

A novel two-stage MBR denitrification process for the treatment of high strength pet food wastewater

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Received 19 January 2005; received in revised form 22 August 2005; accepted 25 August 2005
Available online 3 October 2005

Abstract

A novel paradigm using pre-denitrification process is presented to optimize an existing system of two-stage MBRs treating high strength pet food wastewater. Successive reduction of organics in the 1st stage and almost complete nitrification in the 2nd stage generated effluent meeting stringent surface discharge criteria i.e. BOD₅, TSS and NH₄⁺-N of <10 mg/L at an overall HRT of 6.3 days. Pre-anoxic zone was created by a submerged coil in the path of influent to the 1st stage. Final effluent and the 1st stage mixed liquor were recirculated to the coil. With prevailing high denitrification rates, more than 94% of the recirculated nitrates were denitrified in less than 15 min of effective anoxic residence time. At a recycle ratio of 3:1, total nitrogen was reduced by 84%, aeration energy by 25% and the external alkalinity requirement by 65%, enhancing economical viability of the system.

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Keywords: Pre-denitrification; Two-stage MBR; Energy optimization; Denitrification potential; Nitrogen removal

1. Introduction

Apart from nitrate discharge limits, the reduction in oxygen demand and alkalinity recovery are key benefits that play major role in inclusion of denitrification processes in optimization of new or existing treatment processes. Various conceptualized, studied and operating nitrogen removal processes can largely be classified into three major groups; post-denitrification, pre-denitrification and simultaneous nitrification denitrification (SND) processes [1]. Requirement of external carbon addition and provision of anoxic basin in post-denitrification not only cease possibility of use of influent organic carbon in denitrification, but also pose serious threat of exceeding final effluent BOD criteria in the case of overdosing and nitrogen loading variations. The attractive alternative of SND offers benefits like no additional requirement of reaction space, energy savings, and recovery of alkalinity. DO concentration gradient across large sludge flocs and intermittent aeration are two known basic mechanisms behind SND [2,3]. In the case of high nitrogen loading,

essentiality of external carbon addition for complete denitrification as well as an evident complexity in the steep process control on floc size [4] and DO concentration [5,6] limits acceptability of SND as a preferred treatment option for highly variable influent conditions such as those experienced in many industrial applications. Recirculating nitrified effluent to the anoxic zone upstream of an organics removal step may eliminate the need for external carbon source for denitrification, which renders pre-denitrification the most popular and widely explored treatment, particularly for high strength wastewater where organic carbon is in abundance.

Though conventional studies of denitrification have been driven primarily by the requirement to meet stringent nitrogen discharge criteria, immense work has been done on impact of various carbon sources [7–9], role of diverse microbial cultures kinetics [10–12] and optimization [5]. Research on enhancement and optimization of process designs using pre-denitrification has been limited. Ros and Vrtovsek [13] combined anaerobic, anoxic and aerobic zones in a single reactor as an innovative process design. Introduction of deoxic zone [8], MBR applications [14] and use of bio-electro reactors [15] have also been evaluated in pre-anoxic configurations. Without addition of a separate anoxic basin, Bertanza [5] achieved SND

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Nomenclature

DO_1	DO in 1st stage mixed liquor (mg/L)
N_{in}	NH_3 in 2nd stage influent without recycle (mg/L)
ΔN_{in}	% drop in 2nd stage influent ammonia due to recycle
N_{inr}	NH_3 in 2nd stage influent with recycle (mg/L)
N_o	NO_3 in final effluent in non-denitrifying system (mg/L)
ΔN_o	% drop in NO_3 in final effluent due to recycle
Q	final effluent flow leaving the system (L/d) or 2nd stage influent flow rate in non-denitrifying system (L/d)
Q_a	total flow through anoxic zone (L/d)
Q_{in}	raw wastewater flow to 1st stage (L/d)
Q_r	recycled final effluent flow (L/d)
Q_w	sludge wasted (L/d)
Q_x	mixed liquor recirculation flow (L/d)
R	recycle ratio of Q_r to Q
SDNR	biomass specific denitrification rate (mg NO_3 -N g VSS ⁻¹ min ⁻¹)
SOUR	biomass specific O_2 uptake rate in the 1st stage (mg DO g VSS ⁻¹ min ⁻¹)
T_{deox}	deoxic residence time (min)
V_{anox}	volume of anoxic zone (L)
V_{deox}	volume of deoxic zone (L)
X_1	MLVSS 1st stage (mg/L)
X_a	MLVSS anoxic zone (mg/L)

Greek letters

θ	1st stage HRT (d)
θ_c	1st stage SRT (d)

using ORP/DO control and optimized existing treatment system with no previous provision for denitrification. However in industrial wastewater treatment applications, dynamic loading conditions complicate achievement of SND using DO/ORP control.

Though anaerobic treatment is an attractive and popular approach in the treatment of high strength wastewater, and has been reported to remove up to 90% COD [16], its failure in the treatment of oily wastewater also has been widely experienced [17]. Although the importance of a polishing step post an anaerobic reactor to meet surface discharge criteria is well recognized [18], the sequential configuration of UASB and MBR failed to achieve desired removal of ammonia from the high strength brewery wastewater [19]. Inhibition of nitrifiers by the organics [20] remaining in the 1st stage effluent is postulated to reduce the ammonia removal efficiency of such two stages systems. Two-stage conventional aerobic activated sludge system (CAS), experimented by Liu et al. [21], removed 99% BOD treating high strength oily pet food industry wastewater, but did not achieve the desired nitrification, which was attributed to limitations of clarifiers. In order to overcome these limitations, application of a membrane in the 1st stage aerobic reactor

can create a high rate organics removal step by maintaining high biomass concentration, rendering minimal BOD in the effluent for successful nitrification in the 2nd stage. Complete retention of the nitrifiers in the 2nd stage, which is essential for stable and complete nitrification in the light of low growth of nitrifiers and dynamic influent nitrogen loadings, can be achieved in a 2nd stage as an MBR. The uniqueness of such MBR system lies in its fundamental concept of decoupling the organics removal and the ammonia removal in two separate aerobic stages to meet stringent surface discharge criteria. The innovation in such a two-stage MBRs is apparent, as a critical literature review, and exploration of renowned databases (Scholarsportal.info, Science Citation Index, Current Content Connect and Scifinder Scholar) and profound patent search (USPTO) did not reveal any lab, pilot or full-scale system that employs a two-stage MBR with two separate sludge systems.

