Title: Hybrid Adsorption and Biological Treatment Systems (HABiTS) for Enhanced Nitrogen Removal in Onsite Wastewater Treatment

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Twenty-five United Nations member states in the wider Caribbean region ratified the Cartagena Convention, which covers the marine environment of the Gulf of Mexico, the Caribbean Sea and some parts of the Atlantic Ocean. The Land-Based Sources and Activities protocol (LBS Protocol) of that convention addresses nutrient pollution from sewage discharges, agricultural runoff and other sources. Unfortunately, most Caribbean people use conventional onsite wastewater treatment systems (OWTs), especially septic systems. These systems fail to remove nitrogen effectively, posing a challenge for near shore environments. Passive biological nitrogen removal (BNR) processes have been developed for OWTs that rely on simple packed bed bioreactors, with little energy or chemical inputs and low operations and maintenance (O&M) requirements. This paper provides a case study from Florida on the partnerships and pathways for research to develop an innovative technology, Hybrid Adsorption and Biological Treatment System (HABiTS), for nitrogen reduction in OWTs. HABiTS combine ion exchange materials and BNR to remove nitrogen from septic tank effluent and buffer transient loadings. HABiTS, employs natural zeolite material (e.g. clinoptilolite) and expanded clay in the first stage to achieve both ammonium ion exchange and nitrification. The second stage of HABiTS utilizes tire chips, elemental sulphur pellets and oyster shells for adsorption of nitrate as well as sulphur oxidizing denitrification. Under transient load applications, the nitrogen in excess of the biodegradation capacity during high loading events was partially retained within the ion exchange and adsorption materials and readily available later for the microorganisms during lower loading events. Results from a bench scale bioreactor study with marine wastewater, which is relevant to where seawater is used for toilet flushing, are also presented. Pilot scale tests on the OWT of an engaged stakeholder dependent on the marine environment, would contribute to broader discussions for paradigm shifts for nutrient removal from wastewater.

Introduction

Adopted by twenty-five countries in the Wider Caribbean Region in March 1983, the Cartagena Convention is a regional legal agreement for the protection of the Caribbean Sea. The convention's "Land Based Sources and Activities Protocol" (LBS), was signed in October 1999 and entered into force on 13 August 2010 (United Nations, 1999). An objective of the LBS protocol is to reduce impacts of priority pollutants such as nutrients (nitrogen [N] and phosphorous [P]) by establishing guidelines and implementing best management practices for primary source categories including domestic sewage. Nutrient loading into groundwater and surface water systems has negative impacts on the environment, such as eutrophication, oxygen depletion, and decimation of fish populations (USEPA, 2011). Sources of excess N include domestic and industrial wastewater, agricultural runoff, stormwater runoff, and atmospheric deposition. In the United States and the Caribbean, more sustainable and cost-effective solutions to wastewater treatment are required to minimize water quality degradation and ensure that public health is not compromised. Recent events, such as the red tide bloom in Florida and South Coast sewage crisis in Barbados, both of which are linked to the influx of nutrients to surface water bodies, have further reinforced the need for sustainable wastewater solutions.

While approximately 75% of the United States population is served by centralised wastewater treatment systems (Siegrist et al., 2013), generally, less than 15% of urbanized populations in the Caribbean are connected to centralised systems (Nurse et al., 2012). In the Caribbean context, treatment therefore primarily relies on conventional onsite wastewater treatment systems (OWTs), also known as septic systems. Some places simply flush wastewater into a suck well, which is simply a hole in the ground. Conventional OWTs consist of a septic tank for primary treatment and solids separation and a soil infiltration system for additional biological treatment and pathogen removal. However, many of these OWTs show inconsistent and poor N removal due to factors including poor soil conditions, long idle periods, transient loading conditions, and infrequent maintenance (Oakley et al., 2010). Nitrogen discharges from poorly performing OWTs is particularly acute in Florida and many Caribbean islands since the karstic geology leads to rapid migration of nutrients in the subsurface, eventually affecting the marine environment. Therefore, technological advances have been proposed for improving the performance of OWTs.

