NITROGEN REMOVAL VIA NITRITE FROM REJECT WATER PRODUCED AFTER DEWATERING OF THERMALLY HYDROLYSED AND DIGESTED SLUDGE

E. Statiris[1], C. Noutsopoulos[1], D. Mamais[1], A. Andreadakis[1], S. Malamis[1*]

[1]National Technical University of Athens, 5 IroonPolytechniou St., Zographou Campus, 15780-GR, Athens. Greece

*SimosMalamis: Malamis.simos@gmail.com

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ABSTRACT

A pilot-scale sequencing batch reactor (SBR) having a working volume 5.8 m^3 was developed and applied to remove ammonium nitrogen from sludge reject water via the nitritation/denitritation process. The reject water originating from the dewatering unit of Psyttalia WWTP was characterized by high concentrations of TKN and NH_4-N (>1.5 gN/L and >1 gN/L respectively). The nitritation/denitritation process was achieved as the NOB were gradually inhibited. The SBR operated under 2 different periods reaching a NLR of 0.24±0.08 kg N m^{-3} d^{-1} and achieving 95.3±5.7% NH_4-N and 91.6±7.2% TN removal respectively during the 1st period. The nitrogen uptake rates (AUR) were gradually increased from 2.9±0.5 to 4.2±0.6 mgNO_2-N$gVSS^{-1}h^{-1}$.

INTRODUCTION

Anaerobic digestion sludge liquors are characterized by high ammonium and phosphate content and significant organic carbon concentration with low biodegradability (Gustavsson, 2010; Ge et al., 2015). The treatment of high ammonia effluents with conventional nitrification/denitrification increases the operational costs, while it is difficult to meet the demands in nutrient discharge limits (Rodriguez-Caballero et al., 2013). Reject water could increase up to 30% the nitrogen load at the inlet of the wastewater treatment plant (WWTP); as result the implementation of a side stream treatment to remove nitrogen is beneficial (Aslan et al., 2009; Gustavsson, 2010).

Short–cut nitrification/denitrification (SCND) offers 25% reduction in oxygen demand and 40% reduction in external carbon source required for denitrification compared to the conventional nitrification/denitrification process (Ge et al., 2015).

The most critical parameter in order to inhibit nitrite oxidizing bacteria (NOB) and achieve the nitritation/denitritation process during the treatment of high-strength wastewater is the free ammonia (FA) concentration in the mixed liquor (Wei et al., 2014). According to Anthonisen et al. (1976), FA concentrations of 0.1 to 1.0 mg L^{-1} could inhibit NOB, while at concentrations between 10-150 mg L^{-1} the growth of AOB could also be inhibited. The sequential batch reactors (SBR) seem the most appropriate technology for the application of nitritation/denitritation for sludge reject water treatment (Gustavsson, 2010; Ge et al., 2015). Frison et al. (2013) used an SBR to treat reject water from the anaerobic co-digestion of sewage sludge and the organic fraction of municipal solid waste via the nitrite pathway and reported 90% NH_4-N removal for vNLR of 0.8 kg N m^{-3} d^{-1}.

This work aims to investigate the real potential of the SCND process to remove nitrogen from the reject water produced following the dewatering of thermal hydrolyzed anaerobically digested sludge of Psyttalia WWTP and reports the start-up strategy and first periods of steady state operation.

MATERIALS AND METHODS

A pilot-scale SBR was operated for the treatment of dewatered sludge reject water using the SCND process. During the first weeks of the start-up period, the SBR worked under consecutive aeration phases in order to achieve nitritation, washing out the NOB. The SBR was operated for a total period of 260 d, which can be divided into three periods. The reaction volume of the SBR was 5.8 m^3. The pilot plant was designed in order to take advantage of the readily biodegradable COD contained in the supernatant of the thickened primary sludge. After the start-up, the SBR operated under 5 cycles per day with alterations of aerobic and anoxic phases. During the anoxic phase, primary thickening sludge liquor and acetic acid were added as external carbon source.