In this two-stage MBR system, employing two aerobic submerged membrane bioreactors in series, a small coil of tube receiving recirculated nitrates from the 2nd stage permeate, recycled mixed liquor from the 1st stage MBR and wastewater, is inserted into the 1st stage. A high denitrification rate, facilitated by the high biomass concentration in the 1st stage MBR of >20,000 mg VSS/L, the high 2nd stage permeate nitrates of ~800 mg/L and the excess readily biodegradable organic matter in the influent wastewater, prevails in this short HRT anoxic zone.

1.1. Distinct features

Unlike the common approach in various forms of modified Ludzack–Ettinger processes including conventional systems [8,12] as well as MBRs [14], where mixed liquor from the nitrifying basin is recirculated to the anoxic zone, the presented modified two stages MBR recirculates nitrified permeate only, and not the nitrifiers to the created anoxic zone. Thus, despite nitrates recirculation, the inherent benefit of the two separate sludge systems to remove organics and nitrifiers prevents intermixing of bacterial cultures. Hence, this novel denitrification process eliminates possibilities of loss of nitrifiers through wastage of excess sludge generated due to the organics removal in the 1st stage. Whereas all investigated processes, in the literature either encourage addition of a pre-anoxic basin [22] with mixing devices or various forms of SND with complex control mechanisms, the presented innovation eliminates the need for any additional reaction space or mixing devices with minimal additional construction.

The primary objectives of this paper are presentation of the design approach of this novel system, and the comparative performance evaluation of the two-stage system with and without denitrification. This paper presents detailed data on the achievability of denitrification in this uniquely modified system of two-stage MBR during treatment of high strength pet food wastewater characterized by (Table 1) ammonia concentration of up to 2000 mg/L, total COD and BOD₅ concentration of 20,000 and 10,000 mg/L respectively and oil and grease concentrations of up to 8000 mg/L.

Table 1
Summary of performance of two stages MBR at different HRTs

Parameters	Influent average	Final effluent (average values at steady states run at different combined HRTs)							
		12.5 Days	% Removal	10 Days	% Removal	8.5 Days	% Removal	6.3 Days	% Removal
TSS (mg/L)	4545 ± 5468	0	100	0	100	0	100	0	100
TCOD (mg/L)	20303 ± 8167	1224 ± 296	93.97	703 ± 261	96.54	1208 ± 125	94.05	680 ± 310	96.64
TBOD ₅ (mg/L)	9719 ± 2725	4 ± 4	99.95	6 ± 2	99.93	4 ± 2	99.95	4 ± 0	99.95
NH ₃ -N (mg/L)	1139 ± 342	112 ± 74	90.16	143 ± 55	87.45	137 ± 94	87.97	3.5 ± 3.4	99.69
P (mg/L)	208 ± 69	120 ± 85	42.31	61 ± 46	70.67	117 ± 48	43.75	124 ± 49	40.38
VSS R1 (mg/L)		3230 ± 756		14724 ± 3742		16532 ± 2310		23621 ± 2396	
VSS R2 (mg/L)		3401 ± 390		6733 ± 380		3116 ± 579		3956 ± 431	

Shown values of VSS indicate MLVSS concentrations in R1 and R2 at different HRTs.

2. Materials and methods

2.1. Source of wastewater and two stages MBR

High strength wastewater generated from a pet food industry located in southern Ontario was pretreated onsite by an oil recovery system followed by dissolved air flotation (DAF). DAF effluent was treated in the existing two-stage MBR bench scale system (Fig. 1).

The system consisted of a 20 L storage tank, which was filled with DAF effluent every 2 days, followed by two 25 L activated sludge reactors. These reactors were made from stainless steel and provided with a glass window and a scale to monitor water level. Both the reactors were continuously aerated using compressed air through air diffusers. Zenon membranes (ZW-1, pore opening of 0.04 μm, surface area of 0.047 m²) were employed in the reactors to retain solids and draw permeate only as effluent. Two membranes with total surface area of 0.094 m² were immersed in the 1st stage (R1) reactor while one membrane module (0.047 m² surface area) was used in the 2nd stage (R2) reactor. Operation was closely monitored and carried out for a period of 337 days (prior to the modification) at combined HRTs of 12.5, 10, 8.5 and 6.3 days (which comprise HRTs of 6.25, 5, 3.5 and 2.8 days in the 1st stage reactor and 6.25, 5, 5 and 3.5 days in the 2nd stage reactor) for 85, 19, 62 and 171 days, respectively. While operating at a combined HRT of 8.5 and 6.3 days, sludge retention time (SRT) in the 1st stage reactor was maintained at 12.5 days by direct wasting of reactor mixed liquor. No wasting of sludge was deemed necessary from the 2nd stage reactor. A combined HRT of 6.3 days was used in this work to explore the innovative denitrification process. DO of 1.3 and >2.5 mg/L was maintained in the 1st and the 2nd stage MBR, respectively. pH in the 1st stage was 8.2 while that in the 2nd stage was maintained from 7 to 7.5. Trans-membrane pressure (TMP) was monitored and membranes were cleaned by water flushing and soaking in a 200 ppm solution of NaOCl when fouling reduced the flux and dropped permeate flow below required. The system has been in operation, treating the industrial wastewater at a temperature of 18–20 °C for period of 337 days prior to the modification.

