MetaMateria
Environmental NanoTechnology

Products for Denitrification

Nitrogen pollution is a serious problem in surface and ground water. Nitrate and nitrite are regulated in drinking waters by the Safe Drinking Water Act and have an enforceable MCL (maximum contaminant level) of 10 mg/L. Agricultural practices are among the greater generators of nitrate in groundwater, particularly Confined Animal Feeding Operations (CAFO), such as poultry and other animal farms. MetaMateria's porous composite media shows a great potential for bioremediation of nitrogen. This occurs due to especially high surface area available to support colonies of multiple types of beneficial bacteria. Both nitrification and denitrification is done more efficiently and at higher rates and more cost effective than conventional bioremediation approaches. MetaMateria media ***biologically breaks down 3 times more nitrate to nitrogen gas*** in shorter times and at lower carbon:nitrogen levels.

Testing of MetaMateria bioremediation media (BIO-DN) developed by shows nitrates lowered from 70 mg/L to under 5 mg/L, usually often in under 60 minutes contact time. Lab results show nitrate removal levels three times higher than values found in the literature. This occurs because the composition of the highly porous ceramic contains an electron donor and a solid-phase buffer. BIO-DN's high surface area allows for colonies multiple of beneficial bacteria; consequently aerobic bacteria can exist near the media surface to oxidize ammonia and colonies of autotrophic and/or heterotrophic bacteria exist to convert nitrates to nitrogen gas. The uniform distribution of buffers mitigates acidic conditions of bacteria, allowing a higher effectiveness of bacteria colonies with little change in pH. Many shapes and sizes are available.

Nitrate Removal Approaches in contaminated water use a variety of techniques, such as reverse osmosis, ion exchange, catalysis and biological nitrate reduction (denitrification). In contrast to processes that concentrate nitrates, such as reverse osmosis and ion exchange, biological denitrification converts nitrate to free nitrogen (Dahab 1991, Fernandez, *et.al*, 2008, Mousavi *et al,* 2011, Karansios *et al* 2010). As a treatment option for the removal of nitrate from drinking water, biological denitrification represents a more cost-effective and versatile approach than ion exchange, particularly as the plant size increases (Gauntlett, 1981). Biological denitrification is not only able to remove nitrates but also able to eliminate various toxic micro-pollutants and organic mutagens (Rogalla *et al*., 1990; Kool and Van Kreijl, 1984; Bouwer and Crowe, 1988, and Larzarova *et al*., 1992). Biological denitrification can also be conducted *in situ* whereas ion exchange requires treatment of water done at a water treatment plant.

In recent years, autotrophic denitrification with H_2 has been used for reduction of nitrate from drinking water in lab-scale and full-scale treatment. These studies show that the process is technically and economically feasible for nitrate removal from drinking water supplies (Dries *et al*., 1988; Rutten and Schnoor, 1992; Clifford and Liu, 1993; Sahu *et al*, 2009). In addition, biological denitrification offers flexibility of application in a water aquifer or as a conventional above ground treatment process (Mercado *et al*., 1988; Hiscock *et al*., 1991). As mentioned previously, *in-situ* denitrification employs the aquifer as a reactor for the reduction of nitrate. The major advantage of this process is that the aquifer can serve as both a reactor and filter.

Denitrification (autotrophic denitrification) with sulfur compounds as electron donors, represents an alternative to heterotrophic denitrification, and has been shown to be feasible to remove nitrate from waste water with low carbon to nitrogen ratio (Batchelor *et al.*, 1978). A number of common soil bacteria (such as *Thiobacillus denitrifans* and *Thiomicrospira denitrificans*) can reduce sulfur compounds using electron donors and respire NO^{-}_{3} in the absence of oxygen. Advantages of autotrophic sulfur oxidizing denitrification include: high NO_3^- removal efficiencies, elemental sulfur is significantly less expensive than ethanol or methanol, little

or no carbon source is required, less sludge is produced due to lower biomass yields for autotrophic bacteria and autotrophic sulfur producing bacteria produce less N_2O than heterotrophic denitrifying bacteria

Other treatment options for removal of nitrate from are expensive or create additional water quality problems. Ion exchange is fairly effective for nitrate-contaminated water; however, this process produces large quantities of brine that must be subsequently disposed of (Gauntlett, 1981; Hollò and Czakò, 1987) and is not cost effective. Biological denitrification is effective for removal of nitrate; however, not without operational problems. If sulfur is used as the electron donor, pH will drop due to the generation of acid by the operating bacteria and bacteria effectiveness suffers, even when a buffer is part of the bed.

Engineered Media for Denitrification: MetaMateria BIO products have been used for many years for biological conversion of nitrate (NO_3-N) to nitrogen gas (DN) in waste water and aquaculture systems. Testing shows that anoxic conditions develop within the thickness of the material, while aerobic bacteria exists on surface layers remove any residual oxygen. Testing of regular BIO media in a recirculating (800 gallons) aquaculture environment showed nitrates reduced 10 fold (from 225 to 20 mg/L) once denitrifying bacteria colonies were established (6 grams of nitrate-nitrogen (NO_3-N) per 1.5 kilogram of media).