In Florida, several studies have been conducted to enhance the treatment using passive bioreactors that include passively aerated nitrification (no compressors), denitrification with reactive media (containing a solid electron donor such as wood chips or elemental sulphur) and a limited number of pumps used for operation (FDOH, 2013). Chang et al. (2010) from the University of Central Florida studied a modification of the conventional drainfield design that included a vertical flow area for nitrification (conversion of ammonium [NH_4^+] to nitrate [NO_3^-]) and a horizontal flow area with a combination of sand, tire crumbs and sawdust for denitrification (conversion of NO_3^- to nitrogen gas [$N_{2(g)}$]). Greater removal of total N (TN) was observed in the modified drainfield (70%) compared with a conventional drainfield (50%). Passive N removal systems that are incorporated into the conventional OWT treatment train have also been studied. Conventional nitrifying biofilters with sand media have been shown to improve Total Suspended Solids (TSS) and Total Kjeldahl Nitrogen (TKN) removal (Anderson et al., 1998, USEPA, 2002).

This paper provides a case study from Florida on the partnerships and pathways for research to develop an innovative technology, Hybrid Adsorption and Biological Treatment System (HABiTS), for N removal in OWTs. It first presents results from bench scale studies of HABiTS using simulated septic wastewater influent, and then presents results from a pilot scale HABiTS system installed at a local wastewater treatment plant. Results from a bench scale bioreactor study with marine wastewater using similar N removal techniques as HABiTS is then presented. Finally, conclusions discuss opportunities for pilot scale tests on novel OWTs in the Caribbean and how that can contribute to broader discussions needed for paradigm shifts for nutrient removal from wastewater.

HABiTS Benchscale Studies

The following study was performed by the authors at the University of South Florida. This study was funded by the the USEPA Center for Reinventing Aging Infrastructure for Nutrient Management (RD835569). The study involved collaboration with engineers from private industry and was inspired by previous studies conducted by the Florida Onsite Sewage Nitrogen Reduction Strategies (FOSNRS, 2015) and Krayzelova et al., (2014). The technology developed, called Hybrid Adsorption and Biological Treatment System (HABiTS), combines ion exchange (IX) materials and biological nitrogen removal to effectively remove N and buffer transient loadings (Figure 1). In HABiTS, ionic forms of nitrogen (NH_4^+, NO_3^-) exceeding the system's biodegradation capacity are adsorbed during high loading rate periods, while desorption occurs during low or no loading periods. The desorbed nitrogen is then utilized by the microbial population, effectively regenerating the material. The overall goal of this research was to apply HABiTS for TN removal in OWTs under variable loadings.

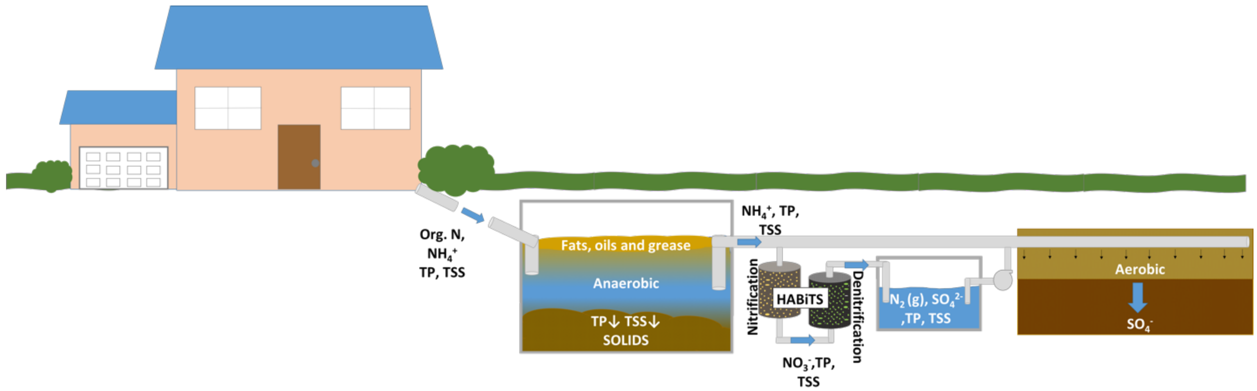

Figure 1. Hybrid Adsorption and Biological Treatment System (HABiTS), enhanced Onsite Wastewater Treatment Systems (OWTS)

