The potential of denitrification for the stabilization of activated sludge Processes affected by low alkalinity problems

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ABSTRACT

In this study, the problems provoked by nitrification of wastewater with low alkalinity were analyzed in a pilot sequencing batch activated sludge reactor (SBR). Decrease in pH resulted in disappearence of protozoa. Deflocculation of the activated sludge floc started below pH 6.5, resulting in enhanced effluent turbidity and loss of bacteria. Nitrification efficiency was affected below pH 6.2. The denitrification activity was not sufficient to keep up the pH, due to a low C/N ratio of the wastewater. was developed. Based on alkalinity and ammonia concentration of the wastewater and the necessary denitrification rate to prevent operational problems, was developed a prognostic diagram. The applicability of this diagram was tested for the SBR with excellent results. The diagram could be applied to optimize the operation of wastewater treatment plants affected by problems with low alkalinity wastewater.

Key words: Alkalinity, activated sludge, nitrification, denitrification

INTRODUCTION

Brazilian environmental legislation contemplates an ammonium reduction down to 20 mg NH_4-N/L (CONAMA, 2005). To fulfill this requirement, only the nitrification of wastewater is necessary. The nitrification is the oxidation of ammonia to nitrate but ammonia has more harmful effects on natural water systems than nitrate. The activated sludge system is the most used treatment among the available systems to achieve nitrification, To guarantee nitrification, activated sludge systems need relatively large volumes and a sufficient aeration, due to the low growth rate of the nitrifying bacteria, and their high sensitivity against alterations of pH, lack of oxygen, high organic loads and toxic substances and low temperatures (Nitrogen Control, 1993).

An important aspect in nitrification in Brazil is the formation of acid as a side product of the nitrification, a fact, that normally does not call much attention because in many cases wastewater is characterized by a sufficient alkalinity to keep the pH above of 7.2, a value registered as sufficient for nitrification (Von Sperling, 1997). But Brazilian wastewater, as the drinking water too, many times has low alkalinity. According to the definition (ATV-Manual, 1997), an alkalinity below $1_{\cdot}, 5$ mmol $HCO₃/L$ or 75 mg CaCO₃ mmol /L in the effluent is the limit in order to avoid operational problems in the treatment process, as deflocculation or destruction of activated sludge flocs. The pH can be stabilized with a continuous addition of carbonate (lime). A more economic solution would be the stabilization of the process through the use of denitrification. The denitrification process has the capacity to recuperate half of the lost alkalinity in result of nitrification (ATV-Manual, 1997; Von Sperling, 1997).

Although denitrification is not demanded by the Brazilian legislation (CONAMA, 2005), it is absolutely recommendable for all activated sludge systems, because of its economic and operational advantages, such as: lower production of excess sludge, less energy for the aeration, better settling of the sludge and besides of all facts, denitrification can be integrated easily in the activated sludge process, especially in the SBR-Process (ATV-Manual, 1997, Nitrogen Control, 1993). The denitrification capacity of wastewater treatment is always limited by two factors. The first limitation is the C (COD): N (TKN) ratio of the wastewater. A relation of 10 C to 1 N is considered sufficient for a full denitrification (ATV-Manual, 1997). On the other hand, a 100% denitrification is not possible, due to the configuration of activated sludge systems, which is the second limitation. The only way to achieve a 100 % denitrification is a post-denitrification using an artificial carbon source. The most common configuration without carbon source is the pre-denitrification, where the efficiency of denitrification depends on the volume of return sludge flow:

 $\eta_{DN} = V_{SR+RC} / (V_{SR+RC} + 1)$ (1)

where : V_{SR+RC} = Volume of sludge return and sludge recirculation flow (ATV-Manual, 1997).

Another possibility is the cascade denitrification where the efficiency of denitrification depends on the number of cascades.

 $\eta_{\text{DN}} = 1 - (1/(\eta_{\text{C}} (1 + V_{\text{SR}})),$ (2) where n_C = number of cascades V_{SR} = Volume of sludge return flow

The alkalinity depends on the relation between bicarbonate and carbonic gas and it is determined by the amount of HCl necessary to adjust 1 liter of water to a pH of 4.3. Depending on the type of carbonate, there are different parameters with different dimensions, as shown in Table 1.

