

Comparison of MarinePure™ Bio-Media versus Other Types of Bio-Media on Ammonia and Nitrite Removal in Freshwater Aquarium Systems

Paul Pustulka
Cermedia General Manager and Development Engineer

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Summary

Based on a CerMedia™ LLC internal study, MarinePure™ bio-media outperformed other types of bio-media in a year long study. Chemical ammonia was used to represent fish waste from food breakdown and respiration. MarinePure™ bio-media was able to eliminate significantly more harmful ammonia and nitrites and convert it to nitrate.

Bio-filters containing MarinePure™ bio-media, with its vast useable surface area and open-flow porosity, will have greater capacity to create healthy water for fish. CerMedia™ LLC refers to this combination of properties as Thin Bio-Film Technology™. By having the large continuous pores, the bio-film in the system can develop in thin sections. This allows the bacteria to have intimate contact with water containing ammonia and nitrite.

Filters with MarinePure™ bio-media can be smaller requiring less initial capital costs. Aquatic systems can carry a higher fish load, which becomes even more important in fish farming situations. They will also be able to adjust quicker to system upsets.

Objective

To compare the effectiveness of various bio-media, using eight identical aquarium set-ups, in their ability to host beneficial bacteria that eliminate ammonia and nitrite.

Background

Starting in July, 2011, in CerMedia's lab in Buffalo, NY, eight identical fresh water aquarium set-ups were assembled to test the ability of several bio-media to house bacteria that converts ammonia to nitrite and then to nitrate. Ammonia occurs in fish tanks as the by-product of fish respiration, fish waste excretion, and un-eaten food breakdown. Ammonia (NH₄) is harmful to fish in small doses. Naturally occurring beneficial bacteria (nitrosomonas) will convert the ammonia to nitrite (NO₂). Nitrite is also harmful to fish. Other bacteria (nitrospira & nitrobacter) will convert the nitrite to nitrate (NO₃). Nitrate is much less harmful to the aquarium occupants but still need to be removed. Nitrate removal is beyond the scope of this experiment, but it is usually accomplished by water changes, plants & algae using it as fertilizer, or another class of bacteria (anoxic) converting the nitrate to nitrogen gas (N₂) which will leave the tank.

Bacteria multiplication usually occurs in bio-films which adhere to almost every surface in the tank and filter system. Bio-filter media is typically designed to have a maximum amount of surface area for the bio-film to attach. A high surface area media should lead to safer (ultimately zero) ammonia and nitrite levels in a tank. There should also be excess surface area available for additional bacteria growth if there is a sudden surge of ammonia due to dead fish or plant life. Another important factor in the media effectiveness is its pore size and openness. If the pores are too small, the bacteria may not fit, or the pores

can be easily plugged by biofilms. If the pores are not interconnected, the interior surface area is not usable. If the pores are too large there will be a significant reduction in surface area per a given volume. The bio-media chosen for the experiment covers the range of surface areas and porosities available to test these ideas.

Method and Set-Up

For this experiment each setup included;

- a) 20 gallon glass aquarium
- b) Fluval 205 canister filter
- c) Top Fin Air-4000 air pump shared between two tanks
- d) 6" inch air stone
- e) Elite 20 watt heater
- f) in-tank thermometers

A picture of the set-up (not including the air pumps and air stones) is shown in Figure 1.

Figure 1
Tank set-ups



The canister filters were assembled per the manufacture's instructions. The supplied sponge mechanical filters were used on each. No additional carbon or polishing filters were used inside the canister filters.

The canister filters contain three trays to hold different treating options; usually one houses the bio-media. For this study, all three trays were used to hold the bio-media, resulting in 1.65 liters of bio-media in each filter.

Bio-media was chosen to represent different media types used in both aquariums and in koi ponds. Each bio-media was randomly assigned a tank. The tank assignments and descriptions are shown in Table 1.

