

Optimization of the aerobic biological treatment of thermophilically treated refractory wastewater

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Abstract

A pilot scale conventional activated sludge was operated for over 600 days to study its effectiveness at further remediating the effluent of an existing industrial site's thermophilic biological treatment stage. During the course of the study, the activated sludge was able to further biodegrade the contaminants in the incoming industrial wastewater in terms of both BOD and nitrogen reductions at varying hydraulic and solids retention times, despite elevated concentrations of soluble copper being present. A limiting hydraulic retention time (HRT) for BOD removal of 1.5 days was observed as well as the loss of nitrification occurred at a solids retention time (SRT) of approximately 6 days. Biokinetic coefficients were determined with the maximum rate of substrate utilization per unit mass of microorganisms, k , of 0.14 mg VSS/(mg sBOD-d) and the Monod half velocity constant, K_s , of 9.4 mg sBOD/L. Simultaneous nitrification and denitrification (SND) of the nitrogenous compounds found in this wastewater was observed throughout the majority of the experimentation while the bulk DO in the system was greater than 1 mg/L. The activated sludge was estimated to contain soluble copper on the order of 1 mg/L throughout the course of operation with no apparent detriment to nitrification. Additionally, the activated sludge was able to biologically remove the main solvents found in the influent wastewater. The removals of trace levels of *N*-nitrosodimethylamine (NDMA) were also observed.

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1. Introduction

The remediation of industrial wastewaters requires more robust treatment schemes than typical municipal wastewater treatment systems. Firstly, industrial wastewater systems have significant flow variability, as attributed to the production schedule of the site. Secondly, the extremely high concentration of the contamination in the industrial effluents can be so great that it would require rather unique treatment processes. This also does not preclude the treatment of solvents and heavy metals that may be present and further complicate the use of biological systems commonly used for wastewater remediation. These issues have led to the use of more unique treatment steps, such as the use of aerobic thermophilic systems. Although the use of thermophilic biological processes

is not new, they are still relatively rare. They have been proven to be able to remediate industrial effluents from the cosmetics industry [1], fermentation industry [2] and the organic chemical industry [3]. Unfortunately, the use of these high temperature biological systems is hindered by the poor settling characteristics, which are commonly observed due to the dispersed growing microorganisms [2,4–9]. To overcome the settling challenges, the use of membranes or significant settled sludge return have been explored. Despite these systems, there was always some remaining carbonaceous and nitrogenous contamination in the final effluent, which then must be discharged to a municipal treatment works for further processing.

Several authors have documented the use of two stage biological treatment systems consisting of both thermophilic and mesophilic (i.e. 30 °C) stages for the treatment of pharmaceutical plants [10], as well as synthetic wastewaters [11,12]. The purpose of this study was to investigate the benefits

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Nomenclature

k	maximum biomass-specific substrate biodegradation rate ($M_s M_x^{-1} t^{-1}$)
K_s	Monod half-velocity substrate concentration ($M_s L^{-3}$)
S	substrate concentration ($M_s L^{-3}$)
U	specific substrate biodegradation rate ($M_s M_x^{-1} t^{-1}$)
X	biomass concentration ($M_x L^{-3}$)
Y	biomass yield ($M_x M_s^{-1}$)
Θ	hydraulic retention time (t)

of utilizing a conventional activated sludge as an additional biological treatment step to further remove the both the soluble and particulate residual biodegradable organic matter, including VOCs, following thermophilic aerobic treatment for an existing organic chemical industrial site. The impact of varying both the hydraulic and solids retention times on the process performance was also undertaken, along with the investigation of the removal of both carbonaceous and nitrogenous contaminants found in the influent wastewater. Additional influent characterization is presented elsewhere [13]. For the sake of brevity, only BOD and TKN results are presented in this study.

The impact that the influent copper had upon the performance of the activated sludge system was also evaluated. The removal of specific organics, such as acetone, MIBK and toluene, along with *N*-nitrosodimethylamine (NDMA) from the industrial influent was also monitored and reported. A biokinetic analysis describing the activated sludge system was undertaken.

2. Materials and methods

2.1. Influent wastewater

The feed wastewater for this study was taken directly from the discharge of the existing patented aerobic bacterial thermophilic consortium, which was described by Lugowski et al. [3], and Quesnel and Nakhla [13,14]. The concentrations of VOCs and semi-volatile organic compounds (SVOCs) in the thermophilic effluent are presented in Table 1.

2.2. Pilot scale activated sludge system

The details of this system are listed by Quesnel and Nakhla [13,14] and will only be briefly described here. A 10 m³ stainless steel vessel was used as the aeration chamber for the completely mixed activated sludge system, with mixing and oxygen being supplied via a coarse bubble diffuser (courtesy of Envirocan, Mississauga, Ont., Canada). Compressed air and pure oxygen with nitrogen were used to aerate the

Table 1

Specific characteristics of the influent thermophilically processed chemical wastewater