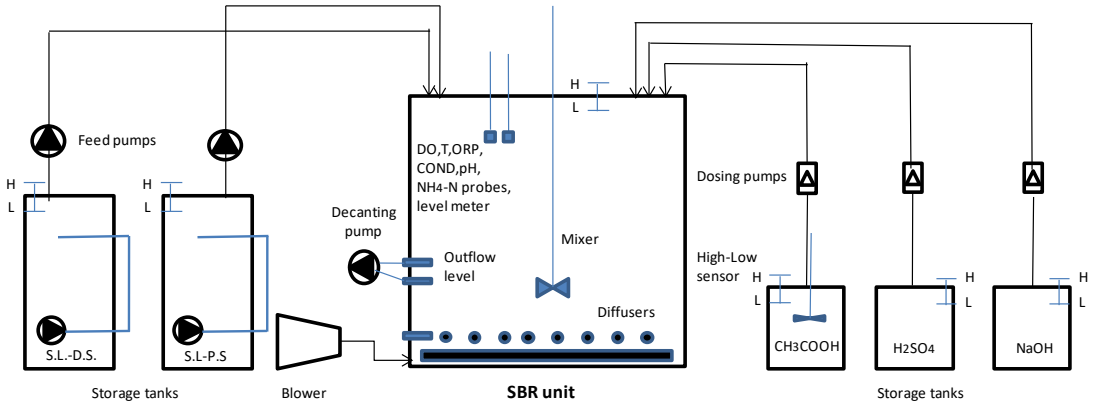

Figure 1: Major units of the pilot-scale SBR treating reject water

SBR operation

Figure 1 illustrates the major units of the pilot system along with their interconnections. The SBR was made of a rectangular stainless steel, with 9m^3 maximum volume. An aeration system with diffusers has been installed in order to meet the oxygen requirements of the system, while the SBR was also equipped with a mixing apparatus. Two 8 m^3 volume storage tanks were used to store the sludge liquors from the dewatering unit and from the primary sludge thickening unit. A number of parameters were measured online in the SBR tank which included pH, ORP, conductivity, DO and ammonia using WTW probes. The pilot plant also included a pH control system and a storage tank for the acetic acid solution (in the form of sodium acetate) which was added as external carbon source.

5.5 m^3 of mixed liquor from the bioreactors of Psyttalia WWTP was used as inoculum. During the first 2 weeks of the start-up period, the SBR worked only under consecutive aeration phases to achieve the short-cut nitrification. The automation system was set to apply 3 cycles per day with a duration of 8h each, that started with feeding, followed by aerobic phase (7h), settling (1h) and decanting.

After the first two weeks of start-up, the SBR operated with 5 cycles per day having the following sequence of phases: feeding, 165 min aerobic, 60 min anoxic, 60 min settling and decanting. During the anoxic phase, primary sludge liquor and acetic acid were added as external carbon source. In period 1 primary sludge liquor was fed to the reactor along with the acetic acid solution, in order to provide for an additional carbon source. However, during the 2nd period, external substrate was provided exclusively in the form of acetic acid as there was no availability of primary sludge reject water.

Biomass ex-situ tests

A significant number of ex-situ batch experiments were conducted and the ammonium oxidation rates via nitrite (AUR) and the denitritation rates (NUR) were determined. During the AUR tests, 700 ml of mixed liquor from the SBR unit was transferred to a stirred glass vessel where solution of NH_4-N was added at similar concentrations to the operational conditions of the SBR unit. A blower was used to provide adequate DO throughout the experiment while the pH was maintained at 7.5±0.5. Mixed liquor samples were collected every one hour, centrifuged, filtered and were characterized for ammonium and nitrite concentrations, while the oxidation rates were calculated at 20 ^{0}C.

During the NUR tests, a similar volume of mixed liquor was transferred to a stirred glass vessel which was covered in order to avoid oxygen ingress. Adequate carbon source in the form of acetic acid was added and the samples were characterized for nitrite and COD concentrations. During the batch test the pH was maintained at 7.5±0.5. Mixed liquor samples were collected every one hour, centrifuged, filtered and were characterized for nitrite, nitrate and COD concentrations while the NUR was calculated at 20 ^{0}C.

