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## Evaluation of nitrite accumulation in biological treatment systems, aiming at shortcut denitrification

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**ABSTRACT.** Biological treatment of landfill leachate faces some difficulties by influence of some physical and chemical characteristics of this sort of effluent, which usually presents high levels of nitrogen – mainly ammonia nitrogen. High concentrations of ammonia nitrogen restrain biodegradation, requiring the nitrogen removal along with landfill leachate treatment in these cases. This work evaluated the nitrite formation in a pilot-scale biological treatment system applied to landfill leachate, aiming at posterior nitrogen removal by shortcut denitrification. Two pilot-scale units (250 L aeration tanks) were monitored simultaneously for 100 days. HRT in both cases was 5 days. Leachate applied on this experimental device was collected in a solid waste landfill in the city of Londrina, Paraná State. That landfill is active since 1972. In the operational conditions observed during this experiment, most of nitrogen removal occurred by ammonia volatilization. Anyway, nitrite formation was obtained in the pilot-scale units and nitrate remained at low levels.

**Keywords:** nitrogen removal, leachate, sanitary landfill.

## Avaliação do acúmulo de nitritos em sistemas de tratamento biológico, visando à desnitrificação de via curta

**RESUMO.** O tratamento de lixiviados de aterro sanitário por processos biológicos enfrenta algumas limitações em função das características físico-químicas deste tipo de efluente, que comumente apresenta elevadas concentrações de nitrogênio – principalmente na forma amoniacal. A presença de N-amoniacal em altas concentrações limita a biodegradação, fazendo necessária a remoção deste nutriente de forma integrada ao tratamento de lixiviados de aterro nestes casos. O presente trabalho buscou avaliar a formação de nitritos em um sistema de tratamento biológico de lixiviados de aterro sanitário em escala piloto, visando posterior remoção complementar dos nitritos pela desnitrificação de via curta. Foram monitoradas duas unidades de tratamento (tanques de aeração de 250 L cada) simultaneamente durante um período de 100 dias. O TDH em ambos os tanques de aeração era de cinco dias. O lixiviado utilizado no experimento foi coletado no Aterro Controlado de Londrina, Estado do Paraná, que está em operação desde a década de 1970. Os resultados mostram que, nas condições operacionais experimentadas neste estudo, a remoção de nitrogênio por volatilização da amônia livre prevaleceu sobre as reações de oxidação nos tanques de aeração. Apesar disso, o sistema mostrou boas possibilidades para posterior desnitrificação de via curta pela formação de nitritos maior que de nitratos.

**Palavras-chave:** remoção de nitrogênio, lixiviado, aterro sanitário.

### Introduction

One of the major environmental problems associated with landfills is the leachate generation, which is the effluent derived from percolation of liquid through the grounded mass of waste. Usually this liquid is called leachate or landfill leachate.

Physical and chemical characteristics of the landfill leachate are determined by a combination of several factors such as rainfall index, characteristics of the waste grounded and landfill age (FERNANDES, 2006). Therefore, it is not

always easy to point a technique as the most adequate for the treatment of this type of effluent.

Nevertheless, it is commonly observed in Brazilian landfills the use of biological processes for the leachate treatment.

The use of biological processes to treat landfill leachate, in general, is not enough to remove properly the pollutants. The leachates from landfills commonly feature high concentrations of nitrogen and organic matter. The nitrogen, in ammonia form, above certain

concentrations and as a function of pH can reduce or inhibit completely the biological activity.

Moreover, in the case of leachates of older landfills, the organic matter tends to be difficult to degradation, making necessary the use of a complementary system of treatment.

According to Li and Zhao (1999), when the concentrations of ammonia nitrogen increased from 50 to 800 mg N-NH<sub>3</sub> L<sup>-1</sup>, the COD removal rate raised from 97.7 to 78.1%.

