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Ozone Application in Aquaculture

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Why Use Ozone?

Intensive production of fish and shellfish in recirculating aquaculture systems can accumulate particulate organic matter (uneaten feed, feces, microorganisms, etc.) and dissolved organic matter (small organic molecules not visible to the human eye). These suspended solids are irritating to the gills and external tissue of the animals; will degrade in the water, contributing to toxic nitrogen waste; and can harbor pathogenic bacteria and toxic algae. For these reasons mechanical filtration units (settling basins, microscreen filters, foam fractionators, etc.) are critical components of aquaculture systems because these filters are designed to remove particulate matter. However, even with the implementation of these mechanical filters, suspended solids are not completely removed and will accumulate in aquaculture systems. Using ozone (fig. 1) in conjunction with filtration can be a highly effective control measure for removing particulate and dissolved organic matter, disinfecting or reducing the load of bacteria in the culture water, reducing levels of algal toxins, removing off-flavor compounds, and purifying shellfish.

Ozone

Advantages

- Improves water clarity and quality.
- Reduces water usage by increasing water recirculation rate.
- Removes pathogens and toxic compounds.
- Reduces off-flavors of fish and shellfish.
- Increases growth rates of animals.

Disadvantages

- Requires trained labor.
- Puts animals and people at risk if used improperly.

Chemistry of Ozone in Freshwater

Ozone in a freshwater environment involves relatively simple chemistry. Ozone (O_3) is an unstable and very strong oxidant that is produced in an ozone generator and delivered into the water using an air or pure oxygen diffuser (i.e., air stone), injector, or low-head oxygenation unit (LHO). On a molecular basis, ozone is typically generated in a silent corona discharge unit that uses electrical discharge on oxygen molecules (O_2) to cause the release of free radicals of oxygen ($O^\bullet$) and ultimately the formation of ozone. This process can be generally described as follows (equation 1; Summerfelt and Hochheimer 1997):

$$3O_2 \leftrightarrow 2O_2 + 2O^\bullet \leftrightarrow 2O_3 \qquad (1)$$

This reaction is reversible, and the free radicals of oxygen are the primary oxidant that provides the benefits of ozone. Several primary factors in water that influence the decomposition of unstable ozone back to stable oxygen are presented in table 1. Quicker ozone removal is desired because it reduces exposure time of animals in the water.

Table 1. Water quality and impacts on ozone efficiency

Water quality factor	Impact on ozone decomposition rate
↑ Bicarbonate concentration	↑ Ozone removal rate
↑ pH	↑ Ozone removal rate
↑ Salinity	↓ Ozone removal rate
↑ Temperature	↑ Ozone removal rate
↑ Total organic carbon	↑ Ozone removal rate

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Chemistry of Ozone in Seawater

The chemistry of ozone in seawater is similar to freshwater systems but is complicated by the many different salts (elements) that are present. Seawater contains numerous primary elements (calcium, chloride, magnesium, potassium, sodium, sulfate, bromide) with trace levels of other elements (beryllium, copper, silicon, etc.). One particular element in seawater that is problematic in ozonated aquaculture systems is bromide (Br^-). Bromide reacts with ozone to form the harmful ozone byproducts hypobromite (OBr^-) and bromate (BrO_3^-; Brookman, Lamsal, and Gagnon 2011). The formation of these two ozone byproducts is presented in equations (2) and (3):

$$O_3 + Br^- \rightarrow O_2 + OBr^-, \qquad (2)$$

$$2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^-. \qquad (3)$$

Both hypobromite and bromate are toxic to aquatic animals at low concentrations. Some refer to the total level of hypobromite and bromate as biocidal bromine. Even though the concentration of these ozone byproducts is generally low, these byproducts are stable and remain in the water for days even after the ozone is turned off. Concentrations of biocidal bromine can be estimated using commercially available DPD (N,N diethyl-p-phenylenediamine) chlorine test kits. Generally in these tests, a powder or tablet is added to a water sample, and a pink color forms that can be quantified using a color wheel or spectrophotometer. Even though this test is designed to measure chlorine (another strong oxidizing agent), in an aquaculture environment these kits effectively estimate biocidal bromine.

System and Application

Ozone generators can be installed to receive air (21 percent oxygen) or oxygen from gas cylinders (90-95 percent pure oxygen). The use of oxygen gas cylinders will result in more efficient ozone generation and is typically more cost-effective. However, if the ozone generator is used intermittently on a small scale, the use of air is often acceptable. The generated ozone gas is then delivered to the water via a diffuser, injector, or turbine. To maximize the efficiency of ozonation in aquaculture systems, ozone is delivered to the water following filtration processes (fig. 2).

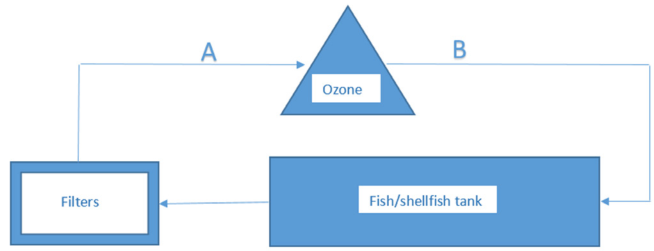

Figure 2. Typical ozone installation in aquaculture systems.