HABiTS was first tested at bench scale by Rodriguez-Gonzalez (2017). In the study, two side-by-side biofilters were constructed, both with a passive aerobic column for nitrification and an anoxic column for sulphur oxidizing denitrification (SOD). The HABiTS treatment contained 20% clinoptilolite and 80% expanded clay for Stage 1 and tire chips, sulphur pellets and oyster shells for Stage 2. The control treatment employed only the expanded clay medium as a biofilm carrier in Stage 1 and non-sorptive plastic carriers instead of the tire scraps for Stage 2. A bench-scale septic tank fed both biofilters at a rate of 1.3 L/day (0.0013 m^3/day). The influent to the septic tank was screened raw domestic wastewater amended with urea to increase the NH_4^+-N concentration to values more commonly reported for OWTs. The influent was applied per the National Sanitation Foundation Standard 40, where 35%, 25% and 45% of the daily volume was distributed between 6 to 8am, 11 to 2pm and 6 to 8pm, respectively. Samples were collected three times per week and analyzed for N species and other water quality parameters. The systems where tested under different operating conditions with varying results. It was observed that at start-up, the nitrifying HABiTS column was able to keep N species concentrations significantly lower than the control column (Rodriguez-Gonzalez, 2017), highlighting the importance of the clinoptilolite in the treatment. The HABiTS column also showed enhanced performance at high loading rates (0.34 m^3/m^2-d; Rodriguez-Gonzalez, 2017). This indicated that IX continued to occur in the HABiTS column and possibly bio-regeneration of the clinoptilolite.

Table 1 shows a partial summary of the results for the HABiTS study that included both nitrification and denitrification columns at a loading rate of 0.21 m^3/m^2-d. At this loading rate, no significant difference was observed in the NH_4^+-N and NO_3^--N concentrations in the effluent of the HABiTS and control column. This indicated that under these conditions nitrification was the predominant N removal mechanism over IX. In the denitrification stage of the treatment, transient NO_2^--N production was observed for the effluent of HABiTS Stage 2 but not for the control Stage 2 column during this period. In HABiTS, leaching of carbon from the tire mulch (Krayzelova et al., 2014), could have allowed partial heterotrophic denitrification to occur resulting in higher NO_2^--N production. In time and due to the high availability of elemental sulphur, SOD start-up was observed and NO_2^--N concentrations dropped to below 1 mg/L. Samples collected during the study indicated faster denitrification in HABiTS, possibly due to the partial heterotrophic denitrification as discussed previously. Because of SOD, the high removal of NO_3^--N correlated with increased SO_4^{2-}-S in the effluent. Under these conditions, HABiTS outperformed the control column by removing 53.94% of the NO_3^--N produced compared to 40.94% removed in the control treatment.

Table 1. Average water quality results for influent, control and HABiTS columns (modified from Rodriguez-Gonzalez et al., 2017).

Parameter	*Influent*	*Control Stage 1*	*Control Stage 2*	*HABiTS Stage 1*	*HABiTS Stage 2*
NH_4^+-N (mg/L)	80.56 ±30.66	19.79 ±17.07	21.82 ±16.08	21.51 ±13.99	20.25 ±12.90
NO_2^--N (mg/L)	0.97 ±0.91	0.50 ±0.54	0.67 ±0.74	0.57 ±0.75	1.49 ±2.98
NO_3^--N (mg/L)	0.07 ±0.17	58.96 ±21.86	25.68 ±15.12	58.60 ±23.47	16.17 ±15.96
TIN (mg/L)	81.59 ±31.74	79.25±39.47	48.18 ±31.94	80.68 ±38.21	37.91 ±31.84
SO_4^{2-}-S (mg/L)	22.48 ±16.22	42.31 ±16.79	74.14 ±23.62	43.48 ±9.02	70.90 ±22.48

HABiTS Pilot Scale Studies

A pilot scale demonstration of HABiTS is currently underway at the Northwest Regional Water Reclamation Facility in Hillsborough County, Florida (Stocks, 2017; Miriyala, 2018). This study is being performed in collaboration with the Hillsborough County Department of Public

