Research Article

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Enhanced landfill leachate treatment in sequencing batch biofilm reactors (SBBRs) amended with zeolite and biochar

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Abstract

BACKGROUND: Biological treatment of landfill leachate is inhibited by high concentrations of ammonia and recalcitrant organic matter. This study investigated the addition of natural adsorbent materials, zeolite (clinoptilolite) and biochar, to enhance biological treatment of landfill leachate in sequencing batch biofilm reactors (SBBRs). Three bench-scale SBBRs were set up with varying types of biofilm support media: (i) lightweight expanded clay aggregate (LECA) as a control (C-SBBR); (ii) LECA + zeolite (CZ-SBBR); and (iii) LECA + zeolite + biochar (CZB-SBBR). SBBRs were operated with alternating anoxic and aerobic stages to promote total nitrogen (TN) removal via nitrification/denitrification.

RESULTS: Excellent TAN removal (>99%) was achieved in all three SBBRs throughout the study, most likely as a result of the favorable environmental conditions and long hydraulic retention time (HRTs) applied (nine or more days). Biochar addition in CZB-SBBR resulted in significantly higher chemical oxygen demand (COD) (61–83%) and color (82–95% as UV456) removals compared with C-SBBR (42–44% for COD and 28–33% for color) and CZ-SBBR (34–45% for COD and 20–35% for color). High effluent nitrate (NO_3^-) concentrations initially were observed in CZB-SBBR, most likely due to limited organic carbon availability for denitrification. However, after >1 year of operation, NO_3^- accumulation declined and TN removal of 81% was achieved, indicating that the main nitrogen removal pathway shifted from simultaneous nitrification/denitrification to partial nitritation/anammox.

CONCLUSIONS: Zeolite/biochar amended SBBRs are a promising approach for enhanced landfill leachate treatment.

Keywords: biochar; landfill leachate; nitritation-anammox; simultaneous nitrification denitrification (SND); sequencing batch biofilm reactors (SBBRs); zeolite mineral

INTRODUCTION

Landfilling is used for management of ≈40% municipal solid waste (MSW) generated worldwide.[1] However, large quantities of landfill leachate are generated because of infiltration of rain and snow through decaying MSW. In the US, landfill leachate typically is collected in underdrains for co-treatment with domestic wastewater in conventional wastewater treatment plants (WWTPs).[2] However, the high concentrations of ammonia, recalcitrant organic matter and color in landfill leachate result in challenges to biological processes at WWTPs. Leachate ammonia concentrations typically are several orders of magnitude higher than those in domestic wastewater, resulting in high oxygen demands for nitrification and high organic carbon (C) requirements for denitrification. High total ammonia nitrogen (TAN) concentrations also lead to high free ammonia (FA) concentrations, which can inhibit ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) involved in nitrification.[3] The low ratios of biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) (0.05–0.2) in leachate result in poor organic matter biodegradability.[4,5] The deep brown color of landfill leachate is caused primarily by dissolved humic compounds, which also are toxic to microorganisms and can disrupt the ultraviolet (UV) disinfection process.[6]

A number of processes have been studied for onsite landfill leachate treatment.[7-9] Sequencing batch reactors (SBRs) often are applied to treat leachate owing to their low costs and flexibility in operating sequence and cycle times. Huang *et al.*[1] found that SBRs removed 40.9% and 85.9% of COD and total nitrogen (TN) from landfill leachate, respectively. A modification of the SBR is the sequencing batch biofilm reactor (SBBR), which incorporates biofilm carrier media into the conventional SBR. Compared with SBRs, SBBRs can retain high biomass concentrations, resulting in increased system stability, resistance to shock loads, enhanced contaminant removals and shorter required hydraulic retention times (HRTs).[10-12] Goh *et al.*[11] used a

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SBBR with sponge cube media to treat synthetic wastewater with an initial TAN concentration of 48 mg L^{-1}; this configuration increased TAN removal from 86% to ~100% compared with an SBR. Bernat *et al.*[13] found that adding polyethylene ring-shaped carriers to SBRs increased denitrification effectiveness and TN removal from aerobically stabilized leachate 1.23- and 1.10-fold, respectively.

Although SBBRs have been successfully used for treatment of low-strength domestic wastewater, the high concentrations of TAN and refractory organic matter in landfill leachate present a challenge that could be addressed through hybrid adsorption and biological treatment processes.[14] Adsorptive media can be used to overcome microbial inhibition by temporarily adsorbing contaminants and allowing more time for their biodegradation. An advantage of this approach is that the adsorbent media is bioregenerated *in situ* by attached biofilms without having to add more adsorbent or generating waste brines that require further treatment.[15]

Natural zeolite minerals, such as chabazite and clinoptilolite, are porous alumino-silicate minerals that have a high ion exchange (IX) capacity and selectivity for ammonium (NH_4^+) ions. Although chabazite has a higher NH_4^+ adsorption capacity, clinoptilolite is the most commonly used zeolite for wastewater treatment owing to its low cost.[16] Zeolite minerals previously have been used to adsorb NH_4^+ from swine wastewater[16] and landfill leachate.[17] Aponte-Morales *et al.*[15] found that adding zeolite (chabazite) to batch bioreactors alleviated FA inhibition to nitrifiers, resulting in an increase in nitrification rate from 0.16 to 0.36 mg N g^{-1} VSS-h (VSS, volatile suspended solids). Importantly, the IX capacity of the bioregenerated chabazite did not decrease even after 40 cycles of operation of a Zeolite-SBR treating anaerobically digested swine waste centrate.[14] Yalcuk and Ugurlu[18] added zeolite to vertical flow constructed wetlands to treat landfill leachate, which enhanced ammonia removal from 48.9% to 62.3%.

Biochar is another adsorbent that can be added to SBBRs to promote removal of color, COD and TAN from landfill leachate. Biochar is a low-cost byproduct of pyrolysis of organic feedstocks, such as wood waste, at high temperature under oxygen (O_2)-limiting conditions.[19] Because of its large surface area, porous structure and active surface functional groups, biochar has excellent adsorbent properties.[20,21] Rozari *et al.*[22] added biochar to constructed wetlands to treat secondary clarified wastewater and found that biochar addition increased the removal efficiencies of TN (71% to 87%), NOx-N [sum of nitrite nitrogen (NO_2^--N) and nitrate nitrogen (NO_3^--N)] (81% to 93%) and TAN (65% to 79%). Compared with zeolite, the most significant advantage of biochar for landfill leachate treatment is its high adsorption capacity for organic matter and metal ions. A study by Khurshid *et al.*[23] showed biochar derived from tea leaves removed 99.5% of COD from produced water with an initial COD concentration of 2400 mg L^{-1}. Shi *et al.*[24] found that biochar addition to a SBR enhanced COD removal from synthetic wastewater with an average influent concentration of 1800 mg L^{-1} from 98% to 100%. Paranavithana *et al.*[25] found that biochar addition to landfill leachate achieved heavy metal adsorption capacities of 30 mmol g^{-1} for cadmium (Cd^{2+}) and 44.8–46.7 mmol g^{-1} for lead (Pb^{2+}). In addition, prior studies also showed that biochar can provide an attachment surface for biofilm growth in wastewater treatment systems.[26,27]

Both zeolite and biochar are promising materials for enhancing biological treatment of domestic wastewater, yet studies of the combined use of these materials for landfill leachate treatment have not been carried out previously. Hence, the overall goal of this study was to enhance N, COD and color removal from landfill leachate in SBBRs amended with zeolite and biochar. Specific objectives were to: (1) evaluate adsorption capacities of zeolite and biochar for NH_4^+ and COD from landfill leachate; (2) compare SBBR treatment performance with and without adsorbent addition; and (3) investigate the effects of HRT and operating time on system stability and contaminant removal.

