

Importance of the ammonia volatilization rates in shallow maturation ponds treating UASB reactor effluent

Fernando Augusto Lopes de Assunção and Marcos von Sperling

ABSTRACT

This study aimed at determining the influence of ammonia volatilization on nitrogen removal in polishing (maturation) ponds treating sanitary effluent from upflow anaerobic sludge blanket (UASB) reactors in the city of Belo Horizonte, Brazil. An apparatus for the capture and absorption of volatilized ammonia in three polishing ponds in series was installed. Volatilized ammonia was captured by a chamber on the surface of the ponds and dissolved in boric acid solution, in order to estimate the amount of ammonia per unit surface area of each pond. Low rates of volatilization, below 0.2 kg/ha.d, in about 75% of samples from all the ponds, were observed. The mass balance of ammonia nitrogen of the ponds showed that the volatilization represented only about 2% of the total removal of nitrogen from the polishing ponds. The results obtained suggest that ammonia volatilization was a mechanism of little importance in nitrogen removal in the investigated polishing ponds.

Key words | ammonia volatilization, maturation ponds, nitrogen removal, polishing ponds

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INTRODUCTION

The mechanisms regarding nitrogen removal in stabilization pond systems have been a matter of great controversy in the technical literature. The major mechanisms are: volatilization of ammonia; nitrate and ammonia assimilation by algae with subsequent sedimentation of organic nitrogen and its retention in the ponds, bottom sludge; nitrification–denitrification. These mechanisms may operate simultaneously or even follow a specific route depending on the characteristics of the ponds and local weather conditions (Ferrara & Avci 1982; Pano & Middlebrooks 1982; Reed 1985; Senzia *et al.* 2002; Craggs 2005; Camargo-Valero & Mara 2007a, b; Camargo-Valero 2008; Picot *et al.* 2009). Among these mechanisms, volatilization of ammonia has been reported, for several years, as the predominant mechanism for nitrogen removal (Pano & Middlebrooks 1982; Reed 1985; von Sperling & Chernicharo 2005; Bastos *et al.* 2007).

Ammonia volatilization is the desorption of free ammonia (NH₃) in the liquid phase to the atmosphere, being a mass transfer process, influenced mainly by the concentrations of NH₃, mixing conditions, temperature and pressure, both in the liquid medium as well as the atmosphere above the liquid. Volatilization is directly related to the partial pressure the gas exerts on the liquid. Considering

that the ammonia present in the liquid tends to diffuse from a more concentrated medium (pond water mass) to a less concentrated one (atmosphere) and considering that the concentration of ammonia in the atmosphere is essentially zero (Zimmo *et al.* 2003), the transfer of ammonia to the atmosphere can be described according to Equation (1):

$$rd\text{NH}_3 = k_l[\text{NH}_3] \quad (1)$$

where: $rd\text{NH}_3$ = rate of NH₃ desorption in the liquid phase (mg/L.d); $[\text{NH}_3]$ = NH₃ concentration in the liquid phase (mg/L); k_l = mass transfer coefficient (d⁻¹).

Stratton (1969) presents a way to evaluate the mass transfer coefficient k_l as a function of the pond depth and temperature, according to Equation (2):

$$k_l = \frac{0.0566}{d} e^{[0.13(T-20)]} \quad (2)$$

where: T = temperature (°C); d = pond depth (m).

The original model developed by Pano & Middlebrooks (1982) states volatilization as a leading mechanism in nitrogen removal and it has been widely used in estimating

effluent concentrations from stabilization ponds. Studies from other researchers comparing experimental data with the data estimated by the model show good fitting and, therefore, it is usually implied that ammonia volatilization is the main route for nitrogen removal in stabilization ponds (Silva *et al.* 1995; Soares *et al.* 1996; Bastos *et al.* 2007). However, most of these studies are based on input and output data, not reflecting the possible transformations in the ponds.

In spite of that, other authors have questioned the importance of ammonia volatilization in the nitrogen balance, highlighting the importance of nitrogen assimilation by algae and its sedimentation in the bottom of ponds (Ferrara & Avci 1982; Camargo-Valero & Mara 2007a, b, 2010; Camargo-Valero 2008; Yamamoto *et al.* 2009; Camargo-Valero *et al.* 2010) and nitrification-denitrification under certain temperature conditions, as the predominant routes of nitrogen removal in ponds systems (Lai & Lam 1997; Picot *et al.* 2009).

