Mechanisms of ammonia removal in a leachate treatment pond at the Taylors Road landfill site – Melbourne, Australia

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Abstract Contaminant levels in landfill leachates can be high; for older landfills, ammonia concentrations in leachates can exceed 1000 mg/L. Before being discharged, such leachates must be treated to reduce ammonia concentrations. Air stripping of ammonia in mechanically aerated ponds is widely used for this purpose. Previous work suggests that more ammonia could be lost by desorption at the pond surface than is lost to the air bubbles generated by the aerators. This has significant design and economic implications for those managing landfill leachates. To determine the fraction of ammonia removed by each of the above mechanisms, an experimental study was conducted on a 3000 m³ leachate treatment pond at the Taylors Road Landfill in Melbourne. Changes in ammonia concentration were followed during a batch stripping process that over 25 days reduced ammonia levels from 780 to 83 mg/L; pH and temperature readings were also taken. Some nitrite and nitrate analyses were also conducted. At least 87% of the ammonia removed from this pond was lost via desorption at the pond surface. Only 10% of the ammonia losses could be accounted for by desorption into the air bubbles generated by the aerators while at most 2-3% was lost through nitrification.

Keywords Ammonia removal; ammonia stripping; landfill; leachate; nitrification; pond

INTRODUCTION

Waste deposited in landfills undergoes slow anaerobic decomposition, often lasting many decades. The leachate that forms in landfills is regularly pumped out and collected. It is rich in contaminants and must be treated before being discharged. A key contaminant is ammonia, an end product of the anaerobic breakdown of proteinaceous and other organic wastes. Concentrations of ammonia within the leachate increase steadily over time and can exceed 1000 mg/L (Welander et al., 1998). At the Taylors Road Landfill site in Melbourne, Australia, concentrations as high as 1300 mg/L have been measured. Wastewaters containing such levels of ammonia must be treated on-site as they cannot be released directly to the environment, or even to sewer. For example, at the above landfill, leachate ammonia concentrations have to be reduced to 150 mg/L before discharge to sewer is permitted.

To achieve the required reductions in ammonia levels, two treatment options are available: microbiological (conversion of ammonia to nitrate by nitrification) and physico-chemical (air stripping). In high strength leachates, concentrations of free (undissociated) ammonia are high enough to inhibit nitrification (Anthonisen et al., 1976), so for such leachates air stripping is the preferred treatment process. The stripping is usually achieved by pumping the leachate into a shallow open pond and then mechanically aerating it using surface aerators. Ammonia concentrations are monitored regularly and aeration continued until prescribed discharge levels are achieved. The pond is then pumped out and refilled with a new batch of leachate. The operational simplicity and effectiveness of this procedure has led to its being widely used around the world.

The main disadvantage of stripping is that it is a lengthy process, often taking weeks to achieve required reductions in ammonia concentrations. Useful cost savings could be made by shortening treatment times: aerator power costs could be reduced, as could land and treatment pond construction costs. Stripping rates can be increased by raising the pH of the leachate, thereby increasing the fraction of the ammonia that is present in the undissociated form (NH_3); this practice is widely used in the chemical industry as it greatly improves mass transfer rates. However, leachates, especially older ones, have a strong buffering capability, making pH adjustment more difficult. In addition, some operational simplicity is lost and the cost of the chemicals needed to raise the pH of the leachate, and subsequently neutralize it, can be significant. The procedure also adds to the TDS of the leachate, which can limit possibilities for re-using the final treated effluent for irrigation.

A simpler way to make ammonia removal from leachate treatment ponds more cost-effective would be to improve the efficiency of the existing process. Little research has been done on mechanisms of ammonia removal from aerated leachate treatment ponds and these are still poorly understood. Several papers have suggested that ammonia losses to air at the surface of aerated wastewater tanks may be more important than losses by desorption into the bubbles generated by aerators (Smith and Arab, 1988; Crisp et al., 1995; Cheung et al., 1997). In Smith and Arab's (1988) laboratory study, 3 to 5 times more ammonia was lost at the water surface than was lost in the air bubbles. If similar loss ratios apply in leachate treatment ponds this could have major implications for both pond design and aerator selection. No published information on loss ratios for actual leachate treatment ponds could be found so a field study was undertaken on an aerated leachate treatment pond at the Taylors Road Landfill, in Melbourne, Australia. The aim of the study was to determine the relative importance of the different ammonia removal mechanisms in this pond.