MATERIALS AND METHODS

Three bench-scale recirculating SBBRs were set up in the Environmental Engineering Laboratory at the University of South Florida (Tampa, FL, USA) with varying biofilm support media: (i) lightweight expanded clay aggregate (LECA) as a control (C-SBBR); (ii) LECA + zeolite (CZ-SBBR); and (iii) LECA + zeolite + biochar (CZB-SBBR). An ideal experimental design also would have included a LECA + biochar SBBR; however, owing to resource limitations we were not able to operate four bench-scale SBBRs at once. The effect of zeolite addition was investigated by comparing C-SBBR and CZ-SBBR. The effect of biochar addition was investigated by comparing CZ-SBBR and CZB-SBBR. In addition, we carried out batch adsorption studies to verify that there were no synergistic or antagonistic effects when zeolite and biochar were combined. Experiments were carried out in different phases (Table 1) over more than a year. Detailed information on all materials and methods was provided previously.[28]

Landfill leachate and SBBR media

Landfill leachate was collected from the Southeast Hillsborough County Landfill in Lithia (FL, USA). The landfill was constructed in 1984 on portions of a phosphate mine. It currently includes a Class 1 landfill, waste tire processing facility, and composting facility for yard waste and biosolids. Leachate was collected from a storage tank in the landfill approximately every two months and was kept at 4 °C until use. Average raw leachate characteristics are shown in Table 2.

LECA was purchased from Trinity Lightweight Aggregate (Livingston, AL, USA). Zeolite (clinoptilolite) was obtained from St Cloud Mining Company's Ash Meadows Plant (Nye County, NV, USA). Biochar was obtained from Biochar Supreme Inc. (Everson, WA, USA). The bulk density and particle size ranges of the media materials used in this study are provided in Table 3. Additional information about biochar properties can be found in Rahman, *et al.*[29]

Batch adsorption studies

Two sets of batch adsorption studies were conducted to investigate the adsorption capacities of zeolite and biochar for NH_4^+ and COD in landfill leachate. The first set was used to investigate the effects of adsorbent dosage on contaminant removal. It also was performed to identify appropriate dosages of the zeolite and biochar to use for the SBBR studies. Varying dosages of zeolite (0, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 g L^{-1}) and biochar (0, 20, 40 and 60 g L^{-1}) were added to duplicate Erlenmeyer flasks filled with 100 mL raw landfill leachate. A second batch adsorption study was carried out to evaluate the potential synergistic/antagonistic effects between biochar and zeolite for contaminant removal. Zeolite (60 g L^{-1}), biochar (40 g L^{-1}) and their combination (60 g L^{-1} zeolite + 40 g L^{-1} biochar based on the CZB-SBBR media zeolite:biochar ratio) were added to 100 mL leachate.

Zeolite and biochar were washed with deionized water (DI) and dried before use. Flasks were covered with parafilm and placed on an orbital shaker at 200 rpm and room temperature (RT; 25 °C). Raw leachate and supernatant samples were collected after 24 h and filtered with 0.45-μm glass fiber filter paper. NH_4^+-N and COD concentrations were measured as described below. The

Table 1. Experimental phases for SBBR operation

Phase	Days of operation	Fill volume per cycle (mL)	Exchange volumetric Rate (%)	HRT (d)	EBCT (d)	Influent TAN (mg L^{-1})	Influent sCOD (mg L^{-1})
1	6	NA	NA	100% recirculation	NA	NA	NA
2	84	113	25	14	47	404	411
3	38	180	40	9	29	394	515
4	270	180	40	9	29	370	510

NA, not applicable.

dosage of zeolite and biochar for the CZ and CZB reactors were calculated based on the following:

$$P_{\text{adsorbent}} = \frac{D_{\text{adsorbent}} \times V_{\text{leachate}}}{\rho \times V_{\text{total}}} \times SF \quad (1)$$

where $P_{\text{adsorbent}}$ is the adsorbent (zeolite or biochar) percentage added to CZ-SBBR and CZB-SBBR (by volume, %), $D_{\text{adsorbent}}$ is the selected zeolite dosage (60 g L^{-1}) or biochar dosage (40 g L^{-1}) based on their adsorption capacity (see Batch adsorption studies section below), V_{leachate} is the pore volume (i.e. leachate volume, L), V_{total} is the total working volume (i.e. media fill volume, mL), ρ is the density of zeolite or biochar (g mL^{-1}), and SF is a safety factor (4 in this study).

SBBR design and operation

Bench-scale SBBRs (Fig. 1) were constructed from 12 cm diameter × 20 cm height acrylic tubing. The working volume for each reactor was ~1.5 L and the pore volume was 450 mL. The SBBRs were filled with the following media materials (by volume): (i) C-SBBR: 100% LECA, (ii) CZ-SBBR: 92% LECA + 8% zeolite, and (iii) CZB-SBBR: 47% LECA + 8% zeolite +45% biochar. Large particle size LECA (Table 3) was added to the top of each reactor to prevent adsorbent materials from floating. All SBBRs were placed in a fume hood at room temperature (25 °C). Leachate was recirculated in the SBBRs using Masterflex L/S 17 peristaltic pumps (Cole-Parmer Instrument Company, LLC, IL, USA). To offset water loss by evaporation, bioreactors were replenished with 50 mL deionized water (DI) every two cycles.

The SBBRs were operated in four phases (see Table 1 for detailed operating information). Phase 1 was operated as an acclimation phase. SBBRs were seeded with ≈110 mL (25%, by volume) landfill leachate mixed with 335 mL treated wastewater (75%) and 5 mL mixed liquor suspended solids (MLSS) with total suspended solids (TSS) of 10 g L^{-1} from the Valrico WWTP (Tampa, FL, USA). Slow recirculation at 60 mL min^{-1} was applied to promote mass transfer and biofilm attachment. One fourth of the pore volume was discharged on day (D)2, D4 and D6 and the reactors were replenished with same amount of raw leachate. The acclimation phase was concluded on D8.