General Points

- Most ozone generators produce a consistent supply of ozone gas when turned on. The dial that determines the amount of ozone delivered to the water is actually controlling the air/gas flow rates through the generator.
- Turning the ozone down delivers less ozone to the water by increasing the flow rate of air/gas into the ozone generator, which effectively results in large bubbles with a low concentration of ozone. Less ozone would be introduced to the water because there will be less contact with the water due to the large bubble surface area.
- Turning the ozone up delivers more ozone to the water by decreasing the flow rate of air/gas into the ozone generator, which effectively results in small bubblies with a high concentration of ozone.
- When purchasing an ozone generator, the manufacturer will assist with sizing the unit. They will also assist with compatible hoses/pipes and fittings.

It is important to minimize the amount of ozone that returns to the fish/shellfish tank. Therefore, ozone concentrations in the water are usually measured after the point of ozone delivery to ensure that excessive ozone is not added. An oxidation-reduction potential meter is required for evaluating the amount of ozone that is delivered to the water. At the point of delivery, ozone oxidation-reduction potential could be as high as 400 to 450 millivolt to be effective. However, a typical rule of thumb for freshwater is to operate below 300 mV oxidation-reduction potential, as measured in the fish or shellfish culture water. Therefore, adequate removal of ozone must be achieved before the ozonated water returns to the culture water.

If ozone is used consistently for days or weeks and is suddenly turned off for an extended period of time, the operator should closely monitor nitrite (NO_2) in the water. Ozone oxidizes nitrite to nitrate (NO_3) very efficiently, essentially outcompeting nitrite-oxidizing bacteria. So, when the ozone is turned off, the population of bacteria might not be sufficient to remove nitrite (Schroeder et al. 2015).

Options for the initial design, installation, and development of effective and safe operating protocols include working with Virginia Cooperative Extension, university faculty members, or private consultants.

The following innovative strategies A and B are optional.

Strategy A

Innovative strategies can be employed to provide more efficient use of ozone while minimizing health risks posed to animals. At Point A (fig. 2) water quality factors (table 1) can be measured to predetermine the dose of ozone that should be delivered. In most cases, the most important water quality factor that predetermines the dose of ozone is the organic carbon in the water. The amount of organic carbon in the water can be determined or estimated using the following laboratory methods (listed in order from most accurate and most difficult to run to least accurate but easiest to run): (1) chemical oxygen demand, (2) total organic carbon, (3) total suspended solids, (4) turbidity, or (5) spectrophotometry (color absorption).

Strategy B

At Point B (fig. 2), the installation of a deozonation unit will minimize the amount of ozone that could be reintroduced to the fish/shellfish tank. A deozonation unit would essentially be an aeration basin (a tank of water aerated using pumped or pressurized air) that would drive the ozone out of the water relatively quickly, an activated carbon filter, or ultraviolet lights. An oxidation-reduction potential sensor after this point could verify that the ozone level in the water is safe to return to the fish/shellfish tank. Often an additional oxidation-reduction potential sensor is installed in the fish or shellfish culture water to ensure that it does not exceed safe levels.

Risks to Aquatic Animals

It is important to minimize residual toxic ozone (e.g., oxygen radicals) in the water to reduce the risk of harming or killing the animals. Ozone attacks the epithelium that covers gill lamella (burning the gills) and decreases the ability of fish and shellfish to regulate ions and minerals in their blood/hemolymph. This leads to organ damage as well as suppressed immunity and an increased risk of disease. Therefore, it is important to manage ozone properly. Damage to gills can typically be observed under a microscope by evidence of blackened or burned branchial tissue. These observations provide an additional tool for managing ozone prior to a major aquaculture kill.

Risks to Employees

Ozone gas that enters the atmosphere can also be toxic to humans. Individuals in buildings that are closed tight, resulting in low building air exchange, are at higher risk. The Occupational Safety and Health Administration (2012) permissible exposure limit to gaseous ozone is 0.1 ppm time-weighted average over an eight-hour workday (OSHA Standards – 29 CFR). The National Institute for Occupational Safety and Health's (2016) Pocket Guide to Chemical Hazards: Ozone provides information about ozone safety.

People who are trained to recognize the smell of ozone can smell a clean, sweet-smelling aroma. It is strongly recommended that an ozone detector with an audible alarm be installed so workers will know when to leave the space when safe levels of ozone in the workspace air are exceeded. Typical symptoms of people exposed to excess ozone begin with acute eye, nose, and respiratory irritation. Chronic exposure can lead to lung and central nervous system damage. The ozone generator should be shut down and those exposed should exit the area.

Conclusion

Working with experienced people in the design and operations of ozone applications is recommended and will help minimize potential issues and hazards. When used properly, ozone can be an excellent, cost-effective addition to aquaculture systems.

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