# The removal of ammonia from sanitary landfill leachate using a series of shallow waste stabilization ponds.

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**Abstract:** This study evaluated the efficiency of a shallow (~0.5m deep) waste stabilization pond series to remove high concentrations of ammonia from sanitary landfill leachate. The pond system was located at EXTRABES, Campina Grande, Paraiba, Northeast Brazil. The pond series was fed with sanitary landfill leachate transported by road tanker to the experimental site from the sanitary landfill of the City of Joao Pessoa, Paraiba. The ammoniacal-N surface loading on the first pond of the series was equivalent to 364 kg ha<sup>-1</sup> d<sup>-1</sup> and the COD surface loading equivalent to 3,676 kg ha<sup>-1</sup> d<sup>-1</sup>. The maximum mean ammonia removal efficiency was 99.5% achieved by the third pond in the series which had an effluent concentration of 5.3 mg L<sup>-1</sup> ammoniacal-N for an accumulative HRT of 39.5 days. The removal process was attributed to ammonia volatilization (stripping) from the pond surfaces as a result of high surface pH values and water temperatures of 22-26°C. Shallow pond systems would appear to be a promising technology for stripping ammonia from landfill leachate under tropical conditions.

Keywords: sanitary landfill leachate; ammonia; volatilization; waste stabilization ponds

#### **INTRODUCTION**

The disposal and treatment of solid waste in a hygienic and environmentally sustainable way is a serious problem, notably in many rapidly industrializing countries including Brazil. The construction of sanitary landfill sites for solid waste disposal resolves part of the problem; however, treatment of the leachate produced is itself an important issue if surface and ground waters are not to be contaminated (Calli, et al. 2005). Apart from the high COD concentrations the leachate also contains high concentrations of ammoniacal-N (amongst other problems), that needs to be removed in a simple, efficient and cost-effective way.

Nitrogen removal processes in waste stabilization ponds have been recently and comprehensively reviewed by Craggs (2005). Of these processes ammonia volatilization (stripping) can account for between 75-98% removal of total N in WSP treating domestic sewage at pH's from 7 to 9 and temperatures in the range 22 to 28°C. It is considered to be the principal route of nitrogen removal in ponds (Pano and Middlebrooks, 1982; Reed, 1985; Pearson et al., 1996). The stripping of ammonia is a physical removal process in which free molecular ammonia is lost by volatilization from the surface of the liquid phase to the atmosphere above. Ammonia in the liquid phase exists in two forms in equilibrium, namely the ionic form  $(NH_4^+)$  and the molecular or gaseous form  $(NH_3)$ . The equilibrium between the ammonium and ammonia species is given in equation 1.

$$NH_4^+$$
 (aqueous) + OH<sup>-</sup>  $\leftrightarrow$  NH<sub>3</sub> (gaseous) + H<sub>2</sub>O (aqueous) (Equation 1)

This equilibrium is dependent on a number of factors the most important of which are temperature and pH. The  $NH_4^+$  ion predominates below pH 7.2 and gaseous ammonia increases proportionally as the equilibrium is displaced to the right in response to increasing pH until at pH 9.2  $NH_3$  accounts for 50% of the total. Furthermore the proportion of  $NH_3$  doubles for every 10°C rise in temperature (Emerson, et al 1975; Athayde, 2000).

Zimmo et al. (2004) claimed that the combined biological processes of nitrification and denitrification accounted for up to 25% of N removal in their shallow (0.9m) experimental ponds. A study at the Melbourne ponds, Australia concluded that these processes could be an important route for nitrogen removal but that the nitrifyer population was unstable and nitrification was inhibited at pH levels above 8.5 and when the oxygen concentration dropped below 6mg L<sup>-1</sup> (Gross et al. 1994). Furthermore ammonium oxidizers are inhibited by high light intensities notably in shallow ponds (Abelovich and Vonshak 1993).

High concentrations of ammonia are toxic to pond microorganisms notably the algae which are responsible for photosynthetic oxygen production. It is the NH<sub>3</sub> form which readily enters microbial cells causing inhibition at high concentrations. An ammoniacal-N concentration of 54mg  $L^{-1}$  can inhibit algal photosynthesis by 90% at pH > 9.0 (20-25°C) seriously diminishing algal growth and oxygen production (Pearson et al. 1987).

In this study we evaluate the suitability and efficiency of using a series of shallow waste stabilization ponds to remove high concentrations of ammoniacal-N from sanitary landfill leachate under tropical conditions.

# MATERIALS AND METHODS.

## Location and design of the experimental system:

The present research was carried out at the Experimental Research Station for the Biological Treatment of Sewage – EXTRABES of the Federal University of Campina Grande (UFCG) and the State University of Paraiba (UEPB), in the city of Campina Grande, Paraiba, Northeast Brazil ( $7^0$  13<sup>°</sup> 11<sup>°</sup> South,  $35^0$  52<sup>°</sup> 31<sup>°</sup> West, at an altitude of 550 m above sea level). The experimental system comprised four shallow ponds in series constructed above ground in clay blocks and faced in concrete the details of which are given in Table 1. Pond inlets and outlets were positioned 5cm below the water surface.