During Phases 2, 3 and 4, SBBRs were operated on a 3.5-day cycle consisting of the following stages: (i) rapid fill; (ii) one-day anoxic react; (iii) 2.5-day aerobic react; and (iv) rapid drain. During the anoxic stage, leachate was recirculated at a flow rate of 30 mL min^{-1} from the bottom of the reactor to a diffuser below the liquid surface to reduce surface turbulence and O_2 transfer from the air. At the end of the anoxic stage, 20 mL effluent was collected for testing. During the aerobic stage, leachate was recirculated at a flow rate of 90 mL min^{-1} from the bottom of the reactor to a perforated tube above the liquid surface to provide aeration. At the end of the operating cycle, a specific amount of effluent was discharged to maintain the target HRT and fresh leachate was added to the reactors for the next cycle. HRT initially was set at 14 days and reduced to nine days on D90 by increasing the decant/filling volume (Table 1). To elucidate the fate of nitrogen species and organic matter, samples were collected for sCOD and nitrogen species analysis from CZB-SBBR every 6 h during Cycle 10 of Phase 3. During Phase 4, only the CZB-SBBR was operated to evaluate its long-term performance. Because of COVID

Table 2. Southeast Hillsborough County average raw landfill leachate characteristics

Parameter	Units	Leachate
pH	NA	7.8 ± 0.07
Electrical Conductivity	μS cm^{-1}	14,00 ± 490
Alkalinity	mg $CaCO_3$ L^{-1}	1900 ± 700
sCOD	mg L^{-1}	450 ± 54
BOD_5	mg L^{-1}	71 ± 5
TSS	mg L^{-1}	42 ± 2
VSS	mg L^{-1}	25 ± 1
TN	mg L^{-1} (as N)	570 ± 180
NH_4^+	mg L^{-1} (as N)	400 ± 7
FA	mg L^{-1} (as N)	15 ± 1
NO_2^-	mg L^{-1} (as N)	70 ± 45
NO_3^-	mg L^{-1} (as N)	BDL

Concentrations of heavy metals of concern in landfill leachate (Cr, Cu, Zn, etc.) were relatively low and therefore not monitored frequently during this study; BDL, below detection limits.

Table 3. Bulk density and particle size of LECA, clinoptilolite and biochar

Material	Bulk density (g mL^{-1})	Particle size
Large LECA	0.8	2~5 mm
Small LECA	0.8	0.6~2 mm
Zeolite (clinoptilolite)	0.9	<0.6 mm
Biochar	0.1	2~4 mm

Large LECA was added as the cover layer of SBBRs; Small LECA was the main medium in the control SBBR.

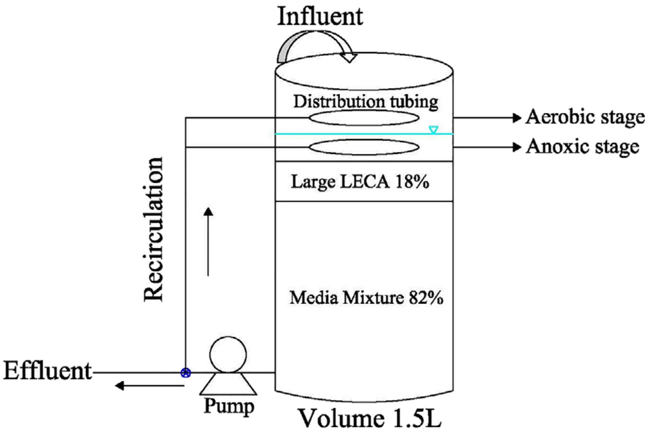

Figure 1. Laboratory-scale SBBR schematic.

limitations, sampling and analysis was carried out less frequently during this phase.

Analytical methods

Dissolved oxygen (DO) and pH were measured *in situ* using an Orion 5 Star Multifunction Meter (Thermo Scientific, Waltham, MA, USA). Raw leachate and SBBR effluent samples at the end of both anoxic and aerobic stages were collected and filtered through the 0.45-μm glass fiber filters for chemical analysis. NH_4^+-N and NOx-N concentrations were measured using a TL-2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO, USA). NO_2^--N was measured using a combination of *Standard Methods 4500*.[30] NO_3^--N was calculated by subtracting NO_2^--N concentration from NOx-N concentration. TN was measured using Hach TNTplus® 827 Total Nitrogen test kits (Hach, Loveland, CO, USA). Total organic nitrogen (TON) was calculated by subtracting the total inorganic nitrogen (TIN) from the TN concentration. sCOD was measured using Lovibond LR test kits (0–150 mg L^{-1}) (Tintometer Inc., Sarasota, FL, USA). *Standard Methods*[30] were used to measure NO_2^--N (4500), UV456 (2120C), BOD_5 (5210B) and alkalinity (2320B). Raw leachate and CZB-SBBR effluent metal concentrations were measured at the end of the study by the ICP-OES at University of South Florida Geochemistry Core Facility.

Data analysis

Statistical significance was determined by Student's *t*-tests using Excel (Microsoft, Redmond, WA, USA). Comparisons with *P*-values of <0.05 were considered as significantly different. Initial concentrations of sCOD and nitrogen species inside the SBBRs were calculated by accounting for dilution of the raw leachate with liquid retained in the SBBRs from the previous cycle:

$$C_{\text{initial}} = \frac{C_{\text{influent}} {}^{*} V_{\text{fill}} + C_{\text{cycle }(n-1)} {}^{*} (V_{\text{leachate}} - V_{\text{fill}})}{V_{\text{leachate}}} \quad (2)$$

where C_{initial} is the actual initial concentrations of sCOD or nitrogen species (mg L^{-1}), C_{influent} is sCOD or nitrogen concentrations in raw landfill leachate (mg L^{-1}), $C_{\text{cycle }(n-1)}$ is the sCOD or nitrogen concentrations in effluent from previous cycle (mg L^{-1}), V_{fill} is the fill volume (113 mL during Phase 2 and 180 mL during phases 3 and 4), and V_{leachate} is the total pore volume (450 mL).

HRT and empty bed contact time (EBCT) were calculated according to:

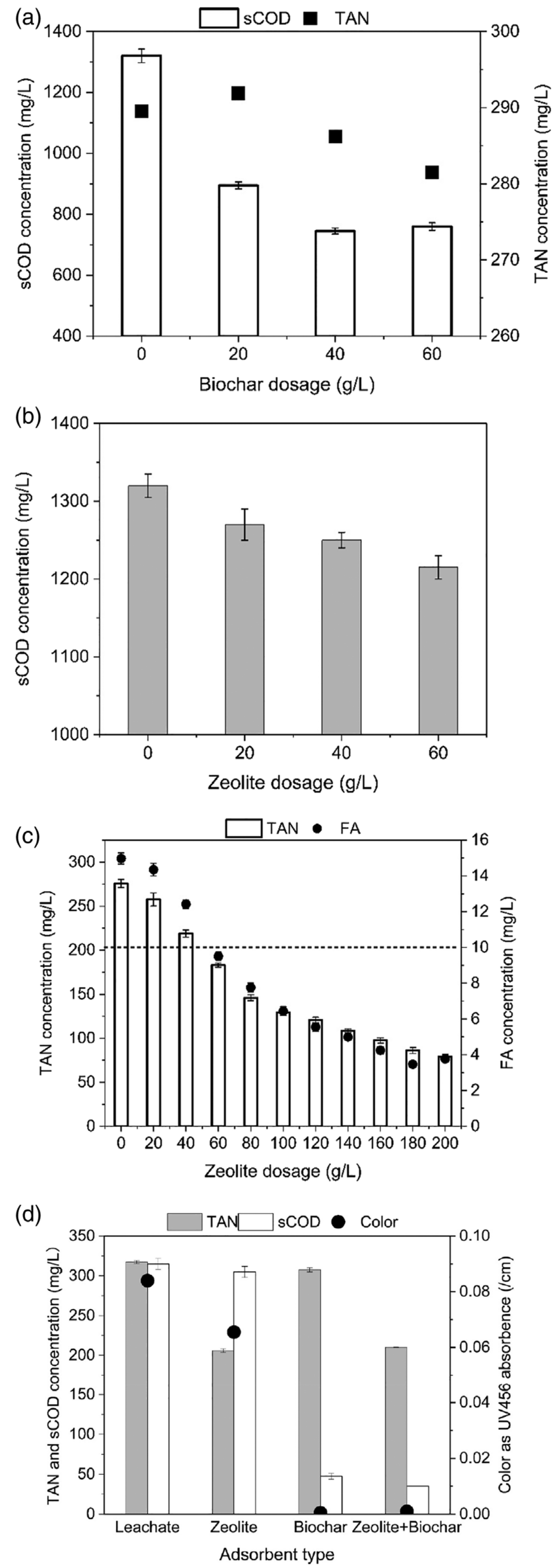

Figure 2. Results from adsorption study with biochar and zeolite: (a) sCOD and NH_4^+ adsorption by biochar; (b) sCOD adsorption by zeolite; (c) NH_4^+ and FA adsorption by zeolite; (d) NH_4^+, sCOD and color adsorption by zeolite (60 g L^{-1})/biochar (40 g L^{-1}).

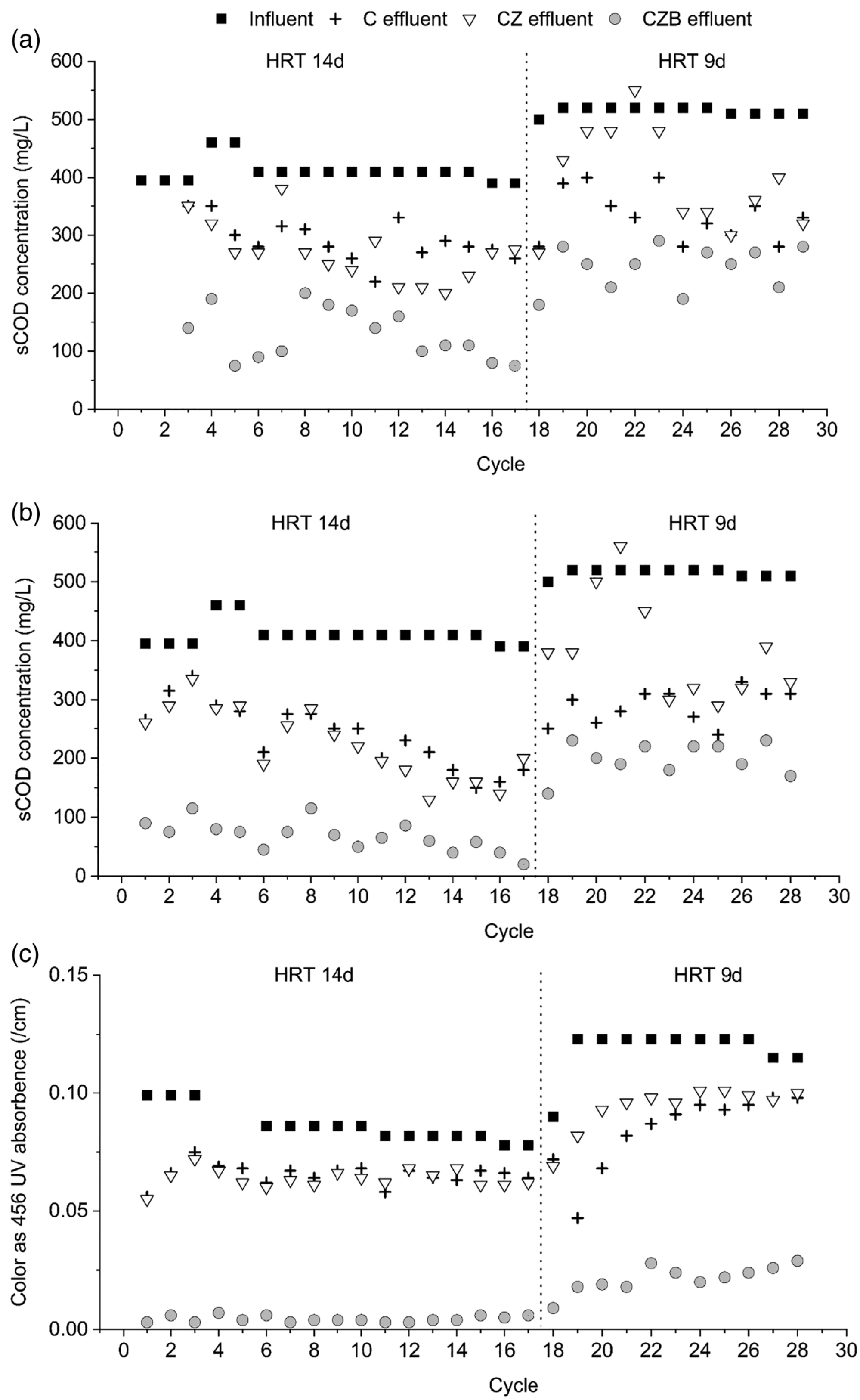

Figure 3. sCOD and color variation during phases 2 and 3: (a) sCOD after anoxic phase; (b) sCOD after aerobic phase (final effluent); (c) color (UV456 absorbance) in final effluent.

$$HRT = \frac{V_{\text{leachate}}}{V_{\text{fill}}} * T_{\text{cycle}} \quad (3)$$

$$EBCT = \frac{V_{\text{total}}}{V_{\text{fill}}} * T_{\text{cycle}} \quad (4)$$

where T_{cycle} is the cycle time (3.5 days) and V_{total} is the working volume of the empty bioreactor (1500 mL).