Volatile organic compounds	Average \pm standard deviation ($\mu\text{g/L}$)
Acetone	165348 \pm 238772 (33–1400000)
Toluene	45421 \pm 122833 (7.6–600000)
Methyl isobutyl ketone	50769 \pm 55215 (50–220000)
Semi-volatile organic compounds [14]	Average (range) in $\mu\text{g/L}$
3-Methyl-nonane	1542 (1010–3026)
Aniline	28765 (1033–56652)
1-Decene	16203 (5434–25876)
C10 hydrocarbon	17041 (8096–25197)
2-Decene	1295 (318–3930)
DPA	3372 (362–7130)
C20 hydrocarbon	1179 (234–2010)
2MBT	1341 (963–1579)
Carboxin	2278 (197–16547)
C17 hydrocarbon	1263 (235–2929)
9-Methyl-nonadecane	1255 (306–1960)
Butylated hydroxytoluene	683 (299–1203)
7-Propyl-tridecane	994 (153–2524)
10-Methylnonadecane	ND

system. The aeration chamber was kept at a constant level through the use of an overflow pipe that flowed to the clarifier. The clarifier was an open topped, conical bottomed gravity settler with a 1.1 m³ capacity. The thickened settled sludges from the clarifier were continuously withdrawn and pumped back into the aeration chamber. Sludge wasting and sludge age control was performed using the thickened sludges by removing a known volume of sludges from the system. The dissolved oxygen (DO), pH, level and temperature of the aeration chamber were continuously monitored.

2.3. Wastewater analyses

BOD₅, TKN, TSS and VSS were all performed by following the Standard Methods [15]. All BODs reported in this study are the standard 5-day BOD (i.e. BOD₅ at 20 °C) The soluble fractions of BOD (sBOD) and TKN (sTKN) were determined by first passing the sample through a 0.45 μm filter and then following the Standard Methods [15]. The influent wastewater was sampled weekly and the pilot scale activated sludge system was sampled twice per week. Ammonia, nitrate and soluble phosphorus concentrations were determined by filtration through Whatman No. 5 filter paper, prior to analysis using Hach methods [16] employing a spectrophotometer (Hach DR/2010, Hach, Loveland, Colorado). As needed, concentrated phosphoric acid was added to the pilot scale activated sludge system to maintain the soluble phosphorous concentration between 3 and 7 mg/L. Volatile organic compound sampling was performed weekly on both the influent wastewater as well as on the pilot scale activated sludge effluent and sludge wasting samples. The sample and analysis were done in accordance with US EPA method 1624 [17]. Copper analysis was performed on the influent, effluent and waste sludge samples weekly, in accordance with EPA

method 6010B [18]. A linear correlation, developed between the effluent TSS of the pilot scale activated sludge system and the effluent copper ($r^2 = 0.73$, data not shown), showed that particulate copper was 0.54% (by wt.) of TSS. This correlation was then used to estimate the soluble copper concentrations in the effluent of the pilot scale system. NDMA analyses were performed weekly on the influent, effluent and return activated sludge samples of the pilot scale system. Samples were taken into amber glass bottles that were pre-certified NDMA free. The samples were stored in a refrigerator at 4 °C until undergoing analysis. Analysis was done by filtering the samples and adjusting pH to 10. The basic solution was serially extracted with dichloromethane, washed with an acidic solution and then concentrated. The sample extracts were analyzed by gas chromatography–low resolution mass spectrometry (GC/MS) using the isotope dilution method.

2.4. HRT optimization

The pilot scale system was set up and operated to determine the minimum hydraulic retention time necessary to effectively biodegrade the thermophilic influent. As shown in Table 1, a total of six different steady state operating stages were evaluated for the minimum HRT determination. Steady state conditions were based upon stable effluent quality, reactor biomass concentrations and operational conditions, such as operating for at least two turnovers of the mean sludge retention time (SRT) prior to determining the effectiveness of the activated sludge. The lone exception was stage 1, which had operated for a total of 28 days.

2.5. SRT optimization

The pilot scale activated sludge system underwent changes in its solids retention time upon the system's performance for carbonaceous and nitrogenous contaminant removal. A long SRT of 30 days was initially targeted for minimization of the sludge wasting rate. However, upon actual calculation of the SRT, which necessitated inclusion of the clarifier effluent solids, the SRT for stage 2 was found to be 20 days. This SRT of 20 days was then targeted for the remainder of the study, with the actual SRT shown in Table 1.

Observed yield calculations were performed during the course of the SRT optimization, and were done in the method described by Quesnel and Nakhla [13].

2.6. Biokinetic calculations

From this study, the biokinetic parameters of k (the maximum rate of substrate utilization per unit mass of microorganisms) and K_s (the half-velocity Monod constant) for the activated sludge were determined. Given the aforementioned problem of poor solids capture of the system clarifier, the effluent sBOD was utilized. Tchobanoglous and Burton [19] list the kinetic expression for the substrate concentration (S)

and the specific substrate utilization rate (U) as follows:

$$U = \frac{kS}{K_s + S} \quad (1)$$

Rearranging,

$$\frac{1}{U} = \frac{K_s}{k} \frac{1}{S} + \frac{1}{k} \quad (2)$$

Thus, a plot of $1/S$, where S is the effluent sBOD in mg/L versus $1/U$ in mg VSS-d/(mg sBOD) and U was calculated as follows:

$$U = \frac{\text{sBOD}_{\text{in}} - \text{sBOD}_{\text{eff}}}{\theta X} \quad (3)$$

where sBOD_{in} is the average influent sBOD concentration in mg/L, sBOD_{eff} the average effluent sBOD concentration in mg/L, θ the HRT in days and X is the biomass concentration in mg VSS/L.

2.7. Nitrogen mass balance calculation

The nitrogen balance was calculated using the following formula:

$$N_{\text{in}} = M_{\text{in}}([\text{TKN}]_{\text{in}} + [\text{NO}_3]_{\text{in}}) \quad (4)$$

where N_{in} is the mass of influent nitrogen in kg/d, M_{in} the influent liquid flowrate in L/d, $[\text{TKN}]_{\text{in}}$ the influent TKN concentration in kg/L and $[\text{NO}_3]_{\text{in}}$ is the influent nitrate concentration in kg/L.