Parameter:	Length	Width	Depth	Volume	HRT	Dispersion
Pond	<b>(m)</b>	( <b>m</b> )	<b>(m)</b>	(m <sup>3</sup> )	(days)	No. (d)
P1	5	1	0.60	3.00	14.3	0.18
P2	5	1	0.55	2.75	13.1	0.18
P3	5	1	0.50	2.50	12.1	0.18
P4	5	1	0.45	2.25	10.5	0.18

Table1. Operational details of the pond series treating the sanitary landfill leachate.

The sanitary landfill leachate used in this study was transported by road tanker from the sanitary landfill site of the city of Joao Pessoa and stored in open  $5m^3$  rigid PVC tanks (depth 1.5m) at the experimental site from where it was pumped to the pond system. The concentration of the leachate received varied between 584 a 1768 mg. L<sup>-1</sup> depending on conditions at the sanitary landfill. In the present study the maximum surface loading on the first pond of the series was equivalent to 364kg of ammoniacal-N ha<sup>-1</sup> d<sup>-1</sup> and 3,676kg of COD ha<sup>-1</sup> d<sup>-1</sup> and the mean ammoniacal-N concentration of the influent leachate was 869.7mg L<sup>-1</sup> (SD $\pm$  29.4). The results presented here are for the highest ammoniacal-N and COD surface loading rates at the shortest HRT during an overall experimental period January and October 2008.

### Samples and Analyses

Samples of the influent leachate and effluent samples from each pond in the series were analysed weekly for COD, solids, volatile fatty acids, ammoniacal-N, alkalinity, dissolved oxygen, pH and

temperature (APHA, 1998). Additionally a series of total water column samples were taken from each pond over several weeks to determine the mean chlorophyll *a* concentrations in each pond using the methanol extraction technique (APHA, 1998). Samples were taken at different depths in the water column of each pond to determine algal speciation and insitu measurements of dissolved oxygen and pH were also made.

#### **RESULTS AND DISCUSSION**

The ammoniacal-N concentration of the raw leachate feeding the pond series decreased with time in the open storage tank feeding the ponds. In this particular set of experiments (Figure 1), the ammonia-N concentration dropped from an initial value of 1768 mg L<sup>-1</sup> to 924 mg L<sup>-1</sup> during the first 9 days of storage, representing a loss of 47.7%. Thereafter the losses were minimal reaching 50.8% after 50 days of storage equal to a remaining mean concentration of 869.7 mg L<sup>-1</sup> (SD± 29.4). The pH of the leachate remained virtually constant during the storage period at a mean value of 8.1 (±0.32).



Figure 1 Reduction in ammoniacal-N concentration with time in the stored sanitary landfill leachate used to feed the shallow pond series.

The mean concentrations of ammonia-N in the influent sanitary landfill leachate feeding the first pond ( $P_0$ ) and the effluents of each of the four ponds in series (P1 to P4 respectively), are presented in Figure 2.



**Figure 2**. Ammonia concentrations in the influent leachate (P0) and in the effluents of each pond in the series (P1-P4).

The effluent of the first pond (P1) with a theoretical HRT of 14.3 days had a mean ammoniacal-N concentration of 175 ( $\pm$ 69) mg L<sup>-1</sup> representing a reduction in ammonia of 80.0%. The effluent ammoniacal-N concentration from the second pond in the series (P2) was 15.9 ( $\pm$ 7.5) mg L<sup>-1</sup>

corresponding to an additional removal of 91.4%. Taking the first two ponds together the overall mean reduction in ammoniacal-N was 98.2% for a combined HRT of 27.4 days and a mean influent concentration of the crude leachate of 869.7 mg L<sup>-1</sup> ammoniacal-N i.e. the mean value from day 9 to day 50 of the experimental period (see figure 1). Ponds 3 and 4 had the same mean effluent ammoniacal-N concentration of 5.3 ( $\pm$  2.0) mg L<sup>-1</sup> for accumulative theoretical HRT's of 39.5 and 50.0 days respectively, representing a further reduction in ammoniacal-N of 38.7% giving a mean maximum removal in the system of 99.5% after three ponds in the series. The P3 and P4 effluent ammoniacal-N values come close to the Brazilian consent values for discharge into surface waters of 5mg/L but the pH of the final effluent would need to be reduced (CONAMA, 2005).

The large reductions in the effluent ammoniacal-N concentrations of ponds P1 and P2 are largely attributed to the process of ammonia volatilization from the pond surfaces at the high pH's and water temperatures and reduced dissolved oxygen concentrations encountered in these shallow ponds which tend to favour volatilization over the nitrification/denitrification route (Table 2).

