Development of an unstructured nitrification-denitrification model in an industrial-scale SBR for treating the liquid wastes from a potato industry

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Abstract

The liquid wastes from potato industries have high nitrogen concentrations (50-500 mg/L). A typical biotreatment technology for such type of wastes is anaerobic digestion followed by aerobic treatment. Anaerobic digestion consumes only the incoming carbon leaving at the outlet high nitrogen amounts which are removed in two stages during the aerobic treatment. The first step requires strong oxidized conditions, so that the organic nitrogen converts to nitrate (nitrification) and the second stage requires anoxic conditions in order the nitrate to be reduced to nitrogen gas (denitrification). This two-stage procedure, typically, requires a carbon to nitrogen ratio of at least 3:1. However, in our case this ratio is lower. This study presents the results of a new nitrification-denitrification method in one stage using a Sequencing Batch Reactor in which the diluted oxygen is varied between 0 (anoxic conditions) to 2.4 (aerobic conditions). The COD inlet was 685 mg/L and the inlet nitrogen was 140 mg/L while the COD outlet was 48 mg/L and the nitrogen 17 mg/L. Moreover, an unstructured nitrification-denitrification model was developed to predict the behavior of the most important variables.

Keywords: SBR system, industrial scale study, liquid wastes from potato industry, modelling

1. Introduction

The Sequencing Batch Reactor (SBR) system is based on the method of activated sludge with the main characteristics being the semi-continuous feeding and the implementation of distinct time intervals in order to achieve the desired treatment. The unit operations involved in an SBR system are similar to those designed for the conventional activated sludge systems. In SBR systems, the successive stages of biological oxidation and precipitation are performed in the same tank. Particularly, the steps occurred in an SBR system are: the feeding of waste, the aeration step, the sedimentation step, and finally, the disposal of the supernatant liquid [Kang *et al*., 2003]. SBR technology offers several advantages over other conventional technologies of biological treatment facilities. Specifically, the cycle format of the operational phases provides the necessary flexibility and adjustability of the microorganisms, and hence, of the entire system, as the time intervals of each phase can be altered and adjusted. In this way, possible changes in treating conditions, in the characteristics of the influent and/or in the requirements of the quality of the effluent can be easily tackled. Another advantage of the SBR technology is the removal of both the COD, and total nitrogen at high levels [Kang *et al*., 2003]. Measurements that were performed on treated effluent from potato industries in Bosnia and Ireland showed a COD removal of 97.1% and 91.3% while the removal of total nitrogen ranged from 97.1% to 97.7%, respectively [Muniraj *et al*.,2013, Kupusovic *et al*.,2009].

Wastewaters from potato industries have increased nitrogen concentrations. Nitrogen in liquid wastes can be in four different forms: as organic nitrogen, as ammonia and as nitrite and nitrate. The main forms are the first two. For pH values around 7, ammonia exists almost entirely in the form of ammonium (NH_4^+). The biological processes for nitrogen removal are performed in the reactor during the aeration and the sedimentation stage. In the first one, the nitrification of nitrogen takes place where the diluted oxygen (DO) is around 0.3-4 mg/L, while the denitrification occurs in the second step where anoxic conditions (DO = 0.3-1.1 mg/L) are imposed [Ciudad *et al*.,2005]. The nitrification reaction takes place in two steps. In the first one, a group of autotrophic microorganisms oxidizes ammonia to nitrites. In the second step, nitrites are oxidized to nitrates [Rodriguez *et al*., 2011]. The stages of the biological oxidation of ammonia are the following:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

(Nitrite stage)

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

(Nitrate stage)

However, the nitrification of ammonia is not sufficient for the biological dissimilation of nitrogen. The final removal of nitrate that is produced via the nitrification is carried out through the process of denitrification. Here, we have the reduction of nitrite and nitrate to nitrogen gas with intermediate products nitric oxide and nitrous oxide.

The denitrification reaction is:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

A group of microorganisms are responsible for the above transformations. They use nitrate as an electron acceptor instead of oxygen for respiration, where the electron donor is the organic carbon. Therefore, it becomes obvious that the denitrification process is promoted in anoxic conditions [Rodriguez *et al*., 2011]. An important factor that affects the rate of both reactions is the pH. The rate of nitrification is substantially reduced for pH values lower than 6.8, while the reaction can be ceased at very high pH values. Optimum pH value to carry out nitrification, successfully, is about 7.2. The effect of pH on the rate of denitrification is not so intense. However, the optimal range is between 7.5 and 7.8 [Wu *et al*., 2007]. In this study, the aerobic biological treatment in an industrial scale SBR waste treatment facility was monitored. Moreover, according to the obtained results, an unstructured nitrification-denitrification model was developed.