Utilities as part of the Facilities Accelerating Science & Technology (FAST) Water Network by the Leaders Innovation Forum for Technology (LIFT) (Stocks, 2017; Miriyala, 2018). The pilot systems are being used to evaluate HABiTS nutrient and pathogen removal performance with (HABiTS R) and without recirculation (HABiTS FF) of nitrified effluent from Stage 1 to a pre-denitrification tank. The pilot systems configurations were similar to bench scale system with nitrifying and denitrifying stages. The first stage contained a mixture of clinoptilolite (16% w/w), expanded clay (82% w/w) and oyster shells (2%). The second stage of both pilot HABiTS contained a mixture of tire mulch (83% w/w), elemental sulphur pellets (13% w/w) and oyster shells (4% w/w). The HABiTS with recirculation (R) had two additional tanks that served as a pre-denitrification tank (32 gallons) and a recirculation tank (40 gallons). Both pilots were fed septic tank effluent at a rate of 35 gallons/day.

Figure 2. Pilot HABiTS at North West Water Reclamation Facility

A partial summary of the results of the pilot study is shown in Table 2 (Henderson et al., 2018). HABiTS with recirculation consistently achieved < 10 mg/L NH_4^+-N in the effluent, likely due to improved moisture content for enhanced biofilm development and/or increased mass transfer of substrates to the biofilm in Stage 1. Moreover, the pre-denitrification step in HABiTS R resulted in reduced organic carbon loads that would otherwise hinder nitrification. Complete denitrification was observed for both systems and could be attributed to both adsorption of NO_3^-

onto the tire chips and the denitrification due to SOD and leaching of organic carbon from the tire chips, which promotes heterotrophic denitrification and enhances NO_3^--N removal. Overall, an 81.7% TIN removal was observed in the final effluent of HABiTS with recirculation (HABiTS R2) and 59.2% in HABiTS without recirculation (HABiTS FF2). Due to this versatility, HABiTS are promising alternatives for passive N removal in OWTS.

Table 2. Average concentrations of NH_4^+-N, NO_2^--N, NO_3^--N, TIN and *E.coli* log removal for the HABiTS pilot (modified from Henderson et al., 2018).

N species	***Recirculation ratio 1:1***			***Recirculation ratio 3:1***		
	Influent	**HABiTS R2**	**HABiTS FF2**	**Influent**	**HABiTS R2**	**HABiTS FF2**
NH_4^+-N (mg L^{-1})	35.95±1.40	6.31±1.52	14.42±1.00	42.00±4.17	9.03±3.60	19.19±4.94
NO_2^--N (mg L^{-1})	0.36±0.24	0.33±0.14	0.3±0.18	0.48±0.31	0.54±0.27	0.48±0.24
NO_3^--N (mg L^{-1})	0.00±0.00	0.00±0.01	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
TIN (mg L^{-1})	36.12±2.68	6.6±8.02	14.72±2.20	42.14±4.98	9.28±4.15	19.45±5.64
E.coli log removal	-	1.40	0.51	-	1.59	1.10

Marine Wastewater Bench Scale Bioreactor

Bench scale experiments to test the performance of different electron donor materials for biological denitrification in marine systems were performed at the University of South Florida (He et al., 2018) through funding from the China Scholarship Council, China (CSC, NO. 201606400027), the US National Science Foundation Partners for International Research and Education (PIRE Grant No. 1243510) and the Florida Sea Grant. A series of microcosm experiments were conducted to compare methanol, fish faecal waste (FW), wood chips, elemental sulphur (S^0) and a combination of wood chips and S^0 for saline wastewater denitrification. The saline wastewater composition was based on studies of a pilot Recirculating Aquaculture System (Boxman et al., 2018), however, the performance of the systems should be similar for wastewater in areas where sea water is used for toilet flushing as is the case of coastal communities in the Caribbean. For the experimental conditions used, a range of denitrification rates were obtained with methanol (23.4 g N/(m^3·d)), and S^0 (3.5 g N/(m^3·d)), and pine wood-sulphur heterotrophicautotrophic denitrification (P-WSHAD) (7.2–11.9 g N/(m^3·d)). Table 3 summarizes the pros and cons of a representative set of the electron donor systems.