Table 1: Equivalent parameters of alkalinity: Ks (ATV Manual 1997)

The alkalinity of wastewater results directly of the alkalinity of the drinking water. The ammonification (or TKN hydrolysis) increases the alkalinity of the wastewater:

 $NTK + H_2O \rightarrow NH_4^+ + OH^-$ (3)

Von Sperling (1998) mentioned the alkalinity of raw wastewater in Brazil with 110-170 mg CaCO₃/L, (or $2.2 - 3.4$ mmol HCO₃-/L). This is, for example, half of the alkalinity of common wastewater in Germany (ATV manual, 1997). The nitrification process consumes alkalinity, the nitrification of 1 mol NH_4-N produces exactly 2 mol of H^{\dagger} :

 $NH_4^+ + 2O_2 \rightarrow NO_3 + H_2O + 2H^+$ (4)

The bicarbonate/carbonic gas system reacts in the form:

$$
2 H^{+} + 2 HCO_{3} \rightarrow 2 H_{2}O + 2 CO_{2} (5)
$$

By this 1 mol NH_4^+ (14 mg NH₄-N/L) uses 2 mol $HCO₃$ (or 122 mg $HCO₃$ -/L, or 100 mg CaCO₃/L,), what means that 1 mg NH_4-N/L consumes 0.14 mmol $HCO₃/L$ (7.14 mg) $CaCO₃/L$). As the hydrolysis of the TKN, the denitrification process also increases the alkalinity (adapted of the ATV Manual, 1997):

$$
NO_3^- + H^+ \blacktriangleright 0.5 N_2 + 0.5 H_2O + 2.5 (O)
$$
 (6)

That means that the denitrification of 1 mol Nitrate recuperated 1 mol HCO₃' (or 0.07 mmol $HCO₃/L$ or 3.57 mg CaCO₃/L for 1 mg NO₃-N/L) accurately the half of what was used for the Nitrate production.

It can be concluded that the final alkalinity after the biological process in a nitrifying reactor depends on the natural alkalinity (Ks) and the Ammonia concentration (NH_4-N_0) of the wastewater. The difference between the Ammonium concentration of the wastewater (NH_4-N_0) and the treated effluent (NH_4-N_0) is the resulting Nitrate concentration (NO_3-N_e) . Considering these facts the calculation for the alkalinity in the effluent (Ks_{n}) follows the equation (Manual ATV 1997):

$$
Ks_e = Ks_o - 0.07 (NH_4-N_o - NH_4-N_e + NO_3-N_e)
$$

mmol HCO₃⁷/L (7)

$$
Ks_e = Ks_o - 3.57 (NH_4-N_o - NH_4-N_e + NO_3-N_e)
$$

mg CaCO₃/L (8)

The concentration of $NH₄-N$ which is oxidized to NO_3-N and not reduced (denitrification) has to be considered twice (because 2 mol $H⁺$ are produced), while the concentration of NH4-N. which is oxidized and reduced to N_2 gas has to be considered only once (because 1mol H^+ is recuperated). This correlation was used for the evaluation of the alkalinity in system RSB.

The objective of this work was to analyze the potential of denitrification on the stabilization of the activated sludge process operating with wastewater with low alkalinity.

MATERIALS AND METHODS

SBR pilot reactor and integration of denitrification

A pilot SBR with volume of 1.3 m^3 was situated in the campus of the University (UFSC, Universidade Federal de Santa Catarina). It was operated with wastewater colleted from a public sewer. The wastewater was pretreated in a septic tank with a retention time of 2-3 days. The SBR worked in three cycles a day, each cycle of 8 h, receiving 400L wastewater (1,200 L per day). The operation of a full cycle (charge, aeration, settling and discharge) was totally automatic and in order to reach a efficient denitrification, the charge and aeration was divided in four steps (repeating the charge and aeration four times). Modeled on the well known cascade denitrification process, this SBR filling strategy was called "cascade filling". In order to obtain a total denitrification of resistant nitrate of the sludge (Figure 1) the first charge of the cycle was larger than the three following (1 x 250 L and 3 x 50 L).