Thus the nitrogen removal should be considered when selecting systems for leachate treatments, since the limitation or inhibition of the degradation by the presence of this component at high concentrations can preclude the biological treatment.

The removal of nitrogen can be performed by means of physical and chemical or biological processes. The definition of the type of treatment to be employed should be subject of specific research, and depends on the goals to be achieved with the treatment system.

As previously discussed, the biological treatment of leachates from landfills can undergo severe limitations due to high concentrations of ammonia nitrogen that this type of effluent usually can present.

Following this reasoning, the physical and chemical processes of removing nitrogen become interesting since permit to reduce the concentrations of ammonia nitrogen to levels that allow the subsequent biological treatment of the effluent.

However it should be considered that physical and chemical processes often generate by-products harmful to the environment. As for example, the ammonia stripping process that releases NH<sub>3</sub> gas.

The ammonia stripping is a process of removal of ammonia gas (NH<sub>3</sub>) in solution in a given effluent, in which the gas is transferred by desorption of the liquid phase to a gaseous phase (LEITE et al., 2009). The biological removal of nitrogen is performed by complete or partial oxidation, followed by a anoxic stage to remove nitrate (denitrification) or nitrite (shortcut denitrification).

In the removal by biological processes, the nitrogen is removed in its molecular form (N<sub>2</sub>), which is easily released into atmosphere (MADIGAN et al., 1997). As there is already a great portion of this gas in the atmosphere, the emission of N<sub>2</sub> caused by this type of process is not a risk to the environment.

The shortcut denitrification features some advantages in relation to the conventional

nitrification/denitrification. The lower demand for aeration during the formation of nitrite and the lower consumption of CDO along the denitrification reflect in lower operating costs in this type of process (SCHMIDT et al., 2003).

In order to accomplish the shortcut denitrification it is necessary to create conditions in the treatment system to limit the activity of bacteria that oxidize the nitrite, preventing the oxidation of nitrite to nitrate, obtaining the desirable accumulation of nitrite.

Yoo et al. (1999) relate the accumulation of nitrite with some factors, such as:

Free ammonia (NH<sub>3</sub>): non-ionized ammonia above certain concentrations inhibits both *Nitrosomonas* and *Nitrobacter* bacteria, but the latter are more sensitive to the presence of free ammonia. Therefore, in some concentrations, the presence of free ammonia favors the accumulation of nitrite.

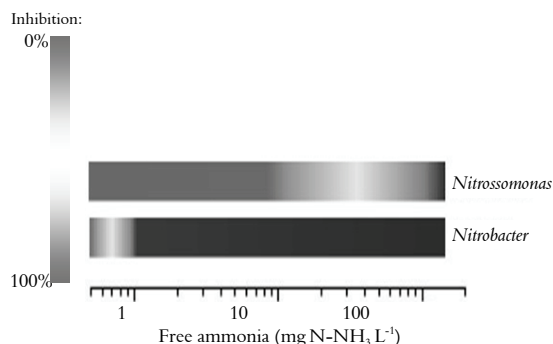
Temperature: studies have shown that *Nitrobacter* bacteria have higher activity at temperatures between 10 and 20°C. In temperatures between 25 and 28°C, the growth rate of ammonia-oxidizing bacteria is higher among the nitrite-oxidizing ones.

Dissolved Oxygen (DO) Concentration (DO) during the nitrification: nitrate ions (NO<sub>3</sub><sup>-</sup>) have one more oxygen molecule than nitrite ions (NO<sub>2</sub><sup>-</sup>). By limiting the concentration of DO, the oxygen is not enough to form nitrate ions.

According to Ruiz et al. (2003) and Ciudad et al. (2005), in a biological treatment system, it is possible to get accumulation of nitrites by maintaining the concentrations of dissolved oxygen around 1.4 mg O<sub>2</sub> L<sup>-1</sup>.