TABLE 1
Test Tank Assignments and Description

| Tank # | Media Description | Comment |
|--------|--|---|
| 1 | MarinePure™ (High Density) | Open porosity aluminosilicate ceramic (<i>MarinePure™ 1.5" Spheres</i>) |
| 2 | Ceramic Sphere | Pelletized ceramic media, $\approx 1/2$ " in diameter |
| 3 | Feather Rock, cut to $3/4$ " cubes | Naturally occurring closed-porosity light weight rock |
| 4 | Porous Stone | Naturally occurring random shaped stone, typically $1/4$ " to 1" long with very fine pores |
| 5 | MarinePure™ (Low Density) cut to $3/4$ " cubes | Open porosity aluminosilicate ceramic (<i>MarinePure™ Plates, Blocks, cartridges & MP2C</i>) |
| 6 | Plastic Bio-Balls | 1.5" diameter plastic balls with "fingers" |
| 7 | Empty Filter | Three media trays were left empty |
| 8 | Sintered Ceramic | Extruded cylindrical ceramic with center hole |

The surface area measurement of the media was performed at an outside lab (TAM Ceramics, Niagara Falls, NY) using Quantachrome Instruments' Monosorb MS9 B.E.T.¹ Surface Area Analyzer. The results are typically expressed in square meters per gram (m²/g) and are shown in Table 2. The weight of the media used to fill the three filter trays (1.65 L) in each filter is also listed. The total surface area due to the bio-media is calculated. The additional surface area from all the other surfaces in each system was estimated. This included amongst other things, the tank sides and walls, the mechanical filter sponge, the air tubes and the canister filter housings. Using these values, the total surface area in each system was tabulated. These values are shown in Table 2.

TABLE 2
Media Surface Area and Weights

| Tank # | Media | Media Surface Area (m ² /g) | Weight of Media (g) | Total Surface Area due to media (m ²) | Additional Surface Area remainder of system (m ²) | Total Surface Area in each system (m ²) |
|--------|-------------------------|--|---------------------|---|---|---|
| 1 | MarinePure™ (HD) | 1.50 | 511.2 | 767 | 18.4 | 785 |
| 2 | Ceramic Sphere | 0.20 | 1117.8 | 224 | 18.4 | 242 |
| 3 | Feather Rock | 0.18 | 684.9 | 123 | 18.4 | 142 |
| 4 | Porous Stone | 2.59 | 1303.7 | 3377 | 18.4 | 3395 |
| 5 | MarinePure™ (LD) | 1.50 | 242.5 | 364 | 18.4 | 382 |
| 6 | Plastic Bio-Balls | * | 174.6 | *0.5 | 18.4 | 18.9 |
| 7 | Empty Filter | NA | 0 | 0 | 18.4 | 18.4 |
| 8 | Sintered Ceramic | 0.10 | 885.2 | 89 | 18.4 | 107 |

* 0.32 m²/Liter via manufacture's technical specifications thus 0.32m²/l*1.65l = 0.5m²

¹ See following link for more information on BET Surface Area. http://en.wikipedia.org/wiki/BET_theory

Pictures of the media used in the study are shown in Figures 2 – 9 below.

Figure 2
Tank #1 MarinePure™ (High Density)



Figure 6
Tank #5 MarinePure™ (Low Density)



Figure 3
Tank #2 Ceramic Spheres



Figure 7
Tank #6 Plastic Bio-Balls



Figure 4
Tank #3 Feather Rock



Figure 8
Tank #7 Empty Filter



Figure 5
Tank #4 Porous Stone



Figure 9
Tank #8 Sintered Ceramic



The tanks were filled with tap water passed through a carbon filter to remove the chlorine. In place of using live fish to eliminate the risk of harming the fish and for a more controllable system, ammonia was added chemically. 30% ACS Reagent grade Ammonium Hydroxide was used. Ammonia Hydroxide was added every weekday to each tank. The following day, approximately 23 hours later, each tank would be tested for residual ammonia and nitrite using API Freshwater Test Kits. Occasionally pH and Nitrate were also tested. The ammonia hydroxide was added using two sizes of Cole Parmer Auto Pipettes, 10 to 100 micro-liters, and 1000 micro-liters. Knowing the actual amount added, the overall concentration of ammonia, more specifically the nitrogen component in the ammonia (N-ammonia) could be calculated in parts per million (ppm).

Based on the daily results, the amount of ammonia hydroxide added would be adjusted for each tank. If there was neither ammonia nor nitrite showing up on the test, the amount of ammonia hydroxide added would be increased. If there was ammonia and/or nitrite remaining in the tank, the amount added would either be kept the same or decreased. Using this method, each system would be pushed independently to determine its effectiveness.