During the AUR and NUR tests and according to the sampling schedule, the pH and temperature of the mixed liquor was also recorded along with MLSS and MLVSS.

FA calculation

The FA concentrations in the mixed liquor of SBR were calculated as a single value at the beginning of each SBR cycle according to Aslan et al. (2009). The pH and temperature were provided by the online probes installed into the SBR while the NH_4-N concentration was measured.

Analytical methods

The SBR performance was evaluated by routine measurements of TKN, NH_4-N, NO_3-N, NO_2-N, TSS, VSS, MLSS, MLVSS, tCOD and sCOD. All analyses were performed according to the Standard Methods (APHA, 2012). DO, temperature, pH and ORP were measured using portable equipment (HACH, HQ40d).

Fluorescence in situ hybridization (FISH)

FISH analysis (Amann et al., 1995) was used to evaluate and calculate the population dynamics of the SBR biomass during different operational periods. Cy3 labeled NIT3oligonucleotide probe was used in order to evaluate the population of NOB while Cy3 labeled Nso1225 oligonucleotide probe was used in order to calculate the population of AOB in the SBR biomass. The same probes were also used by Wei et al. (2014). The population dynamics of AON and NOB were calculated in triplicate as percentage of the total biomass using the Image-pro software.

RESULTS AND DISCUSSION

The produced sludge of the Psyttalia WWTP undergoes thermal hydrolysis prior to the anaerobic digestion process. As a result, the reject water from the dewatering process is characterized by very high TKN and ammonium nitrogen concentrations. The influent TKN concentration ranged on average between 1500 to 2000 mg L^{-1}, while the ammonium nitrogen was on average equal to 1100-1640 mg L^{-1}. The measured TKN and NH_4-N average values of influent reject water during the periods of operation were much higher than these reported in other works (Frison et al., 2013, 2015). The influent characteristics of the pilot-scale SBR with regard to TKN, ammonium nitrogen, soluble COD and phosphorus are summarized in Figure 2.

Table 1: Influent characteristics of reject water produced after thermal hydrolysis and anaerobic digestion (average values ±standard deviation)

Parameter	**Start-up (Days 1-85)**	**1st period (Days 85-185)**	**2nd period (Days 185-258)**
TKN (mgN L^{-1})	1507±408	2008±312	1790±422
NH_4-N (mgN L^{-1})	1093±346	1640±378	1098±272
TP (mgP L^{-1})	131±55	144±56	258±99
PO_4-P (mgP L^{-1})	21±7	50±23	129±56
sCOD (mgO_2 L^{-1})	1855±464	2168±440	2742±560

The reject water produced after the thermal hydrolysis and anaerobic digestion processes is also characterized by high concentrations of total and soluble COD with the first depending on the TSS concentration of the supernatant stream. After thermal

hydrolysis and anaerobic digestion, only a small part of approximately 5-8% of the fraction of soluble COD is biodegradable. Even though, the soluble COD concentration was always above 1800 mg L^{-1}.

A conservative approach was selected during the start-up, and the nitrogen loading rate (NLR) was set at 0.07±0.05kg N m^{-3} d^{-1} with the addition of a specific volume of reject water per cycle. The pH was adjusted at 7.4±0.4.

With an NLR of about 0.04 kg N m^{-3} d^{-1}, conventional nitrification was responsible for the ammonium nitrogen oxidation during the first days of operation. During the next weeks, the increase of NLR above 0.10 kg N m^{-3} d^{-1} led to nitrite accumulation in the mixed liquor and inhibition of NOB as recorded by the minimal concentrations of nitrates in the effluent stream. The FA concentration during the start-up was always above 2 mgN L^{-1}. On the contrary, the FNA concentration was always below 0.01 mgN L^{-1} during the start-up period; therefore FNA concentration in the mixed liquor did not inhibit the NOB activity.

The results of the operation of the reactor for the three experimental periods are summarized in Table 1.

