Hybrid Adsorption and Biological Treatment System (HABiTS) for enhanced nitrogen removal in onsite wastewater treatment systems


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Abstract
A Hybrid Adsorption and Biological Treatment System (HABiTS) was investigated for efficient nitrification in on-site wastewater treatment. Variable septic tank effluent loading experiments were carried out in bench-scale columns, with and without zeolite addition. Enhanced NH$_4^+$-N removal (80%) was observed in the HABiTS column that combined expanded clay and clinoptilolite compared with a control column with only expanded clay (73%) during phases with high nitrogen loads. The enhancement was attributed to NH$_4^+$ adsorption by clinoptilolite during high loading rate periods and subsequent bioregeneration by nitrifying bacteria during low loading rate periods. Similar treatment efficiency for the both the HABiTS and control column was observed during low loading rate periods.

Keywords
Ion exchange, nitrification, on-site wastewater treatment, zeolite

INTRODUCTION
Centralized wastewater treatment involves collecting and conveying sewage from individual residences to large wastewater treatment systems. However, in many rural and suburban areas, where there are low population densities and large distances between households, the cost of centralized treatment is prohibitive. Onsite wastewater treatment systems (OWTs) are an alternative to centralized systems that have been used for decades worldwide. In the United States, for example, OWTs treat close to a third of the wastewater produced (USEPA, 2002). Similar numbers are reported for other developed countries, such as France (20%), and OWTs are even more prevalent in developing countries (Petitjean et al., 2016; Libralato et al., 2012). The cost effectiveness of OWTs is attributed to their simple operation, low energy and maintenance requirements and little to no chemical use (USEPA, 1999). Regardless of these benefits, there are still major challenges in OWT application, including limitations due to high water table elevations and proximity to drinking water supplies and environmentally sensitive areas (FDOH, 2013). In particular, the limited nitrogen (N) removal in conventional OWTs (USEPA, 1999) can result in nutrient contamination of ground and surface water (Liu et al, 2009). In addition, variable water usage and long idle times (e.g. during vacations) result in highly variable loading rates, which affect the biological treatment process (USEPA, 2002).

Conventional OWTs consist of a septic tank for primary treatment and solids separation and a soil infiltration system for biological treatment and pathogen removal. A number of technologies have been developed to provide enhanced treatment in OWT. For example, multi-chambered...
settling tanks have been shown to improve solids removal. Moussavi et al. (2010) investigated an upflow septic tank as opposed to the conventional horizontal flow system. Improved removal of total suspended solids (TSS) and chemical oxygen demand (COD) was observed at retention times as low as 24 hours. However, these modifications had little effect on N removal. Oh et al. (2014) studied the use of recycled rubber particles as filter media for the treatment of septic tank effluent and observed 93% removal of TSS and 90% removal of $\text{NH}_4^+$-N. Chang et al. (2010) studied a modification of the conventional drainfield design that included a vertical flow area for nitrification and a horizontal flow area with a combination of sand, tire crumbs and sawdust for denitrification. Greater removal of total N (TN) was observed in the modified drainfield (70%) compared with a conventional drainfield (50%). Passive N removal OWTs that include nitrification and denitrification bioreactors placed between the septic tank and drainfield have also been studied. Conventional nitrifying biofilters with sand media have been found to improve TSS and TKN removal (Anderson et al., 1998, USEPA, 2002). Passive aeration through the biofilter has been shown to provide sufficient dissolved oxygen (DO) for nitrification; however, transient loadings can result in variable N concentrations in the effluent (Petitjean et al., 2016).

This study investigated a Hybrid Adsorption and Biological Treatment System (HABiTS), which is a modification of passive N removal OWTs. HABiTS employs a combination of ion exchange (IX) and biological N removal (BNR) to enhance the performance of OWTs. HABiTS have the potential to overcome variable loading rates by adsorbing N loads in excess of the system biodegradation capacity during high loading rate periods. During low loading rate periods, N containing ions ($\text{NH}_4^+$ or $\text{NO}_3^-$) are desorbed and can be subsequently utilized by the microbial population. In our prior research, Krayzelova et al. (2014) demonstrated this concept using scrap tire chips as an $\text{NO}_3^-$ IX medium in sulfur oxidizing denitrification bioreactors. This paper focuses on the application of the HABiTS to nitrifying biofilters used in passive N removing OWTs.