The effluent nitrogen was determined using the following formula:

$$N_{\text{out}} = M_{\text{in}}([\text{TKN}]_{\text{eff}} + [\text{NO}_3]_{\text{eff}}) + M_{\text{WAS}}([\text{TKN}]_{\text{WAS}} + [\text{NO}_3]_{\text{WAS}}) \quad (5)$$

where N_{out} is the total effluent nitrogen in kg/d, $[\text{TKN}]_{\text{eff}}$ the effluent TKN concentration in kg/L, $[\text{NO}_3]_{\text{eff}}$ the effluent nitrate concentration in kg/L, M_{WAS} the mass of sludge wasted in kg/d, $[\text{TKN}]_{\text{WAS}}$ and $[\text{NO}_3]_{\text{WAS}}$ are the TKN and nitrate concentrations in the wasted sludge from the system in kg/L.

After stage 3, a correlation between the particulate TKN (pTKN) and the TSS was made and used to determine the WAS pTKN from stages 4 to 7. This correlation ($r^2 = 0.87$, not shown) indicated that the ratio of pTKN to TSS by mass was 0.045 (i.e. 4.5%). Also, the WAS nitrate monitoring was discontinued and the effluent nitrate concentration was used for the WAS nitrate concentration after establishing that no statistically significant differences at the 95% confidence level between the WAS and effluent nitrates existed.

Table 2
Steady state operational data for the activated sludge system

Stage (days of operation)	HRT (days)	Target SRT (days)	Actual SRT (days)	Q_g/Q_l	$F:M$ (mg BOD/mg VSS-d)	Volumetric loading (kg BOD/m ³ -d)	MLVSS (mg/L)
1 (98–125)	5.4	30	31.4	418	0.06	0.44	7238 ± 1229
2 (129–226)	4.3	30	20.6	308	0.04	0.33	7750 ± 1760
3 (227–292)	3.1	20	19.7	247	0.07	0.50	7769 ± 1277
4 (293–357)	2.8	20	14.5	220	0.08	0.54	6631 ± 1138
5 (358–419)	2.2	20	13.4	183	0.04	0.34	7522 ± 958
6 (420–489)	1.9	20	17.2	181	0.11	0.94	8112 ± 2059
7 (550–628)	2.3	10	6.3	96	0.11	0.33	2796 ± 194

Note: HRT, hydraulic retention time; SRT, solids retention time; Q_g/Q_l , ratio of gas flowrate to liquid flowrate; $F:M$, food to microorganism ratio, MLVSS, mixed liquor volatile suspended solids.

3. Results and discussion

3.1. Organics removal

3.1.1. HRT optimization

In all the cases, the food to microorganism ratios ($F:M$) were very low in the 0.04–0.11 mg BOD/(mg VSS-d) range, as shown in Table 2. The $F:M$ ratios listed here are similar to those systems reported from the pharmaceutical industry of 0.11 mg BOD/(mg VSS-d) [20], organic chemical industry of 0.10 mg BOD/(mg VSS-d) [20] and paper mills of 0.11 mg BOD/(mg VSS-d) [20].

Routine microscopic analysis revealed no proliferation of filaments, nor any pin-floc, yet the clarifier was exhibiting poor solids capture, resulting in high concentrations of TSS in the effluent [13,14]. As demonstrated by Quesnel and Nakhla [13], the SVI for the initial stages remained very constant at approximately 100 mL/g, and this trend continued throughout the course of the operation of the pilot scale system. Thus, the focus of this performance assessment was on the soluble fractions of organics in the effluent of the pilot scale activated sludge system, so as not to confuse the results obtained with the poor clarifier performance.

As shown in Table 2, the steady state mixed liquor VSS (MLVSS) for the various stages with the exception of stage 7, were all on the order of 7500 mg/L, even though the SRT was adjusted throughout the course of the study. The ratio of actual HRT to SRT varied narrowly from 5:1 to 6:1 as shown in Table 2 (excluding stages 6 and 7 with ratios of 9:1 and 3:1). This is of the same order as the activated sludge system described by Becares [21] and Garcia-Olivares and Becares [22] treating a chemical–pharmaceutical wastewater. Table 2 also displays the volumetric loading that the system treated during this course of study. In reviewing all the operational characteristics of this system, namely the long SRTs, high MLVSS, low $F:M$ and the BOD volumetric loading, this system would be comparable to an extended aeration system. As shown in Table 2, the BOD volumetric loading that this system was subjected to was always less than 1 kg BOD/(m³-d), which would be indicative of an extended aeration system [19].

In stages 1–6, the minimum HRT that could be sustained was 1.9 days. Stage 6B was initiated with a further reduction in the HRT down to 1.5 days, commencing on day 490. However, as demonstrated in Fig. 1, which displays the impact of a further reduction of HRT in the pilot scale activated sludge system, the effluent sBOD increased sharply after the commencement of stage 6B and the end of stage 6, with an HRT of 1.9 days ended at day 489. The breakthrough of sBOD detected in the effluent of the system is displayed in the inset of Fig. 1. Also noted at this time, the routine microscopic analysis of the biomass revealed the disappearance of all higher groups, leading the authors to hypothesize that the system