2. Materials and Methods

2.1 Description of the SBR system

The monitoring of the biological treatment was performed in the facilities of the potato industry TASTYFOODS.SA, in Agios Stefanos, in the region of Attikis. The biological treatment system is based on the combination of an anaerobic and an aerobic reactor that operate in series. The liquid wastes from the plant, after a pretreatment step for removing the solids, are fed into an anaerobic UASB reactor. Subsequently, the effluent of the UASB is fed into the SBR that follows. The working volume of the reactor is approximately 950 m^3 and the inflow of the waste is 9-12 m^3/h. A complete cycle of the SBR is 8 h. During a cycle, the following operations are occurred: the feeding of the SBR (30 minutes), the aeration period (240 minutes), the stirring of the waste in anoxic conditions (30 minutes), the sedimentation of the sludge (120 minutes), and finally, the decanting of the supernatant (60 minutes). The controlling parameter for the aeration time is the dissolved oxygen (DO). Aeration is completed when the value of DO reaches 2.5 mg/L. If this does not occur, then there is a maximum limitation of 240 minutes. The monitoring of the biological treatment facility lasted for 14 individual cycles.

2.2 Analytical methods

During each cycle, the DO values, pH and Redox Potential (ORP) were recorded continuously. Samples were taken every half hour for further analysis. The soluble chemical oxygen demand (sCOD), ammonia (NH_3-N), nitrate, total suspended solids (TSS), volatile suspended solids (VSS) and volatile solids as percentage of total solids (%VS) were measured. Also, in the inlet and outlet of the reactor, pH, TSS, VSS, sCOD, Total Kjeldahl Nitrogen (TKN) and concentrations of NH_3-N and NO_3^-N were analysed. Analyses were performed according to standard analysis methods [APHA, 1998].

2.3 Development of an unstructured model

An unstructured model so as to predict the behavior of the most important variables during the cycle of SBR was developed. The model was based on the most important biochemical reactions that take place during the SBR cycle. In Figure 1, the two different bioroutes (route 1 and route 2) of the consumption of TOC are illustrated together with the bioconversion of TKN to N_2. Route 1 requires oxygen while route 2 is activated in anoxic conditions.
There are three groups of different microorganisms that are involved in the three bioroutes of Figure 1.

$$\frac{dX1}{dt} = Y_c \cdot \frac{d(TOC)_1}{dt} - X1 * k_{dc} \quad \text{Eq.1}$$

$$\frac{dX2}{dt} = Y_{cd} \cdot \frac{d(TOC)_2}{dt} - X2 * k_{dc} \quad \text{Eq.2}$$

$$\frac{dX3}{dt} = Y_n \cdot \frac{d(N-NH_4)}{dt} - X3 * k_{dn} \quad \text{Eq.3}$$

Where, X1, X2 and X3 are the three different biomass groups, Y_c, Y_{cd} and Y_n are the yield coefficients of X1, X2 and X3 while k_{dc}, and k_{dn} are the decay rates of the three reactions. The hydrolysis of the Total Kjeldahl Nitrogen (TKN), the oxidation of ammonia (NH_3-N) and the nitrates (NO_3-N) reduction are simulated by using Eq.4, Eq.5 and Eq.6, respectively.

$$\frac{d(TKN)}{dt} = -k_h \cdot (X1 + X2) \cdot TKN_t \quad \text{Eq.4}$$

$$\frac{d(N-NH_4)}{dt} = -\frac{k_{mn} \cdot X3 \cdot (N-NH_4)_t}{K_{Sn} + (N-NH_4)_t} \cdot \frac{DO}{DO + K_{DOn}} \cdot \frac{(ALK)}{K_{SALK} + (ALK)} \cdot (-2{,}2 + 0{,}395 \cdot pH) \quad \text{Eq.5}$$

$$\frac{d(N-NO_3)}{dt} = -\frac{k_{md} \cdot (X1+X2) \cdot (N-NO_3)_t}{K_{Sd} + (N-NO_3)_t} \cdot \frac{K_{DOd}}{DO + K_{DOd}} \quad \text{Eq.6}$$