Henze et al. (1997) assert that ammonia concentrations can limit partial or totally the activity of the bacteria *Nitrosomonas* and *Nitrobacter*. The first are partially inhibited by concentrations of free ammonia from 0.1 mg N-NH<sub>3</sub> L<sup>-1</sup>, with total inhibition at 1 mg N-NH<sub>3</sub> L<sup>-1</sup>; *Nitrobacter*, in turn, are inhibited from 10 mg N-NH<sub>3</sub> L<sup>-1</sup>, with total inhibition at 150 mg N-NH<sub>3</sub> L<sup>-1</sup>, as shown in Figure 1.

In this way, a concentration range of free ammonia between 1 and 10 mg N-NH<sub>3</sub> L<sup>-1</sup> is needed to accumulation of nitrite. As one can see in Figure 1, in this range of values, the inhibition of ammonia-oxidizing bacteria is null, whereas the inhibition of nitrite-oxidizing ones is total.



**Figure 1.** Inhibition of the bacteria *Nitrosomonas* and *Nitrobacter* as a function of the free ammonia concentration – modified from Henze et al. (1997).

According to Bae et al. (2002), the optimal conditions for nitrite accumulation are: pH equal to 8, DO around 1.5 mg O<sub>2</sub> L<sup>-1</sup>, and temperature around 30°C.

As observed in Equation 1, the temperature and pH are crucial to the balance between the forms of ammonia nitrogen (free ammonia - NH<sub>3</sub> and ammonium ion - NH<sub>4</sub><sup>+</sup>). Therefore, the pH and the temperature are decisive for obtaining accumulation of nitrite, once they interfere directly on the concentration of free ammonia in the effluent to be treated.

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + 10^{pKa - pH}} \quad (1)$$

where:

[NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>] = concentration of ammonia nitrogen

K<sub>a</sub> = maximum ionization constant for ammonia

pK<sub>a</sub> = 4×10<sup>-8</sup>×t<sup>3</sup> + 5×10<sup>-5</sup>×t<sup>2</sup> - 0.0356×t + 10.072

t = temperature in °C.

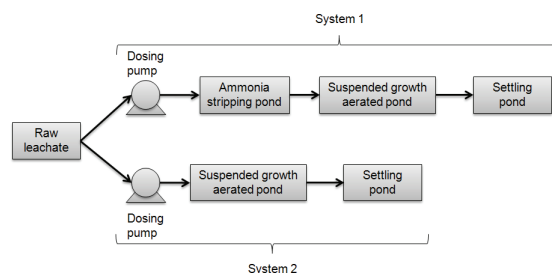
In agreement with Kim et al. (2006), with temperatures around 5°C using landfill leachate with concentration of ammonia nitrogen of 1,200 mg N-NH<sub>3</sub> L<sup>-1</sup>, it was possible to obtain accumulation of nitrite in the order of 700 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup>. And with increasing temperature to 25°C, there was no formation of nitrite and nitrate.

The goal of the present study is to evaluate the accumulation of nitrite through biological treatment systems (suspended growth aerated pond) applied to landfill leachate. By means of this analysis, we intend to investigate which possibilities that this type of treatment system have in relation to nitrogen removal by shortcut denitrification.

## Material and methods

For this study, two lines were built for leachate treatment in a pilot scale, which consisted of suspended growth aerated pond followed by a settling pond. One of the treatment lines was preceded by a stripping pond without changes on natural pH, to minimize the concentrations of ammonia nitrogen (system 1), and another line received directly the raw leachate. In this way, we aimed at assessing the influence of the variation in the concentrations of ammonia nitrogen in the formation of nitrite in biological treatment.

The Figure 2 shows the flowchart of the experimental devices used.



**Figure 2.** Flowchart of the experimental devices used.

Each aerobic pond was compounded of tanks of 250 L and diameter of 0.90 m, operated with HRT of five days. The decanters consisted of tanks of 100 L with HRT of two days. For the system monitoring, the parameters listed in Table 1 were determined.