Table 3: Summary of denitrification performance using different electron donors in marine water (modified from He et al., 2018). SOD – sulphur and oyster shells, P-WC – pine wood chips, PO-WSHAD – pine wood chips, oyster shells & elemental sulphur.

Substrates	Advantages	Disadvantages	Recommended treatment application for saline wastewater
Methanol	High denitrification rate.	High cost. Chemical handling and safety concerns. NO_2^- accumulation.	Centralized systems. Requires chemical feed system and optimization of system operating conditions to control NO_2^- production and prevent overdosing.
SOD	Low cost. Stable NO_3^- removal. Low NO_2^- accumulation.	Requires oyster shells or limestone for alkalinity. SO_4^{2-} generation.	Passive OWTs. Requires periodic sulphur replenishment (every 2-3 years).
P-WC	Bioavailable carbon source. High proportion of rbCOD to total COD.	Carbon becomes less bioavailable over time.	Passive OWTs. Prior studies have shown wood chips can continue denitrifying for up to 15 years.
PO-WSHAD	High denitrification rate. Low SO_4^{2-} generation. Adequate alkalinity source.	Pilot scale systems needed to demonstrate performance.	Passive OWTs. Combines benefits of both S^0 and WC.

Locations such as the cayes in Belize where toilets are flushed with marine water would be ideal sites for installing and testing the performance of a bioreactor system that enhances denitrification. Places like Belize's Laughing Bird Caye National Park (LBCNP), a World Heritage Site and popular tourist destination managed by the Southern Environmental Association (SEA) have invested in wastewater management systems that improve the quality of water in the surrounding reef. Fragments of Hope, a Non-Governmental Organization based in Belize, has restored corals at this site since 2006 following destruction by hurricane Iris in 2001. Their work there documents the longest record of reef restoration in the world, and is recognized for its example of success. Given the proximity of the restored reef sites to the OWT installed by a local business, EcoFriendly Solutions Ltd., there is recent history of moving the OWT because of erosion and its potential contribution to algae growth (Figure 3). Through support from PIRE, training activities with SEA rangers and tour guides to the area were conducted to raise awareness of treatment process and maintenance. These initiatives revealed high levels of interest and inquiry on whether this type of information could be shared with tourists. Testing of the new system for performance with respect to N removal has not been undertaken and consideration of denitrification technology would have to consider supply and cost of materials like sulphur.

Figure 3. Restroom facilities and OWT installed by Ecofriendly Solutions Ltd. at Laughing Bird Caye National Park, Belize. Pictures taken in a) March 2017 showing algae covered rocks and interventions to combat erosion and b) March 2018 showing relocation of OWT with increased treatment capacity.

Conclusions

The three case studies presented to reduce N levels in wastewater systems all link environmental engineering research and education with a real-world context and local partner. The HABiTS Bench Scale study was fashioned off of a residential pilot system installed at a local home, the HABiTS Pilot Study was run at a research site built at the Northwest Regional Water Reclamation Facility in Hillsborough County, Florida, and the Marine Wastewater Bench Scale Bioreactor was partnered with a recirculating aquaculture system pilot at the Mote Marine Lab in Sarasota, FL. LBCNP Belize presents an ideal location with a valuable and vulnerable reef right next to an OWT with limited land for nutrient uptake. USF faculty and students along with staff from the wastewater treatment plant lead educational tours for students and practitioners at the HABiTS pilot site. This hands-on experience improves understanding of nutrient management options for OWTs. With so many community centers, national heritage sites, and schools in the

Caribbean region that use OWTs, installing the types of nutrient management pilots discussed in this paper could help to initiate discussions on such potential solutions to nutrient pollution.

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References

Anderson, D. L., Tyl, M. B., Otis, R. J., Mayer, T. G., & Sherman, K. M., (1998). Onsite wastewater nutrient reduction systems (OWNRS) for nutrient sensitive environments. In On-Site Wastewater Treatment: Proceedings of the Eighth National Symposium on Individual and Small Community Sewage Systems, ed. DM Sievers. American Society of Agricultural Engineers, St. Joseph, MI.