2.2. Modifications of the existing system

Simple and inexpensive modifications incorporated in the existing system are shown by dark lines in Fig. 1b. A coil tube

with a hold up volume of 460 mL (ID 1 in., length 3 ft.) was submerged in the mixed liquor of the 1st stage. The coil was placed such that one unsubmerged end can receive all influents, which would flow by gravity to the other submerged end. The unsubmerged end of the coil served as a junction of three streams – 1.28*Q* of influent from the storage tank, 3*Q* of recirculated final effluent and 3*Q* of recirculated mixed liquor from the 1st stage, where *Q* is the final effluent flow rate of 7 L/d. First stage bioreactor mixed liquor was circulated to the anoxic reactor i.e. unsubmerged end of the coil using a peristaltic pump. Hold up volume of the mixed liquor path from the 1st stage bulk zone to the anoxic zone entry point was 70 mL (diameter 3/8 in., length 3 ft.). Dimensions of the flow paths not specified here do not bear any significance on the performance of the process. To achieve the required flows in the modified system, membrane filtration area was doubled to 0.188 and 0.094 m² in 1st stage and 2nd stage, respectively, using additional membrane modules.

2.3. Membrane cleaning

Membranes were cleaned online by air scouring and offline by water flushing and soaking in 200 ppm solution of NaOCl. For the first 200 days, intermittent air scouring was used, where consecutive aeration and pumping was attempted with different combinations of pumping and aeration time (each between 300 and 600 s). From day 200 onwards, simultaneous air scouring and permeate pumping was implemented. On intermittent aeration, TMP in both the stages remained around 10–12 psi (68.9–81.7 kPa), while continuous air scouring reduced TMP below 4 psi (27.5 kPa). To prevent measurable drop in flows, membranes were cleaned offline every second day for the first 200 days and every seventh day after day 200. Throughout the study period, independent of the mixed liquor concentrations, TMPs remained almost constant between successive cleanings, and varied mainly with air scouring methods. Detailed variations in the fluxes were not measured, as it was not in the scope of the presented study.

2.4. Analytical methods used

Samples of the influent, 1st stage permeate and the 2nd stage permeate (final effluent) and mixed liquor of both reactors were collected (2–3 samples per week) and analyzed for total suspended solids (TSS), volatile suspended solids (VSS), BOD₅ and

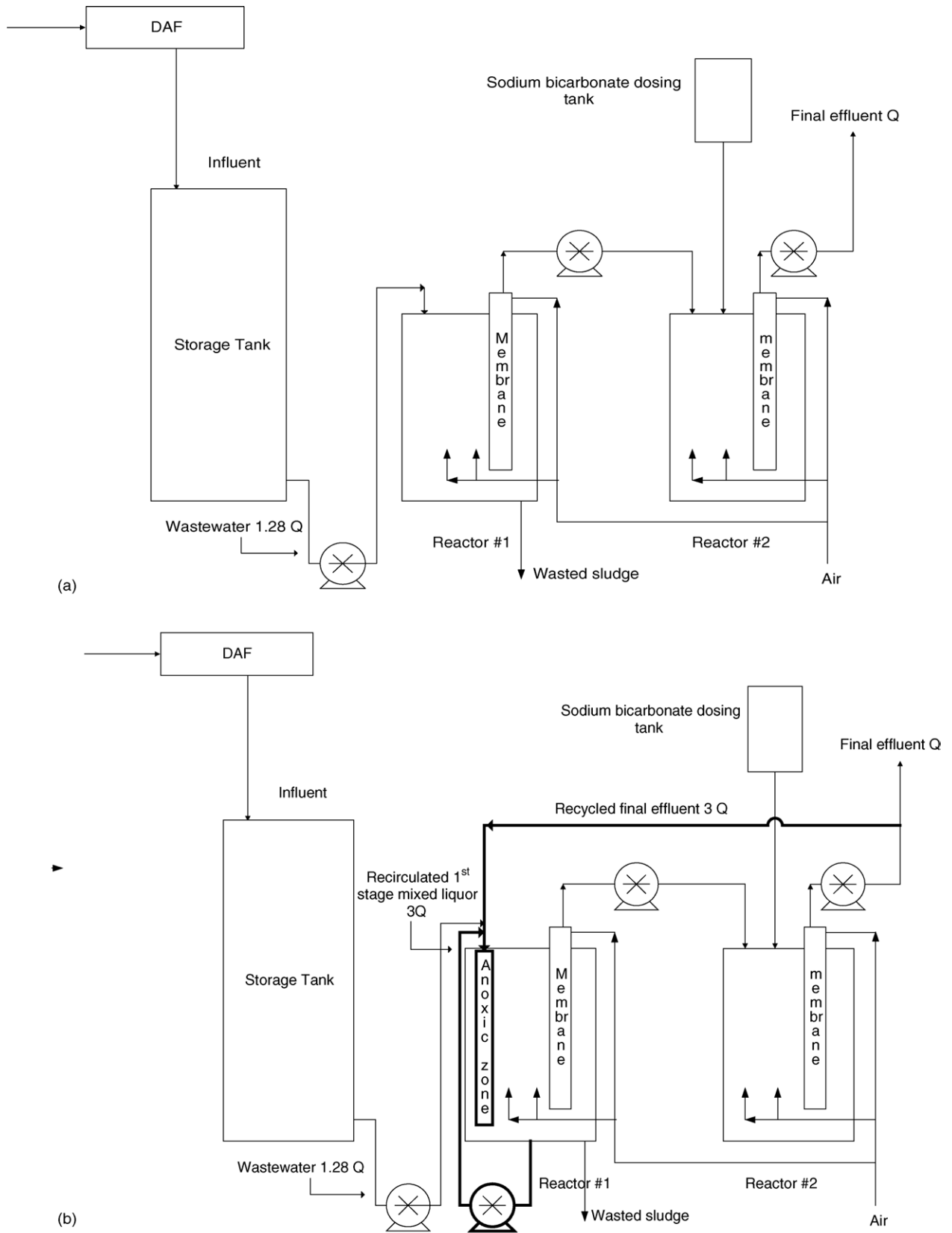


Fig. 1. (a) Bench scale system of two-stage MBR before modification. (b) Modified two-stage MBR (modifications shown by dark lines).