THEORY
Ammonia is present in water mainly as the ammonium ion NH_4^+, which exists in equilibrium with the undissociated form NH_3. The fraction of ammonia present in the undissociated or free ammonia form, f, is a function of pKa, the acid equilibrium constant, and of pH, and is given by:

$$f = \frac{1}{1+10^{pKa-pH}}$$ (1)

Hence the concentration of free ammonia in the liquid phase, C_L (mg/L), is given by:

$$C_L = f \times C_T$$ (2)

where C_T is the concentration of ammonia (total) in the liquid phase (mg/L).

Since only undissociated ammonia molecules can be transported from water to air, C_L is a key parameter in mass transfer relationships. For ammonia desorption at the pond surface, the mass transfer rate is liquid film controlled and is given by (Skelland, 1974):

$$\frac{N}{V} = K_L a \times C_L$$ (3)

where:
N = mass of ammonia transferred per unit time (mg/h); V = lagoon volume (L); $K_L a$ = overall ammonia transfer coefficient (h^{-1}).

A different approach can be used to determine the amounts of ammonia lost to the bubbles created by the aerators. The ammonia concentration in air bubbles rising through water containing dissolved ammonia reaches its equilibrium value very quickly (Bayley, 1967). The partial pressure of ammonia in the air bubbles at equilibrium (P (atm)) is given by (Bayley, 1967):

$$P = \frac{C_L}{H}$$ (4)

where H is the Henry's Law constant (mg/l.atm). H is primarily a function of temperature, T (ºC), and is given by (Srinath and Loehr, 1974):

$$H = 3.564 \times 10^6 \exp(-0.0525 \times T) \tag{5}$$

If pond temperature, pH and ammonia concentration are known, the value of P can be readily determined using equations (1), (2), (5) and (4). If air bubbles are assumed to be saturated with ammonia when they emerge from the pond, the Ideal Gas Law can be used to determine the mass of ammonia removed by each litre of air bubbled through the pond. Provided aerator air flow rates are known, rates of ammonia loss via the bubbles can readily be estimated. In practice airflow rates will not be known exactly, but a good estimate of their value can be made using aerator specifications.

METHODOLOGY

Study area
Taylors Road Landfill is located in Lyndhurst, 30 km southeast of Melbourne, Australia and is owned and operated by SITA Environmental Solutions. At present leachate collected from around the landfill site is treated in a system of ponds. This comprises four composite-lined ponds: two 720 m³ ponds (Ponds A and B), used mainly as discharge ponds, and two larger 3000 m³ ponds (Ponds C and D). Treatment is carried out primarily in Ponds C and D, both equipped with two 22kW high speed floating aerators that achieve a high level of mixing. Manufacturer's specifications state that each aerator supplies 1330 L/s of air. Aeration is continued until ammonia concentrations fall to 150 mg/L, the level specified in SITA's Trade Waste Agreement with the local water authority, South East Water Limited. The pond contents are then batch discharged to sewer.

Experimental work
The experimental procedure was as follows. Pond D (40m x 30m x 2.5m) was filled with leachate and, once full, isolated for 25 days. The experiment was conducted in autumn 2008, beginning on April 11th and ending on May 6th. During the experimental period neither inflows to the pond, nor outflows from the pond, were allowed. The aerators were run continuously during the experiment.

To characterize the pond's behaviour, samples were collected from the pond on 34 separate occasions over the 25 day period. On each occasion samples were taken at four different sampling points and combined to give a composite sample. Measurements of pond pH and temperature were taken at the time of sampling. Ammonia concentrations were determined according to procedures in Standard Methods (2005). For samples taken towards the end of the experimental period, nitrate and nitrite concentrations were also measured, again using procedures in Standard Methods (2005).

RESULTS AND DISCUSSION

Ammonia and pH values obtained during the monitoring period of the experiment are shown in Figure 1. The ammonia concentration data have been subjected to limited smoothing to eliminate a few obvious inaccuracies. The ammonia concentration decreased steadily from an initial value of 780 mg/L to 83 mg/L at the end of the experiment, 25 days later. The pH value was 7.8 initially but rose quite rapidly to around 9.0, remaining at or slightly above this value for the remainder of the experiment. Air stripping of carbon dioxide from the leachate is believed to be the cause of the early pH increase (Marttinen et al., 2002) but this was not confirmed experimentally. Sample temperature fluctuated according to weather conditions and the time of day at which samples were taken. As shown in Table 1, temperatures declined slowly over the experimental period. Samples were usually taken near the start or end of the day, so measured temperatures should encompass much of the diurnal pond temperature range.
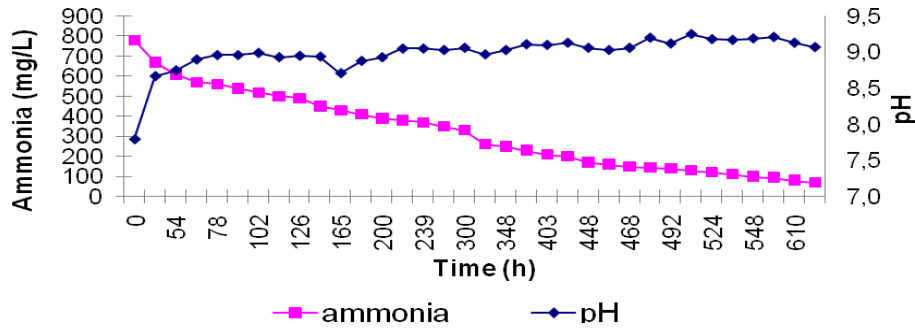
Figure 1: Changes with time of ammonia and pH levels in pond D