Early on in the test there was a wide range in pH which appeared to be affecting bacteria growth and ammonia conversion. To remedy this, sodium bicarbonate (baking soda) was added to keep the pH approximately 8.3. An additional benefit of using baking soda is that it contains important ingredients for bio-film and bacteria growth. Once the baking soda was added, the systems stabilized and ammonia conversions became more predictable. Baking soda was then only added to each tank when the pH started to drop.

For tank maintenance the following steps were performed. Nitrates (NO_3) were controlled with an 80% water change about once a week. About once a month the filters were opened and excess bio-film was squeezed off the mechanical sponge filters. The bio-media, still in the media trays were dunked several times in used tank water.

Temperature was maintained on all the tanks between 75 °F and 77 °F by adjusting the heaters as necessary.

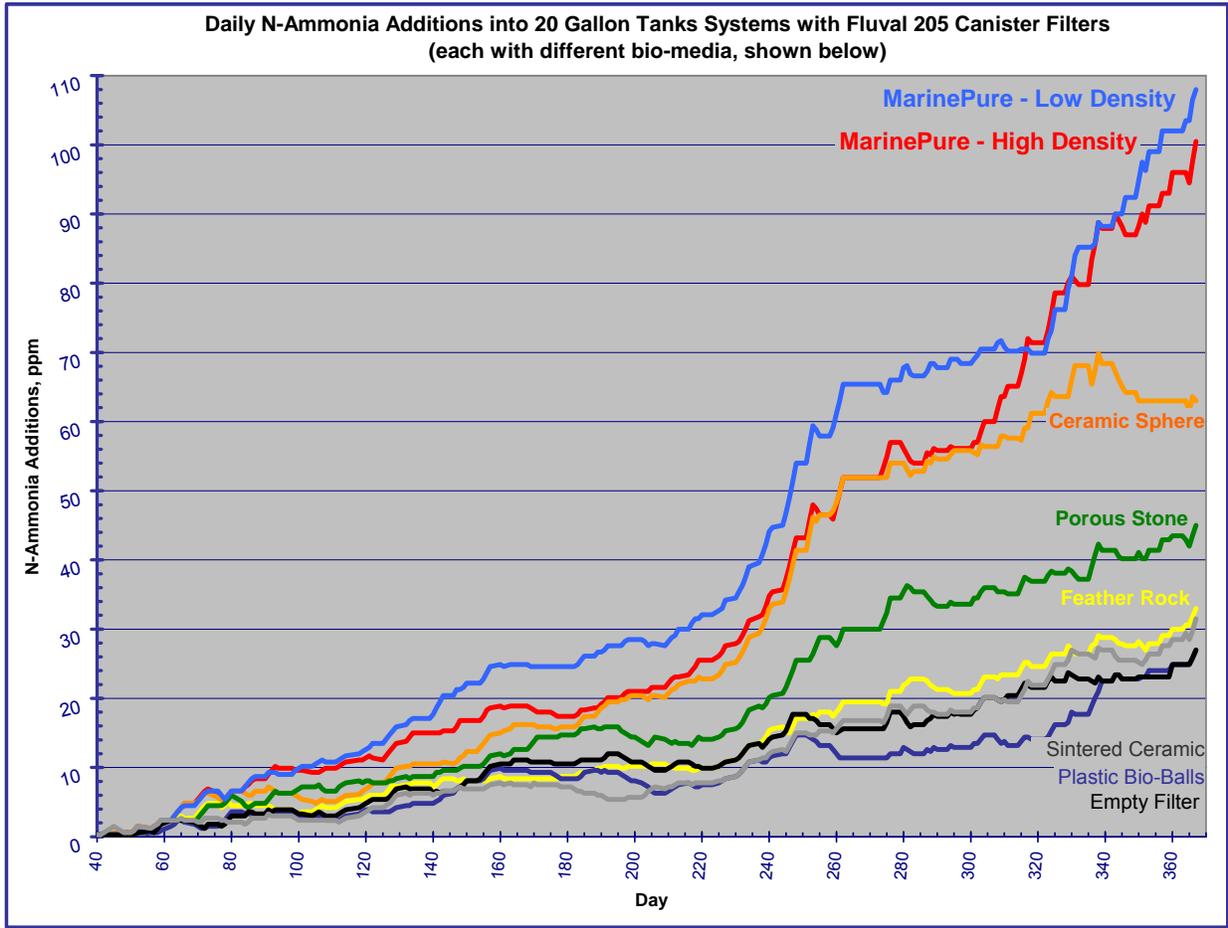
Results

The nitrogen cycle was accomplished in the tanks without using any biological additives. The bacteria appeared naturally. The tank closest to the lab door, Tank #8, cycled first in just over 4 weeks. The other tanks followed soon after and all were completed within 6 weeks.