Zeolite materials have the ability to adsorb positively charged ions, such as $\text{NH}_4^+$ (Wen et al., 2006; Rodriguez-Gonzalez et al. 2015). Lahav and Green (1999) used zeolite as an adsorbent in a two-stage nitrification system, where adsorption of $\text{NH}_4^+$ took place in one stage and bioregeneration of $\text{NH}_4^+$ laden regenerant brine took place in a second stage. In a prior study in our laboratory, the zeolite material chabazite was added to a sequencing batch reactor (Zeo-SBR) treating high $\text{NH}_4^+$ strength wastewater from anaerobic digestion of swine manure (Aponte-Morales et al., 2016). Addition of chabazite reduced the inhibition of free ammonia to nitrifying bacteria and allowed for complete N removal with the addition of an electron donor during the denitrification stage. Clinoptilolite, a lower cost zeolite material, has also been studied for the enhancement of N removal in passive N removing OWTs (Hirst et al. 2013; Rodriguez-Gonzalez et al., 2015); however, no prior studies have compared HABiTs with conventional packed bed nitrification reactors under transient loading conditions.

The goal of this research was to compare HABiTS and conventional media nitrifying biofilter performance with septic tank effluent under variable loading rates. The first part of this work which included material selection, characterization and modelling is presented elsewhere (Rodriguez-Gonzalez et al. 2015).
METHODOLOGY

Influent wastewater
Effluent from a 30 L bench-scale septic tank (hereafter referred to as influent) was used to feed the columns described below. The influent was applied at varying rates according to the National Sanitation Foundation Standard 40 for variable loading, where 35%, 25% and 45% of the daily volume was distributed between 6 to 8am, 11 to 2pm and 6 to 8pm, respectively. The septic tank was fed with screened raw sewage from the Falkenburg Advanced Wastewater Treatment plant in Tampa, FL. Due to the low concentration (~30 mg/L) of NH₄⁺-N in the sewage, urea was added to the sewage to increase NH₄⁺-N to a target concentration of 100 mg/L, which lies in the range of septic tank effluent concentrations recorded by Lowe et al. (2009). Note that due to the variability of the wastewater collected from the treatment plant there was significant variability in the influent composition, similar to real OWTs.

HABiTS and control column studies
Two side-by-side nitrifying biofilter columns (88.9 mm diameter, 406 mm length) were constructed. One was designated as the control column and employed an expanded clay medium (1.38-2.38 mm; Riverlite, Big River, Alpharetta, GA) as a biofilm carrier. The material selection was based on its low cost and prior studies using this material in OWTs (Hirst et al., 2013) and its low capacity for NH₄⁺ adsorption (Rodriguez-Gonzalez et al. 2015). The HABiTS column contained a mixture of 20% clinoptilolite (2-2.38 mm, Zeox Mineral Materials Corp, Cortaro, AZ) and 80% expanded clay. The clinoptilolite dose was calculated to be able to withstand typical NH₄⁺ loads over a 14 day period with no nitrification (e.g. due to biofilm dye-off after a long idle period or after shock loading of a toxicant) based on the measured adsorption capacity of 14 mg NH₄⁺/g (Rodriguez-Gonzalez et al., 2015). The media materials were rinsed with deionized water for 15 minutes and dried at 105 (±3) °C for 24 hours (Rodriguez-Gonzalez et al., 2015). No chemical conditioning was performed. The columns were flushed with deionized water to remove fines and then flushed with 15L of local groundwater to reduce some of the Na⁺ loads from the clinoptilolite that could hinder nitrification (Aponte-Morales et al., 2016). At the end of the groundwater flush, effluent Na⁺ from the columns was 100.36 and 22.4 mg/L for HABiTS and control column, respectively.