Camargo-Valero (2008), using gas capture chambers on the surface of a maturation pond in Bradford, England, obtained an ammonia volatilization rate ranging from 0 to 27 g/ha.d, while theoretical models estimated rates varying from 107 to 812 g/ha.d and, as a result, the authors concluded that models for estimating ammonia volatilization overestimate this route of removal. The same authors conducted studies introducing isotopes of nitrogen ($^{15}\text{NH}_4\text{Cl}$) at the beginning of the maturation ponds under conditions that favoured volatilization. However, they verified that the ^{15}N accumulated predominantly in the particulate organic nitrogen and, thus, they suggested that the assimilation by the biomass would be the main destination of nitrogen in these ponds (Camargo-Valero & Mara 2007a, b).

This study aims to aggregate information about the relative importance of ammonia volatilization in nitrogen removal in polishing (maturation) ponds treating sanitary effluent from anaerobic upflow anaerobic sludge blanket (UASB) reactors operating in a warm-climate region, quantifying the loss of ammonia from the pond surface and the rates of volatilization and comparing them with models for estimating volatilization.

MATERIAL AND METHODS

Description of the study area

The project was developed at the Experimental Sewage Treatment Plant UFMG/Copasa, which is part of the

Centre for Research and Training in Sanitation located at Arrudas Wastewater Treatment Plant in the city of Belo Horizonte, Brazil (coordinates 19°53'42" S and 43°52'42" W). The system receives typical sanitary sewage. The experimental apparatus consisted of a UASB reactor, followed by three polishing ponds in series and a coarse rock filter (Figure 1).

The treatment system was designed to treat a population equivalent of 200 inhabitants. The UASB reactor has an effective height of 4.5 m and a diameter of 2.0 m. It operated with an average influent flow of 29 m³/d and hydraulic retention time of 11.7 h.

The three polishing ponds operated in series and the rock filter was installed at the final third of the last pond. The main physical and operational characteristics of the ponds are presented in Table 1.

Laboratory tests for the determination of the volatilized ammonia

Initial tests included the development of an apparatus for ammonia absorption based on the work of Camargo-Valero & Mara (2007a), Zimmo *et al.* (2003) and Stratton (1969) to assess the ammonia absorption capacity by boric acid in laboratory scale. The apparatus consisted of a 2 L container filled with 400 mL of ammonium chloride solution (40 mg NH₃-N/L). Inlet air, which passed through the free atmosphere of the bottle with ammonium chloride solution, was injected into the container using an aquarium-type air compressor. The gas enriched with volatilized ammonia was bubbled in 180 mL of boric acid at 3% in three sequential flasks (Figure 2). The pH of the ammonium chloride solution was adjusted to around 9.0 by adding NaOH and a borate buffer solution. Temperature was maintained at around 30 °C and a magnetic stirrer was used to mix the solution.

The tests were performed over 48 h periods, and the amount of ammonia volatilized was measured by the

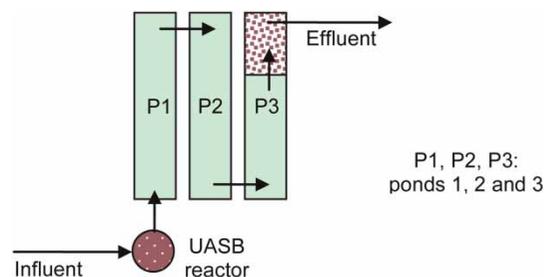
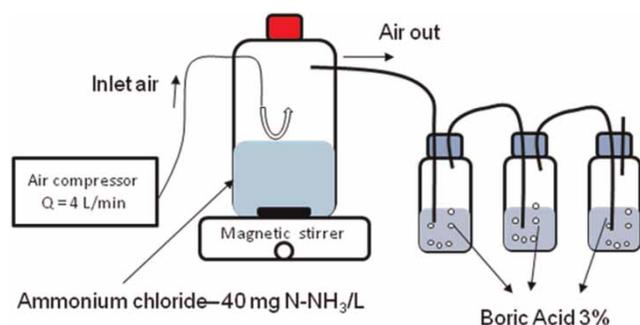


Figure 1 | Flowchart of the treatment system investigated.