Increases in Ammonia Hydroxide were fairly slow at first, and then progress more rapidly as the capabilities of each set-up was realized.

The graph below, (Figure 10) shows the daily N-ammonia (ppm) additions over the year of the study. Note how each line goes up and down, signaling the bacteria in each is struggling to keep up to the increasing ammonia challenge.

FIGURE 10
Ammonia Additions in Test Tanks

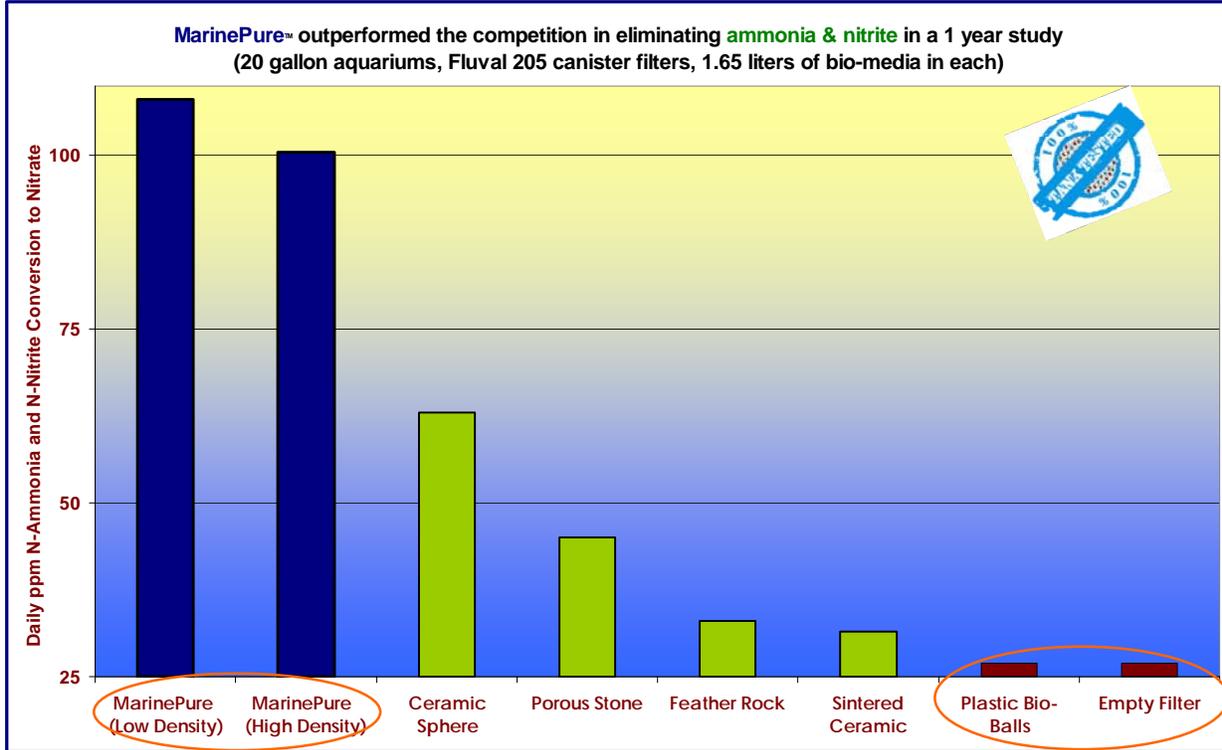


The study was stopped at after 1 year in order to free up the tanks and space to perform additional tests. There are plans to continue similar tests with the MarinePure™ samples to determine their ultimate capabilities. Others media and filtration types will also be investigated.

The results show that the MarinePure™ products greatly outperform the competing products on eliminating ammonia and nitrite.