Figure 1. Experimental setup schematic
During column operation, the influent was distributed over the top of the unsaturated columns according to the NSF Standard 40 described above. The columns were studied in three different phases. In the first phase the columns were fed at a rate of 2.1 L/day resulting in a hydraulic loading rate (HLR) of 0.34 m³/m²-day. In this phase the columns were monitored to observe the effect of IX and the length of time required for nitrification start-up. Phase II began several weeks after Phase I at the same loading rate. Phase III began after Phase II when lower flowrate was applied, 1.3L/day (HLR = 0.21 m³/m²-day) to improve nitrification.

Backwashing was performed once on day 37 during the Phase II study period to improve column hydraulics. Backwashing was performed with a mixture of groundwater and septic tank effluent to avoid any major desorption of NH₄⁺ from the HABiTS columns that would give an advantage over the control column. The columns were filled from the bottom, drained twice, overflowed for 5 minutes at a rate of 250 mL/min, drained again and then were immediately connected back to the influent pumps. During Phase III no backwashing was performed; however, the column media were re-distributed on day 87 to improve column hydraulics.

Analytical Methods
Samples were collected at least three times per week during the noon dosing period. A portion of the samples was filtered through a 0.45 µm mixed Cellulose Esters filter (FisherScientific, Waltham, MA). TSS/VSS concentrations were measured using Standard Methods 2540 D (APHA et al., 2012). TN concentrations were measured in both unfiltered and filtered samples using HACH (Loveland Co) TNT plus 827 test kits (MDL: 0.140 mg/L). Concentrations of anions (NO₂⁻, NO₃, Cl⁻, PO₄³⁻, SO₄²⁻) and cations (NH₄⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺) were measured in the filtered samples using a Metrohm 881 Compact IC Pro (Herisau, Switzerland) ion chromatography system. pH and dissolved oxygen (DO) were measured using an Oakton Acorn Series meter (Orion 5 Star ThermoScientific) and calibrated electrodes. Chemical oxygen demand (COD) was measured for unfiltered and filtered samples with the Vario Tube Test (Loveland Co) COD LR test kits (MDL: 0-150 mg/L), according to the Standard Methods (APHA et al., 2012).

Statistical analysis
Statistical analyses were performed to compare the performance of the two studied columns. A two sample t-test assuming equal variances was performed in Excel 2011 for N species results from both columns with α=0.05.

RESULTS AND DISCUSSION
Influent and effluent NH₄⁺-N, Na⁺, NO₂⁻-N, and NO₃⁻-N concentrations during Phase I are shown in Figure 2. During the start-up phase, removal of NH₄⁺-N in HABiTS ranged from 75 to 85%, which was significantly greater than the control. As shown in Figure 2b, the ion exchanged with NH₄⁺ was Na⁺; however, the effluent Na⁺ concentration only reached a maximum of 210 mg/L on day 2 and decreased to the influent value within 12 days. High Na⁺ concentrations are of concern due to the inhibitory effect of Na⁺ on nitrifying bacteria. However, Na⁺ concentrations observed in this study were much lower than the value reported by Sanchez et al. (2004) to inhibit nitrification of 8,000 mg/L. The groundwater flush prior to Phase I reduced the load of Na⁺, as was also observed in batch studies (Rodriguez-Gonzalez et al., 2015). Other
cations present, such as Mg$^{2+}$, Ca$^{2+}$ and K$^+$ showed little difference from influent (not shown). In contrast, in the control effluent NH$_4^+$-N concentrations only started to decrease after day 7 (Figure 2a), which coincided with increases in effluent NO$_2^-$-N concentrations (Figure 2c). Some NO$_2^-$ was also observed in HABiTS but to a lesser extent. Start-up of nitrification within both columns occurred much faster than in gravel/sand filters studied by Petitjean et al. (2016), where nitrification was observed after 12 days at a HLR of 0.117 m$^3$/m$^2$-day. It is important to note that neither of the columns was seeded with active nitrifying biomass, indicating that some nitrifying microorganisms were likely present in the influent feed. Transient accumulation of NO$_2^-$ during start-up was consistent with literature showing that NH$_4^+$ oxidation kinetics are faster than NO$_2^-$ oxidation (Almutairi & Weatherley, 2015).