The leachate used during the monitoring period was collected from the controlled landfill of the city of Londrina, Paraná State, which is operating since the 70's.

**Table 1.** Physical and chemical characteristics of the leachate used during the operation of the systems.

| Parameter        | Sample          |                 |                |                |                 |                 |
|------------------|-----------------|-----------------|----------------|----------------|-----------------|-----------------|
|                  | Input System 1  | Input System 2  | Pond 1         | Pond 2         | Output System 1 | Output System 2 |
| Alkalinity       | 3 times a week  | 3 times a week  | 3 times a week | 3 times a week | 3 times a week  | 3 times a week  |
| pH               | 3 times a week  | 3 times a week  | 3 times a week | 3 times a week | 3 times a week  | 3 times a week  |
| Ammonia nitrogen | 3 times a week  | 3 times a week  | -              | -              | 3 times a week  | 3 times a week  |
| TKN              | 1 time per week | 1 time per week | -              | -              | 1 time per week | 1 time per week |
| Nitrite          | 2 times a week  | 2 times a week  | 2 times a week | 2 times a week | 2 times a week  | 2 times a week  |
| Nitrate          | 2 times a week  | 2 times a week  | 2 times a week | 2 times a week | 2 times a week  | 2 times a week  |

The collection of the leachate was made by a water truck previously prepared for this purpose, and stored in the Laboratory of Hydraulics and Sanitation of the State University of Londrina (UEL), into a tank of 5,000 L, from where it was taken for treatment in the in pilot scale systems. In the Table 2 are given the physical and chemical characteristics of the leachate used in the present study.

**Table 2.** Physical and chemical characteristics of the leachate collected from a controlled landfill of the city of Londrina, Paraná State.

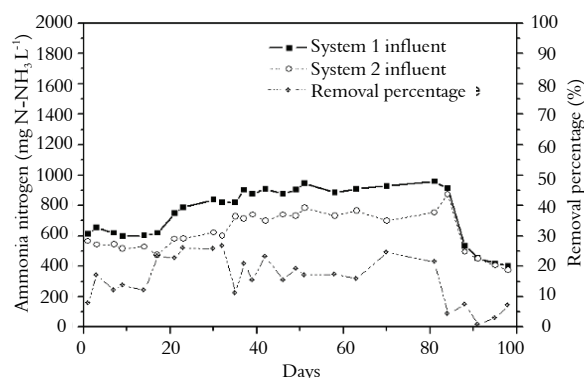
| Parameter                 | Mean* | Unit               |
|---------------------------|-------|--------------------|
| Fixed Total Solids        | 5,526 | mg L <sup>-1</sup> |
| Volatile Total Solids     | 2,218 | mg L <sup>-1</sup> |
| Volatile Suspended Solids | 65    | mg L <sup>-1</sup> |
| BDO                       | 176   | mg L <sup>-1</sup> |
| CDO                       | 2,430 | mg L <sup>-1</sup> |
| pH                        | 8.34  | -                  |
| Alkalinity                | 5,734 | mg L <sup>-1</sup> |
| TKN                       | 1,272 | mg L <sup>-1</sup> |
| Ammonia nitrogen          | 1,075 | mg L <sup>-1</sup> |
| Nitrate                   | 4     | mg L <sup>-1</sup> |
| Nitrite                   | 0.0   | mg L <sup>-1</sup> |
| Phosphorus                | 2.8   | mg L <sup>-1</sup> |

\*mean values obtained during a monitoring period from March 2007 to February 2008.

Laboratory analyses were performed following the standardized procedures from "Standard Methods for the Examination of Water and Wastewater".