Figure 11 is a graphic showing the results at the end of the year long study. It shows how much ammonia could be converted to nitrate in 1 day using 1.65 L of media in a 20 gallon system after slowly building up the bio-film and bacteria in each system.

FIGURE 11
Final N-Ammonia Elimination Results



Discussion

The high concentrations of ammonia used in this study would be deadly to marine life. If the total volume of the system was much larger (dilute the same quantity of ammonia), but the filter remained the same size, you could calculate how much fish food the ammonia represents, the fish load that is sustained by the food, and what the size of the tank or pond is needed for this fish load. This is done in Table 3. The table shows the conversion of the ammonia to feed rate, fish load and ultimately tank/pond size. The calculations are standardized on 1 liter of media. No adjustments were taken for theoretical increases in system surface area such as pond walls. Also not taken into consideration is the turnover rate of the tank water through the filter. For the lab experiment, the turnover rate was about 6 times per hour. This may be typical of smaller systems, but for larger systems a turnover rate of 1 to 2 times per hour is more appropriate. Using the assumption that food is 40% protein and protein breaks down to ammonia, the amount of food theoretically used in the study is calculated. To assume the amount of fish load, it was assumed the fish should daily receive food weighing 2% of their weight. A fish load of 250 gallons per 20” fish (typical of Koi hobby) gives the ponds size.

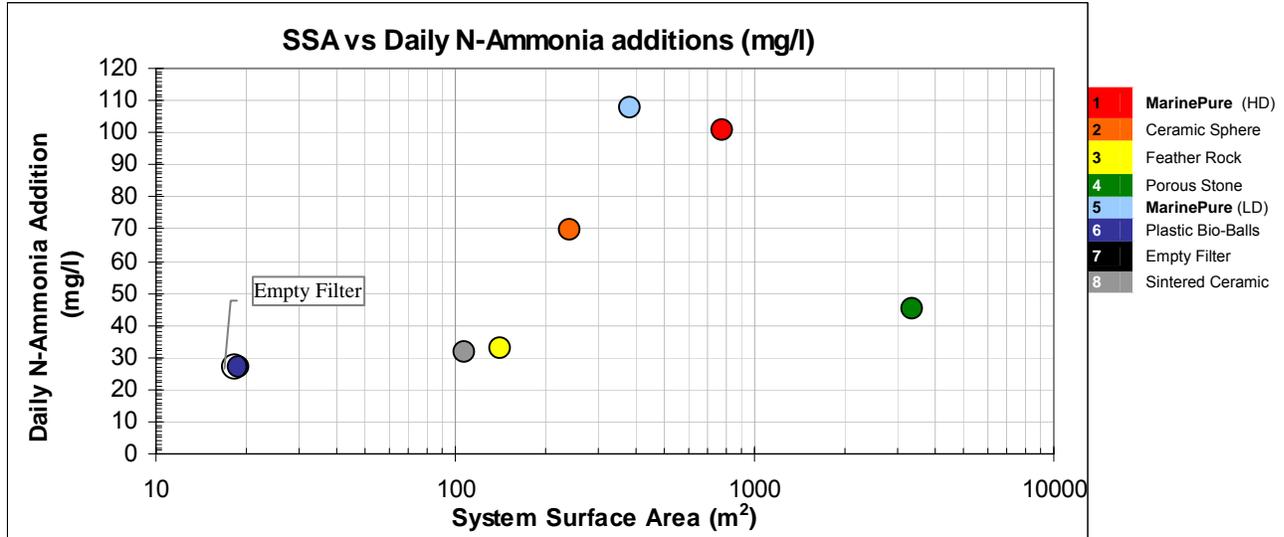
TABLE 3
Loading Capacities of Different Bio-Media
(Used in systems with standard equipment including mechanical filters)

| TANK # | Media | Conversion to Grams of Food Per Day per Liter of Media | Typical Fish Load (lbs) | Tank/Pond size (Gal) for 1 Liter of Media |
|--------|-------------------|--|-------------------------|---|
| 1 | MarinePure™ (HD) | 197.6 | 21.7 | 1279 |
| 2 | Ceramic Sphere | 137.5 | 15.1 | 890 |
| 3 | Feather Rock | 64.9 | 7.1 | 420 |
| 4 | Porous Stone | 88.5 | 9.7 | 573 |
| 5 | MarinePure™ (LD) | 212.4 | 23.4 | 1375 |
| 6 | Plastic Bio-Balls | 53.1 | 5.8 | 344 |
| 7 | Empty Filter | 53.1 | 5.8 | 344 |
| 8 | Sintered Ceramic | 61.9 | 6.8 | 401 |