alkalinity using standard methods [23]. COD and ammonia-N were analyzed using HACH Odyssey Analyzer and COD heating reactor with standard HACH testing kit. HPLC (Waters 515 HPLC Pump, Waters 432 Conductivity detector) was employed to determine nitrite-N, nitrate-N and phosphorous. All ammonia, nitrate, and nitrite results reported here are as nitrogen. For analysis of soluble parameters, samples were filtered through 0.45 μm filter (Wheaton). Dissolved oxygen (DO) was measured with a portable DO meter (YSI Dissolved Oxygen Meter Model 50).

3. Results and discussion

3.1. Performance of the existing treatment system of two-stage MBR

While the detailed performance of the two-stage MBR has been reported elsewhere [24], Table 1 presents a summary of the various operational conditions for the system as well as final effluent quality achieved. Despite the huge variability in the influent, as apparent from the standard deviations, the system consistently generated effluent meeting stringent surface discharge criteria of TSS, BOD₅ and ammonia <10 mg/L during the experimented HRT run of 6.3 days. Even at an average COD loading of 7 kg COD/m³ d, corresponding to the influent flow rate of 9 L/d and a 1st stage HRT of 2.8 days with 40% deviations in the influent COD concentrations, the final effluent COD always remained below 1500 mg/L, which strongly articulates the robustness of the system derived from the high MLTSS of up to 35,000 mg/L. As depicted in Table 2, more than 99% of BOD₅ was removed in the 1st stage, articulating 1st stage as a primary organic removal step.

Contrarily to literature [17,25], even at oil and grease concentrations more than 5000 mg/L, satisfactory performance of the system in contaminant removal, where oil and grease concentration in the 1st stage effluent as low as 11 mg/L, was achieved (Table 2). The removal of oil and grease is attributed mainly to the biodegradable nature of the oil and grease in the influent, and very high concentration of biomass, affecting hydrolysis of O&G. Treating wastewater with very high concentrations of influent ammonia and TKN up to 2000 and 2500 mg/L, respec-

tively, 47% of ammonia was removed in the 1st stage primarily due to cell synthesis and volatilization at an operating pH of 8.3. In the absence of inhibitory organics, the 2nd stage nitrified almost all the ammonia to nitrates consistently keeping final effluent ammonia concentration below 10 mg/L. Membranes affected an additional 5–37% removal of soluble COD. High biomass concentrations averaging 23.6 g/L and consequently lower F/M ratio of 0.5 g COD/g VSS day were achieved in the 1st stage, contributing to a relatively low observed sludge yield of 0.19 g VSS/g COD (obtained from the plot of cumulative VSS produced versus cumulative COD consumed with an R^2 of 0.99, not shown here).

Operation at an overall HRT of 3.0 days and SRT of 25 days increased the MLSS concentrations to over 50 g/L, rapidly clogging the membrane and reducing its flux to less than 15% of the nominal design flux of the membrane. Such operation was thus deemed unfeasible and the modification to the system was undertaken following resumption of the HRT and SRT of 12.5 and 6.3 days.

3.2. Denitrifying two-stage MBR system

3.2.1. Rationale

Stoichiometrically insufficient alkalinity in influent and apparent loss of alkalinity in the 1st stage probably due to CO₂ stripping [26], necessitated the addition of 4.5 kg of NaHCO₃ dosing per m³ of the system influent to achieve complete nitrification. In a batch experiment of anoxic respiration of organics present in the waste, using mixed liquor from the 1st stage, at a VSS concentration of 12,200 mg/L and a F/M ratio of 0.4 g COD/g VSS, 5.6 g of COD was degraded for each gram of NO₃-N denitrified (found from a plot of COD consumed versus nitrates reduced, $R^2 = 0.86$, not shown here).

Final effluent NO₃ concentrations averaging about 750 mg/L, were equivalent to the 1st stage effluent TKN. Considering HRT and SRT of 2.7 and 12.5 days in the 1st stage respectively and an HRT of 3.6 days and infinite SRT in the 2nd stage, final effluent leaving the system was around 78% of the influent flow. This implies that for each liter of influent wastewater, 585 mg of NO_x was wasted in the final effluent, with a potential to degrade around 3200 mg i.e. around 15% of the influent COD. This

Table 2
Detailed performance of an existing two-stage MBR system (HRT: 6.3 d, SRT: 12.5 d)

Parameters	Influent/DAF effluent average	1st stage effluent	% Removal in the 1st stage	Final effluent	% Removal in overall system
TSS (mg/L)	4545 ± 5468	0	100	0	100
VSS (mg/L)	4080 ± 4890	0	100	0	100
TCOD (mg/L)	20303 ± 8167	702 ± 202	96.54	680 ± 310	96.64
SCOD (mg/L)	12807 ± 3300	–	–	–	–
TBOD ₅ (mg/L)	9719 ± 2725	14 ± 3	99.85	4 ± 0	99.95
SBOD ₅ (mg/L)	7940 ± 3050	–	–	–	–
NH ₃ -N (mg/L)	1139 ± 342	603 ± 157	47.05	3.5 ± 3.4	99.47
NO ₃ -N (mg/L)	3.9 ± 4	4 ± 10	0	750 ± 180	–99.46
TKN (mg/L)	1750 ± 470	752 ± 193	57.60	11 ± 4	99.37
Alkalinity (mg/L)	3400 ± 1040	2433 ± 880	–	315 ± 900	–
O&G (mg/L)	2893 ± 3000	15 ± 4	99.50	–	–