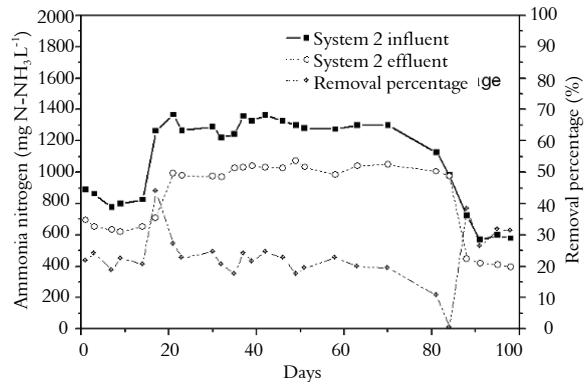
## Results and discussion

The Figures 3 and 4 show, respectively, the evolution of ammonia nitrogen over time in the system 1 (preceded by stripping) and in the system 2. The average removals of ammonia nitrogen in the systems 1 and 2 were 15.8 and 22.9%.



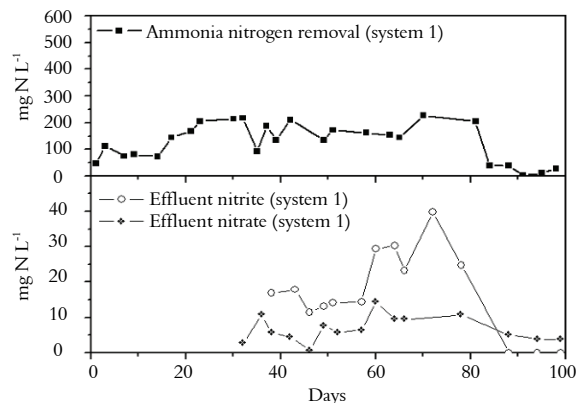
**Figure 3.** Evolution of ammonia nitrogen over time in the system 1, and removal percentage.

In the system 2, the initial concentration of ammonia nitrogen is greater, and consequently the concentration of free ammonia is higher.

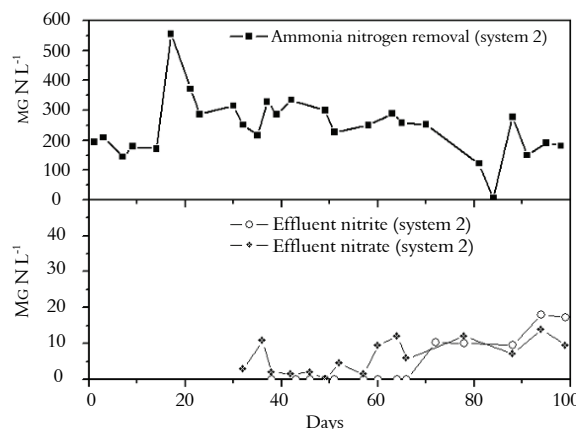


**Figure 4.** Evolution of ammonia nitrogen over time in the system 2, and removal percentage.

The evolution of the removal of ammonia nitrogen, nitrite and nitrate over time in the systems 1 and 2 is presented in the Figures 5 and 6, respectively.



**Figure 5.** Evolution of the removal of ammonia nitrogen, nitrite and nitrate in the system 1 over time.



**Figure 6.** Evolution of the removal of ammonia nitrogen, nitrite and nitrate in the system 2 over time.

The concentrations of nitrite and nitrate in the system 1 did not exceed 40 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup> and 15 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>, respectively – values that even summed

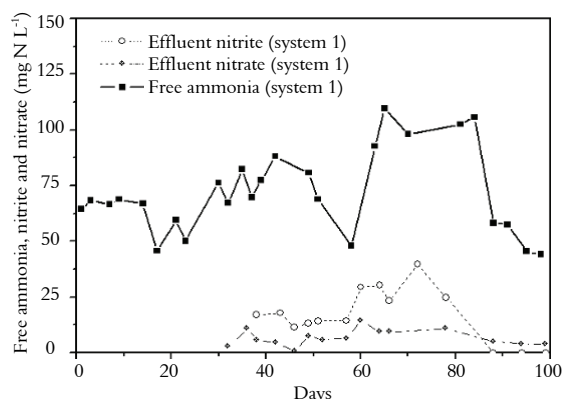
remain below the removal of ammonia nitrogen that ranged from 100 and 200 mg N-NH<sub>3</sub> L<sup>-1</sup> for most of the monitoring period.