Where: k_h is the hydrolysis coefficient, k_{mn} is the maximum ammonia oxidation rate for heterotrophics, k_{sn} is the half coefficient for autotrophics, k_{DOn} is the oxygen half coefficient for nitrification autotrophics, k_{DOd} is the oxygen half coefficient for denitrification heterotrophics, k_{md} is the denitrification rate coefficient, k_{sd} is the half coefficient for denitrification heterotrophic bacteria, DO is the diluted oxygen in the tank, ALK is the alkalinity of the effluent and K_{sALK} is the alkaline half coefficient for the nitrification autotrophics The biodegradation of TOC is described by using Eq.7 and 8. Eq.7 is based on route 1, while Eq.8 is based on route 2.

$$\frac{d(TOC)_1}{dt} = -\frac{k_{mc} \cdot X1 \cdot TOC_t}{K_{Sc} + TOC_t} \cdot \frac{DO}{DO + K_{DOc1}} \quad \text{Eq.7}$$

$$\frac{d(TOC)_2}{dt} = -\frac{k_{mc} \cdot X2 \cdot TOC_t}{K_{Sc} + TOC_t} \cdot \frac{K_{DOn}}{DO + K_{DOc2}} \cdot \frac{(N-NO_3)}{K_{Sd} + (N-NO_3)} \quad \text{Eq.8}$$

Finally, the degradation of the alkalinity is simulated by using Eq.9:

$$\frac{d(ALK)}{dt} = -7{,}14 \cdot \frac{d(N-NH_4)}{dt} + 3{,}57 \cdot \frac{d(N-NO_3)}{dt} \quad \text{Eq.9}$$

3. Results

Table 1 shows the average experimental values of the most important variables at the inlet and outlet of the SBR while Table 2 shows the average experimental values for each

operational phase of the SBR. The pH inlet has a typical value of a liquid effluent coming out from a UASB digester. The pH is then stabilized at 7.7-7.8, as a result of the nitrification bacteria action. The rapid increase in TSS after initiation of aeration is the result of mixing the feeding with the aerobic sludge while during the precipitation stage TSS are reduced to zero. Regarding the carbon assimilation (C), it seems that the COD inlet is easily degradable, and hence, its removal remains at high percentages throughout the SBR cycle (>92%). Similar behavior is noticed on the assimilation of nitrogen (N), as the % removal of TKN reached 88%.

The SBR accomplishes conversion of organic nitrogen and ammonia to nitrogen gas through the conversion of ammonia to nitrites and then reduction of nitrites to nitrogen gas, by passing the oxidation of nitrite to nitrate. The phenomenon of nitrification-denitrification via reduction of nitrites to nitrogen gas is a strategy that has been followed in various reports [Wu *et al*.,2007, Pambrun *et al*.,2008, Dobbeleers *et al*., 2016]. The ORP values remain in negative levels through the entire cycle, which also indicates the prevalence of the reducing conditions.

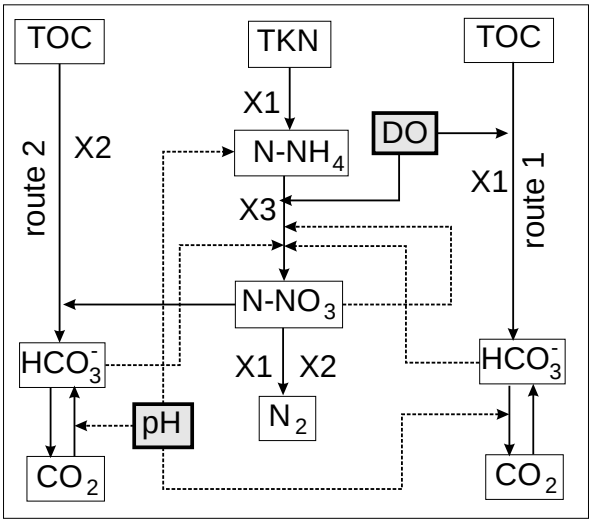

Figure 1 The different bioroutes for assimilating TOC and TKN in the examined SBR system