![Graphs](image)

**Figure 2.** NH$_4^+$-N (a), Na$^+$ (b), NO$_2^-$N (c), and NO$_3^-$N (d) daily variation in the influent (○), control (▲) and HABiTS (□) columns effluent for Phase I under HLR of 0.34 m$^3$/m$^2$-d.

Based on the amount of clinoptilolite added, saturation of the HABiTS media and breakthrough should have occurred within 14 days of start-up. The low effluent NH$_4^+$ concentrations in HABiTS after 14 days, showed that nitrifying biofilms were bio-regenerating the clinoptilolite. Meladonic & Weatherley (2008) also saw considerable retardation of NH$_4^+$-N breakthrough due to nitrification in clinoptilolite columns treating synthetic wastewater. In the case of HABiTS, however, little production NO$_2^-$ and NO$_3^-$ was observed. Based on the average effluent NO$_2^-$ and NO$_3^-$ concentrations, only 9.24% of the NH$_4^+$-N removed was due to nitrification, possibly due to simultaneous nitrification/denitrification in anoxic zones within HABiTS. However this phenomenon was not observed in Phases II and III and was not studied further. Statistically
significant differences were observed for NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{-} (p<0.05), showing improved performance for HABiTS during start-up. This result also highlights the efficiency of HABiTS to reduce start-up periods by maintaining low N concentrations while nitrifying biofilms are being established. Almutairi & Weatherly (2015) observed similar results when testing multiple IX columns, with and without the addition of external aeration and nitrifying biomass. Huang et al. (2015) tested clinoptilolite for NH\textsubscript{4}\textsuperscript{+}-N removal in groundwater and also reported on the robustness of the treatment in the case of insufficient biological activity. Increasing the clinoptilolite percentage in the HABiTS column would likely have resulted in greater removal of NH\textsubscript{4}\textsuperscript{+} and longer periods of sustained IX but would have defeated the goal of keeping these systems cost-effective and promoting hybrid IX and biological treatment. Such was the case for further studies from Hirst et al. (2013). Although high NH\textsubscript{4}\textsuperscript{+} removal was observed in pilot scale nitrifying biofilters with 100% clinoptilolite media, the material was not selected for full scale tests due to cost constraints (FOSNRS, 2015).

N species concentrations during Phases II and III are shown in Figure 3. A summary of the N results and additional water quality parameters measured are shown in Table 2. During Phase II, NH\textsubscript{4}\textsuperscript{+}-N concentrations (Figure 3a, Table 2) in the influent were highly variable (57.49 ±19.78), which affected the variability of the effluent of the control column (15.78±9.24). During this period; however, the average HABiTS effluent NH\textsubscript{4}\textsuperscript{+}-N concentration was less than 15 mg/L, with little variation (11.03±3.45) and were significantly lower than effluent concentrations in the control column. Hirst et al. (2013) reported that little effluent NH\textsubscript{4}\textsuperscript{+}-N variability was observed in a nitrifying biofilter with a clinoptilolite medium. No significant differences were observed in NO\textsubscript{2}\textsuperscript{-}-N and NO\textsubscript{3}\textsuperscript{-}-N effluent concentrations from the columns (Figure 3b-c). This was a clear indication that both IX and bio-regeneration of the clinoptilolite continued to occur in the HABiTS column. Another indication of the effect of IX in HABiTS was the high NO\textsubscript{3}\textsuperscript{-} concentrations recovered from HABiTS when compared to the control column within the first flush due to stored concentrations from the previous study. No significant difference was observed in the other cations and anions from both columns (Table 2).

A 7-day gap in results between days 30 and 37 was due to column and equipment maintenance as well as a required system backwash due to clogging and increased head loss within the columns. Based on NH\textsubscript{4}\textsuperscript{+}-N removal, there was no significant impact on the treatment performance due to backwashing for either column, with the exception in variability in TSS/VSS concentrations (Table 2), most likely due to release of biomass during the first flush after backwash. Although not desirable, backwashing after over two months of intermittent treatment is not uncommon. In studies by Petitjean et al. (2016) clogging of a sand column was observed within 45 days of operation under varying HLR (0.07-0.117 m\textsuperscript{3}/m\textsuperscript{2}-d). In this study the particle size was about half that of Petitjean et al. (2016) and the HLR during Phase I was about three times higher. In order to address the clogging problem, the HLR was decreased in Phase III.