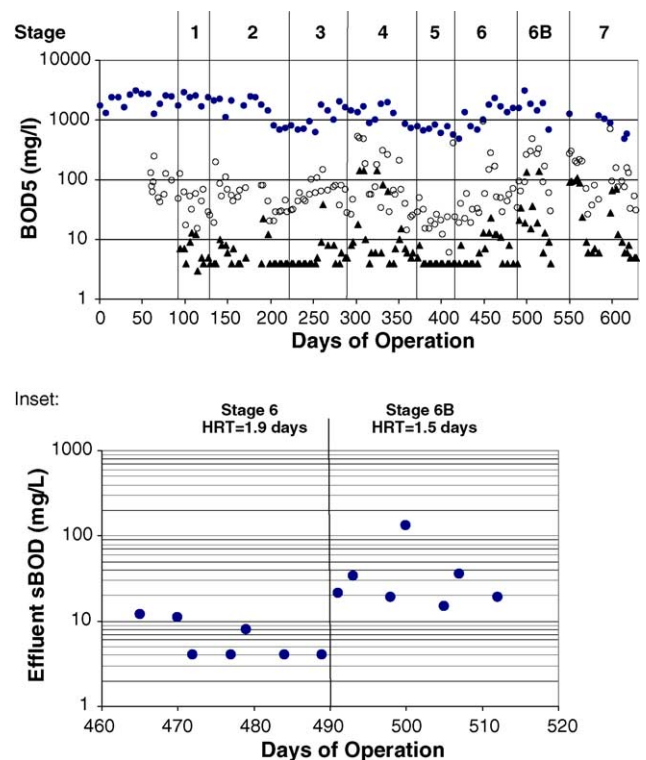


Fig. 1. BOD₅ concentrations for the activated sludge system with total BOD influent (●), total BOD effluent (○) and soluble BOD effluent (▲). Inset: Soluble BOD breakthrough due to HRT reduction from 1.9 to 1.5 days in the pilot scale activated sludge system.

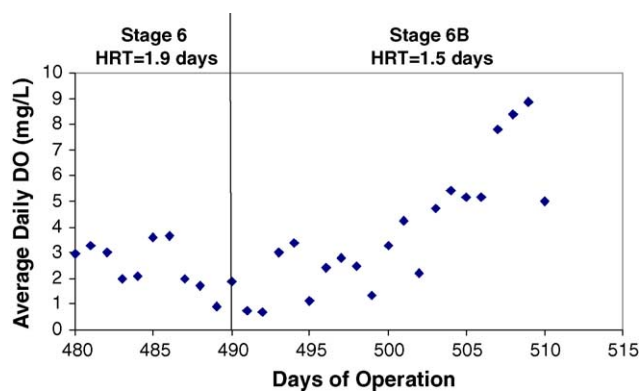


Fig. 2. Impact of HRT reduction to the daily average DO concentration in the activated sludge system.

was beginning to collapse. Fig. 2 illustrates the average daily DO concentrations in the aeration tank during stages 6 and 6B. It is evident that the system operated at DOs well above 0.5 mg/L, and this is comparable to the average DO during the course of experimentation was 3.4 ± 1.7 mg/L. Further analysis of the DO data during this stage 6B, recorded automatically every 30 s, indicated that the DO fell below 0.5 mg/L for only 8% of the time. This clearly indicated that despite the high BOD loading of $1.4 \text{ kg BOD}/(\text{m}^3\text{-d})$ on average during stage 6B, the aeration system was able to meet the oxygen demand of the stage 6B MLVSS of 13,840 mg/L. While it may be argued that DO diffusional limitations inside the biological flocs may have contributed to the breakthrough of sBOD, the absence of literature on the correlation between TSS concentrations and floc size, combined with the lack of specific measurements of floc sizes in this study, preclude conclusive assessment of the such a hypothesis. However, it is interesting to note that no increase in SND efficiency was observed during this phase, relative to other operational periods. It must be asserted that both the influent and effluent sTKN during this period essentially were similar to the other operational stages with the system achieving sTKN removal efficiencies of 68%. During stage 6, the DO was less than 0.5 mg/L for about 1% of the time at an MLVSS of 8112 mg/L, and the system was experiencing simultaneous nitrification denitrification without BOD breakthrough. Zhang et al. [23] have shown that there was no correlation between floc size and MLSS in conventional activated sludge although in MBRs, such a correlation exists. Thus, the observed breakthrough in effluent sBOD concentrations may be more indicative of

kinetic limitations than of diffusional limitations inside the floc. To salvage the system, the HRT was increased back to a previously demonstrated stable operating value of 2.3 days, and additional sludge injections from the neighbouring municipal plant were undertaken to reseed the bioreactor on day 512. Stage 7 did not commence until approximately two sludge age turnovers had passed, on day 550, to minimize the impact of the reseeded of the bioreactor.

Table 3 displays the mass of BOD entering and exiting the pilot scale system during the steady state operating stages, along with the average percent BOD₅ removal. As shown, this system was capable of removing significant amounts of the residual BOD₅ from the influent wastewater. Table 3 shows that the mass of effluent BOD₅ was very consistent throughout the course of operation. It should be pointed out that the values listed in Table 3 reflect the total BOD₅ mass balance. As seen in Fig. 1, overall there is an order of magnitude reduction in total BOD₅ across the system, and another order of magnitude reduction when comparing the effluent sBOD to the influent total BOD. Throughout the course of operation, the effluent sBOD of the activated sludge system was at or near the method detection limit of 4 mg/L. The system stability was noteworthy as the effluent sBOD was virtually constant despite large increases in the influent BOD concentrations. An example is shown in Fig. 1, during stage 3, where the influent BOD concentration increased from approximately 800–1500 mg/L, yet the effluent BOD concentration remained in the 10 mg/L range. Only during stage 4, there was a brief period of time that sBOD breakthrough was experienced, as shown in Fig. 1. It is to be stated that during stage 4, the pilot activated sludge system was plagued with numerous power outages which resulted in the impairment of the biomass, as indicated by the low average specific oxygen uptake rate (SOUR) during this stage 4 of $5 \pm 1 \text{ mg O}_2/\text{g VSS-h}$, when compared to the other measured SOURs of 7.2 ± 3.5 , 9.2 ± 1.8 and $11.1 \pm 4.2 \text{ mg O}_2/(\text{g VSS-h})$ for stages 1–3, respectively [13]. To remedy this situation, supplemental additions of methanol were manually added to the pilot scale system for a brief period of time (5 days), which contributed the breakthrough in sBOD seen in Fig. 1.