FA concentration was calculated as in Hansen *et al.*[31]:

$$\frac{FA}{TAN}=\left(1+\frac{10^{-pH}}{10^{-\left(\left[0.09018+\frac{2729.92}{T(k)}\right)\right)}}\right)^{-1} \quad (5)$$

RESULTS AND DISCUSSION

Batch adsorption studies

Adsorption capacities of zeolite and biochar for sCOD and NH_4^+ were evaluated though batch adsorption studies. As shown in Fig. 2(a), biochar had a high adsorption capacity for sCOD with the highest removal efficiency of 44% at dosage of 40 g L^{-1}. However, biochar had a much lower adsorption capacity for NH_4^+ (< 3%). Increasing the biochar dosage to 60 g L^{-1} did not result in additional sCOD removal, possibly due to overlapping of adsorption sites or insufficient driving force for mass transfer to the surface.[32] Shehzad *et al.*[33] showed much higher sCOD (84.94%) and TAN removals (95.77%) by biochar with average influent concentrations of 700 and 3330 mg L^{-1}, respectively, which might have been due to effective biochar activation by pre-treatment with potassium hydroxide. Rahman *et al.*[29] used the same biochar material for TAN adsorption from stormwater and achieved a higher TAN adsorption capacity (3.5 mg g^{-1}) than in this study (0.13 mg g^{-1}). This likely was caused by competition with NH_4^+ for adsorption sites on the biochar surface by cations in the landfill leachate such as K^+.

By contrast, zeolite had a much higher adsorption capacity for NH_4^+ than sCOD [Fig. 2(b) and (c)]. The highest TAN and sCOD removals were 71% and 8% at dosages of 200 g L^{-1} and 60 g L^{-1}, respectively. Aponte-Morales *et al.*[15] showed that zeolite (chabazite) removed 88% of TAN from anaerobically digested swine waste centrate with an initial TAN concentration of 806 mg L^{-1}. Aziz *et al.*[34] found that 100 g L^{-1} zeolite achieved TAN and sCOD removals of 53.1% and 22.5% from landfill leachate, respectively. As FA and NH_4^+ rapidly equilibrate in aqueous solution, adsorption of NH_4^+ by zeolite decreases FA concentrations and reduces its inhibition to nitrifiers.[15] As shown in Fig. 2(c), FA concentrations decreased with increasing zeolite dosage. At a zeolite dosage of 60 g L^{-1}, the FA concentration was <10 mg L^{-1}, which has been shown to inhibit AOB.[3]

Based on the preliminary adsorption studies, three SBBRs (C-SBBR, CZ-SBBR and CZB-SBBR) were constructed. Based on Eqn (1), 60 g L^{-1} zeolite and 40 g L^{-1} biochar were selected, corresponding to 8% (by volume) of zeolite addition in CZ-SBBR and CZB-SBBR and 45% (by volume) of biochar addition in CZB-SBBR.

The combined effects of zeolite and biochar are shown in Fig. 2 (d). The combination of zeolite and biochar removed 34% of TAN, which is similar to zeolite only (35%) ($P > 0.05$). Adding both zeolite and biochar removed 89% of sCOD, which is higher than biochar/zeolite individually, but similar to the sum of zeolite only (3%) and biochar only (85%). Greater than 99% color removal was achieved in either biochar only or combination of zeolite and biochar. These results show that there are no obvious synergistic or antagonistic effects between zeolite and biochar addition.

Effects of adsorbent addition and HRT on SBBR performance

sCOD

The landfill leachate treated in this study had a low BOD_5:COD (~ 0.16, Table 2), which hindered the biodegradation of organic matter in SBBRs. The sCOD concentrations in raw leachate, intermediate samples collected at the end of the anoxic stage and final effluent samples are shown in Fig. 3. The sCOD balance for the three reactors is shown in Fig. 4. Note that the 'initial' concentration shown in Fig. 4 takes into account dilution of leachate with treated leachate from the previous cycle and is not the raw leachate concentration. The addition of zeolite to CZ-SBBR did not improve sCOD removal compared with C-SBBR. sCOD removal efficiencies for C-SBBR and CZ-SBBR during Phase 2 were 41.9% and 45.4%, respectively. sCOD removal efficiencies for C-SBBR and CZ-SBBR during Phase 3 were 44.0% and 34.2%, respectively. sCOD removals within the C-SBBR and CZ-SBBRs were achieved primarily during the aerobic stage, especially during Phase 2 (Fig. 4). Similar results were observed in previous studies.[11,35]

Addition of biochar to CZB-SBBR resulted in greater sCOD removal than in C-SBBR and SZ-SBBR. sCOD removal efficiencies for CZB-SBBR were 83.4% during Phase 2 and 61.3% during Phase 3 [Fig. 3(a) and (b)]. The enhanced performance most likely was a result of the combined effects of adsorption and biodegradation. Biochar both adsorbs recalcitrant organic matter and provides an attachment surface for microbial biofilms.[26,33] The adsorbed recalcitrant organic matter may be slowly degraded to simple organic molecules by hydrolytic bacteria and then consumed by either denitrifiers in the anoxic stage or aerobic heterotrophs in aerobic stage, thus regenerating the active adsorption sites on the biochar surface. Prior studies showed that activated carbon can be bioregenerated *in situ* by organic matter degradation and desorption.[36] In addition, biochar has been shown to oxidize or reduce organic compounds, either directly through redox-active functional groups[37] or indirectly through persistent free radicals generated from O_2, such as hydroxyls.[38-40]

Fresh leachate was obtained from the landfill at the beginning of Phase 3, which had a higher sCOD concentration [Fig. 3(a)

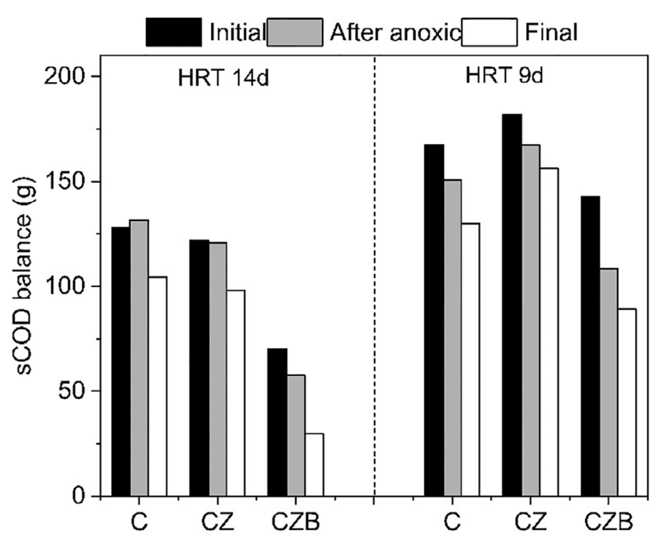

Figure 4. sCOD balance within three SBBRs during Phase 2 and 3.