SCOD, SBOD₅ in both the stages permeate are equivalent to their corresponding TCOD, TBOD₅; –ve removal indicates rise i.e. nitrates generation.

translates to significant savings potential in aeration energy. Parallel generation of 3.5 g of alkalinity per gram of nitrate reduced in this process can effectively address the issue of huge requirement of external alkalinity addition.

Availability of readily biodegradable carbon is a key issue in anoxic respiration or denitrification. Volatile fatty acids like acetic acid [7], propionic acid and butyric acids are widely accepted as desired carbon sources for denitrification. Readily biodegradable COD as reflected by VFAs in the influent averaging 7600 mg COD/L, constituted more than 35% of the total COD. Acetic acid at about 3520 mg/L, was the main VFA, thus pointing to the high denitrification potential of the system.

3.2.2. System design equations

Fig. 1b illustrates the adopted pre-denitrification flow scheme, which can be described as a modified version of MLE process [1] to fit in the existing two stages MBR system. In the path of influent wastewater to the 1st stage MBR, an anoxic reaction space is to be provided where three streams— influent as an organic carbon source, final effluent as a source of NO_x and recirculated 1st stage mixed liquor containing denitrifying heterotrophic biomass were mixed and transferred to the 1st stage MBR after sufficient residence time in the anoxic zone.

3.2.2.1. Flow balance in the modified system. About 9 L/d of raw wastewater (Q_{in}) entered to the system through the anoxic zone. About 7 L/d of final effluent (Q) and 2 L/d of waste sludge (Q_w) were the two streams that left the system. Apart from the influent, the 1st stage received 21 L/d of the recycled final effluent (Q_r) through the anoxic zone. The third stream entering the anoxic reactor was 21 L/d of the recirculated 1st stage mixed liquor (Q_x) i.e. total flow through the anoxic zone (Q_a) was 51 L/d or equivalent to $7.28Q$. Though all liquid entering to the anoxic zone ultimately entered in the 1st stage bulk zone, due to the 21 L/d of recycled mixed liquor, the net flow entering the 1st stage is only 30 L/d. As 2 L/d of mixed liquor was wasted directly from the 1st stage, the flow from the 1st stage to the 2nd stage was 28 L/d, which was equivalent to the total flow out of the 2nd stage i.e. sum of the final effluent leaving the system and final effluent recycled to the anoxic zone.

Listed below are the design equations, developed based on mass balances in the modified two-stage MBR and reaction kinetics, are discussed further in the following sections. Design assumptions considered are: (1) complete removal of the ammonia by nitrification process in the 2nd stage, (2) complete removal of nitrates entering the anoxic zone by its conversion to gaseous nitrogen products and (3) absence of active biomass in system influent. It is apparent from Table 2 that the 2nd stage effluent nitrates are the same as 2nd stage influent TKN, i.e. almost complete nitrification was achieved all the time. Since the TKN loading to the 2nd stage remained the same in the modified system, the first assumption is valid. The second assumption reflecting the design objective to achieve complete denitrification in the anoxic reactor is validated by the comparison of the 1st stage nitrates in the system with and without denitrification. The data comparison presented in Table 3 corroborates that denitrification efficiency was about 97.5%. The third one is based on a basic assumption used in common practice

$$\frac{Q}{Q_{in}} (\%) = \frac{Q_{in} - Q_w}{Q_{in}} \times 100 = \left[1 - \left(\frac{\theta}{\theta_c} \right) \right] \times 100 \quad (1)$$

$$N_{inr}(Q + RQ) = N_{in}Q \quad (2)$$

$$\Delta N_{in} = \frac{N_{in} - N_{inr}}{N_{in}} = \Delta N_o = \left[1 - \frac{1}{1 + R} \right] \times 100$$

$$T_{deox} = \frac{DO_1 - 0.2}{X_1 \text{ SOUR}} \quad (3)$$

$$V_{deox} = \frac{Q_x T_{deox}}{1440} \quad (4)$$

$$V_{anox} = \frac{Q N_o [1 - 1/(1 + R)]}{1440 \text{ SDNR } X_a}, \quad X_a = \frac{X_1 Q_x}{Q_a} \quad (5)$$

$$Q_a = Q_r + Q_x + Q_{in} = 3Q + 3Q + 1.28Q = 7.28Q$$

3.2.3. Design parameters

3.2.3.1. Determination of recycle ratio. It is an established fact that in pre-denitrification, nitrate concentration in the final effluent stoichiometrically depends upon recirculation ratio and

Table 3
Comparison of nitrogen removal in non-denitrifying and denitrifying system

Parameters	Non-denitrifying system			Denitrifying system		
	Influent	1st stage effluent	2nd stage effluent	Influent	1st stage effluent	2nd stage effluent
$\text{NH}_3\text{-N}$ (mg/L)	1139 ± 342	603 ± 157	3.5 ± 3.4	1302 ± 231	308 ± 77	1.9 ± 1.8
$\text{NH}_3\text{-N}$ (g/d)	10.3	4.2	0.02	11.7	8.6	0.01
TKN (mg/L)	1750 ± 470	752 ± 193	11 ± 4	1950 ± 774	369 ± 93	12 ± 5
TKN (g/d)	15.7	5.4	0.07	17.5	10.3	0.08
$\text{NO}_3\text{-N}$ (mg/L)	0	17 ± 38	730 ± 150	0	17 ± 22	386 ± 205
$\text{NO}_3\text{-N}$ (g/d)	0	0.1	5.1	0	0.5	2.7
Total N (mg/L)	1717 ± 540	771 ± 139	771 ± 153	1950 ± 774	386 ± 111	388 ± 205
Total N (g/d) (% removal in the system)	15.5	5.4	5.4 (65%)	17.5	10.8	2.7 (84%)

