OMA Gas Membrane Ammonia Concentration

Supplementary Information for "Negative Carbon via Ocean Afforestation"

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Background

After macroalgae (seaweed) is digested anaerobically and the methane and carbon dioxide are captured, the remaining solution has a concentration of ammonia/ammonium of about 0.1% (1,000 mg/L-N), plus many other important plant nutrients. In most cases the residue will be recirculated to nourish the Ocean Macroalgal Afforestation (OMA or Ocean Afforestation) ecosystem. However, in some locations there is excess nitrogen from agricultural runoff, which has created ocean dead zones. This excess nitrogen could be removed and returned to support terrestrial agriculture, while the remaining ammonia/ammonium solution can be recirculated to the ocean ecosystem.

This paper describes a novel method (patent pending) to capture the excess nitrogen and separate it from the sea salt so it is useful for terrestrial agriculture. In addition, the method can also be used to move organic nitrogen from locations where it is excess (ocean or lake dead zones) to start or expand an Ocean Afforestation ecosystem.

Salt concentration issues

When seaweed is digested anaerobically in seawater, the resulting ammonia solution is too dilute and too salty for use as terrestrial fertilizer unless the ammonia can be concentrated without the sea salt. Fresh water may have total dissolved solids (TDS) up to about 2,000 mg/L before it is unsuitable for most terrestrial agriculture (although some plants are more salt-tolerant. In contrast, ocean water is about 32,000 mg/L TDS.

Gas membranes can remove ammonia

Anaerobic digestate liquid contains ammonia in two forms: ammonium (NH_4^+) and ammonia (NH_3), in equilibrium. Ammonium is an ion. Ammonia is a dissolved gas. If some ammonia is removed, more of the ammonium converts to ammonia. Higher pH favors a higher ammonia concentration. Lower pH favors a higher ammonium concentration.

The gas membrane shown in Figure 1 is designed to allow the gas (ammonia) to pass while denying the ammonium, water, and salts. On the outside of the membrane is digestate. The inside has water with some sulfuric acid (H_2SO_4) or sulfurous acid (H_2SO_3). When the ammonia crosses the membrane, it immediately becomes ammonium in the form of either ammonium sulfate $(NH_4)_2SO_4$ or ammonium sulfite $(NH_4)_2SO_3$. Ammonium sulfate is agricultural fertilizer.

Because there is no ammonia on the "inside" of the membrane, osmotic pressure keeps ammonia moving through the membrane. Figure 1 is a cross-section of a single membrane tube inside a container. The actual containers are often lengths of pipe perhaps a foot in diameter with a thousand membrane tubes. Each membrane tube may be a millimeter in diameter. The membrane container has been an off-the-shelf item for decades. The actual membranes continue to improve rapidly.