Table 1 | Physical and operational characteristics of the polishing ponds

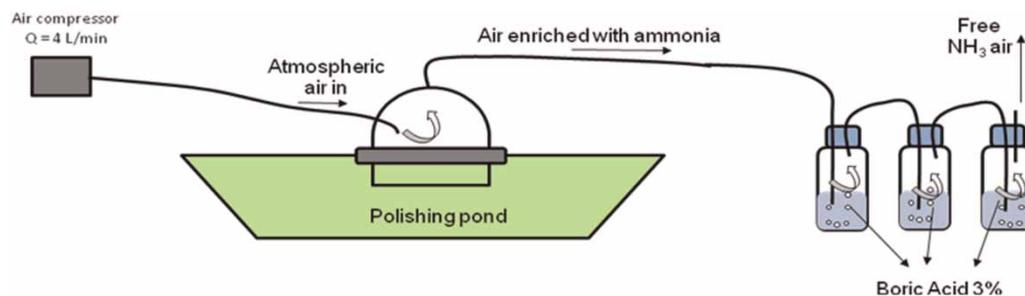
Characteristics	Unit	Pond 1	Pond 2	Pond 3
Length at the bottom	m	25.0	25.0	16.5
Width at the bottom	m	5.3	5.3	5.3
Liquid depth	m	0.8	0.8	0.6
Internal embankment slopes	°	45	45	45
Surface area	m ²	184	184	138
Influent flow (mean)	m ³ /d	29	29	29
Hydraulic retention time (mean)	D	4.3	4.3	1.5
Hydraulic loading rate (mean)	m ³ /m ² .d	0.15	0.15	0.22
Surface organic loading rate (mean)	kgBOD ₅ /ha.d	70	58	76

**Figure 2** | Schematics of the laboratory apparatus for ammonia capture.

difference in N-NH₃ concentration in the solution at the beginning and end of the test period. The 3% boric acid solution enriched with ammonia nitrogen was analysed for this parameter, allowing the estimation of the percentage of volatilized ammonia that was actually captured by the acid solution.

Field apparatus for the determination of the volatilized ammonia in the ponds

The field apparatus for capturing volatilized ammonia comprised three acrylic chambers (one chamber installed in the

**Figure 3** | Schematics of the field apparatus for capturing ammonia.

centre of each polishing pond). **Figure 3** shows a schematic of the functioning of the apparatus. The capture and absorption apparatus for volatilized ammonia consisted of inserting inlet air, using aquarium-type compressors, at one end of the chamber. This air was used to 'wash' the ammonia-enriched atmosphere of the chamber. The air was then bubbled into a 3% boric acid solution, leading to the dissociation of the ammonia gas into ammonium ion, allowing the determination of ammonia nitrogen, which was made according to the *Standard Methods for the Examination of Water and Wastewater (APHA/AWWA/WEF 1995)*.

Figure 4 shows a chamber installed on the surface of the first polishing pond. The diameter and height of the chamber cylindrical part was 0.50 m. The chambers had flaps of approximately 0.15 m submerged in the pond to prevent air from escaping from the sides. It was necessary to use weights on the edges of the chamber in order to keep those edges totally submerged, thus preventing loss of gas.

The aquarium-type air compressor used had a 4 L/min air capacity. It was connected to the chamber through transparent plastic hoses which showed possible obstructions due to liquid condensation and allowed their removal to