Removal is enhanced further using BIO-DN, which also contains electron donors to support autotrophic bacteria colonies and include a carbonate buffer to control pH. BIO-DN operates with lower dissolved carbon for nitrate reduction, either naturally available or supplemented by additions of commercial products. BIO-DN is much more effective than plastic media or urethane foam or most other products on the market. In fact, over 700 pounds of plastic products (e.g. bio-balls) are needed to equal the surface area available with 1 pound of BIO media. Consequently, multiple colonies of bacteria can exist (aerobic at the surface and anaerobic and autotrophic bacteria inside), which are particularly effective used together. When tested in an up-flow column filled using 1.6 cm balls of BIO-DN media, **over 35 kg/m^3/day of nitrate was removed**; this is three times higher than best values reported in the literature.

Bacteria Availability: The greatest limitation of any biological treatment system is the quantity of active microorganisms available to consume the contaminant(s). In an aerobic basin the quantity depends on the type and amount of aeration/recirculation, but is typically limited to under 3,000 mg/L (approximately 3 kg of microbes per m^3 of system volume[1]).. In an attached growth system, the limitation is a function of the surface area of the media on which the microbes are attached. To reduce the footprint of a system, it is best to maximize the surface area per unit volume. Commonly used media have surface areas on the order of a hundred to one thousand square meters per cubic meter of media (m^2/m^3). Typical bacteria found in industrial treatment systems range from 2 to 5 microns in size, have a density near that of water (~1 g/cc). Therefore, a single layer of microbes covering this area would provide about 2 kg of microbes per m^3 of system volume.[2] An active colony 5 layers thick reaches 10 kg per m^3.

MetaMateria's porous products have a surface area above 2,000,000 m^2/m^3. An average pore size for biofilm growth is 25-50 microns, which is large enough to efficiently conduct water at a low pressure drop and support a relatively thick bio-film. A single layer of microbes covering this area would provide about 200 – 800 kg of microbes per m^3 of system volume.[3] Even with a very conservative assumption that 90% of the pores are unavailable; this area would still provide 20–80 kg of microbes per m^3 of system volume. With specific bacteria concentrations, this will be at least an order of magnitude higher than competitive media systems. Considerably higher volumetric efficiency is expected, which results in reduced capital equipment and operating costs for many system designs.

[1] 5000 mg/L by wt. * 1,000 kg/m^3 = 5kg/m^3
[2] Using 1,000 m^2/m^3 of media: 1,000 m^2 * 2 micrometer microbe thickness * 1,000 kg/m^3 = 2 kg microbes
[3] Using 100,000 m^2/m^3 of media: 100,000 m2 * 2 micrometer microbe thickness * 1,000 kg/m^3 = 200 kg microbes

Contact Efficiency – Minimizing Hydraulic Retention Time (HRT)

Hydraulic retention time (HRT) is the average time required for wastewater to be held within the system volume to provide enough contact for contaminant reduction. In short, this is a statistical average of time required for a contaminant to have a reactive contact with a microbe. In a suspended system, water and microbes are circulated and aerated (for an aerobic system) which can be time consuming to ensure a sufficient quantity of contaminant is reacted. In a packed bed or other attached growth system, water is circulated or passed over media to improve the HRT. Some low efficiency systems, such as a simple aerated basin, may have HRTs on the order of days, requiring a tank size 1,440 times the GPM flow rate for every 24 hours of HRT. More efficient designs including some attached growth systems and MBRs have much shorter HRTs, but typically are still on the order of several hours or more. The large number of interconnected pores and channels within the porous media provides a unique structure that forces wastewater to remain in close proximity (on the order of hundreds of microns or less) to the active biofilm that exists on the cell walls. This small diffusion distance enables the reduction of contaminants with a very short HRT. HRTs as low as 10 minutes have provided an 80% reduction in ammonia concentration. HRTs of only 6 minutes for denitrification have consistently yielded reductions of 30 ppm in laboratory testing. This high surface area also provides an ideal base for development and nourishment of many types of beneficial bacteria, which can lead to systems with a smaller footprint. Considerable unused capacity is available to handle changes (spikes) in nutrient levels. Even just 10% of the media surface area is over 50 times greater than alternative media forms.

Summary

All types of Bio-Lair products are used for years for biological conversion of nitrate (NO_3-N) to nitrogen gas (denitrification) in water systems. A higher performance is seen compared with most other commercial products. Testing shows that anoxic conditions develop within the thickness of the material, while aerobic bacteria on the surface layer removes any residual oxygen. BIO-DN is product made with an electron donor (sulfur) to support autotrophic bacteria colonies and a carbonate buffer to control pH. The BIO-DN product removes up to 5 times more nitrate than regular BIO-Lair media.

Benefits of BIO-DN include:

- Can function at moderate dissolved oxygen concentrations (typically DO of <5 ppm)
- Works at a much lower C:N or BOD:N ratio, typically under 3 BOD:N
- The sulfur to carbonate ratio is typically 1:1, versus 3:1 for other sulfur denitrification
- High denitrification rates of over 30 Kg/m^3/day (gm/L/Day) were achieved in Lab tests
- Performance is usually limited by the availability of nutrients (nitrates, phosphates)
- Residence time (EBCT) is typically 15-60 minutes, much shorter than other media

Because BIO-DN provides high denitrification, it allows reactor volume to be reduced, which in turn lowers capital cost and reduces system footprint. BIO-DN media has less effect on pH of effluent water, even with sulfur in the media, eliminating a need for additional buffering agents. Less carbon also means lower operating costs.

BIO media can also be used with MetaMateria's PO4 media to remove additional phosphorus.

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