

# Ion Exchange/Anammox Process for Nitrogen Removal from Wastewater

## INTRODUCTION

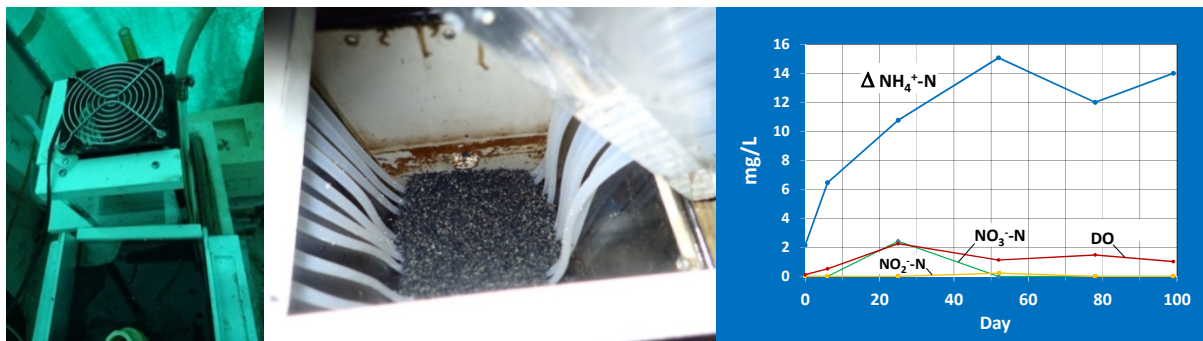
Nitrogen from onsite wastewater systems adversely affects surface and ground water quality, with particularly acute effects in estuarine waters (US EPA, 2002). This paper presents the Anaerobic/Ion Exchange/Anammox (AN/IX/ANM) process for onsite nitrogen removal. AN/IX/ANM evolves from the Anaerobic/Ion Exchange (AN/IX) process, in which wastewater nitrogen is recovered by anaerobic ion exchange of  $\text{NH}_4^+$  on clinoptilolite, a natural zeolite (Smith and Smith, 2015a,b,c). AN/IX/ANM extends AN/IX by adding controlled delivery of oxygen to clinoptilolite media beds in order to foster nitrogen removal through nitrification and anammox. The coupling in single reactors of nitrification (partial nitrification of ammonia to nitrite:  $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ ) with anammox ( $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2$ ) provides a metabolic pathway for complete mineralization of ammonium to nitrogen gas ( $\text{N}_2$ ) (Du et al., 2015; Ma et al., 2015b). AN/IX/ANM can be used for in situ regeneration of exhausted clinoptilolite media, and can also operate in a continuous nitrogen removal mode that couples anaerobic ion exchange with the metabolic platform of nitrification/anammox. The goal of AN/IX/ANM is a passive and low cost process for resilient nitrogen removal in onsite wastewater systems.

## MATERIAL AND METHODS

A 57 L AN/IX prototype was operated for over two years on onsite wastewater to remove  $\text{NH}_4^+$  by ion exchange on clinoptilolite. The AN/IX reactor contained an initial upflow anaerobic solids blanket chamber followed by three ion exchange chambers packed with granular clinoptilolite. Effluent  $\text{NH}_4^+$  remained below detection for over 300 days but the capacity of clinoptilolite to remove  $\text{NH}_4^+$  was exhausted after 2 years (Smith and Smith, 2015b). To evaluate AN/IX/ANM, the third ion exchange chamber (AN/IX Chamber 4) was fitted with a permeable tubular membrane array placed laterally across the flow path for controlled oxygenation by diffusive flux through the membrane (Figure 1). The array consisted of nine tubes (peroxide cured silicone; 7.9 mm o.d., 0.79 mm wall thickness;  $\text{O}_2$  permeability of  $7,961 \text{ cm}^3\text{-mm} / \text{cm}^2\text{-sec-cm Hg} \times 10^{-10}$ ). Silicone membranes in pressurized hollow fiber configuration were previously used to permeate  $\text{O}_2$  and  $\text{H}_2$  into biofilm reactors for biological nitrogen removal from combined urine and condensate for spacecraft life support (Smith et al., 2008). Air circulation through membrane lumen was provided by a 15W impeller fan removing air on a 10 minute on/20 minute off cycle. Wastewater flow was continued through the experiment.

## RESULTS AND DISCUSSION

Following installation of the membrane array, Chamber 4  $\text{NH}_4^+\text{-N}$  concentration decreased to less than the influent concentration (Figure 1). The concentration difference across Chamber 4 reached



**Figure 1.** Micro- $\text{O}_2$  Permeation to IX Media in AN/IX Chamber 4. Left: manifold with air circulator. Center: tubular membrane array. Right: solute time profiles.

ca. 14 mg/L around Day 40  $\text{NO}_3^-$  accumulated Day 40 but subsided by Day 40, while little  $\text{NO}_2^-$  was observed. Chamber 4 DO remained less than 2 mg/L throughout. Nitrogen removal appeared to be enabled by limited  $\text{O}_2$  flux to zeolite media by diffusive flux through permeable membranes. Lowering of the  $\text{NH}_4^+$ -N concentration in Chamber 4 is hypothesized to have resulted in  $\text{NH}_4^+$ -N release from zeolite due to the reversibility of  $\text{NH}_4^+$ -N sorption. In this case, the actual mass removal of  $\text{NH}_4^+$ -N in Chamber 4 would be greater than reflected by the decline in  $\text{NH}_4^+$ -N concentration alone. In-situ desorption of spent media is one aspect of the AN/IX/ANM process that can be operatively employed in onsite wastewater systems.

These results are preliminary but consistent with nitrification/anammox metabolism in Chamber 4. The main requirements for establishing nitrification/anammox are effective retention of microbial populations, a supply of  $\text{NO}_2^-$ , and the prevention of nitrite oxidation (Ma et al., 2015b). The granular clinoptilolite media in Chamber 4 provide excellent biomass retention. One of the most effective methods to prevent nitrite oxidation is oxygen limitation (Varas et al., 2015; Ma et al., 2015a; Qiao et al. 2013; Kwak et al. 2012), and diffusional limitation of  $\text{O}_2$  has been identified as an operative factor in establishing nitrification with nitrate oxidation (Malvonny et al., 2015). It appears quite possible that permeable membrane arrays can be configured in AN/IX/ANM to satisfy the controlled  $\text{O}_2$  delivery requirement.

## CONCLUSIONS

AN/IX/ANM has potential to be a passive and low cost system for nitrogen removal from onsite wastewater. Specifically designed experiments will confirm the initial results, verify nitrification/anammox metabolism within clinoptilolite media, and develop operating and design experience.

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