Figure 1: One cycle (8 h) of the pilot SBR, working with the idea of cascade filling in four steps

In order to determine a correlation of alkalinity and denitrification efficiency the following analyses program was carried out:

 Three times per week parameters of influent and effluent: Alkalinity, COD and SS according to the Standard Methods of Water Examinations (1998); NH₄-N, NO₃-N, NO₂-N, PO4-P with colorimetric method (kit of Merck) Once a week a cycle of 8 h was analyzed, with control of pH , O_2 and temperature and sampling at the end of the anoxic and aerobic phases (sample of filtered sludge) for analyses of: COD, NH_4-N , NO₃-N, NO₂-N, and alkalinity. SVI_{30} (Sludge Volume Index)

and.microscopy analyses of the activated sludge were carried out once a week. After the first negative experiences with low pH values, for pH values below 7.0 lime was added. Approximately 50 g of lime per week were used to keep pH around 7.0.

Denitrification efficiency

According to Figure 1 in the SBR process with the principle of cascade filling, theoretically only the volume of the last filling can't be denitrified, that means a denitrification efficiency of :

$$
\eta_{DN} = 1 - ((V_{\text{feed}} / V_{\text{last step}})
$$
 (9)

where V_{feed} = Volume of total cycle filling V_{last} _{step} = Volume of last step filling

The pilot SBR with filling in four steps (350L : 50L) would have a theoretically maximum denitrification efficiency of 87.5%.

RESULTS AND DISCUSSION

Operation of the pilot SBR

Nitrification started a week after the inoculation of the pilot reactor with activated sludge. After five weeks and temperatures around 20-25°C, the nitrification process was stabilized with effluent concentrations below 1 mg NH4-N/L. Probably the relatively long stabilization time was due to the low pH and other inhibitory factors. Without limewater addition, it was observed that:

- 1 Between a pH of 6.8 6.0 the protozoa's disappeared. The last surviving organisms were amoebae (Figure 2A)
- 2 Below 6.5 the activated sludge flocs started to disintegrate (deflocculation), resulting in turbid effluent and enhanced bacterial loss
- 3 Between pH of 6.2 6.0 the nitrification was affected and an intensive growth of

fingered and amorphous zoogleal organisms was observed (Figure 2B).

4 Filamentous bacteria (Figure 2D), like type 021N and sulfur bacteria (Jenkins et al., 1993) were observed during all the operation. This organism contributed to a increasing SVI_{30} (Sludge Volume Index), which increased from 120 to 180 mL/g, indicating bulking sludge and sedimentation problems.

Figure 2: Microscopic analyses to detect floc formation problems in operation phases.

The most important objective of further investigations was the improvement of denitrification until the theoretical technical limitation of 87.5% (equation 9) to keep the pH constant without addition of lime. But the results showed that the denitrification was limited by the low COD/BOD_5 concentration (low C/N) ratio), reported also by Hoffmann et al (2004). Figure 3A shows one of the first cycle results, done at the beginning of nitrification stabilization ($4th$ week). The cycle in Figure 3B was obtained two months later, accidentally a day with high COD concentration in wastewater.

• Figure 3A shows the same nitrification velocity in all the four aerated nitrification phases. The denitrification velocity was higher in the first anoxic phase with the higher organic load (250L wastewater) and decreased in the three following anoxic phases with load of 50L wastewater. Although the denitrification seemed to have a high efficiency, nitrate concentration at the end of the cycle was higher than in the beginning. Sometimes nitrate concentration increased up to 20 mg NO_3-N/L (Table 2).

• The wastewater in Figure 3B had a higher COD/N ratio. At first high loading phase, an efficient denitrification process was observed and at subsequent following phases, the denitrification was lower, but the cycle resulted in lower nitrate concentration than at the beginning. The problem in example 3B was the nitrification. To improve the denitrification, the aeration was reduced to guarantee the total absence of oxygen during the anoxic phases, as shown in the second diagram. With uncommonly high organic load of the wastewater, this aeration was not sufficient for total nitrification the nitrification was limited by the oxygen lack.

Figure 3: Results of monitoring of 2 cycles of 8h (6 h denitrification e nitrification, 1 h sedimentation and 1 h for removing of treated wastewater**)**

Also, the alkalinity and the pH were analyzed, (Figure 3). For better visualization, the alkalinity in 3A and 3B was calculated in mmol $HCO₃$ -/L (Table 1), the more common unit in Brazil being mg $CaCO₃/L$, which was noted in the Figure.