Total N values presented are based on calculated values for each samples (total N = TKN + NO_3); 1st and 2nd stage effluent mass/d calculated based on flow rate Q (7 L/d) in non-denitrifying system and $3Q$ (21 L/d) in denitrifying system.

subsequent dilution effect [27,28]. Assuming complete denitrification in the pre-denitrification zone, considering complete nitrification in the following nitrification step, Eq. (2) specifies % drop in final effluent nitrates at a given recycle ratio R , where R is the ratio of recycled final effluent flow rate to flow rate of final effluent leaving the system. In this study, system performance at the typical recycle ratio of 3, was studied with 75% targeted decrease in the final effluent NO_3^- .

3.2.3.2. Provision of anoxic environment and availability of facultative anaerobes. DO concentrations above 1 mg/L [20] are inhibitory to denitrification. Pochana and Keller [4] found that DO concentrations <0.2 mg/L are essential in the anoxic basin for effective denitrification, thus substantiating the criticality of the anoxic environment for the process.

Determination of biomass specific oxygen uptake rate (SOUR) is essential in the 1st stage to determine the residence time and ultimately size of the deoxic zone. Biomass specific oxygen requirement was determined by a batch experiment in which mixed liquor from the 1st stage was aerated for extended period of 2.5 days to induce endogenous respiration. Oxygen uptake rate (OUR) was measured in such different samples with biomass concentrations of 31.8, 15.2 and 5.8 g VSS/L. DO concentration was increased up to saturation level and then allowed to drop below 0.7 mg/L and DO variations were recorded with time (Fig. 2a). SOUR was determined from a plot of OUR versus biomass concentration (Fig. 2b), to be 0.14 mg DO reduced/g VSS min.

The flow path of the recirculated mixed liquor between the point of withdrawal from the bulk phase of the 1st stage MBR to the point of entry in the anoxic zone (Fig. 1) can serve as a deoxic zone to bring DO from 1st stage operating concentration of 1.3 mg/L to the desired DO of 0.2 mg/L. From Eq. (3), with an average MLVSS of 23.6 g/L in the existing 1st stage and the aforementioned SOUR, the minimum deoxic residence time is around 30 s. It is noteworthy that the work of Pochana and Keller [4] indicated that the primary resistance to mass transfer of oxygen is inside the biological floc, and is governed by the floc size,

not the external mass transfer in the bulk liquid. Thus, mixing is expected to affect SOUR to the extent that it impacts floc size. In this study, the conformance of all three mixed liquor concentrations at one specific SOUR clearly suggests that the floc size may not have been strongly impacted by mixing. Furthermore, while steady state 1st stage BOD_5 is around 14 mg/L, the actual oxygen uptake rate in the 1st stage is expected to be higher than the determined endogenous SOUR. Though variations in mass transfer between the batch test determining SOUR and the anoxic reactor are conceivable, the use of SOUR in deoxic reactor size calculation adds a safety margin. The actual size of deoxic zone depends upon recirculated mixed liquor flow rate, which would determine available concentration of biomass for denitrification and ultimately size of the anoxic zone. In order to maintain high biomass concentrations in the anoxic zone, in this work mixed liquor recirculation rate of $3Q$ was employed. Using Eq. (4), at a recirculation rate of 21 L/d ($3Q$ as Q is 7 L/d), the required deoxic volume is less than 10 mL. This required volume and its criticality increases, if MLVSS concentration in the 1st stage mixed liquor decreases. Provision of this zone is essential to mitigate DO interference in the denitrification process and eliminate possibilities of oxic consumption of available readily biodegradable carbon in the influent. Due to the high concentration of MLVSS, a 3/8 in. ID \times 3 ft. long 70 mL tubing was used.

3.2.3.3. Denitrification rate, biomass specific denitrification rate and sizing of denitrification reactor. Size of the denitrification reactor i.e. required anoxic zone residence time depends upon the rate of denitrification, biomass specific rate of denitrification, and availability of denitrifying biomass. Data collected from a batch test to determine NO_3^- reduction rate during anoxic respiration using influent as a carbon source are graphically presented in Fig. 3. At the two biomass concentrations studied of 12.2 and 15.5 g/L, a higher rate of denitrification was observed in the first 10 min, i.e. 27 mg of NO_3^- reduction/min. A distinguishable drop in the reaction rate was observed after 10 min with excellent repeatability. Consuming readily biodegradable