3.1.2. SRT optimization

The impact of SRT upon BOD₅ removal for this system was further evaluated. Since it has been elaborated above

Table 3
BOD mass balance for the activated sludge system

Stage	Influent BOD (kg/d)	Effluent BOD (kg/d)	WAS BOD (kg/d)	Average removal (%)
1	3.6 ± 0.7	0.06 ± 0.03	0.09 ± 0.02	98.4
2	2.8 ± 1.3	0.10 ± 0.04	0.26 ± 0.04	96.5
3	4.1 ± 1.1	0.20 ± 0.04	0.31 ± 0.08	95.3
4	4.5 ± 1.6	0.42 ± 0.37	0.38 ± 0.29	90.8
5	2.8 ± 0.6	0.37 ± 0.65	0.22 ± 0.15	86.6
6	7.6 ± 2.1	0.35 ± 0.31	0.13 ± 0.03	95.5
7	2.7 ± 1.4	0.30 ± 0.16	0.31 ± 0.20	88.9

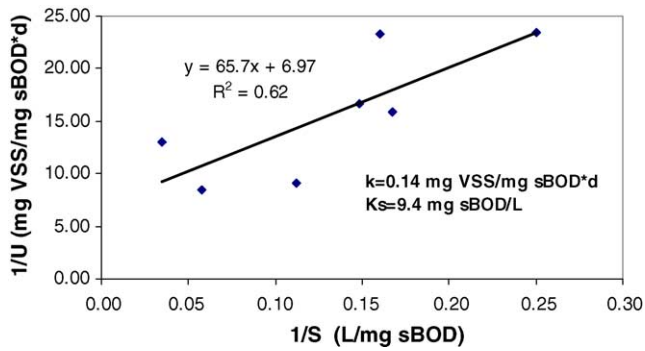


Fig. 3. Biokinetic constants derived from the steady state operational data of the activated sludge system.

that the HRT in this system was not limiting in the 5.4 days to at least 1.9 days, comparison of the system performance at identical volumetric loadings can be used to assess the impact of SRT. Scrutiny of the various operational stages indicated that the volumetric BOD loading remained constant at 0.33 kg BOD/(m³-d) during stages 2, 5 and 7, while the actual SRT decreased from 20.7 to 13.4, to 6.3 days, respectively. It is apparent that the reduction of SRT from 20.7 to 13.4 days decreased the BOD₅ removal efficiency from 96.5 to 88.9%, which remained almost constant upon further reduction to 6.4 day SRT. In fact, the average effluent sBOD concentrations from the system depicted in Fig. 1, remained essentially constant at the method detection limit of 4 mg/L, clearly emphasizing that the differences in BOD removal are related to the effluent suspended solids (i.e. particulate BOD due to the clarifier limitations). The average effluent TSS during stages 2, 5 and 7 were 347 ± 92, 489 ± 363 and 552 ± 115 mg/L, respectively. As shown in Table 2, stage 2 is characterized with a large HRT of 4.3 days and stages 5 and 7 have a relatively low HRT of approximately 2.2 days. Thus, the reduction in BOD₅ removal is due to the increase in the influent flowrate to the pilot activated sludge system.

The relationship between 1/U and 1/S, displayed in Fig. 3 for the determination of k and K_s ($r^2=0.63$), resulted in a k value of 0.14 mg sBOD/(mg VSS-d) and a K_s value of 9.4 mg sBOD/L. The low k value was indicative of a wastewater that was difficult to biodegrade and is comparable to the 0.07 d⁻¹ found in the second stage of a two-step activated sludge system treating a chemical-pharmaceutical wastewater [22] and the 0.17 d⁻¹ observed in a dyeing industry wastewater [24]. These k values are lower than those reported for several different pulp and paper mills in the range of 4.4–13.6 d⁻¹ [20], petroleum refinery wastewaters with k values of approximately 4 d⁻¹ [20] and a ceramic industry wastewater of 1.4 d⁻¹ [25]. For comparison, municipal wastewaters have k values ranging from 2 to 10 d⁻¹ [19].

The observed yields of biomass from this course of experimentation were determined with the results shown in Table 4. The low observed yield during stage 6 was attributed to the large variation in the influent VSS, which resulted in an atypically low value. The stage 7 observed

Table 4

Observed yield from the activated sludge system treating the thermophilically processed chemical wastewater

Stage	Observed yield (mg VSS/mg BOD)
1	0.16
2	0.25
3	0.23
4	0.30
5	0.36
6	0.07
7	0.54

yield of 0.54 mg VSS/(mg BOD), was the largest and this was attributed to the fact that there would have been a substantially reduced endogenous respiration at an SRT of approximately 6 days when compared to the other stages operating at SRTs greater than 13 days. The observed yields found here translate to comparable true yields published in the literature for industrial wastewater systems such as pharmaceutical wastewaters [20] and textile wastewaters [26].

