# Marine Aquarium Chemical Filtration

**Marine aquarium chemical filtration is very important in a reef tank but is often misunderstood.**

*By J. Charles Delbeek*

The topic of chemical filtration is described in just about every textbook written on marine aquariums, yet few people really seem to understand its capabilities, limitations and applications. There are numerous forms of filtration that could fall under the category of chemical filtration depending on their mode of operation. For the purposes of this article, we will limit our discussion to the common forms of chemical filtration used in reef systems: activated carbon, foam fractionation (also known as protein skimming), molecular adsorbants and ozone.

Due to the various biological processes that occur in an aquarium, a build-up of organic substances takes place. These substances are referred to as organic because they all contain the element carbon in their chemical composition. The list of substances is quite lengthy and includes such items as amino acids, proteins, phenols, creosols, terpenoids, fats, carbohydrates, hydrocarbons, plant hormones, vitamins, carotenoids and various organic acids such as fatty, acetic, lactic, glycolic, malic and citric (deGraaf, 1981; Moe, 1989). Fortunately, these various substances can be lumped together under the all-encompassing term of dissolved organic carbon (DOC). Taken as a whole, these DOCs often have various deleterious effects on aquarium inhabitants, including reduced growth, reduced disease resistance and metabolic stress.

DOCs are processed in different ways in an aquarium. Some are mineralized into ammonia by bacteria present in the tank. The ammonia is then oxidized by nitrifying bacteria into nitrite and then into the final product, nitrate. Unless utilized by plants as food, nitrate tends to accumulate in the aquarium water. Many organic substances are not mineralized but also tend to accumulate in the aquarium. This is why water changes are usually advocated as part of aquarium maintenance. Hobbyists are often under the impression that the purpose of a water change is to lower the nitrate concentration. While water changes do reduce nitrate levels, a more significant result is that the DOC content of the water is also lowered. Because nitrate is easier to measure than DOC, and because nitrate and DOC concentrations are often directly related, nitrate levels can be used as a yard stick to determine when a water change is needed.

The concept behind chemical filtration is that if much of the DOC can be removed before it accumulates or is converted into ammonia, the need for water changes can be reduced, the load on the biological filter will be less and nitrate levels will decrease. The result will be improved growth and health for the fish and invertebrates in the tank.

I would like to make it very clear that I am not saying that the use of chemical filtration eliminates the need for water changes. Water changes are still essential. To begin with, no method of chemical filtration is 100 percent efficient, and many substances in aquarium water are difficult to remove by chemical filtration. In addition, water changes provide other benefits, such as helping maintain the correct pH and appropriate levels of trace elements and calcium. Even in the most carefully maintained aquarium, the effects of a water change on the inhabitants can be quite revealing. Colors improve and the animals exhibit greater alertness and activity. The primary benefit of chemical filtration is to help maintain a much lower concentration of DOC in your tank, which becomes extremely important when dealing with invertebrates such as hard corals.

## Activated Carbon

Many of us remember our early experiences with aquarium filtration when we were less "sophisticated" about filters. I am thinking particularly of using charcoal in the corner box filter of a freshwater tank. This form of chemical filtration consisted of small, shiny, irregularly shaped pieces of bone or wood charcoal. Charcoal, of course, is not really suitable for use in aquariums.

The material of choice is always "activated" carbon. The term activated refers to carbon that has been subjected to very high pressures and temperatures to drive out all impurities and gases, leaving behind extremely porous and pure grains of carbon. Particle size, the type of gas used, the activation temperature and, in some instances, the addition of inorganic salts (zinc, copper, phosphate, silicate and sulphate) before activation all provide carbon with specific adsorption characteristics (Moe, 1989). Therefore, activated carbon can be tailored to the specific types of impurities that one wishes to remove. By creating this extremely porous structure within the carbon grains, the effect is that of an efficient sponge that can absorb many compounds from the passing water.

Activated carbon will remove a wide variety of organic molecules by simply trapping them in the carbon pores (absorption) or by chemically bonding them (adsorption). Adsorption relies on the fact that many organic molecules are polar in nature.