<b>Table 2</b> . Results for the influent leachate (P0), pond effluents and in-pond parameters.									
Parameter/ Pond	PO	P1	P2	P3	P4				
$pH^1$	$8.1 \pm 0.3$	$8.6\pm0.4$	$9.1 \pm 0.4$	$9.2 \pm 0.4$	$9.2 \pm 0.4$				
pH <sup>2</sup>	ND	$9.1 \pm 0.07$	$9.6 \pm 0.06$	$9.7 \pm 0.08$	$9.7\pm0.09$				
Temp $(^{\circ}C)^{1}$	$22.8 \pm 0.9$	$22.8\pm0.8$	$22.9 \pm 0.7$	$22.7\pm0.8$	$26.0 \pm 2.4$				
DO $(\text{mg L}^{-1})^2$	ND	$2.7 \pm 0.4$	$2.6 \pm 0.4$	$2.6 \pm 0.4$	$2.5 \pm 0.3$				
Chl <i>a</i> ( $\mu$ g L <sup>-1</sup> ) <sup>3</sup>	ND	$296 \pm 84.7$	$545 \pm 131.4$	$364 \pm 363.7$	$169.2 \pm 37.3$				
TSS $(mg L^{-1})^1$	$288 \pm 53$	$380 \pm 96$	$490 \pm 67$	$519 \pm 152$	$348\pm109$				
VFA $(mg L^{-1})^1$	$625 \pm 456$	$491\pm304$	$415 \pm 276$	$456 \pm 144$	$470 \pm 185$				
1	- 2								

<sup>1</sup>Effluent; <sup>2</sup>Pond top 5cm; <sup>3</sup>Water column; ND = Not Determined;  $\pm$  = Standard Deviation.

Total alkalinity values for the influent leachate and the pond effluents are presented in Figure 3. The consumption of alkalinity in the ponds will be influenced by the biological removal of  $CO_2$  (notably algal photosynthesis) and also by the volatilization of ammonia gas. In the case of ammonia gas, for each mole of gas volatilised there is the consumption of 1 meq L<sup>-1</sup> of total alkalinity (Emerson, 1975). The total alkalinity of the influent leachate to the pond series was 4,932 ( $\pm$ 752) mg L<sup>-1</sup> CaCO3 L<sup>-1</sup> which reduced to 3545 ( $\pm$  562) mg L<sup>-1</sup> in the effluent of pond 1 and to 3171( $\pm$  868) mg L<sup>-1</sup> CaCO<sub>3</sub> in the final effluent (Figure 3). This consumption of total alkalinity along the pond series amounted to a mean reduction of 35.7% with the largest drop occurring in pond 1 (28.1%), which is presumably a result of the considerable volatilization of gaseous ammonia from the surface of the first pond.



**Figure 3**. Total alkalinity concentrations in the influent to the pond series (P0) and in each of the pond effluents (P1-P4).

The COD declined steadily through the pond system giving a final effluent concentration of 2,972mg  $L^{-1}$  (Figure 4), representing an overall removal efficiency of 67% for the series and 47% after the first three ponds.



**Figure 4**. COD concentrations in the influent leachate (P0) and each pond effluent (P1-P4) in the series.

The ammonia concentration  $(175 \text{ mg L}^{-1})$  in the first pond (P1) was not sufficient to inhibit the development of a healthy algal population as shown by the chlorophyll *a* concentration (Table 2). All the ponds contained a monoculture of the same flagellate green alga genus Chlamydomonas known to be tolerant to high organic loadings and high sulphide concentrations but interestingly not noted for ammonia tolerance (Pearson et al. 1987). The pond chlorophyll *a* (chl *a*) concentrations (Table 2) were relatively low compared to conventional pond systems designed to treat domestic sewage but sufficient for algal photosynthesis to raise pond pH's above 9, reaching a maximum mean value of 9.7 in P3. This increase in pH favours the formation of NH<sub>3</sub>-N and its subsequent volatilization from the pond surfaces. The total suspended solids (TSS) in the pond effluents were high even in the final effluent (P4) and were higher than in the influent raw leachate presumably as a result of the presence of the microalgae.

### CONCLUSIONS

1. The shallow pond series removed up to 99.5% of the ammoniacal-N in the sanitary landfill leachate, giving a concentration of 5.2 mg  $L^{-1}$  ammoniacal-N in the effluent of the third pond (P3) for an accumulative HRT of 39.5 days. However additional treatment would be necessary to reduce solids and COD, perhaps by advanced oxidative processes, before discharge to surface waters.

2. Surface loadings of ammoniacal-N of 364 kg ha<sup>-1</sup> d<sup>-1</sup> and COD of 3,676 kg ha<sup>-1</sup> d<sup>-1</sup> (on the first pond of the series) did not produce odour and did not inhibit the developed of a healthy, actively photosynthesising algal population capable of elevating pond pH. The apparent ammonia tolerance of the Chlamydomonas species warrants further attention.

3. High surface pH values in the ponds, low dissolved oxygen concentrations and high water temperatures and solar intensities would favour ammonia volatilisation over nitrification/denitrification as the principal route of nitrogen removal from the ponds.

4. Shallow waste stabilization pond systems appear to be a promising alternative to other ammoniastripping technologies at least under tropical conditions. They do not require the addition of chemicals to raise the pH, are easy to construct, maintain and operate and are energy efficient. Furthermore they can accommodate shock hydraulic loads of leachate leaving sanitary landfills during periods of excessive rainfall.

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