Cermedia does not recommend running large systems with such a small bio-filter as shown in the table above. Physically, it would be very difficult to run a 1300 gallon pond through 1 liter of media six times in 1 hour. This study just shows the potential of MarinePure™ bio-media and how it compares to other types of bio-media. Typically large aquariums and ponds are tuned over 1 or two times per hour. This would suggest 3 to 6 liters of MarinePure™ bio-media would be needed plus an additional safety amount.

To compare the bio-media in a different way the following graph was prepared, see Figure 12 below. The bottom axis shows the total amount of surface area in the system, the side axis shows the daily N-ammonia converted.

FIGURE 12



There are four important topics to take note from this graph.

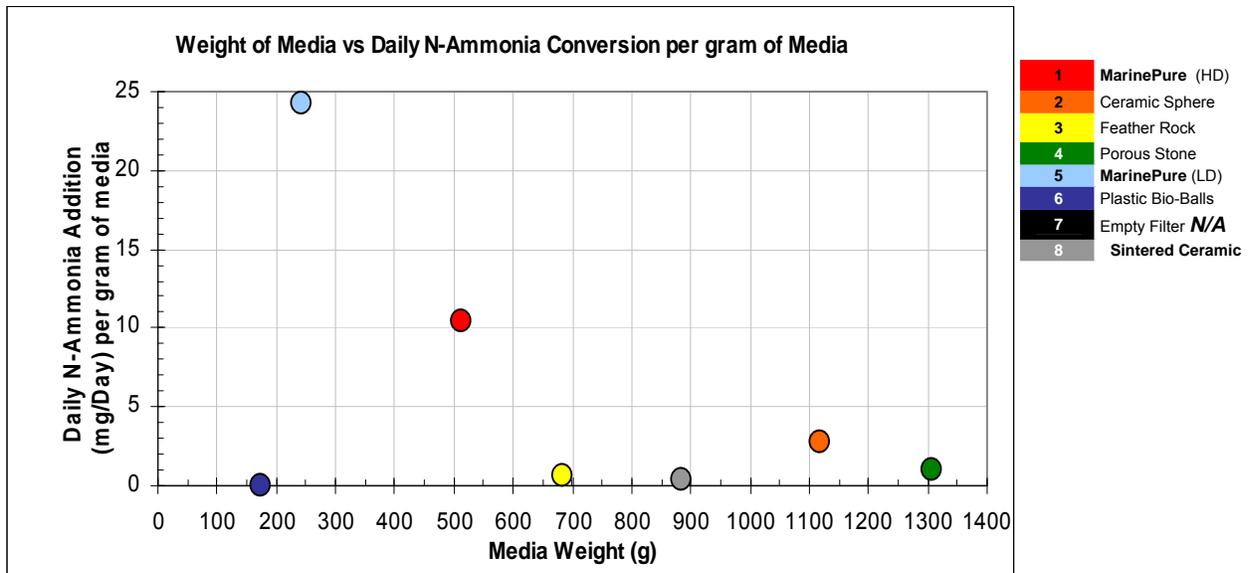
- 1) The filter filled with plastic bio-balls is near equivalent to the empty filter. The plastic bio-balls add virtually no additional benefit.
- 2) The additional surface area from the sintered ceramics media and feather rock adds only a little to the ammonia conversion.
- 3) The huge amount of surface area in the porous stone also adds very little to the systems abilities. In fact, the manufacture states that most of the porosity of the system is too small to house

bacteria. Due to the small pores, it is probably very difficult for water to travel quickly through the media and most of the biological activity takes place to the outside.

- 4) The surface area in the ceramic sphere and the two MarinePure™ products are the only products where it appears that the increased surface area plays a significant role in ammonia conversion, with the impact of MarinePure™ bio-media almost twice that of the ceramic sphere. This difference might even be greater than shown because looking back at Figure 10; it appears the ceramic sphere may be reaching its full potential while the MarinePure™ products were still improving when the study ended.