This means that the two ends of a molecule differ in their affinity for water. One side is repelled by water and is termed hydrophobic ("water hating") while the other end is attracted to water and is called hydrophilic ("water loving"). When a polar molecule comes close to a polar surface such as activated carbon, they become attached to each other, effectively removing the molecule from solution. Moe (1989) gives a detailed discussion of the properties of activated carbon and the factors that determine its efficiency.

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Perhaps the most common mistake made in using activated carbon in reef aquariums is its placement in trickle filters. It is the nature of flowing water to take the path of least resistance. When activated carbon is used in outside power filters, for example, it is placed so that the water must flow through the carbon, not around it. This lesson appears to have had little impact on many of the designers of trickle filters. All too often, bags of activated carbon are placed in the sumps of trickle filters in such a manner that the majority of the water passes around the carbon, not through it. In a correctly designed sump, all of the water is forced to flow through the carbon chamber.

In a trickle filter in which the flow of water cannot be controlled, there are a couple of options available. One is to hook up a canister filter filled with activated carbon to the sump so that water is pumped out through the canister filter and then back to the sump. The other is to build an in-line contact chamber in the return from the trickle filter to the tank. This consists of a section of PVC pipe with hose fittings at both ends. The pipe is filled with activated carbon and placed in the return line so that all of the water returning to the tank passes through it. Thiel (1988, 1989) and Moe (1989) describe the construction and placement of this type of unit.

There are two commonly asked questions concerning the use of activated carbon: 1) how much to use and 2) how often to replace it. These questions are very difficult to quantify simply because no two systems are identical. Differences in bioloads and the kinds of fish and invertebrates being kept greatly influence the composition and quantity of DOC produced. For example, aquariums filled with marine algae will produce a greater variety of DOC than systems with very little algal growth. Thiel (1988) recommends using 36 ounces of activated carbon per 50 gallons of water and Wilkens and Birkholtz (1986) recommend 500 grams per 100 liters, which is roughly equivalent. These figures are quite generous, and it may be possible to use somewhat smaller quantities. The real indicators as to whether there is adequate amounts of carbon in the system are the condition of the animals being kept and the color of the water (a yellowish tint indicates a build-up of DOCs).

Careful observation of the tank and its inhabitants is the key. Too many aquarists today are turning toward technological wizardry to maintain their aquariums. Hobbyists are constantly talking about ozone, redox potential and carbon dioxide systems, yet many of them cannot correctly identify their tank inhabitants or do not fully understand what pH is. The marine life in our aquariums is far more sensitive to water chemistry than any meter, and it is therefore better to spend time watching them than looking at test instruments. Observing these animals will keep you attuned to the conditions in your tank.

As with the quantity of carbon, it is difficult to recommend a specific time period after which the carbon should be replaced. Various authors of marine texts have stated that carbon should remain active for five to seven months before needing replacement (Moe, 1989; Wilkens and Birkholtz, 1986). Generally, the presence of a yellowish tint in the water can be used as a guide to determining whether the carbon needs to be replaced, because the substances that tint the water are easily removed by carbon and will start to accumulate in the water when the carbon becomes saturated.

Moe (1989) describes the following method for using water color as an indicator of carbon activity. Obtain a strip of white plastic and color one half very light yellow with a marker. Place the strip in the water and observe from a distance. When you can no longer distinguish the yellow half from the white half, the water contains significant amounts of DOC and it is time to replace the activated carbon in the filter.

Because activated carbon is a very porous material, nitrifying bacteria will quickly colonize it. If you use large amounts of activated carbon and replace all of it at the same time, the sudden loss of a large population of nitrifying bacteria could lead to elevated ammonia or nitrite levels. It might be wiser to replace 30 percent of the carbon and rinse the remaining 70 percent with seawater (Wilkens and Birkholtz, 1986). The new carbon can be placed in a separate bag and located in front of the old carbon in the filter. This will preserve a large amount of the bacteria that have colonized the carbon. Because only a portion of the carbon is being replaced each time, the maintenance schedule for the carbon may need to be increased in frequency.