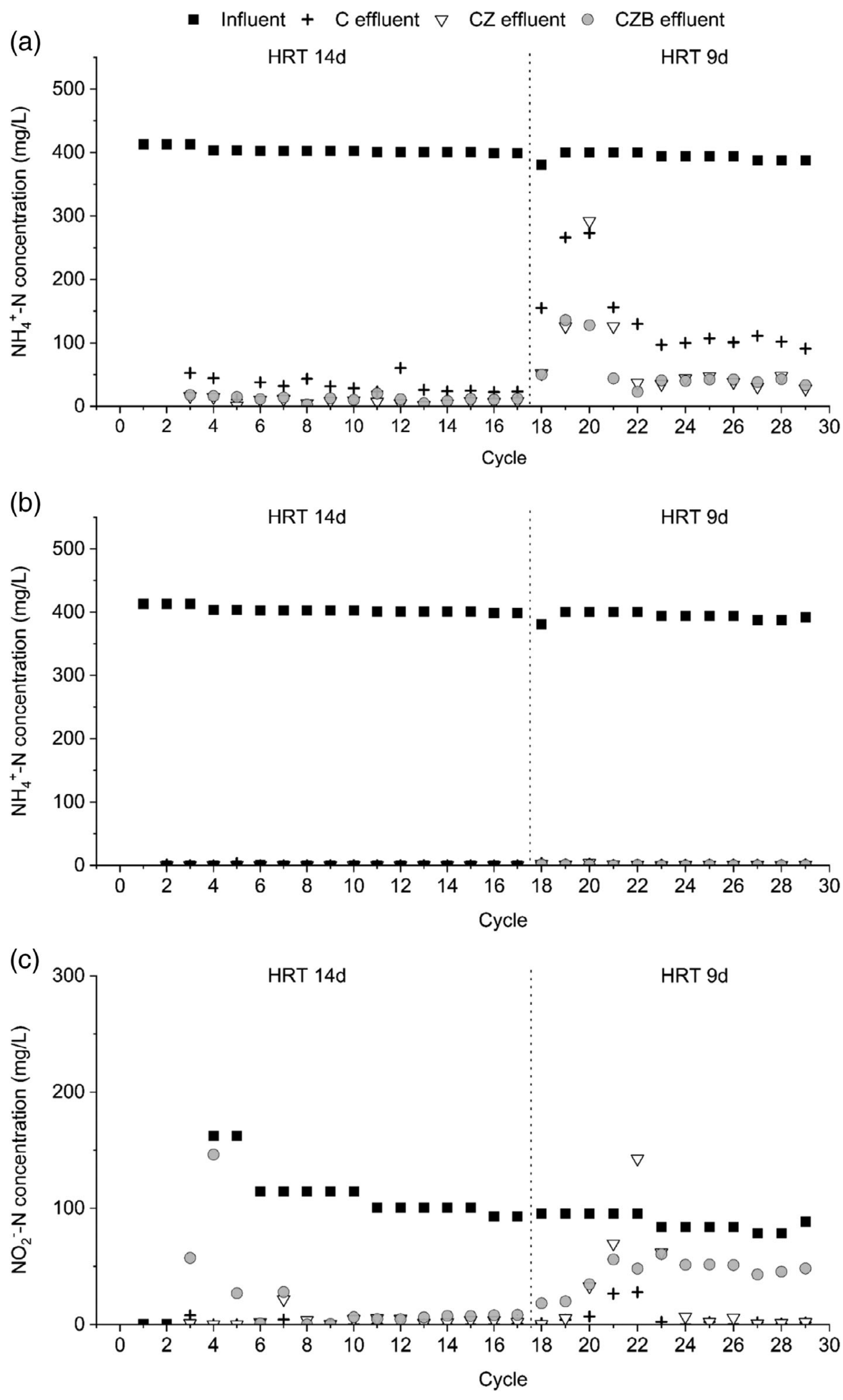

Figure 5. Nitrogen species variation during phases 2 and 3: (a) NH_4^+-N after anoxic phase; (b) NH_4^+-N in final effluent; (c) NO_2^--N after anoxic phase; (d) NO_2^--N in final effluent; (e) NO_3^--N after anoxic phase; (f) NO_3^--N in final effluent.

and (b)]. Decreased HRT and increased influent COD concentration resulted in a decrease in sCOD removals for all SBBRs compared with Phase 2. Wang *et al.*[41] also reported that the COD removal from landfill leachate within SBBRs decreased from 67.7% to 46.2% when the HRT was decreased from ten to five days. However, the percentage of sCOD removed during the anoxic stage increased for all three reactors (Fig. 4). This may have been a consequence of the greater biodegradability of the sCOD; however, BOD_5 was not measured during this period.