The removal of ammonia nitrogen of the aeration ponds does not occur only through its oxidation. Part of this nitrogen is lost to the atmosphere by volatilization.

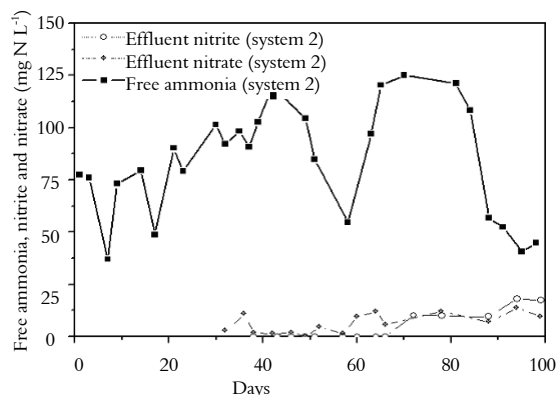
In the system 2, the formation of nitrite and nitrate was even lower, not surpassing 18 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup> and 14 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>, respectively, and the removal of ammonia nitrogen varied between 200 and 300 mg N-NH<sub>3</sub> L<sup>-1</sup> during most of the monitoring period. Higher levels of free ammonia favored the volatilization of this part of ammonia nitrogen, resulting in a greater removal in this case.

As above noted, the removal of ammonia nitrogen in aeration ponds is not due to only its oxidation, but also due to the volatilization of free ammonia. This fact is evidenced by the results presented in the Figures 5 and 6, where it is possible to verify that the removal of ammonia nitrogen is higher than the formation to nitrite and nitrate in both cases.

In the Figures 7 and 8 is shown the evolution of free ammonia, nitrite and nitrate over time in the systems 1 and 2.



**Figure 7.** Evolution of free ammonia, nitrite and nitrate in the aeration pond, over time in the system 1.



**Figure 8.** Evolution of free ammonia, nitrite and nitrate in the aeration pond, over time in the system 2.

From the Figures 7 and 8, it is possible to observe that the concentrations of free ammonia in both cases

are at levels able to inhibit partially the formation of nitrites, and totally the formation of nitrate, according to theoretical values illustrated in Figure 1.

In this way, the oxidation of ammonia nitrogen was limited by concentrations of free ammonia, prevailing thus the loss of ammonia by volatilization.

In the system 1, the concentration of free ammonia in the period between 0 and 58 days was kept between 45 and 88 mg N-NH<sub>3</sub> L<sup>-1</sup>, comprising periods relatively stable. From the 58<sup>th</sup> day, there was an increase in free ammonia, achieving a level of 105 mg N-NH<sub>3</sub> L<sup>-1</sup>.

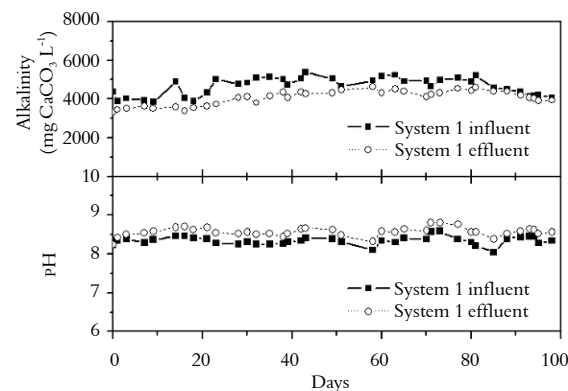
These variations were reflected in the formation of nitrite and nitrate. In initial period, the concentrations of nitrite and nitrate reached 40 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup> and 15 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> respectively. In the following period, there was a reduction in the formation of nitrite and nitrate, and from the 78<sup>th</sup> day, the formation of nitrite was virtually zero, and nitrate did not exceed 10 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>.