Table 1 Characteristics of the waste from the inlet and outlet of the SBR

	pH	**TSS (mg/L)**	**VSS (mg/L)**	**sCOD (mg/L)**	**TKN (mg/L)**	**NH_3-N (mg/L)**	**NO_3^- (mg/L)**
Inlet	7.58	2550	1060	685	140	11.8	4.4
Outlet	7.59			48	16.7	3.1	5.4
% Removal				93	88.1		

Table 2 Experimental results from monitoring the SBR system from the different operational phases

Operational Phase	**Time (min)**	**TSS (mg/L)**	**VSS (mg/L)**	**% VS**	**NO_3^- (mg/L)**	**NH_3-N (mg/L)**	**pH**	**DO (mg/L)**	**ORP**	**% Removal sCOD (mg/L)**
Start of aeration + Feeding	0	12823 (±1103)	8204 (±783)	64.2 (±5)	2.72 (±1.26)	13.97 (±2.86)	7.7 (±0.08)	0.9 (±0.29)	-91.2 (±82.5)	88.6 (±1.6)
Aeration	30	13948 (±889)	8819 (±547)	63.3 (±1)	2.56 (±1.2)	15.15 (±4.59)	7.77 (±0.07)	1.2 (±0.31)	-85.3 (±83)	89.4 (±1,1)
	60	13179 (±1290)	8260 (±989)	58.6 (±3)	2.16 (±0.77)	16.50 (±3.99)	7.79 (±0.07)	1.2 (±0.27)	-104.1 (±78.6)	90.0 (±1)
	90	13490 (±709)	8720 (±395)	64,9 (±1)	2.51 (±0.82)	14.45 (±2.64)	7.79 (±0.07)	0.9 (±0.24)	-130.7 (±91.8)	91.6 (±0.8)
	120	13975 (±666)	8698 (±598)	61.1 (±2)	2.57 (±1)	12.30 (±2.41)	7.81 (±0.07)	1.1 (±0.26)	-120.4 (±92.6)	90.9 (±0.8)

Operational Phase	Time (min)	TSS (mg/L)	VSS (mg/L)	% VS	NO_3^- (mg/L)	NH_3-N (mg/L)	pH	DO (mg/L)	ORP	% Removal sCOD (mg/L)
	150	14309 (±600)	9720 (±858)	65.6 (±3)	2.30 (±0.56)	8.54 (±1.26)	7.82 (±0.09)	1.2 (±0.22)	-79.0 (±102)	91.9 (±0.7)
	180	12245 (±1274)	7455 (±789)	63.6 (±5)	3.64 (±1.72)	9.19 (±1.59)	7.8 (±0.09)	1.6 (±0.35)	-57.1 (±103)	91.9 (±0.5)
	210	12714 (±493)	8216 (±894)	64.3 (±6)	2.18 (±0.39)	6.77 (±1.03)	7.78 (±0.08)	1.6 (±0.3)	-39.8 (±107)	91.0 (±0.6)
Start of the Mixer	240	11950 (±888)	7614 (±685)	63.8 (±5)	2.30 (±0.39)	6.88 (±0.84)	7.79 (±0.09)	1.6 (±0.33)	-33.3 (±109)	91.7 (±0.8)
	270	10560 (±1485)	7973 (±454)	63.2 (±1)	1.97 (±0.25)	8.15 (±1.67)	7.82 (±0.09)	2.1 (±0.29)	-22.1 (±90.2)	90.9 (±0.7)
	300	9403 (±1782)	5906 (±932)	54.8 (±5)	3.45 (±1.09)	5.53 (±0.88)	7.76 (±0.08)	1.8 (±0.47)	-39.4 (±88.9)	91.1 (±0.9)
Precipitation	330	6489 (±1469)	4242 (±948)	65.1 (±9)	3.96 (±0.96)	6.28 (±0.86)	7.75 (±0.08)	0.7 (±0.26)	-43.2 (±88.5)	89.9 (±1)
	360	9750 (±3082)	6011 (±937)	61.5 (±1)	4.05 (±0.82)	6.69 (±0.95)	7.73 (±0.12)	0.1 (±0.05)	-46.8 (±96.5)	91.9 (±0.7)
	390				4.82 (±0.99)	6.10 (±0.72)	7.7 (±0.14)	0 (±0)	-100.5 (±80.6)	90.6 (±1.3)
Disposal	420				3.24 (±1.07)	5.36 (±1.56)	7.7 (±0.21)	0 (±0)	-282.3 (±33.9)	91.1 (±1.7)