1 In Figure 3A, the two parameters shoed high

alterations, pH and alkalinity increase clearly in the anoxic filling phase and decrease during the nitrification. As a result of the first nitrification phase, the alkalinity reduced to the recommended value for operation stability of 75 mg $CaCO₃/L$. This cycle finishesd with 20 mg $CaCO₃/L$. Alterations of this type characterized a wastewater with an insufficient natural alkalinity.

2 Figure 3B did not show these high alterations of pH and alkalinity, whereas the alkalinity of the wastewater was nearly the same. The lower nitrification activity (lower concentration of NH_4-N_0 in the wastewater as well as higher concentration of NH_4-N_e in the effluent) and the strong increase of alkalinity in the first denitrification phase resulted in a stabilization of pH and in an alkalinity value above 75 mg $CaCO₃/L$ during the whole operation cycle.

Correlation between Nitrification, Alkalinity and Denitrification

The results of all of the monitoring cycles of the pilot SBR were analyzed through the equation 9, which calculated the theoretical alkalinity after nitrification and denitrification. The objective was to compare analytical results and the theoretical values. Table 2 shows the results of the analyses and calculation during three months of operation.

Table 2: Characterization of influent and effluent wastewater of the pilot SBR and comparison of the calculated alkalinity with the real alkalinity

After the anaerobic pretreatment in the septic tank, the wastewater showed an average alkalinity of 234 mg CaCO₃/L, with a minimum of 185 mg $CaCO₃/L$ and a maximum of 275 mg $CaCO₃/L$ and a pH value of 7.0. The COD concentration in wastewater showed a variation between 253 and 673 mg COD/L, ammonia concentrations between 25.5 and 44.4 mg NH_4-N/L , resulting in an average COD : N ration of about 10:1 but it is a well known fact that not the whole COD was available for denitrification. The treated effluent showed:

- A concentration of 79 mg COD/L as non degradable COD in this process with a sludge age of 25 days.
- An almost complete nitrification was achieved. Some times the higher ammonia effluent concentrations were provoked by an insufficient aeration.
- The average denitrification efficiency was about 65%, with nitrate concentration in the treated effluent of 12.8 mg NO₃-N/L (Table 2).
- Even on days with higher denitrification rates, as the day 09/01/04 (Table 2 and Figure 3A) with 78% denitrification, a decreasing alkalinity during the cycle was observed, due to the total nitrification of the wastewater with high ammonia concentration $(44.5 \text{ mg } NH_4\text{-N})$ and low alkalinity (235 CaCO₃/L) on this day. The days with high alkalinity and low ammonia concentration, for example at days 05/03, 07/03, 11/03, 14/03, 16/03 and 18/03/04 the alkalinity in the reactor was kept above 75 mg $CaCO₃/L$, which was the limit for stable operation. In most of the days, the alkalinity of the treated wastewater was below this limit at the end of the process (Table 2).

The last column shows the result of the calculation of the value of theoretical alkalinity at the end of the process $(Ks_{\rm sc}, \text{given in equation 8})$. A good correlation between the real and theoretical value was observed, even if 5% higher values were analyzed with calculation. The reduced alkalinity in the real treatment could be explained for example by the formation of organic acids and H_2S in the septic tank. Analyses showed concentrations up to 50 mg H_2S/L in the effluent of septic tank. In one case presence of filamentous sulfur bacteria

was also noted in the activated sludge system (Figure 2 D) which oxidized sulfite (S_2) in the aerobic phase to sulfate $(SO₄²)$ (Jenkins et al. 1997). Despite this temporary problem, there were cycles with good accordance between the calculated and analyzed value of alkalinity, as on the days 21/01, 5/02, 11/02, 13/02, 20/02, 25/02, 01/03, 13/03, 14/03, 18/03, 19/03 and 20/03.