Figure 13 below shows the comparison between the weights of the bio-media used in the study and the amount of ammonia it could convert per gram of media. The surface area and ammonia conversion from the empty filter have been subtracted out.

FIGURE 13



MarinePure™ bio-media is a fired ceramic that would have a high density if it was not filled with voids. It is light in weight because of the large porosity. This graph shows that MarinePure™ bio-media uses its mass more efficiently than the other media. With MarinePure™ bio-media's open pores, the entire surface area within the system is available to passing water, making it useful to hosting bio-film and bacteria. The large open pores allow for a lower pressure drop across a filter, lowering the demands on pumps. For large systems, the weight savings on the media becomes considerable.

The previous two figures lead to the discussion about why MarinePure™ bio-media is the most efficient at ammonia conversion; MarinePure's large surface area combined with an open flow structure gives MarinePure™ its Thin-Film Bio-Technology™. By having the large continuous pores, the bio-film in the system can develop in thin sections. This allows the bacteria to have intimate contact with water containing ammonia and nitrite. Other media will develop thicker films over time. The bottom layers of the film will die off and will plug smaller pores. When MarinePure's thin bio-films do slough off, they are easily flushed from the media via the open porosity.

Conclusion

Based on a CerMedia™ LLC internal study, MarinePure™ bio-media outperformed other types of bio-media in a year long study. Chemical ammonia was used to represent fish waste from food breakdown and respiration. MarinePure™ bio-media was able to eliminate significantly more harmful ammonia and nitrites and convert it to nitrate.

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Information for MarinePure™

MarinePure™ bio-media is designed to be a substrate for bio-filtration, specifically to target ammonia and nitrite removal and to minimize nitrates. MarinePure™ bio-media is suitable for both freshwater and saltwater environments. MarinePure™ can be used fully submerged or in trickle/shower filters. It should not be used in moving bed filters.

SURFACE AREA FOR MARINEPURE™ PRODUCTS

| Product Description | Surface Area per Piece | | Surface Area per Pack Volume | | |
|-------------------------|------------------------|--------------------|-----------------------------------|---------------------|-------------------------------------|
| | (m ²) | (ft ²) | (m ² /m ³) | (m ² /l) | (ft ² /ft ³) |
| <i>8x8x1" Plate</i> | 540 | 5,750 | n/a | n/a | n/a |
| <i>8x8x4" Block</i> | 2,150 | 23,000 | n/a | n/a | n/a |
| <i>Type C Cartridge</i> | 200 | 2,200 | n/a | n/a | n/a |
| <i>Type E Cartridge</i> | 270 | 2,900 | n/a | n/a | n/a |
| <i>1.5" Sphere</i> | 22 | 240 | 435,000 | 435 | 132,000 |
| <i>MP2C</i> | 67 | 720 | 336,000 | 340 | 102,000 |

(Nitrification) Recommended MarinePure™ bio-media amounts to eliminate ammonia and nitrite in an active filter, for a typical bio-load

| Tank Size (gallons) | <i>Spheres</i> | <i>Plates</i> | <i>Blocks*</i> | <i>MP2C (for pond filters)</i> |
|---------------------|----------------|---------------|----------------|--------------------------------|
| 50 | < 1 quart | <1 plate | <1 block | na |
| 100 | 1 quart | 1 plate | <1 block | na |
| 250 | 2 quarts | 2 plates | 1 block | ½ cu ft |
| 500 | 1-2 gallons | 3 - 4 plates | 1 - 2 blocks | ½ - 1 cu ft |
| 2500 | 3 - 4 gallons | 12 plates | 4 blocks | 2 cu ft |
| 10,000 | na | na | na | 8 cu ft |

* MarinePure's thick blocks are designed to be used in passive systems to control Nitrates (see below). If used in active systems they will eliminate ammonia and nitrites.

(Denitrification) Recommended MarinePure™ bio-media amounts to minimize nitrates in a passive filter, for a typical bio-load

| Tank Size (gallons) | Blocks in passive location |
|---------------------|-----------------------------------|
| 50 | 1 block |
| 100 | 1 block |
| 250 | 2 blocks |
| 500 | 3 blocks |
| 2500 | 15 blocks |
| 10,000 | 60 blocks |