The addition of activated carbon to a filtration system that has not contained carbon previously also requires caution. Wilkens and Birkholtz (1986) recommend that when activated carbon is added to an established aquarium, it be done gradually. For example, 20 grams of carbon per 100 liters of water (1½ ounces per 26 gallons) can be added monthly to the filter until a sufficient total quantity is reached. The sudden addition of a large quantity of activated carbon to an established aquarium can remove such a large amount of DOC that the animals may become severely shocked.

There are numerous brands of activated carbon being marketed today, some of which have fancy names, such as "research grade." Unfortunately, not all activated carbon is created equal, and the levels of efficiency and quality vary greatly from brand to brand. Ideally, the grains of activated carbon should be small, dull black in color and as dustless as possible. Recent studies of activated carbon-filtered aquarium water have shown that certain brands of activated carbon appear to actually add phosphate to the water, which is exactly what we are trying to avoid (J. Sprung, personal communication)!

A different problem is that as activated carbon ages, some of the substances it has adsorbed and absorbed may be released back into the water (Thiel, 1988, 1989). If the activated carbon is changed on a regular basis, however, this problem can be avoided. A final caveat concerning activated carbon is that, along with the other forms of chemical filtration to be mentioned in this article, it indiscriminately removes substances from the water, including some useful ones. Therefore, regular water changes take on added importance when chemical filtration is present.

Foam Fractionation
A method of chemical filtration that has been available for decades but only recently has become popular is foam fractionation (protein skimming). A foam fractionator consists of a column through which a very fine mixture of air and water is pumped. If you have spent any time along an ocean shore, you may have noticed varying amounts of foam. This foam is produced by the action of the waves, which combines air, water and certain polar organics to form a stable foam. A foam fractionator works in a similar manner. If the foam is collected, proteins and other organics can removed from the water before they are mineralized into nitrogen-containing compounds and other toxins. As a result, the quality of the tank water is improved and is easier to maintain.

Of the various chemical filtration methods available, only foam fractionation completely removes most organics before they begin to break down (Moe, 1989). The list of substances removed by fractionation includes amino acids, proteins, metals such as copper and zinc complexed with the proteins, fats, carbohydrates, phosphate, iodine, fatty acids and phenols. A more detailed discussion of foam fractionators, including their operation and construction, will appear in a future issue of AFI.

In my opinion, a foam fractionator is an indispensable piece of equipment for a marine aquarium, particularly in a reef system. Foam fractionators have been used in European aquariums for years and are often the sole form of filtration in these tanks. This level of filtration, however, cannot be achieved with the smaller, inside-the-tank fractionators that have been commonly sold for years in North America. What is required are larger, external models, which are only now becoming more common in North America. These units have traditionally been imported from Europe, but a number of companies in North America have introduced a variety of models.

Although the majority of fractionators sold today are driven by wooden airstones, some models are available that incorporate a venturi design. A venturi fractionator utilizes a strong water pump and a small air inlet, creating a suction that forms a fine mixture of air and water in the fractionator. Such devices are more powerful and require less maintenance than the standard wooden airstone-driven models. Because of their efficiency, they can also be smaller in size.

There are a few items of concern to keep in mind using a foam fractionator. First, the continuous removal of small amounts of seawater by the fractionator, along with replenishment of evaporated water with freshwater, can lead to a gradual lowering of salinity. Therefore, the periodic addition of seawater may be necessary to maintain the desired level of salinity. Secondly, efficient fractionators can remove some trace elements. Periodic water changes or the addition of trace elements may be necessary to maintain sufficient levels of these elements. Finally, the addition of certain kinds of buffers and molecular adsorption filter pads can cause a fractionator to foam excessively. The best solution for this is to turn down the skimmer for a day and then gradually restart it.