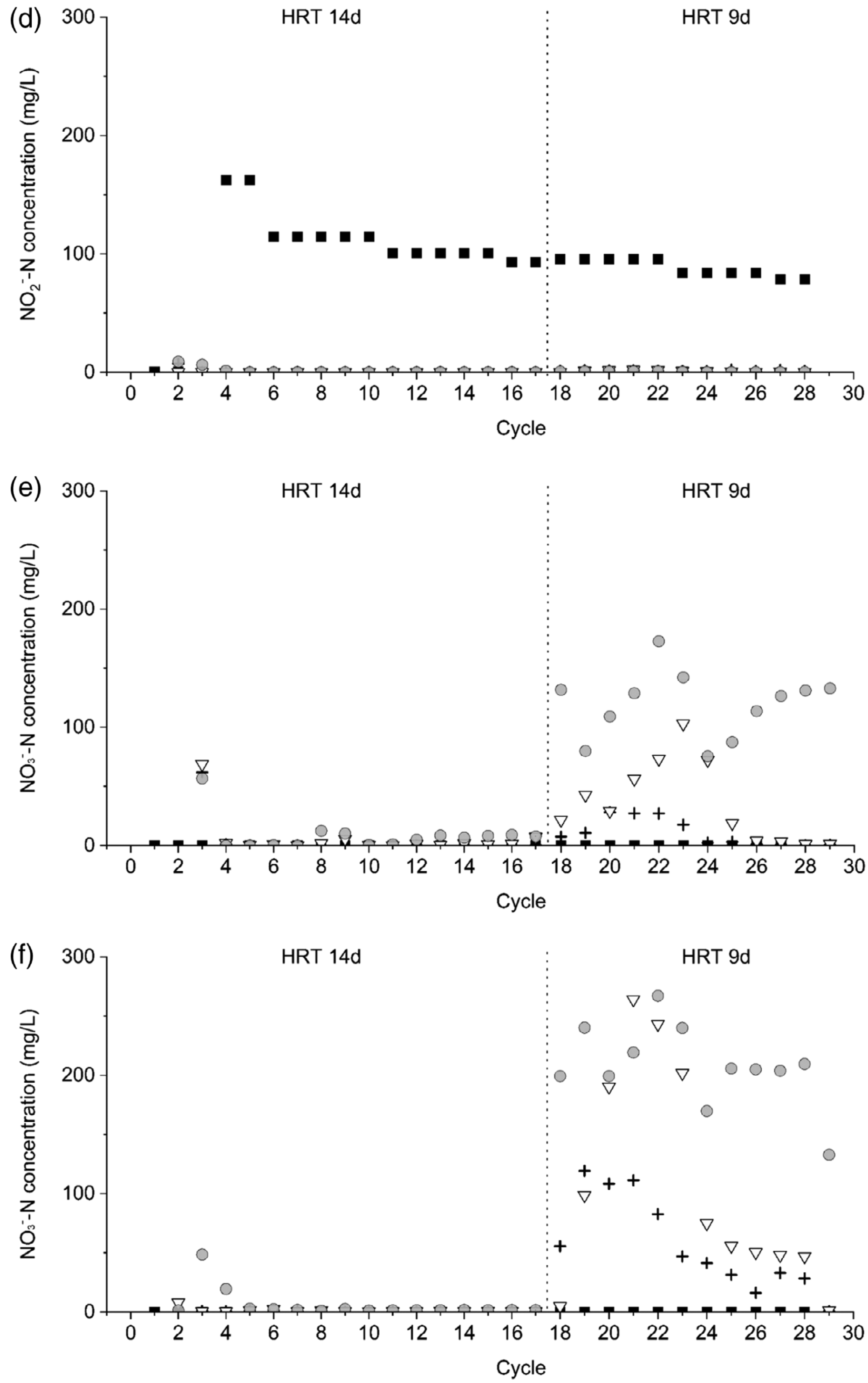

Figure 5 (Continued)

Color removal

The overall color removal performance (as UV456 absorbance) for the three reactors is shown in Fig. 3(c). Zeolite addition did not contribute to color removal for CZ-SBBR (35% during Phase 2 and 20% during Phase 3) compared with C-SBBR (33% during Phase 2 and 28% during Phase 3). CZB-SBBR achieved the best color removals of 95% during Phase 2 and 82% during Phase 3. Decreasing the HRT resulted in decreased color removals in all three SBBRs. The overall pattern of color removal performance was similar to sCOD removals, indicating that the deep color of the landfill leachate was caused mainly by organic compounds, which is consistent with prior studies.[42]

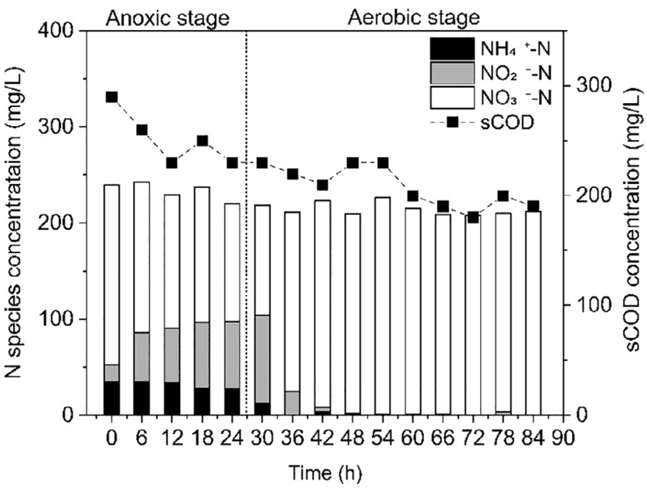

Figure 6. Variations of nitrogen species and sCOD at Cycle 10 during Phase 3.

Nitrogen removal

Nitrogen species removal performances at the end of the anoxic and aerobic stages of the SBBR cycles for Phases 2 and 3 are shown in Fig. 5. Greater than 99% TAN removals were observed for all three SBBRs throughout the study (Fig. 5(a) and (b)). Ammonia oxidation was observed during both anoxic and aerobic stages. Although recirculation was done slowly and below the liquid level during the anoxic stage, the reactors were not sealed and some O transfer occurred from the atmosphere (Fig. 1). It is likely that this aeration strategy resulted in the formation of aerobic zones at the top of the reactor and anaerobic zones at the bottom. TIN removals >99% were observed for all three SBBRs during Phase 2 but decreased to 90% for C-SBBR, 85% for CZ-SBBR and 58% for CZB-SBBR at shorter HRT during Phase 3. Decreasing HRT resulted in high NO_3^--N accumulation in CZB-SBBR.

Patterns of NH_4^+, NO_2^- and NO_3^- elucidate the effects of zeolite and biochar on nitrogen cycling pathways in the SBBRs. For C-SBBR and CZ-SBBR, high FA concentrations in the landfill leachate [≈39 mg L^{-1} in Phase 2; ≈67 mg L^{-1} in Phase 3 based on Eqn (5)] favored AOB growth and NOB suppression (Anthonisen *et al.*, 1976). Thus, partial nitritation/anammox might have contributed to high TIN removal within C-SBBR and CZ-SBBR, even without NO_2^--N/NO_3^--N accumulation [Fig. 6(c)–(f)] or sCOD consumption (Fig. 4). During Phase 3, zeolite addition reduced FA stress for nitritation during the anoxic stage through adsorption compared with C-SBBR [Fig. 5(a)]. Prior studies also showed that zeolite addition to SBBRs can prompt nitritation-anammox by maintaining an appropriate FA concentration.[43,44]

For CZB-SBBR; however, the adsorption study showed that the combination of 8% zeolite and 45% biochar addition theoretically can contribute to ≈24 mg L^{-1} and ≈1 mg L^{-1} FA removal, respectively, which may reduce NOB suppression, resulting in complete nitrification. In addition, previous studies showed that biochar can enhance nitrification performance.[45,46] Biochar also can accelerate denitrification during anoxic conditions due to its abundant redox-active functional components on biochar surface, such as phenolic moieties.[43,47,48] Thus, addition of both zeolite and biochar likely prompted simultaneous nitrification denitrification (SND) for nitrogen removal. However, as landfill leachate has a low BOD_5/COD (≈0.16) and low COD/TN (<1), serious NOx (NO_2^--N and NO_3^--N) accumulation was observed during the anoxic stage [Fig. 5(c) and (e)] and NO_3^--N accumulation during the aerobic stage [Fig. 5(f)]. This most likely was due to limited readily biodegradable organic C availability for denitrification during the anoxic stage and good nitrification performance during the aerobic stage. Similar results also were reported in previous studies.[49,50] To further remove NO_2^-/NO_3^-, a low-cost solid C source, such as wood chips, might be used to enhance denitrification. Additional discussion of NOx accumulation is provided in the next section, which discusses dynamic performance of CZB-SBBR.