Table 2: SBR operating conditions and effluent values (average values ±standard deviation)

Parameter	**Start-up (Days 1-85)**	**1st period (Days 85-185)**	**2nd period (Days 185-258)**
pH	8.4±0.15	8.3±0.3	8.3±0.2
MLSS (mg L^{-1})	2205±1097	6440±1296	7333±1570
MLVSS (mg L^{-1})	1635±866	4807±944	5287±1038
NLR (kg N m^{-3} d^{-1})	0.07±0.05	0.24±0.08	0.23±0.04
NH_4-$N_{effluent}$ (mg L^{-1})	210±311	70.7±90	97.5±43.3
NO_2-$N_{effluent}$ (mg L^{-1})	9.2±11.6	34±46	211±201
$sCOD_{effluent}$ (mg L^{-1})	723±443	861±205	2034±1230
AUR (mgNO_2-Ng VSS^{-1} h^{-1})	2.5±1	2.9±0.5	4.2±0.6
NUR (mgNO_2-N g VSS^{-1} h^{-1})	3±0.7	3.9±0.8	9.4±5.5
$TN_{removal}$ (%)	82.2±25.9	91.6±7.2	73.4±11.2
NH_4-$N_{removal}$ (%)	83.3±25.6	95.3±5.7	91.3±4.3
Carbon source	-	Sodium acetate Primary reject water	Sodium acetate

During the 1st period under stable operation, the average NLR was 0.24±0.08 kg N $m^{-3}d^{-1}$ and the SBR achieved 95.3±5.7% NH_4-N and 91.6±7.2% TN removal respectively. The denitritation process was implemented by using adequate external carbon source in the form of acetic acid and reject water from the primary sludge thickening unit of Psyttalia WWTP.

The 2nd period lasted from days 185 to 258 and an NLR of 0.23±0.04 kg N m^{-3} $d^{-1}$was established. The main difference compared to the1st period was that only sodium acetate was added as carbon source during the denitritation phase. The pilot plant achieved 91.3±4.3% and 73.2±11.2% removal of NH_4-N and TN respectively. In some cases the SBR effluent contained high concentrations of nitrite resulting in lower TN removal. The latter was due to some problems with the feeding pump of acetic acid for a part of this period resulting in higher concentration of nitrite in the treated effluent.

Similar results reported by Frison et al. (2015) who treated reject water using a lab-scale SBR and achieved TN removal between 72-96% by applying NLR of 0.45-0.53 kg N $m^{-3}d^{-1}$. At the same period the stabilization of the pilot plant led to the increase of AUR to 4.2±0.6 kg N m^{-3} d^{-1}. The denitritation rates during the 2nd period of operation with acetic acid as substrate for denitritation were on average equal to 9.4±5.5 mgNO_2-Ng $VSS^{-1}h^{-1}$. Similar denitritation rates with the use of acetic acid as substrate, has been also reported by Kulikowska (2012) who reached NUR of 9.12 mgNO_2-Ng $VSS^{-1}h^{-1}$ using a two stage SBR system treating landfill leachate via nitrite.

AOB and NOB population dynamics were investigated by Fluorescence in situ hybridization (FISH) technique, which showed that during the 1st period the 36.9% of the bacterial population was NOB and the 23.4% AOB. During the 2nd period the biomass composition changed as the NOB population decreased to 22.1%, while AOB population increased to 27.3%. Despite the fact that NOB populations were detectable during these periods, the oxidation of nitrite to nitrate was limited probably due to the inhibition of the NOB metabolism.

CONCLUSİONS

The pilot-scale SBR treated reject water produced after the thermal hydrolysis and anaerobic digestion that contained high amounts of TKN and ammonium nitrogen

(1500-2000 and 1100-1640 mg L^{-1} respectively) and achieved satisfactory NH_4-N (95.3±5.7% & 91.3±4.3%) and TN (91.6±7.2% &73.4±11.2) removals during 1st and 2nd period. The NLR was almost the same during 1st and 2nd period (0.24±0.08 and0.23±0.04 Kg N m^{-3} d^{-1} respectively) and was accompanied by a significant increase of nitrogen uptake rates (AUR) from 2.9±0.5 to 4.2±0.6 mgNO_2-N$gVSS^{-1}$ h^{-1} resulting in the maintenance of satisfactory NH_4-N removal (>91%).

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