As conclusion to this result, equation 8 was used to develop a diagram that determined the necessity of denitrification, depending on the ammonia concentration and the alkalinity of wastewater with the objective to keep the alkalinity in the activated sludge and effluent above 75 mmol CaCO₃/l. It was calculated 100% nitrification (100% oxidation of ammonia-N to nitrate-N), as it was normal for dimensioning of wastewater treatment plant. Figure 4 shows the result of the calculation. The area below the line "without DN" was characterized by such an high ammonia to alkalinity ratio that did not need denitrification for alkalinity recuperation. The area above the line "100% DN" characterized the area where the correlation between ammonia concentration and alkalinity was limited and even in case of 100% denitrification the alkalinity would be reduced below 75 mg $CaCO₃/L$. However, a denitrification of 100% only could be reached with a postdenitrification by an additional carbon source. The denitrification rates between these two limits (20, 40, 60 and 80%) determined the possibility to keep the alkalinity and pH (Figure 4):

- **1 Example 1:** The wastewater in case of the investigated pilot SBR with 235 mg $CaCO₃/L$ (Table 2) would not need any denitrification until a nitrification of 22 mg NH4-N/L. The denitrification of 65% would be sufficient to neutralize the acid, produced as a result of nitrification of 32 mg NH_4-N in the influent wastewater.
- **2 Example 2:** In reality the pilot plant had to nitrify on average **37.4 mg NH4-N /L**, (Table

2) this would need about 80% denitrification with the given alkalinity of 235 $CaCO₃/L$ (example 1). With the realized denitrification of 65%, an alkalinity of approximately 260 $CaCO₃/L$ would be necessary to stabilize the operation.

3 Example 3: According Von Sperling (1997),

an alkalinity of 170 mg $CaCO₃/L$ is normal in the Brazilian wastewater. Corresponding to the calculation, a nitrification of only 20 mg NH4-N/L, for example, would require a 60% denitrification to stabilize the pH. With concentrations above 30 mg NH4-N/L, no denitrification could prevent the necessity of lime water to stabilize the operation.

Figure 4: Prognostic diagram for the denitrification necessity, resulting of the necessity to keep the alkalinity in the rector above of 75 mg $CaCO₃/L$.

CONCLUSION

The results obtained with an activated sludge of a pilot SBR showed that decreasing values of pH, provoked by acid formation during the nitrification have negative effects of process stability, destruction of activated sludge flocs was observed and the loss of active biomass. Alkalinity of more than 75 mg $CaCO₃/L$ could prevent the rise of pH during the operation. The wastewater with the average alkalinity of 234 mg $CaCO₃/L$ and ammonium concentration of 37 mg NH4-N/L did not have a sufficient natural alkalinity to keep up the pH during the nitrification process. The presented diagram showed that a constant

denitrification of at least 80% would be necessary to keep up the pH. This would be the absolute maximum for a denitrification without external carbon sources. In the pilot SBR with the principle of cascade filling in three steps, a denitrification of 87% was calculated as theoretically possible, but with the given wastewater only a denitrification of 65% was realized, due to the relatively low C:N ratio. The monitoring of the different cycles showed clearly an influence of the concentration of COD/BOD_5 in the wastewater. Due to the pretreatment in a septic tank the concentration of COD/BOD_5 was relatively low and the H₂S, formed in the anaerobic pretreatment process,

influenced the alkalinity. It could be very likely that operational problems caused by the low pH and the low alkalinity periodically happened in most of aerobic treatment plants in Brazil, which always would result in a low efficiency of the biological process. The pH could be increased for example by lime or lime water addition, but the most economic solution consisted in the controlled improvement of denitrification, a process which could recovery 50% of the lost alkalinity by nitrification. The experiences with the pilot reactor proved that the denitrification increased the pH significantly and hence, it was a secure way to prevent operational problems. It could save energy and produce lower sludge excess volume in activated sludge systems.

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RESUMO

Os problemas provocados pela nitrificação no esgoto com baixa alcalinidade foram analisados num reator piloto do tipo lodo ativado seqüencial por batelada (RSB), alimentado por esgoto urbano. A diminuição do pH se mostrou em três níveis: Com pH de 6,8 - 6,0 os protozoários, responsáveis para a filtração da fase liquida, desaparecerem; os flocos de lodo ativado começaram a se destruir abaixo pH 6,5 resultando em elevação da turbidez no efluente final e abaixo de pH 6,2-6,0 a nitrificação foi afetada. A influência da desnitrificação para manter o pH foi analisada.

Devido a baixa relação C:N no esgoto pré-tratado, a desnitrificação não se mostrou suficiente para manter o pH estável. Este trabalho apresenta o cálculo da alcalinidade que considera a influência da nitrificação e desnitrificação, de acordo com os resultados obtidos no RSB. Baseado nesse cálculo, foi desenvolvida uma recomendação na forma gráfica para usar em ETE´s afetadas por baixa alcalinidade.

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