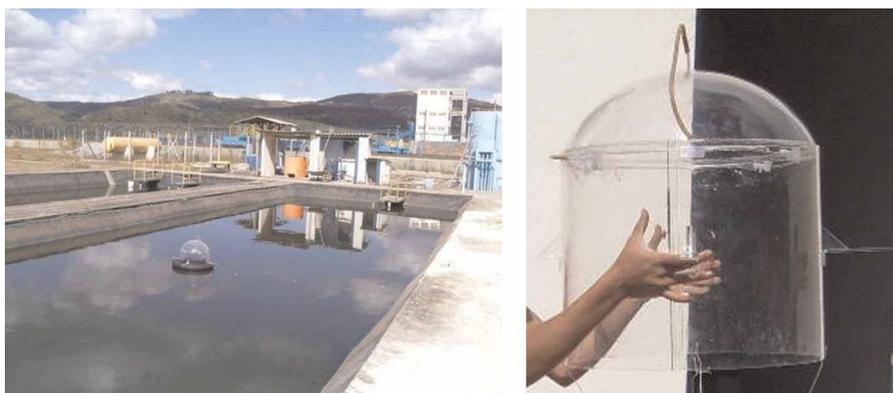


Figure 4 | Capture chamber for volatilized ammonia installed in pond 1.

obtain a perfect flow of the air sent to the flasks of boric acid. A total of three interconnected 200 mL flasks were filled with 60 mL boric acid at 3% solution. The air removed from the chamber was sent to the first flask which, interconnected to the second and third ones, provided a 'triple cleaning' of the ammonia-enriched air.

The ammonia capture and absorption system was monitored at set intervals. In the first stage monitoring was done weekly, and in later stages it was done at shorter intervals (daily, or every other day). The boric acid samples were sent to the laboratory for determination of ammonia concentration.

Based on the concentration of ammonia in the boric acid solution, the volume of boric acid and the chamber area, the amount of ammonia that was volatilized in the chamber area was calculated, thereby determining the rate of volatilization (kg/ha.d). In order to determine the ammonia mass balance in the ponds, the value of the volatilization rate was applied to the total surface area of the polishing ponds, taking into consideration the

efficiency of ammonia capture in the boric acid established in the laboratory.

RESULTS AND DISCUSSION

Determination of the efficiency of ammonia capture using the laboratory apparatus

The laboratory tests were conducted from 14 January to 1 February, 2008. The 3% boric acid solution reached a mean efficiency for volatilized ammonia capture of 95.8% (Table 2). The capture efficiency was substantially greater than that obtained by Camargo-Valero & Mara (2007a, b), who obtained 54% capture using a 2% solution of boric acid with 600 mL volume distributed among three sequential containers. There were no substantial differences observed in the efficiency of the boric acid, therefore the mean value was adopted and extrapolated to field conditions.

Table 2 | Efficiency of ammonia capture in boric acid in the laboratory

Test period	Ammonia concentration		Volatilized ammonia (mg)	Ammonia in boric acid solution (mg)	Capture efficiency (%)
	Start (mg/L)	End (mg/L)			
14-Jan to 16-Jan-08	34.16	14.84	8.17	7.98	97.6
16-Jan to 18-Jan-08	35.84	18.48	7.59	7.43	97.9
21-Jan to 23-Jan-08	32.20	14.56	7.57	7.17	94.8
23-Jan to 25-Jan-08	38.56	18.23	8.13	7.58	93.2
27-Jan to 29-Jan-08	35.12	19.30	6.33	6.13	96.9
30-Jan to 1-Feb-08	36.23	17.68	7.42	7.00	94.4
Mean capture efficiency of volatilized ammonia					95.8

Determination of volatilized ammonia in the field (polishing ponds)

Figure 5 shows the ammonia concentration along the pond system, in which the sequential decay can be clearly observed. Further details regarding the behaviour of ammonia in the pond system may be obtained in Assunção & von Sperling (2011).

The volatilization of ammonia was measured in 38 experiments conducted in the three polishing ponds. The basic descriptive statistics of the observed rates of volatilization (mass of volatilized ammonia per unit area of the ponds) are shown in Table 3.