For each sample, values of C_L and P were determined from the corresponding temperature, pH and ammonia concentration data using equations (1), (2), (4) and (5). pKa values, which vary with temperature, were calculated from information provided in Crisp (1992).

The experimental period was divided up into 33 intervals, with the length of each interval, I_i, being the time that elapsed between the taking of sample i and the taking of the succeeding sample $i+1$. For each interval, average values of pond temperature (T_{ave}), ammonia partial pressure (P_{ave}) and free ammonia concentration (C_{Lave}) were determined. Using the approach outlined earlier, the relevant values of T_{ave} and P_{ave} were used to estimate the mass of ammonia lost via desorption into bubbles (AB) during each interval. The overall ammonia loss (TA) from the lagoon over this interval is given by:

$$TA = V \times (C_{Ti} - C_{T(i+1)}) \qquad (6)$$

where C_{Ti} and $C_{T(i+1)}$ are the ammonia concentrations at the start and the end of the interval concerned, and V is the volume of the lagoon (L). The overall ammonia loss through the surface (AS) in this interval is the difference between TA and AB. From the computed value of AS the values of N, the mass flux of ammonia through the lagoon surface, and of N/V, were determined. The values of the above parameters for each interval are shown in Table 1.

Table 1 shows that the ammonia removed in the air bubbled through the pond represents only around 10% of the overall loss. Analyses of samples taken over the last third of the test run showed the pond water to have virtually constant nitrate and nitrite concentrations of 8-9 mg/L and 4-5 mg/L respectively over this period. This nitrite and nitrate are likely to have been formed prior to or at the start of the run since only within the first 2 to 3 days were the combined inhibitory effects of pH and free ammonia low enough to permit some nitrification (Anthonisen et al., 1976). On this basis, and assuming that denitrification would be insignificant in the well-aerated pond waters, at most 2-3% of the overall ammonia loss can be attributed to nitrite and nitrate formation. Evidently, by far the most important losses are those occurring through the lagoon surface.

Figure 2 shows a plot of N/V versus C_{Lave} from which the overall mass transfer coefficient (K_La) for the pond studied here (Pond D) was determined. From equation (3) the value of K_La should be equal to the slope of the line of best fit through the points on this graph, which is 0.0155 h^{-1}. This parameter reflects the rate at which disturbances generated by the aerator system cause ammonia to be transferred from water to air at the water surface and serves as a measure of the efficiency of this transfer process.

