate reacts with the chlorine according to the equation

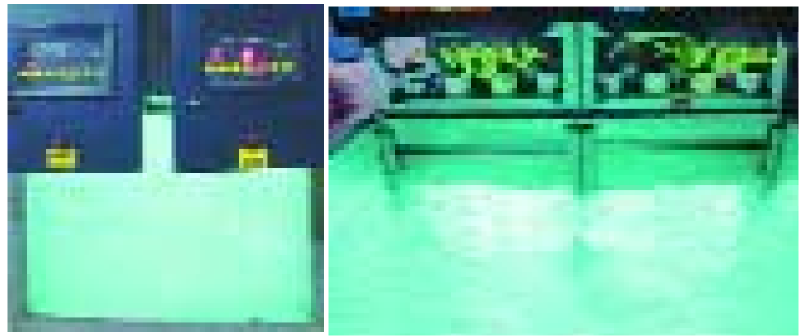
$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2S0_4 + S + 2HCl$$

Sodium thiosulphate also reacts with hydrochloric acid (produced in the previous reaction) to form breakdown products such as sulphur, salt and water:

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + S + SO_2$$

The dose required will vary with the pH of the water, but is approximately 2 to 7 parts sodium thiosulphate per one part chlorine. It is important to note that sodium thiosulphate will also bind the chlorine in chloramines, thereby releasing ammonia. The pH of the water will dictate whether the ammonia released will exist in the form of toxic ammonia, or the less toxic ammonium ion. At a pH above neutral (pH=7), the release will increase the toxic ammonia concentration and can have a detrimental effect on the fish. At a low pH, the ammonia will shift to the less toxic ammonium ion. Sodium thiosulphate will also remove oxygen from the water which should be aerated before it enters the culture system. There are many commercially available products that contain sodium thiosulphate in the suitable concentrations for dechlorination purposes. Other reducing agents such as sodium sulphite (Na_2SO_3) are also available but sodium thiosulphate is the best choice for small hatcheries and aquaculture systems as it is inexpensive, effective and safe.

The use of heavy aeration for dechlorination involves using vigorous bubble diffusers or aerated packed columns where the chlorine dissipates into the air. This process is slow, especially when the initial chlorine concentrations are low and the effort is to reduce them further. In addition, heavy aeration is not effective for removing chloramines from the water in an intensive commercial system as the chlorine-ammonia bond is not broken by aeration.



(left) Control panel of UV irradiation system. (right) Inlet side of an UV dechlorination system.

Activated carbon (charcoal) filters remove both chlorine and chloramines effectively. Activated carbon is a specialized filter media used principally for dechlorination or removal of organic compounds and the colour from water. Thus, activated carbon has the added benefit of removing chemicals such as fluorine and other contaminants that may be present at low concentrations. The length of contact time of the incoming water with the activated carbon is crucial to its removal capacity. Effective water treatment often requires large volumes of the media.

The activated carbon media, once spent, can be ‘re-activated’ with high pressure steam. This leaves the carbon with numerous minute spores or binding sites on its surface. As an aside, the higher the specific surface area of the media (or the smaller the media particles), the more binding sides there will be for a given mass. Contaminant molecules in the water supply travel into the pores and are trapped there. The media does not become exhausted by the chlorine, but rather by other contaminants present in the water. Eventually all the pores become filled and the activated carbon needs to be changed or re-activated.

Outlet side of an UV dechlorination systems

The frequency of changing will depend on the type and concentration of the contaminants in the water supply. During service, the filter media will need to be backwashed to remove particulate debris that accumulates on the surface of the carbon, and also to prevent channelling or short-circuiting of water through the filter bed. Backwashing frequency is usually controlled by a timer which will activate the backwash system at pre-set intervals. Activated carbon filters would not be practical or economical for large volumes of incoming municipal water.

However, in an intensive recirculation facility, the amount of new incoming water is relatively low, and an activated carbon filter may be ideal.

The use of UV light energy is a relatively new method of dechlorination. UV light applied at a sufficient dosage has been proven to destroy free chlorine. UV light is also capable of destroying chloramine compounds, although the required dosage is significantly higher. UV dechlorination has several advantages over othersystems. First, activated carbon filters can serve as a breeding ground for bacterial colonies that can be detrimental to the aquatic population.

Secondly, UV dechlorination technology has the added benefit of disinfection during the dechlorination process resulting in an extremely clean water supply. On the other hand, UV systems are expensive and have high maintenance costs. They are only effective with clean water (any organics present in the water will decrease the effectiveness) and must be properly sized to handle the maximum flow rate at the end of the bulb life.

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