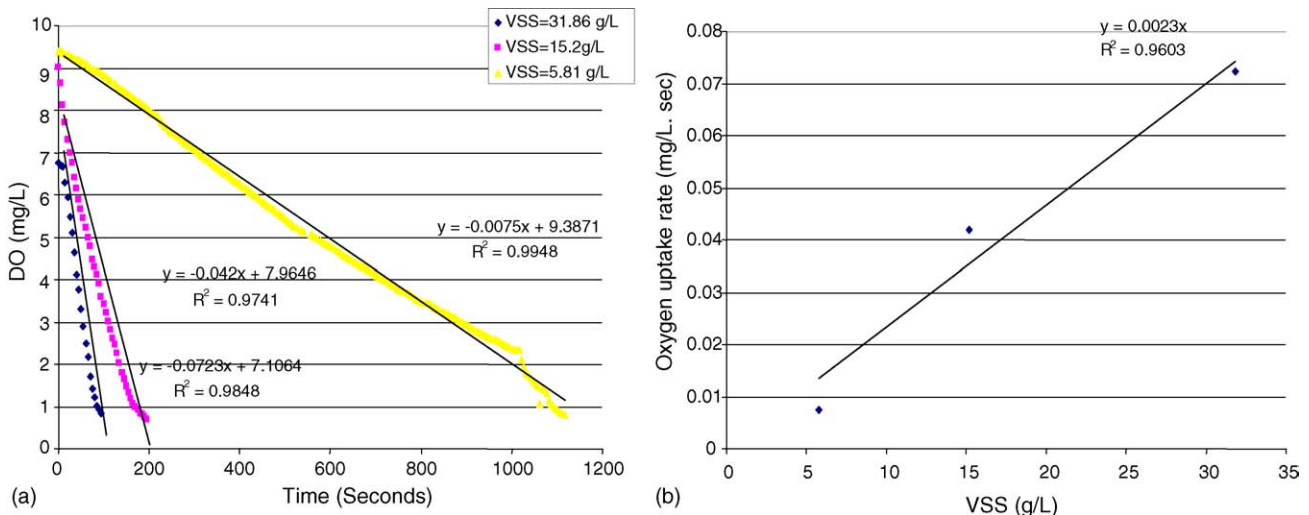


Fig. 2. (a) Oxygen uptake rate at different biomass concentration. (b) Biomass specific oxygen uptake rate.

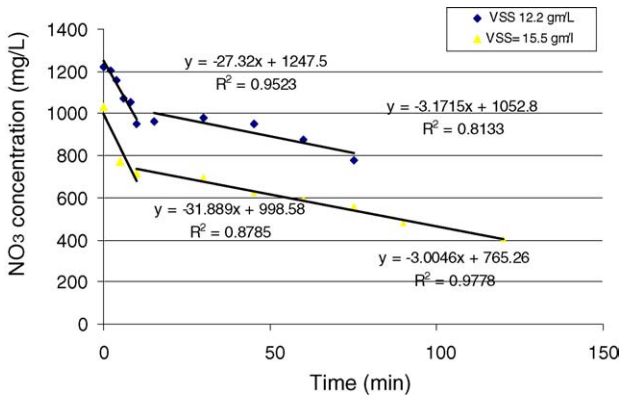


Fig. 3. Denitrification rate.

substrate, similar trends of very high denitrification rate during the first 30 min were experienced by Kujawa and Klapwijk [29]. Biomass specific denitrification rate was found to be between 2.0 and 2.2 mg NO₃-N/g VSS min or 120–144 mg NO₃-N/g VSS h, which is around two times higher than the maximum nitrate reduction rate of 50 mg NO₃-N/g VSS h observed by Glass and Silverstein [30] in denitrification of high-nitrate wastewater. This high denitrification rate was probably due to presence of abundant acetic acid in influent. Constantin and Fick [7] also attributed very biomass specific denitrification rate of 10–80 mM NO₃/g VSS h (140–1120 mg NO₃-N/g VSS h) to excess availability of acetic acid as substrate.

Denitrification reactor volume can be found using Eq. (5), where amount of NO₃ to be removed is based on final effluent NO₃ concentration requirement. Using values of *R*, *Q* and NO₃ concentration of 3, 7 L/d and 750 mg/L respectively, with an influent flow of 1.28*Q*, recycled final effluent of 3*Q* and recirculated mixed liquor of 3*Q* as discussed earlier, 1st stage MLVSS of 23.6 g/L would yield an anoxic zone MLVSS concentration of 9.7 g/L. Combining all the information the required reactor volume was calculated to be 0.140 L, which is about 0.5% of the 1st stage reactor volume of 25 L. The volume of the anoxic reactor is dictated by the quantity of denitrifying biomass, which in turn is influenced by the recirculation rate and MLVSS concentration in the 1st stage. In light of potential variability in influent

ammonia, a safety factor of three was applied to the minimum required volume of the anoxic zone, i.e. three times higher volume of anoxic zone or a coil with hold up volume of 0.46 L was provided in the 1st stage.

3.2.4. Modified system performance

The distinctive ability of the existing MBR system to operate at biomass concentration >20 g/L coupled with specific influent characteristics offered higher rate of denitrification and deoxygenation. As mentioned earlier the required size of the anoxic zone being less than 1% of 1st stage reactor volume, led to an innovative design of anoxic zone created by a coil of tube submerged in to the 1st stage mixed liquor (Fig. 1). Total flow rate handled by this anoxic zone is 7.28*Q* (51 L/d), which gives an effective anoxic residence time of 14 min or an anoxic HRT of 1.1 h, based on the raw influent wastewater flow.

The modified bench scale system was operated over a period of 38 days, which is around three turnovers of the mean SRTs in the 1st stage. Fig. 4 compares performance of the system before modification during day 0–42 with that after modification during days 43–79, with time span of three mean SRTs in each phase. Same comparison of the steady state data is presented in Table 3. As anticipated due to almost complete nitrification in the 2nd stage, recirculated final effluent did not contain any ammonia and hence it diluted ammonia concentration in the 1st stage effluent down to 308 mg/L. Quantitative data presented in Table 3 depicts achievability of denitrification in the modified system. At steady state, the non-denitrifying system generated 5.1 g NO₃/d in the final effluent, which is comparable to around 5.3 g TKN/d in the 1st stage effluent. Due to variability in the influent, the average influent TKN concentration in the modified system jumped from 1750 to 1950 g/L (not shown in the table), unproportionally the 1st stage effluent TKN increased from 5.3 to 10.3 g/d, i.e. the 1st stage TKN removal efficiency decreased from 66 to 41%. This drop in the removal efficiency is postulated to be the consequence of reduced ammonia stripping in the 1st stage, corresponding to the drop in free ammonia concentration in the 1st stage reactor. At the experimented recycle ratio of 3, the system denitrified 7.6 g/d of generated nitrates and reduced final effluent nitrates by around 74%, as predicted by