The free ammonia concentration over time in the system 2 had great variability (between 37 and 121 mg N-NH<sub>3</sub> L<sup>-1</sup>). Although this has not been occurred constantly, the system 2 presented high levels of free ammonia, sufficient to limit the formation of nitrite and nitrate for most of the monitoring period.

Considering the system 2, the formation of nitrite and nitrate was lower than in the system 1, as a function of the higher concentrations of free ammonia observed in this case.

In both cases, it is believed that the removal of nitrogen through volatilization of free ammonia prevailed on the reactions of nitrogen oxidations. This occurred due to the high levels of free ammonia in the aeration ponds, which inhibited the activity of the bacteria *Nitrosomonas* and *Nitrobacter*.

The evolution of alkalinity and pH over time is presented in Figures 9 and 10.



**Figure 9.** Evolution of alkalinity and pH over time in the system 1.

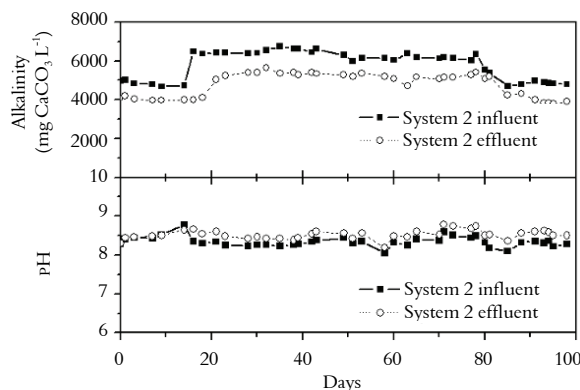


Figure 10. Evolution of alkalinity and pH over time in the system 2.

In the system 1, despite the consumption of alkalinity of up to  $1,316 \text{ mg CaCO}_3 \text{ L}^{-1}$ , the pH remained constant throughout the monitored period. In the system 2, a similar situation was registered: even with alkalinity consumption of up to  $2,483 \text{ mg CaCO}_3 \text{ L}^{-1}$ , there was no reduction in the pH over time.

As previously mentioned, the nitrogen removal of aeration ponds takes place by means of two different reactions: by the nitrogen oxidation and by the volatilization of free ammonia. Both reactions release ions  $\text{H}^+$  that cause the consumption of alkalinity.

The leachate used in this experiment presents a high natural alkalinity as can be seen in the Table 2. Even with alkalinity consumption in the aeration ponds, the remaining alkalinity maintained the pH close to the natural conditions of the leachate.

## Conclusion

As regard to the formation of nitrite in the pilot scale systems, the results allow concluding that, under operating conditions, the removal of ammonia nitrogen by the ammonia volatilization prevailed onto the nitrogen oxidation. This occurred due to the high levels of free ammonia in the aeration ponds, which inhibited the activity of the bacteria *Nitrosomonas* and *Nitrobacter*, preventing partially the nitrogen oxidation.

In the case of the leachate used in this experiment, even under natural conditions of pH and temperature, the free ammonia concentrations were kept high (between 25 and  $125 \text{ mg N-NH}_3 \text{ L}^{-1}$ ). The high levels of free ammonia observed in this case resulted from the high concentrations of ammonia nitrogen of the leachate.

Both the oxidation as the volatilization of ammonia nitrogen caused the consumption of alkalinity. But the high natural alkalinity of the

leachate allowed the nitrogen removal without the need to complement the alkalinity in the aeration ponds.

The obtaining of accumulation of nitrite in suspended growth aerated pond presents good possibilities in landfill leachates. The high concentrations of ammonia nitrogen of the leachate associated with its natural pH maintain the free ammonia at satisfactory levels for the nitrite accumulation.

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