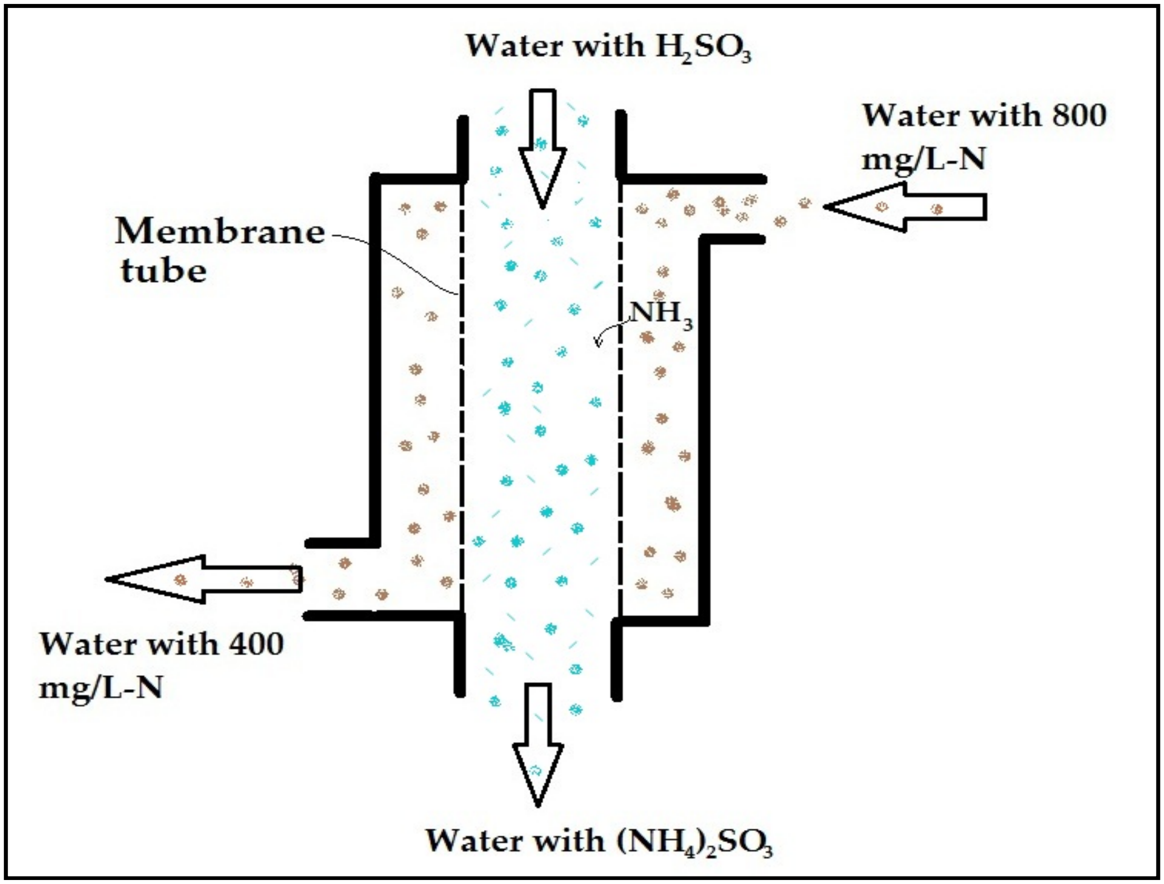

Figure 1 – Cross-section of a single membrane tube: changes in water composition

In Figure 1, the brown-dot water represents the water from the anaerobic digestion process flowing around the outside of the membrane tube. It contains ammonium and ammonia in equilibrium. The blue-dot/line water represents the dilute sulfurous acid flowing in the center of the membrane tube. Upward (counter-flow) of the acid may be more effective. Alkalinity will be consumed and the pH will drop as the ammonium continues converting to ammonia within the brown-dot water:

Acid source

The currently used process involves buying 98% concentrated sulfuric acid, an extremely dangerous liquid. The concentrated acid allows for quick one-pass extraction of ammonia from the filtrate.

However, metallic sulfur is relatively easier and much less dangerous than sulfuric acid to transport and store. Sulfur burners are typically used in terrestrial agriculture to reduce the pH of irrigation water. A sulfur burner will inexpensively produce relatively dilute sulfurous acid, which can be used in the processes shown in Figures 2 and 3 to produce commercial concentrations of liquid ammonium sulfate. The overall reaction from sulfur burner to ammonium sulfite is:

$$2NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2SO_3$$

Neither sulfurous acid or ammonium sulfite are stable. They will convert to sulfuric acid or ammonium sulfate over time with ambient oxygen.

System description

A tanker ship or barge would arrive at the nutrient remediation OMA site full of the appropriate water. The tanker is represented by the open top rectangle at the bottom right of Figure 2. This fresh or saltwater is circulated through the burner and the gas membrane, increasing in ammonium sulfate concentration with each pass. Dissolved oxygen may be added after each pass through the burner or at the end when the acid/fertilizer is in storage. Digestate (the liquid left over from anaerobic digestion) is passed through a filter to remove solid particles. The digestate with reduced ammonia concentration is recycled back to the OMA operation.