Table 1: Experimental results: mass transfer

Interval Nº	Length of interval (h)	P ave (atm)	T ave (ºC)	C_L ave (mg/L)	AB (kg)	TA (kg)	AS (kg)	N (kg/h)	N/V (g.h^{-1}m^{-3})
1	21	4.6 x 10^{-5}	20.9	59.2	6.5	330.0	323.5	15.4	5.1
2	33	7.45 x 10^{-5}	18.6	99.7	16.7	180.0	163.3	4.9	1.6
3	15	7.23 x 10^{-5}	17.1	104.1	7.4	120.0	112.6	7.5	2.5
4	9	7.16 x 10^{-5}	15.7	111.5	4.4	30.0	25.6	2.8	0.9
5	15	7.31 x 10^{-5}	15.7	114.2	7.5	60.0	52.5	3.5	1.2
6	9	6.47 x 10^{-5}	14.7	106.6	4.0	60.0	56.0	6.2	2.1
7	15	6.45 x 10^{-5}	15.3	103.2	6.7	60.0	53.3	3.6	1.2
8	9	6.84 x 10^{-5}	16.4	103.3	4.2	30.0	25.8	2.9	1.0
9	24	7.01 x 10^{-5}	17.0	102.6	11.5	120.0	108.5	4.5	1.5
10	15	4.90 x 10^{-5}	15.7	74.4	5.1	60.0	54.9	3.7	1.2
11	7	4.34 x 10^{-5}	15.8	65.9	2.1	60.0	57.9	8.3	2.8
12	28	5.74 x 10^{-5}	17.3	82.7	11.0	60.0	49.0	1.8	0.6
13	15	5.82 x 10^{-5}	16.4	88.0	6.0	30.0	24.0	1.6	0.5
14	24	5.47 x 10^{-5}	15.1	88.2	9.0	30.0	21.0	0.9	0.3
15	24	4.79 x 10^{-5}	14.4	80.1	7.9	60.0	52.1	2.2	0.7
16	37	5.35 x 10^{-5}	15.8	82.6	13.6	60.0	46.4	1.3	0.4
17	37	4.59 x 10^{-5}	15.8	69.9	7.6	210.0	202.4	5.5	1.8
18	24	3.29 x 10^{-5}	14.8	53.9	5.4	30.0	24.6	1.0	0.3
19	24	3.33 x 10^{-5}	14.3	55.9	5.1	60.0	54.9	2.3	0.8
20	22	3.54 x 10^{-5}	15.1	56.8	8.0	60.0	52.0	2.4	0.8
21	33	3.28 x 10^{-5}	14.7	53.1	6.1	30.0	23.9	0.7	0.2
22	27	2.20 x 10^{-5}	12.5	40.7	2.8	90.0	87.2	3.2	1.1
23	18	1.84 x 10^{-5}	12.8	33.6	0.6	30.0	29.4	1.6	0.5
24	5	1.80 x 10^{-5}	13.2	32.2	1.9	30.0	28.1	5.6	1.9
25	15	1.88 x 10^{-5}	12.6	34.6	1.2	30.0	28.8	1.9	0.6
26	9	1.86 x 10^{-5}	12.3	34.7	1.9	15.0	13.1	1.5	0.5
27	15	1.78 x 10^{-5}	12.1	33.7	1.0	30.0	29.0	1.9	0.6
28	8	1.70 x 10^{-5}	11.9	32.6	2.8	30.0	27.2	3.4	1.1
29	24	1.42 x 10^{-5}	11.6	27.5	1.5	30.0	28.5	1.2	0.4
30	15	1.30 x 10^{-5}	11.6	25.2	0.8	30.0	29.2	1.9	0.6
31	9	1.40 x 10^{-5}	12.6	25.7	0.9	15.0	14.1	1.6	0.5
32	24	1.23 x 10^{-5}	12.8	22.4	0.8	45.0	44.2	1.8	0.6
33	38	9.26 x 10^{-6}	12.8	16.9	0.6	30.0	29.4	0.8	0.3

Pave = average partial pressure; Tave = average temperature; AB = overall ammonia loss in bubbles; TA = total ammonia loss; AS = overall ammonia loss in surface; N = average mass flux from the surface of the lagoon, C_L ave = average concentration of free ammonia in the liquid phase.
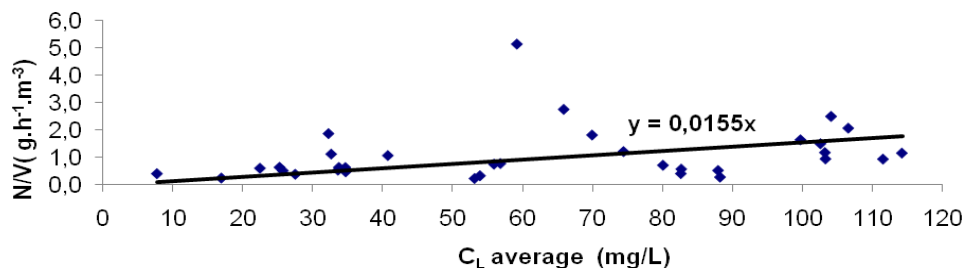

Figure 2: Plot for determining the value of $K_L a$, the overall ammonia transfer coefficient

CONCLUSIONS

For Pond D at the Taylors Road Landfill site only around 10% of the total ammonia removed is accounted for by diffusion of ammonia into the bubbles produced by the surface aerators. Losses attributable to nitrification are 2-3% at most. Desorption of ammonia to atmosphere at the lagoon surface is the dominant removal process in Pond D, accounting for at least 87% of the ammonia removed. This result provides confirmation in the field of previous laboratory findings. Evidently the extent of surface disturbance generated by aerators is a potentially very important factor when choosing a surface aerator for use on a leachate treatment pond.

The K_La value for Pond D under its present operating conditions was estimated to be 0.0155 h^{-1}. At this stage there are no published K_La values for leachate ponds to compare this value with.

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