3.2. Nitrogen removal

During the course of the system's operation, the removal of the nitrogenous contaminants was also monitored. As previously mentioned, the system was limited to a minimum HRT of 1.9 days. The influent and effluent concentrations of TKN and sTKN were plotted and are displayed on Fig. 4. It is apparent that the system was able to achieve approximately 70% sTKN removal throughout this study with the exceptions of stages 4 and 7, which were characterized by the loss of nitrification as evidenced by the rapid increase in effluent sTKN and the decrease in effluent nitrates. As shown in Fig. 4, during stage 4 (days 275–300), there was a loss of nitrification, as reflected by the rapid increase in the effluent sTKN due to the aforementioned operational problems. It is noteworthy that during the low SRT stage, there was a clear breakthrough of ammonia, as shown in Fig. 5. This would imply that there was a limiting SRT for nitrification for this system, in the range of 6 days. This stage is also characterized

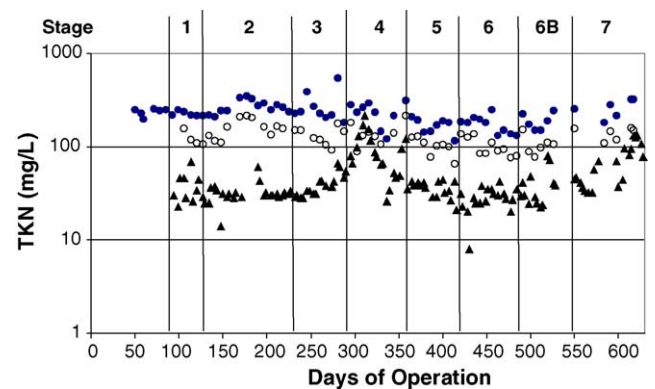


Fig. 4. TKN concentrations for the activated sludge system, with total TKN influent (●), soluble TKN influent (○) and soluble TKN effluent (▲).

Table 5
Nitrogen mass balance for the activated sludge system

Stage	Influent nitrogen (kg/d)	Effluent nitrogen (kg/d)	WAS nitrogen (kg/d)	$N_{out}/N_{in} \times 100$ (%)
1	0.57	0.24	0.06	53
2	0.57	0.18	0.22	71
3	0.91	0.40	0.16	62
4	0.47	0.30	0.16	96
5	0.62	0.20	0.18	61
6	0.63	0.43	0.11	85
7	1.03	0.66	0.28	92

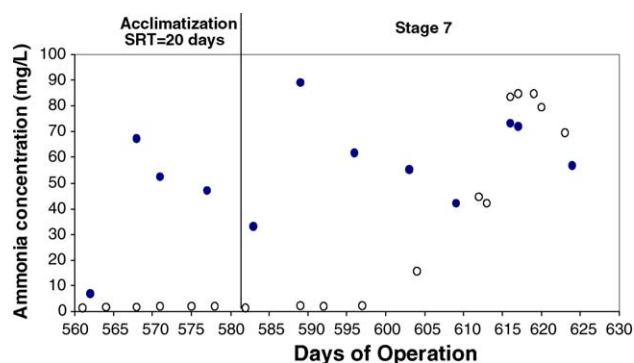


Fig. 5. Influent ammonia (●) and effluent ammonia (○), highlighting the breakthrough of ammonia due to change in activated sludge SRT reduction from 20 to 6.3 days.

with a closed nitrogen balance, as shown in Table 5 and will be discussed later. Furthermore, the disappearance of nitrification at an SRT of 6 days is contradictory to Eckenfelder [20] who reported nitrification in municipal wastewaters SRTs of 4 days at 22–24 °C. During stage 7, which started on day 550 and continued until day 628, a rapid increase in the sTKN in the effluent was observed. Unlike stage 4, there were no external factors impacting the operation of the activated sludge system. Furthermore, during this time, offline experiments were performed to determine the maximum rate of nitrification. A sample of biomass was taken on day 592 and the maximum nitrification rate was found to be 0.25 kg/m³-d ($r^2 = 0.91$, data not shown) and yet on day 597, the maximum nitrification rate was calculated to the reduced rate of 0.11 kg/m³-d ($r^2 = 0.84$, data not shown). This was a clear indication that the system was slowly losing its ability to nitrify the influent wastewater. Then, as shown in Fig. 5, the loss of nitrification was more pronounced with the commencing of the steady state sampling at the reduced SRT of 6.3 days, which commenced on day 602.

From this operation, a mass balance on nitrogen for the varying stages was undertaken and tabulated in Table 5. As shown in Table 5, the nitrogen balance for the first six operating stages could not be closed, with the exception of stage 4, due to the aforementioned operational problems.

Outside of stage 4 and its operational problems, the nitrogen balances could not be closed for the other six stages. This would imply that the nitrogen in the wastewater was undergoing simultaneous nitrification and denitrification (SND). SND has been reported in the literature, being observed

mainly in wastewaters that contain readily biodegradable substrates such as methanol, acetate, sugars and the like. There are documented cases of denitrification occurring with the carbon sources such as acrylamide [27], toluene [28] and acetone [29]. It is noteworthy to state that the wastewater treated in this study contained varying concentrations of volatile organic compounds (VOC), namely acetone, toluene and methyl isobutyl ketone (MIBK), as discussed later.