Phase III commenced after 52 days of treatment. During Phase III HLR was reduced to 0.21 m\textsuperscript{3}/m\textsuperscript{2}-day to achieve more complete nitrification and reduce clogging. Similar removal performance was observed in both columns under the lower HLR condition. Effluent NH\textsubscript{4}\textsuperscript{+}-N concentrations were comparable to that of Phase II. This result was different from that of Luo et al. (2014) where decreased NH\textsubscript{4}\textsuperscript{+} removal was observed with increasing HLR in a system that combined soil and clinoptilolite. The increased effluent NH\textsubscript{4}\textsuperscript{+}-N concentration was most likely
due to an increase in influent NH$_4^+$-N concentrations (+30 mg/L) around day 90. In this phase, nitrification completely dominated the removal processes of NH$_4^+$ for both control and HABiTS columns. This was supported by the observed reduction in effluent pH as well as high effluent NO$_3^-$-N concentrations observed (Figure 3). Although some heterotrophic degradation occurred in the columns based on more than 50% removal of COD (Table 2), average effluent DO concentrations were > 4 mg/L showing that lack of oxygen was probably not the cause for incomplete nitrification.

![NH$_4^+$-N, NO$_2^-$-N, and NO$_3^-$-N daily variation in the influent (○), control (▲) and HABiTS (□) columns effluent for Phase II and III under variable HLR.](image)

In terms of performance, HABiTS could have been affected by slow desorption of the retained NH$_4^+$ during the previous high loading period in Phase II. Similar results were observed by Miladonic & Weatherly (2008) when testing clinoptilolite columns at varying loading rates. Another indication of improved nitrification was the effluent NO$_2^-$ concentrations in both
columns, which decreased about ten times achieving less than 3 mg/L. No statistical difference was observed for any N species under this loading rate. Further studies are being performed investigating the hourly N concentration variation in both columns. Preliminary results show enhanced removal in HABiTS, during the evening hours where 40% of the daily volume is distributed.

Table 1: Water quality results for influent, control and HABiTS column during Phase II and III.

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<th>PHASE II</th>
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<th>PHASE III</th>
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<td></td>
<td>HLR = 0.34 m³/m²-d</td>
<td></td>
<td>HLR = 0.21 m³/m²-d</td>
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<tr>
<td>pH</td>
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<td>Control</td>
<td>HABiTS</td>
<td>Influent</td>
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<td></td>
<td>7.20 ± 0.40</td>
<td>6.68 ± 0.38</td>
<td>6.59 ± 0.41</td>
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<td>DO (mg/L)</td>
<td>0.81 ± 0.39</td>
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<td>0.59 ± 0.30</td>
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<td>TSS (mg/L)</td>
<td>38.12 ± 22.32</td>
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<td>VSS (mg/L)</td>
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<td>NO₂⁻-N (mg/L)</td>
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<td>NO₃⁻-N (mg/L)</td>
<td>0.10 ± 0.23</td>
<td>32.78 ± 17.43</td>
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<td>Na⁺ (mg/L)</td>
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<td>K⁺ (mg/L)</td>
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CONCLUSIONS

Hybrid Adsorption and Biological Treatment System (HABiTS) are a promising alternative for passive N removal in OWTs. The goal of this research was to compare HABiTS and conventional media nitrifying biofilter performance under variable loading of septic tank effluent. Results show that the combined IX and nitrification in HABiTS can sustain variable loading and achieve over 80% removal of $\text{NH}_4^+$ concentrations at loading rates higher than 0.34 m$^3$/m$^2$-day when compared to the conventional media column with 73% removal. Under lower loading rates the biological treatment was enhanced and dominated the $\text{NH}_4^+$ removal processes in both columns. The addition of a denitrification stage is expected to effectively reduce N concentrations and lower the environmental impact of OWTs.

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