The observed volatilization rates varied from 0.003 to 0.821 kg/ha.d in the three polishing ponds. These values were still higher than those reported by Camargo-Valero & Mara (2007a, b) who, in a similar study, found volatilization rates varying between 0.000 and 0.027 kg/ha.d in maturation ponds. The values observed by Zimmo *et al.* (2003), from 0.105 to 0.223 kg/ha.d, are of the same order of magnitude as the mean values observed in the present

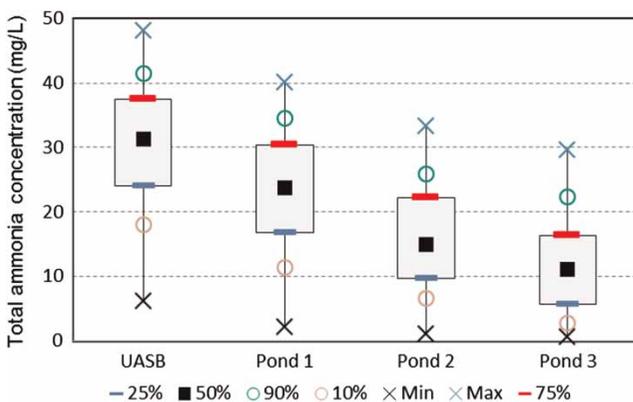


Figure 5 | Box-plot of total ammonia concentration along the polishing ponds.

Table 3 | Descriptive statistics of the rate of ammonia volatilization (kg/ha.d)

Statistics	Pond 1	Pond 2	Pond 3
Number of samples	38	31	31
Arithmetic mean	0.112	0.151	0.098
Geometric mean	0.098	0.078	0.040
Median	0.103	0.080	0.028
Minimum	0.020	0.005	0.003
Maximum	0.249	0.821	0.567
Standard deviation	0.053	0.181	0.140
Coefficient of variation	2.100	0.832	0.695

study. Both studies reinforce the evidence of mean volatilization rates around 0.100 kg/ha.d, such as those found in the present study. The volatilization rate observed is best seen in the box-plot in Figure 6 and in the time series shown in Figure 7.

The rates of volatilization in ponds 2 and 3, during the 2008 monitoring period, showed higher values at the beginning, tending to decrease at the end of this stage. During the 2009 monitoring period, pond 3 showed lower volatilization rates than the other ponds in most of its results, in spite of this pond having a shallower depth, which could in principle lead to higher volatilization rates for this pond in relation to the others.

The role of volatilization in ammonia removal, expressed as the mean load removed, is shown in Figure 8, in which a minute portion of the load removed as a function of volatilization is observed. Figures 9–11 show the mass balance for ammonia during the monitoring in the three polishing ponds, confirming the small role played by volatilization during the period studied.

Figure 12 shows that the percentages of ammonia removal in relation to the total removal observed in the polishing ponds hardly represent more than 3%. The values are

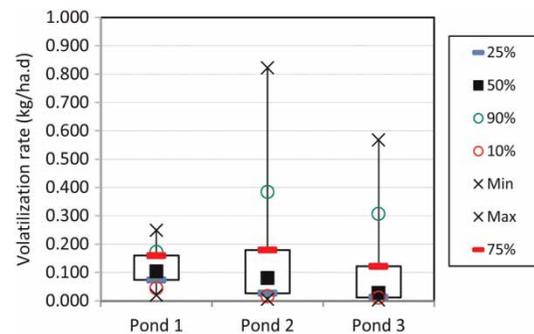


Figure 6 | Box-plot of the volatilization rate observed in the polishing ponds.

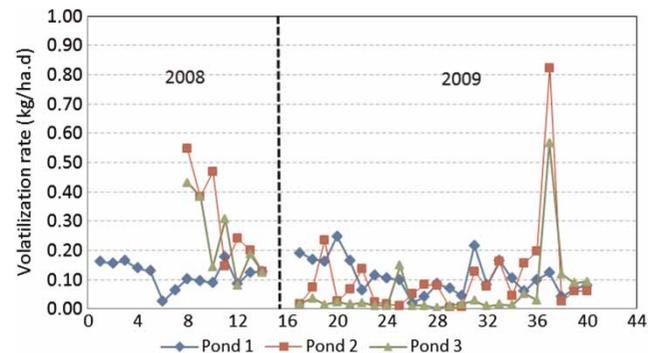


Figure 7 | Time series of the volatilization rate in the polishing ponds.