Dynamic changes in sCOD and N-species for CZB-SBBR

During Cycle 10 of Phase 3, liquid samples were collected every 6 h from CZB-SBBR and the fate of sCOD and N-species were investigated over an operating cycle (Fig. 6). The high initial NO_3^- concentration present in the reactor at the beginning of the anoxic stage was due to carry-over of NO_3^- from the previous cycle. During the anoxic stage, net TAN removal of 23% was observed within 24 h, most likely due to nitrification in aerobic zones at the top of the reactor. NO_3^--N concentrations decreased from 187 to 122 mg L^{-1} and sCOD concentrations decreased from 290 to 230 mg L^{-1}. However, owing to limited biodegradable organic C availability, 65% of NO_3^- remained in the reactor and NO_2^- concentrations also slightly accumulated over time. During the aerobic stage, all of the remaining NH_4^+ and NO_2^- were converted to NO_3^- within 24 h. This efficient conversion agrees with Kim *et al.*,[51] who found that 20 mg L^{-1} TAN was

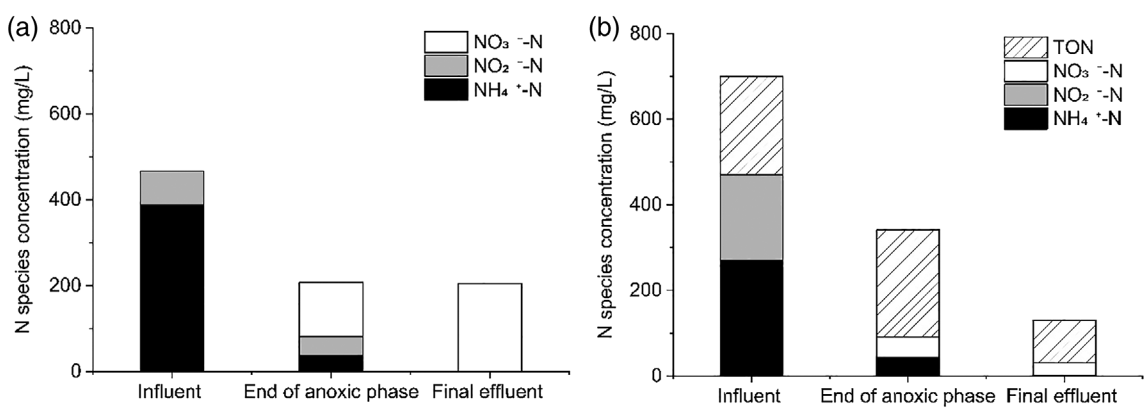

Figure 7. Nitrogen species within CZB: (a) during Phase 3 with short-term operation; (b) during Phase 4 with long-term operation.

Table 4. Raw leachate and CZB-SBBR effluent during Phase 4

Parameter	Raw leachate	End of anoxic stage	Final effluent	Overall removal (%)
sCOD (mg L^{-1})	510 ± 22	290 ± 14	250 ± 10	51
Color as UV456 absorbance (A)	0.174 ± 0.02	–	0.05 ± 0.01	71
NH_4^+ (mg L^{-1} as N)	370 ± 63	25 ± 15	1.0 ± 0.9	99.7
NO_2^- (mg L^{-1} as N)	100 ± 140	0.2 ± 0.16	0.02 ± 0.01	100
NO_3^- (mg L^{-1} as N)	0.4 ± 0.5	24 ± 34	12 ± 15	−2900

–, not measured.

removed in the aerobic stage of SBBRs within 3.5 h. Regarding sCOD, 7% of sCOD was removed within 18 h and then sCOD concentrations gradually decreased during the remaining time, reaching a maximum removal efficiency of 34%. Previous studies showed that sCOD removal from domestic wastewater was mainly completed within 0.5–3 h.[51-53] The low biodegradability of sCOD in landfill leachate in this study extended the degradation time for removal. The results of the dynamic study indicate that CZB-SBBR could be operated at a shorter HRT (e.g. five days) and achieve similar TIN and sCOD removal performance.

Long term CZB-SBBR performance

In order to investigate the long-term performance of CZB-SBBR, the reactor was maintained for an additional 9 months with feeding two times per week to maintain an HRT of nine days (Phase 4). Water quality data collection was less frequent during this period; however, additional measurements of dissolved organic nitrogen (DON) were made. A comparison of nitrogen removals at the end of phases 3 and 4 is shown in Fig. 7. Greater than 99% NH_4^+ removal was observed in both phases. However, compared with Phase 3, Phase 4 exhibited greater overall TIN removal efficiency (93% *versus* 57%) due to lower NO_3^--N accumulation (29 *versus* 204 mg L^{-1}). The enhanced performance likely was a result of the growth and enrichment of anammox bacteria, such as *Brocadia anammoxidan*, which might be induced by the serious NO_2^- accumulation in CZB-SBBR during the anoxic stage [Fig. 5(c)]. Anammox activity tests confirmed the presence of anammox (data not shown). DON removal was negligible during the anoxic stage but reached 60% during the aerobic stage. Prior studies have shown that DON in landfill leachate is poorly biodegradable.[6,54]

Effluent sCOD concentration (≈250 mg L^{-1}) and color (≈0.05 cm^{-1}) (Table 4) were higher at the end of Phase 4 than Phase 3 (≈200 mg L^{-1} for sCOD and ≈0.02 cm^{-1} for color). This may indicate that biochar slowly loses its adsorptive capacity for recalcitrant organic matter over time, as the trend of decreased color removal also was observed at the end of Phase 3 [Fig. 3(c)]. Hence, supplementing SBBRs with fresh biochar is recommended for sustained organic matter/color removal.

Trace concentrations of heavy metals can promote microbial growth but cause inhibition or death at high concentrations.[55] Although metals data collection was limited in this study, the main metal species measured in raw landfill leachate were barium (Ba), copper (Cu) and zinc (Zn), at concentrations of 250, 95 and 32 μg L^{-1}, respectively. Effluent Ba, Cu and Zn concentrations for CZB-SBBR were 238, 305 and 53 μg L^{-1}, respectively. Similar Ba concentrations were reported in previous studies of landfill leachate.[56,57] Cu concentrations in CZB-SBBR were above the values that have been shown to be toxic to microorganisms in prior studies (50–560 μg L^{-1} for nitrifiers; 10–4000 μg L^{-1} for denitrifiers).[58-60] A Zn concentration of 80–500 μg L^{-1} also can inhibit the growth and activity of nitrifiers.[55,61] Previous studies showed that biochar addition can lower the metal solubility by increasing system pH and adsorb metal ions by its surface functional groups (i.e. hydroxyl), which alleviates metal toxicity to microbes.[62,63] No significant metal removal was achieved in this study, likely due to the occupation of the adsorption sites on biochar by organic compounds.

CONCLUSIONS

Three laboratory-scale SBBRs, with and without adsorbent addition, were set up to investigate the effects of biochar, zeolite, HRT and operating time on removal of nitrogen species, organic matter and color from landfill leachate. All three SBBRs achieved excellent TAN removals (>99%) throughout the study, most likely as a result of the long HRT and favorable conditions for TAN oxidation. Although batch studies showed that clinoptilolite had a high IX capacity for NH_4^+ in landfill leachate, its addition to the SBBRs reduced TIN removal via the partial nitritation/anammox pathway in short-term studies. Biochar addition enhanced sCOD and color removal but decreased the availability of bioavailable organic C needed to drive denitrification in the biochar amended SBBR. After a long period of operation (over one year) high TN removals were observed, most likely due to enhanced anammox activity. Results from this study were used to design adsorbent amended hybrid subsurface flow constructed wetlands, which are currently being operated at pilot-scale at a landfill site.[64]

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