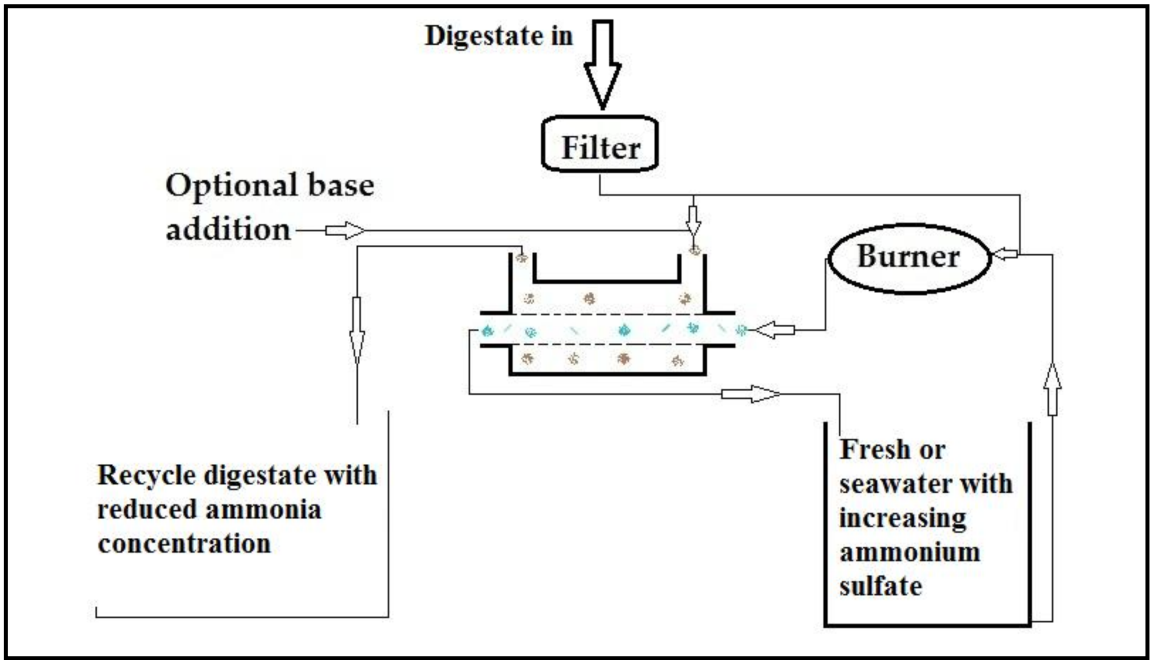

Figure 2 – System schematic with single pass filtrate and multiple pass burner

When recovering nitrogen from the ocean for terrestrial agriculture, the storage tank would initially be a ship or barge filled with fresh water. As the fresh water is circulated through the burner and the membrane unit, it concentrates ammonium (without the salts from seawater). The anaerobic digestion water with reduced ammonium would be spread to grow more seaweed forest.

If the end use is to start or expand an OMA ecosystem, the ammonium concentrating fluid can be seawater, rather than fresh water.

This recirculation arrangement will increase the concentration (more fertilizer or disinfectant in less volume) even though the sulfur burner produces relatively dilute acid with each pass.

Figure 3 shows an arrangement for further reducing the amount of ammonia left in the digestate. This is highly schematic in that the second burner and second gas membrane are unnecessary as the liquids can be arranged to cycle through the same equipment multiple times.

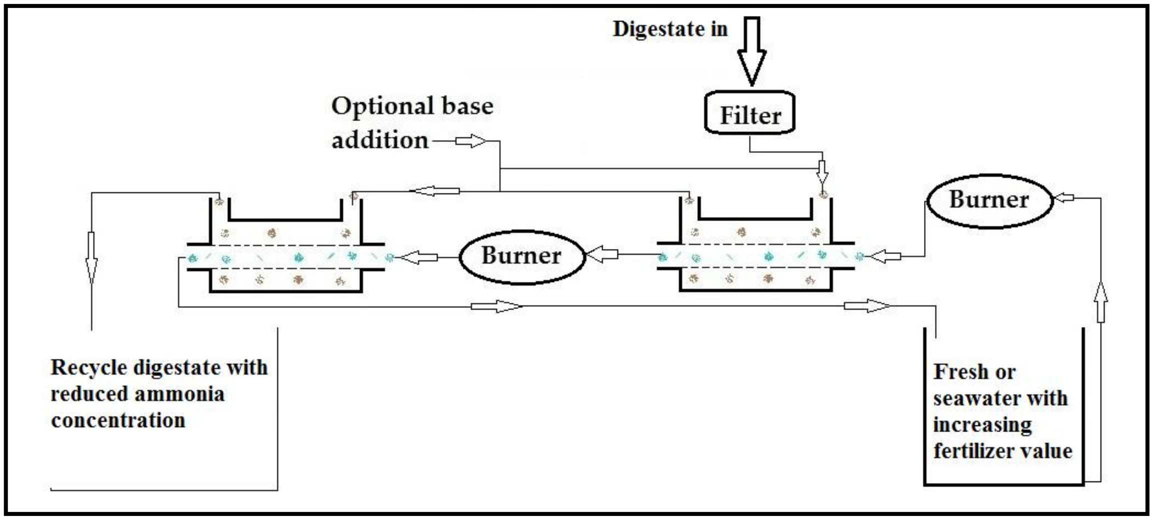

Figure 3 – System schematic of double-pass filtrate

Figures 2 and 3 are simplified for clarity. For example, the pumps are not shown and the optional spray or fine bubble aeration in the storage tank are not shown. Also, the pipes could be arranged for one burner and one membrane unit to be almost as effective as the two of each in Figure 3.

Struvite is also a product of anaerobic digestion which could be recovered with relatively little salt. Struvite (magnesium ammonium phosphate) is a phosphate mineral with formula: $NH_4MgPO_4 \cdot 6H_2O$. Existing struvite recovery processes include Ostara Nutrient Recovery Technologies. Struvite comes out of solution with increasing pH. Therefore a struvite recovery process could operate in conjunction with the ammonia recovery between the optional base addition and the gas membrane.

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