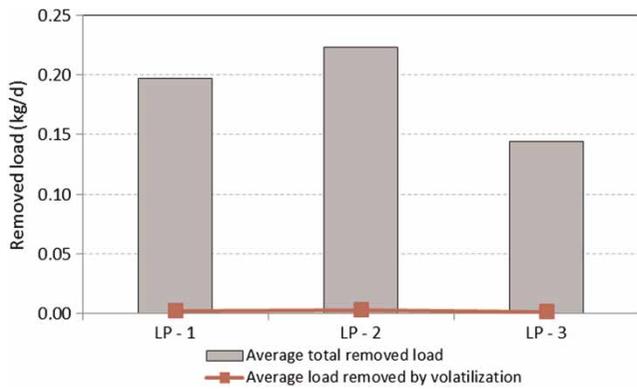


Figure 8 | Comparison between the mean load removed by volatilization and the total mean load of ammonia removed from the ponds.

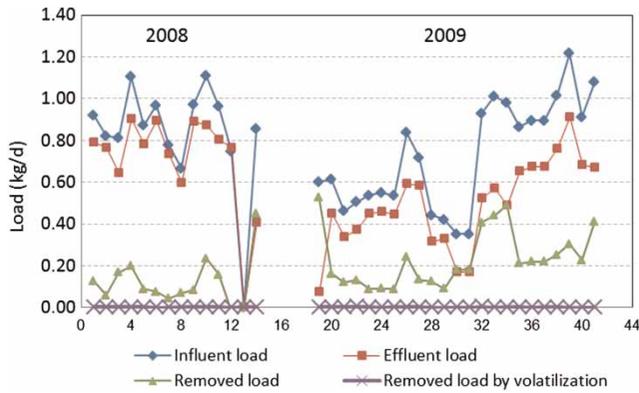


Figure 9 | Ammonia mass balance during the study period in pond 1.

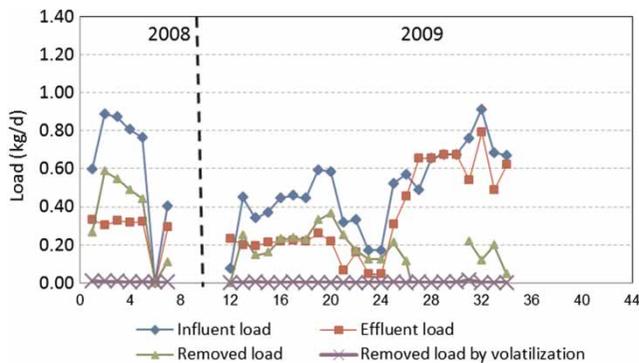


Figure 10 | Ammonia mass balance during the study period in pond 2.

in line with the data observed by *Zimmo et al. (2003)*, who found variations between 1.5 and 3.8%, and also with the study by *Camargo-Valero & Mara (2007a, b)*, which indicated a 3% mean removal due to volatilization. *Senzia et al. (2002)* found that the amount of volatilized ammonia did not represent more than 0.1% in relation to the other

transformations through pond modelling, as the mean load removed by modelled volatilization was around 0.008 kg/ha.d.

Camargo-Valero & Mara (2007a, b), using *Stratton's (1969)* model (Equations (1) and (2)), simulated the rate of ammonia volatilization as a function of the volume and area of the maturation ponds studied. *Figures 13–15* show the plotted values of volatilization rates observed in the

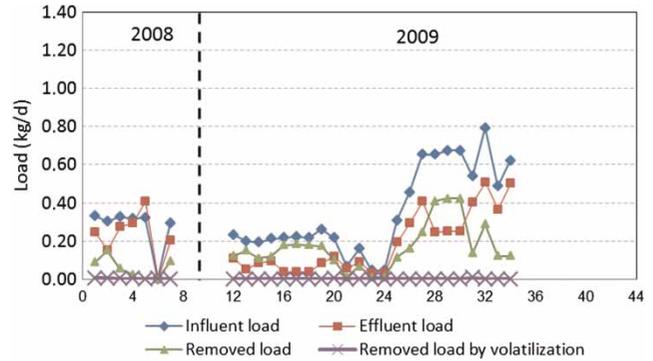


Figure 11 | Ammonia mass balance during the study period in pond 3.