3.2.1. Impact of copper

Copper is known as a toxic heavy metal that reportedly inhibits nitrification at low concentrations, in the range of 0.1–0.5 mg/L [30]. The aforementioned correlation (Section 2.3) of copper to the effluent TSS then used to estimate the soluble fraction of copper in the system, as Hu et al. [31] reported that the inhibition of copper is due to this fraction and not the sorbed or intracellular fraction. As depicted in Fig. 6, the total copper entering the system and the estimated soluble copper concentration exiting the system are shown over the course of this study. The total copper in the influent is only impacted by the production schedule of the industrial site. The estimated soluble copper effluent concentration was observed to be consistently above 1 mg/L throughout the course of experimentation, with no apparent detriment to the ability of the system to nitrify.

3.3. Specific organics removal

3.3.1. Volatile organic compounds

As mentioned by Quesnel and Nakhla [13,14], the influent wastewater was laden with volatile organic compounds,

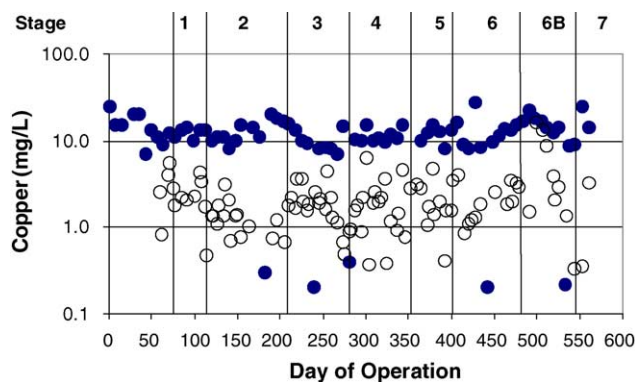


Fig. 6. Influent total copper concentration (●) and the estimated effluent soluble copper concentration (○) concentrations over the course of operation of the activated sludge system.

namely acetone, toluene and MIBK. The influent and effluent concentrations of these organics were monitored in this activated sludge system and are displayed in Fig. 7. A fate analysis was performed during stages 1–3, and as discussed elsewhere [13], biodegradation was the main removal mechanism of acetone at 92%, toluene at 86% and MIBK at 90%. Headspace measurements performed on the system during this time demonstrated that volatilization accounted for the removal of 8% of the acetone, 14% of the toluene and 9% of the MIBK while adsorption onto the sludges was found to be negligible [13].

VOC influent and effluent monitoring continued throughout the course of the duration of this experiment, however, headspace measurements were halted. As shown in Fig. 7, the VOC concentrations measured in the influent to the acti-

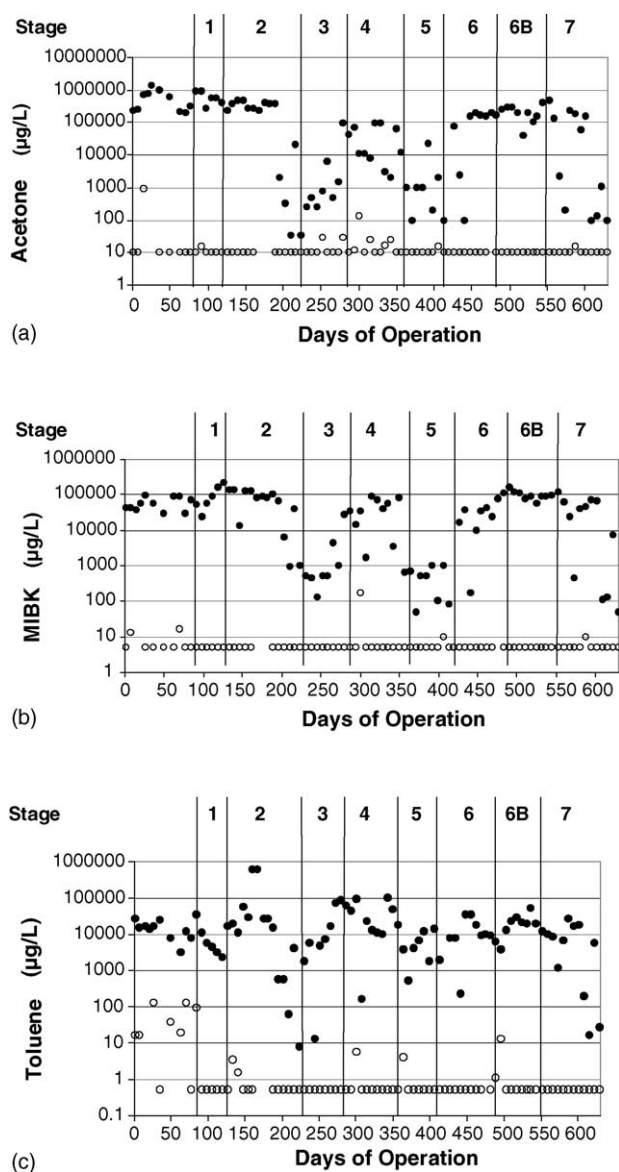


Fig. 7. Acetone (a), MIBK (b) and toluene (c) concentrations in the influent (●) and effluent (○) of the activated sludge system over the course of operation.

vated sludge were never greater after than those measured during stages 1–3. This fact along with the known implication that the ratio of gas flowrate to liquid flowrate (Q_g/Q_l) during the stages 4–7 was less than stages 1–3, as shown in Table 2. By maintaining approximately the same gas flow rate while increasing the influent wastewater feedrate, the impact of volatilization during the other stages would not be greater than during the aforementioned measured periods.