Molecular Adsorption Filters
This form of chemical filtration is a relatively new addition to marine aquariums. At the moment, the hobbyist market is dominated by a single product, Polyfilter(TM), marketed by Polybio Marine Inc. This type of filtration consists of various styrene or acrylic polymers that selectively adsorb polar organics and nitrogen-containing compounds onto their surface (Moe, 1989). Some authors (Thiel, 1988) claim that these products will remove phosphate from the aquarium. Although I do not measure phosphate in my own aquarium, I have noticed that the growth of red microalgae visibly slowed after the addition of such a filter pad.

If the ionic interference caused by seawater can be overcome, and molecular adsorbants become more specific for particular substances, we should see a proliferation of such filter products in the future. For example, products that selectively remove nitrate and phosphate down to the parts per billion level would be especially useful. As with activated carbon, molecular adsorbants should be situated so that water is forced through the medium, not around it. At this time, it is not known whether long-term use of such filters will lead to trace element depletion.

Ozone
Ozone is a naturally occurring gas in the upper atmosphere, where its ultraviolet-absorbing properties have been given wide exposure in relation to its recent depletion caused by chlorofluorocarbons. Ozone is a powerful oxidant that consists of three atoms of oxygen (O3). O3 readily releases what is an extra oxygen atom to become O2, which is more stable. It is this property that we utilize in an aquarium. The oxidizing ability of ozone breaks down organics and nitrite. Unfortunately, other products, such as hypochlorite and hypobromite, can also be produced in this process and can damage delicate invertebrates and fish gills (Moe, 1989).

Ozone is generally used in conjunction with a foam fractionator or pressurized air reactor. Ozone is mixed with air and introduced into a contact chamber. There, the ozone-air mixture mixes with the aquarium water and organics are oxidized. The effluent water is then passed through a container of activated carbon before being returned to the aquarium, which removes any residual ozone and any harmful by-products that may have been produced.

Used in conjunction with a redox controller, precise regulation of a system's redox potential can be obtained. Stated simply, redox potential is the ability of the aquarium water to oxidize and/or reduce substances in the water. Measurements of redox potential in the ocean vary from 350 to 400 millivolts (Moe, 1989) to as low as 160 to 190 millivolts (Wilkens and Birkholtz, 1986). However, caution is advised in any comparisons due to differences in measuring conditions, techniques and equipment used. Recommended redox levels in marine tanks range from 375 to 450 millivolts, but each aquarist must judge the appropriate value on the basis of the appearance of the aquarium. Differences in probe placement, frequency of tank maintenance, bioload and so on all affect redox readings. It is not so much the numerical value that is important but the appearance of the aquarium's inhabitants. Once a redox level is reached at which you feel your tank looks best, that is where to keep it. Do not strive for specific redox levels simply because they are recommended by others.

Although many periodicals and books make note of the quite common use of ozone in Europe (i.e., Moe, 1989), I have read numerous articles from both Germany and Holland that advocate not using ozone. It is unclear what the exact basis of this opposition is, but the main criticisms appear to be that ozone is not necessary to maintain a successful tank, that its use will cause problems in the long run and that the various by-products produced are potentially dangerous to the inhabitants (Hebbinghaus, 1989; Stuber, 1989; Wilkens and Birkholtz, 1986). Nonetheless, I have seen many beautiful aquariums here in North America that use ozone, in conjunction with redox controllers, on a continuous basis.

One thing that I and others have noticed, though, is that reef systems run with ozone tend to have higher nitrate levels than reef systems that do not. This may be a reflection of the increase in nitrate production caused by the oxidation of nitrite into nitrate by ozone and/or some inhibitory ozone effect on denitrification of nitrate. Stuber (1989) reports the growth of more than 11 species of reef-building hard corals without the use of ozone in an aquarium with a measured redox of 180 millivolts! Both Moe (1989) and Thiel (1988, 1989) go into much more detail on redox and ozone and their application to reef systems. I urge you to consult these references for additional information.

Whether used by itself or in conjunction with biological and mechanical filtration, it is safe to say that chemical filtration is an important component of a reef aquarium filtration system. Therefore, it should be considered an essential element in any reef tank.