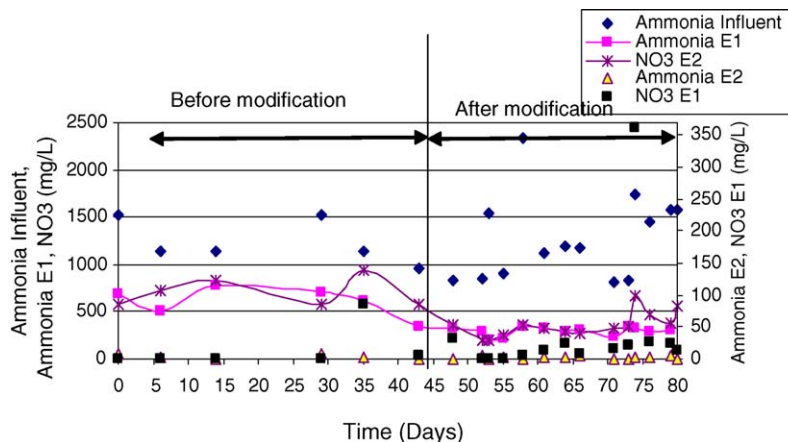


Fig. 4. Denitrification process performance.

Eq. (2). Concentration of nitrates in the final effluent, which is directly proportional to the 1st stage effluent ammonia, followed the same trend as can clearly be seen in Fig. 4. Excellent performance of the anoxic zone is apparent as it denitrified 7.6 g/d or more than 94% of the nitrates recycled ($R \times \text{NO}_3$ discharged) from the final effluent to the anoxic zone, effectively reducing total effluent nitrogen by 84%. Trends in variations in 1st stage effluent ammonia and final effluent nitrate concentrations seemed to be affected equally by variations in DAF effluent or the system influent ammonia concentration.

On day 74 due to an operational problem, recycled final effluent bypassed the anoxic zone and entered directly the 1st stage mixed liquor bulk phase. This was clearly seen to be reflected in the system performance by a rise in nitrate concentrations in the 1st stage permeate from 16 to 360 mg/L, which affected an increase in the 2nd stage effluent nitrate concentrations from 300 to 440 mg/L. This incidence empathetically proved the effectiveness of the installed anoxic zone in achieving denitrification. A similar rising trend in the final effluent nitrates can be seen in the absence of denitrification on day 80 when recirculation was stopped. Furthermore, it is apparent that this denitrifying two-stage MBR system also stabilized nitrification immensely. Though influent ammonia concentration on day 58 reached as high as 2300 mg/L i.e. around two times its average value, no rise in the final effluent ammonia was observed.

Due to the intrinsic limitation of a low oxygen transfer efficiency (less than 1%) in the bench-scale reactor with height of only 30 cm, impact of anoxic respiration on the reduction in air consumption in the 1st stage could not be measured. Around 1150 mg/L $\text{NO}_3\text{-N}$ ($3Q \times 369$ mg/L) in the final effluent or 8.1 g $\text{NO}_3\text{-N}$ /d equivalent to 890 mg $\text{NO}_3\text{-N}$ /L of wastewater treated, was denitrified. This process theoretically reduced 4980 mg/L or 25% of the influent COD with potential savings of 3.6 kg O_2 [calculated as $4980 \times (1 - 1.42Y_{\text{obs}})$] or 5.9 kWh aeration energy/ M^3 of wastewater treated corresponding to 1.6 kWh/kg of O_2 supplied [31]. The most attractive benefit of denitrification was the recovery of alkalinity, which effectively reduced external alkalinity requirements from 4.5 to 1.6 g $\text{NaHCO}_3\text{/L}$ of wastewater, translating to a 65% savings in chemical costs.

4. Summary and conclusions

Presented innovation using denitrification process, proved to be an excellent means to optimize an existing treatment system of the two stages MBR, without providing any additional reaction space and hence minimal additional construction to retrofit. Conceptualization, implementation and impacts studied in this work can be summarized as follows:

- Stable performance of the two-stage MBR, even in the presence of O&G concentrations of more than 5000 mg/L was achieved. Removing 96.6% of total COD, 99.9% of BOD_5 and 99.7% of ammonia, the system achieved stringent surface discharge criteria of TSS, BOD_5 and ammonia <10 mg/L. O&G was reduced in the 1st stage MBR to 10–15 mg/L.

- With 35% of influent COD as a readily biodegradable carbon, the system achieved high denitrification rates of 120–144 mg $\text{NO}_3\text{-N/g}$ VSS h.
- By virtue of the high denitrification rate, the modified system denitrified more than 94% of the recycled nitrates in an effective anoxic residence time of only 14 min or the system anoxic HRT of 1.1 h, based on influent wastewater flow. This eliminated the requirement for a separate denitrification reactor and associated mixing devices, thus facilitating retrofit of the existing reactor with a tubular coil occupying less than 1% of the 1st stage reactor volume.
- Implementation of the modification scheme potentially saved around 5.9 kWh on aeration/ M^3 of wastewater treated and decreased the external alkalinity requirement by 65%.
- While this study demonstrated feasibility of using an innovative pre-anoxic bioreactor, the size of the anoxic zone can further be optimized.

Acknowledgement

Financial support for this study provided by CRES Tech (CRESTech Project # WR02WST93) is gratefully appreciated.

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