3.3.2. NDMA

The site had a maximum allowable discharge limit of 0.20 µg/L of NDMA to the sewer. The impact of the activated sludge treatment on NDMA was monitored to determine if there would be any benefits to NDMA removal from the wastewater. NDMA has been reported to be non-volatile, have a low octanol–water partition coefficient and be highly soluble in water [32]. There is a lack of information regarding the removal of NDMA from industrial wastewaters using biological treatment, despite the abundance of literature available on physical–chemical treatment such as GAC adsorption [33–35], carbonaceous resins [35] and UV-oxidation [36–38].

The influent and effluent NDMA concentrations measured from the activated sludge pilot scale system are shown in Fig. 8. The influent wastewater NDMA concentration ranged from the method detection limit (MDL) of 0.20 µg/L to a high of 40.7 µg/L. The effluent wastewater NDMA concentration ranged from the MDL of 0.04 µg/L to a high of 9 µg/L. The discrepancy between the MDL for the two wastewaters was due to background matrix effects in the influent wastewater, resulting in a larger MDL in comparison to the activated sludge treated effluent. The removal of NDMA as shown in Fig. 8, was expected to be due to biodegradation, given NDMA's aforementioned physical and chemical properties. This was significant since the removal of NDMA was occurring in the presence of known toxins and inhibitory compounds, such as copper and VOCs.

Kaplan and Kaplan [33] reported the biodegradation of NDMA from lake water with salts after 114 days with ini-

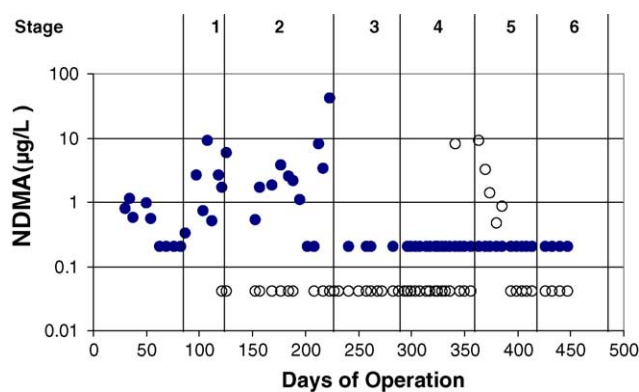


Fig. 8. NDMA concentrations in the influent (●) and effluent (○) of the activated sludge system.

tial concentrations ranging from 0.03 to 15,000 $\mu\text{g/L}$ with percent removals ranging from 16.4 to 78.6. Gunnison et al. [34] reported NDMA biodegradation after 30 days using incubated subsurface soils with initial concentrations ranging from 50 to 50,000 $\mu\text{g/L}$, with 40–70% removals. Sedlak et al. [39] reported NDMA removals from seven different municipal treatment works over a 21 month consecutive period, all of these plants employed activated sludges or dissolved oxygen activated sludges for secondary treatment, with the average influent concentration of 0.080 $\mu\text{g/L}$ of NDMA and the median secondary effluent concentration of NDMA of 0.046 $\mu\text{g/L}$ of NDMA. Industrial wastewater effluents contributed only a maximum of 11% of two of the treatment works investigated by Sedlak et al. [39] and a low of less than 2% for one of the plants.

Of the cited literature, only Sedlak et al. [39] reported on the biodegradation of NDMA in full scale municipal wastewater treatment systems, which were clearly not as toxic, and even then no listing of the operational conditions of the municipal plants was provided. Furthermore, the results obtained were for a pilot scale sized system and not a bench top set up operating for extremely long periods of time [33,34]. This was significant, since this site requires the utilization of GAC and as needed, UV-oxidation to be able to achieve the sewer discharge criterion. This could result in a substantial cost savings to the site.

However, for an unknown reason the system temporarily lost the ability to biodegrade NDMA day 342, and days 364–386, but regained it again on day 394, as shown in Fig. 8. The initial loss of the activated sludge system's ability to remove NDMA occurred during stage 4, when as mentioned earlier, there were numerous power outages being experienced. Due to the complex nature of the influent wastewater, and the matrix effect on the NDMA analysis alluded to above, the influent NDMA concentration was significantly lower than the effluent during the aforementioned upset period.

4. Summary and conclusions

A conventional activated sludge employed as a secondary biological treatment step was able to remove virtually all residual biodegradable organic matter, as well as VOCs, from a thermophilic aerobic bacterial consortium treating a chemical manufacturer's wastewater. In particular, the following specific conclusions can be drawn:

- The system was able to achieve an effluent soluble BOD of less than 10 mg/L approximately 75% of the time.
- An inherent stability of the system to maintain the effluent quality irrespective of fluctuations in the influent concentrations was experienced.
- A limiting HRT for treating the organics in this wastewater of 1.5 days was delineated.
- Nitrogen mass balances revealed that simultaneous nitrification and denitrification of the wastewater occurred

despite maintaining the bulk DO in the range of 1–3 mg/L as well as in the presence of high soluble copper concentration.

- A limiting SRT for nitrification on the order of 6 days was observed for this wastewater.
- Simultaneous removal of acetone, toluene and methyl isobutyl ketone despite varying influent concentrations down to method detection limits. Biodegradation was found as the primary pathway for VOC removal, with volatilization being secondary and adsorption being negligible.
- Apparent biodegradation of NDMA from feed concentrations ranging from 0.04 to 41 $\mu\text{g/L}$ to the method detection limit of 0.04 $\mu\text{g/L}$ was observed.

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