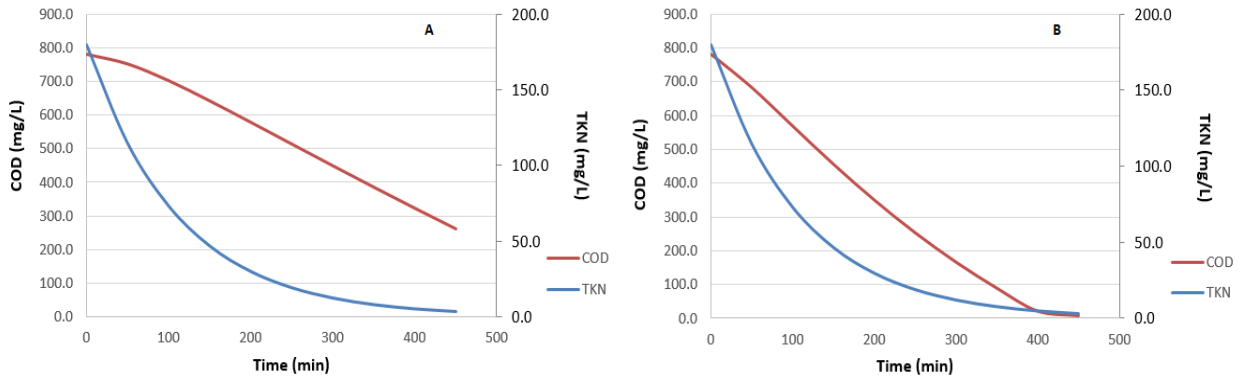

Figure 2 Consumption of COD and TKN for different DO values; Fig2A DO=0.1 mg/L; Fig2B DO=0.5 mg/L

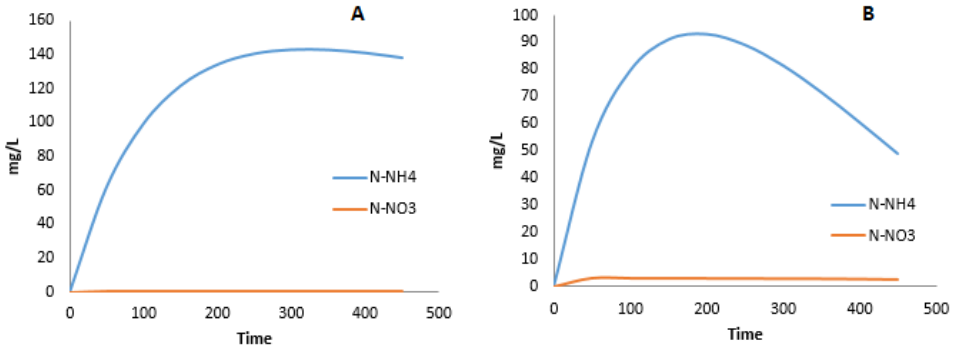

Figure 3 Concentration of N-NH_4 and N-NO_3 for different DO values; Fig3A DO=0.1 mg/L; Fig3B DO=0.5 mg/L

In Figure 2, modelling results of the assimilation of COD and TKN are demonstrated for different DO values. In Figure 2A, the DO value is 0.1 mg/L while in Figure 2B, the DO value is 0.5 mg/L. Although, the COD, in both cases, is almost completely consumed, the TKN is completely consumed only in the second case. In Figure 3,

modelling results of the fluctuations of N-NH4 and N-NO3 concentrations for different DO values (0.1 and 0.5 mg/l) are shown. It becomes obvious that for DO concentrations between 0.1 and 0.5 mg/L, when the initial concentration of TKN is high, the nitrification-denitrification process is promoted simultaneously (i.e. from both bioroutes) at anoxic conditions.

4. Conclusions

In this study, the monitoring of an industrial scale SBR system involving, nitrification-denitrification processes in one stage, was carried out. The feeding of the reactor was performed by using pretreated liquid wastes from a potato industry. The waste has been pretreated previously with an UASB reactor, and hence, it contains a low organic load and high values of nitrogen. It was found that both the carbon and the nitrogen were assimilated succesfully in the SBR, 93% and 88%, respecively. The carbon assimilation is accomplished through the reduction step rather than the oxidation step. Moreover, the development of an unsturctured model was used to simulate the DO effect on the TKN consumption.

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