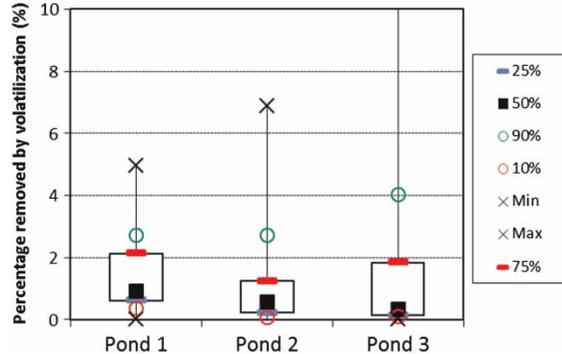


Figure 12 | Percentage of ammonia removal due to volatilization in relation to total ammonia removed.

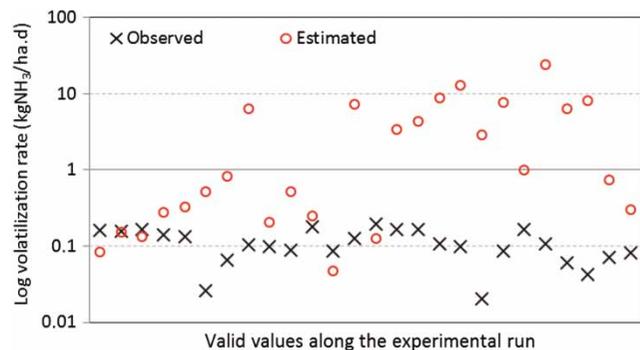


Figure 13 | Observed volatilization rate values compared with modelled values in pond 1.

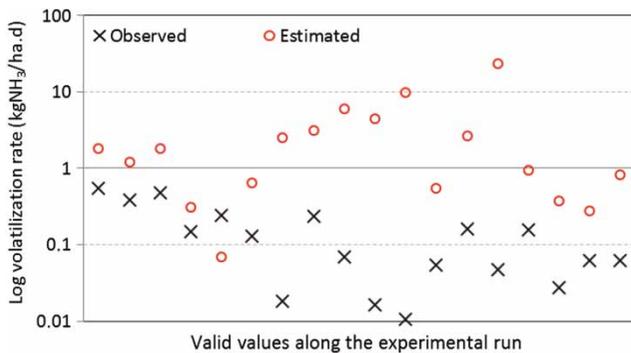


Figure 14 | Observed volatilization rate values compared with modelled values in pond 2.

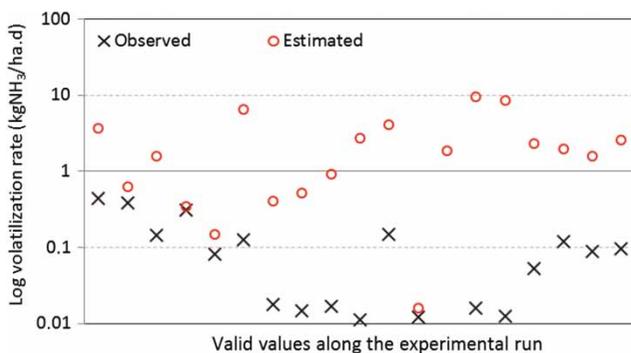


Figure 15 | Observed volatilization rate values compared with modelled values in pond 3.

current study and the estimated values (log-scale) according to this model, as a function of the concentration of free ammonia in the ponds. It is observed that the model overestimates the rates of observed volatilization in most of the results, confirming the findings from Camargo-Valero & Mara (2007a, b).

CONCLUSIONS

The values for the ammonia captured by the apparatus installed in the polishing ponds showed that the mechanism of ammonia loss by volatilization through the pond surface was a mechanism of little importance in the removal of total ammonia nitrogen. The mean rates of volatilization obtained from the ponds varied from about 0.10 to 0.15 kgN/ha.d (75% of the samples below 0.20 kgN/ha.d), which represented only about 2% of the total ammonia nitrogen removed.

The results indicated that the mechanisms for removal of ammonia by volatilization, believed by many authors to be the principal route in nitrogen removal, may not be of

great importance. This corroborates recent studies that point in the same direction.

Stratton's model (1969) for estimating volatilized ammonia was not precise for the estimate of volatilized loads. Parameters that influence volatilization and the establishment of more realistic models in relation to shallow polishing (maturation) ponds treating effluents from anaerobic reactors should be further investigated.

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