Boxman, S.E., Kruglick, A., McCarthy, B., Brennan, N.P., Nystrom, M., Ergas, S.J., Hanson, T., Main, K.L., Trotz, M.A., (2015). Performance evaluation of a commercial land-based integrated multi-trophic aquaculture system using constructed wetlands and geotextile bags for solids treatment. Aquac. Eng. 69, 23–36.

Chang, N. B., Wanielista, M., Daranpob, A., Xuan, Z., & Hossain, F., (2010). New performance-based passive septic tank underground drainfield for nutrient and pathogen removal using sorption media. Environmental Engineering Science, 27(6), 469-482.

FDOH, (2013). Standards for Onsite Sewage Treatment and Disposal Systems, Chapter 64E-6, Florida Administrative Code. Florida Department of Health (FDOH).

FOSNRS, (2015). Florida Onsite Sewage Nitrogen Reduction Strategies Study: Final Report. Retrieved from the Florida Department of Health (FDOH) website: www.floridahealth.gov

He, Q., Zhang, D., Main, K., Feng, C., & Ergas, S. J. (2018). Biological denitrification in marine aquaculture systems: A multiple electron donor microcosm study. *Bioresource technology*, *263*, 340-349.

Henderson M. (2017). The Fate of Fecal Indicator Bacteria in Passive Nitrogen Reduction Systems. Master's Thesis, Department of Civil & Environmental Engineering, University of South Florida, Tampa, U.S.A.

Henderson, M.B., Miriyala, A., Stocks, J.L., Rodriguez-Gonzalez, L., Zhang, D., Ghebremichael, K., Mihelcic, J., Ergas, S.J. (2018) Passive Hybrid Adsorption And Biological Treatment Systems For Removal Of Nitrogen And E. Coli From Wastewater. Selected for Oral presentation and conference proceedings at IWA SWWS2018 Conference on Small Water & Wastewater Systems and Resources Oriented Sanitation.

Krayzelova, L., Lynn, T.J., Banihani, Q., Bartacek, J., Jenicek, P., Ergas, S.J. (2014). A Tire-Sulfur Hybrid Adsorption Denitrification (T-SHAD) process for decentralized wastewater treatment. Water Res, 61, 191-199.

Miriyala A. (2018). Impact of Nitrified Effluent Recirculation on the Performance of Passive Onsite Hybrid Adsorption and Biological Treatment Systems. Master's Thesis, Department of Civil & Environmental Engineering, University of South Florida, Tampa, U.S.A.

Nurse, L., Cashman, A., & Mwansa, J. (2012). Confronting the challenges of sewerage management in the Caribbean: a case study from the island of Barbados. *Environment: Science and Policy for Sustainable Development*, *54*(2), 30-43.

Oakley, S. M., Gold, A. J., Oczkowski, A. J. (2010). Nitrogen control through decentralized wastewater treatment: process performance and alternative management strategies. Ecol. Eng. 2010, 36(11), 1520-1531.

Rodriguez-Gonzalez, L. (2017). Advanced Treatment Technologies for Mitigation of Nitrogen and Off-flavor Compounds in Onsite Wastewater Treatment and Recirculating Aquaculture Systems. Doctoral dissertation, Department of Civil & Environmental Engineering, University of South Florida, Tampa, U.S.A.

Siegrist, R. L., McCray, J. E., Lowe, K. S., Cath, T. Y.; Munakata-Marr, J. (2013). Onsite and

Decentralised Wastewater Systems: Advances from a decade of research and educational efforts. Water 2013, 77-84.

Stocks, J. L. (2017). Enhancement of Two Passive Decentralized Biological Nitrogen Removal Systems. Master's Thesis, Department of Civil & Environmental Engineering, University of South Florida, Tampa, U.S.A.

United Nations (1999). Protocol concerning pollution from land-based sources and activities to the convention for the protection and development of the marine environment of the wider Caribbean region.

USEPA, (2002). Onsite Wastewater Treatment Systems Manual. EPA 625-R-00-008. United States Environmental Protection Agency. Office of Research and Development, Washington D.C., USA.

USEPA (2011). Reactive Nitrogen in the United States: An Analysis of Inputs, Flows, Consequences, and Management Options - A Report of the Science Advisory Board. EPA-SAB-11-013.