

Desorption rate of volatile compounds in polishing ponds

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Abstract Increase of pH in polishing ponds can be predicted quantitatively from variations in alkalinity and acidity. These variables are affected by processes that develop simultaneously in ponds: (1) CO₂ desorption, (2) biological CO₂ removal by photosynthesis and (3) NH₃ desorption. An experimental investigation was carried out to determine the desorption rate of carbon dioxide and ammonium. It is shown that CO₂ and NH₃ desorption can be described by Fick's law, which describes desorption of a gaseous compounds from water as a first order process with respect to the degree of oversaturation which is the driving force of the process. An experimental investigation was carried out to determine the desorption rate constant. The value of the constant proved to be inversely proportional to the depth of the pond (H) and its value at 26 °C was established as $K_{CO_2} = 0.34/H \text{ d}^{-1}$ for carbon dioxide and $K_{NH_3} = 0.33/H \text{ d}^{-1}$ for ammonium.

Keywords digested sewage; nutrient removal; pos treatment; waste stabilization ponds.

INTRODUCTION

High rate anaerobic reactors like UASB (upflow anaerobic sludge blanket) have a high efficiency of organic material removal at short retention times, but are inefficient for pathogen and nutrient removal. (Van Haandel & Lettinga, 1994). When nitrogen removal is desirable, polishing ponds can be used a post treatment alternative. In these ponds the pH tends to rise and this in turns triggers of ammonium desorption from the liquid phase to the air. Cavalcanti *et al* (2001) have shown that pH in polishing ponds rises principal due to the removal of CO₂ by physical desorption and photosynthetic consumption by algae. The low turbidity of the anaerobic effluent permits a high photosynthesis rate (CO₂ consumption) and the oxidation rate (CO₂ production) is low due to a low organic material concentration, so that there is a net CO₂ removal. Carbon dioxide desorption will occur when the liquid phase is supersaturated with the gas which occurs at a concentration of about 0.5 mg/L. Ammonium desorption will take place at any concentration and is equivalent to the removal of a strong base to the liquid phase, reducing the alkalinity and increasing the acidity and therefore is another factor in pH variation. A third process with possibility of affecting pH is the precipitation of calcium carbonate.

Van Haandel and Lettinga (1994) have shown that pH in waste water and treatment plants is determined by the carbonic species distribution which in turn define the alkalinity and acidity as defined by Loewenthal and Marais (1976):

$$(a) \text{ Alkalinity} \quad \text{Alk} = 2[\text{CO}_3^{=}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (1)$$

$$(b) \text{ Acidity} \quad \text{Ac} = 2[\text{CO}_2] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \quad (2)$$

$$(c) \text{ pH} \quad \text{pH} = -\log(\text{H}^+) \quad (3)$$

The interrelation of pH, acidity and alkalinity can be expressed by the Deffeyes equation obtained by rearranging Eqs (1, 2 and 3) (Deffeyes, 1956):

$$\text{Alk} = [\text{Ac} + 10^{(\text{pH}-\text{pK}_1)} - 10^{-\text{pH}}] * [1 + 2 \cdot 10^{(\text{pH}-\text{pK}_2)}] / [1 + 2 \cdot 10^{(\text{pK}_1-\text{pH})}] \quad (4)$$

Where:

$$\text{pK}_1 = -\log K_1 = 6.33 \text{ and } \text{pK}_2 = -\log K_2 = 10.33 \text{ (at } 25^\circ\text{C)}$$

K_1, K_2 = dissociation constants of the carbonic system.

It will prove to be convenient to derive an expression to link the CO₂ concentration explicitly to alkalinity and pH. From the dissociation of carbon dioxide and Eq (4):

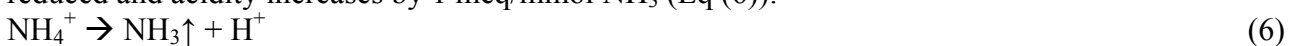
$$[\text{CO}_{2,l}] = \text{Alk} / \{ (2 \cdot 10^{(\text{pH}-\text{pK}_2)+1}) \cdot 10^{(\text{pH}-\text{pK}_1)} + 10^{(\text{pH}-\text{pK}_w)} - 10^{-\text{pH}} \}$$

(5)

Figure 1 is a graphical representation of Eq (4): for different pH values the linear relationship of Eq (4) is drawn. Point 1 represents the ionic equilibrium for a pH of 7.0 and an alkalinity of 7 meq/L (350 mgCaCO₃/L), which could well be characteristic for the effluent of a UASB reactor treating sewage. The removal of CO₂ and NH₃ in ponds can now be evaluated by considering the variation of alkalinity and acidity by these processes. From definition of alkalinity in Eq (2), it is not affected by CO₂ removal. However Eq (2) shows that acidity is affected: there is a decrease of 2 meq of acidity for a CO₂ increase of 1 mmol. Hence when CO₂ removal occurs the ionic equilibrium point is displaced vertically down by 2 meq/mmol removed CO₂.

Figure 2 also shows a curve for the acidity-alkalinity relationship for water that is saturated with CO₂ (0.5 mgCO₂/L). It can be seen that the liquid at point 1 is initially oversaturated, as is to be expected for an anaerobic effluent. However as CO₂ removal proceeds the degree of over saturation decreases and when pH reaches a value of about 8,8 desorption is no longer possible.

If a higher pH is to be reached, biological CO₂ removal by photosynthesis is the only alternative. For the example the maximum CO₂ desorption is 10.2-6.4 = 3.8 meq/L or 1.9 mmol CO₂/L. At pH levels higher than about 8.8 the process is reversed and CO₂ starts to be absorbed by the pond from the atmosphere. Desorption of ammonium is equivalent to the addition of a strong acid: alkalinity is reduced and acidity increases by 1 meq/mmol NH₃ (Eq (6)):



Hence the ionic equilibrium point is displaced in upward direction with an angle of 135°. It will be shown that a high rate of ammonium desorption is only feasible if the pH value is high. In Figure 1, desorption of 3 meq/L (42 mgN/L) is depicted for a final pH of 9.5. It can be seen that under these conditions the final alkalinity and acidity have values of about 4.0 and 3,4 meq/L respectively. For the example there is a need to reduce the acidity by 10.2-0.4 = 9.8 meq/L by CO₂ removal but the maximum removal by desorption is only 3.8 meq/L, so that at least 9.8-3.8 = 6.0 meq/L = 3 mmol have to be removed biologically by photosynthesis. Figure 1 is useful to estimate the extent of CO₂ and NH₃ removal but it does not reveal the rate of the processes. The rates of desorption can be expressed by Fick's law:

$$r_d = (dC/dt)_d = K_d(C-C_s) \quad (7)$$

where

r_d : desorption rate

K_d : desorption constant

C : concentration of the desorbing compound

C_s : saturation concentration (= 0 for ammonium (no ammonium in air) and = 0,01 mmolCO₂/L at 25 °C (Loewenthal and Marais, 1976)).

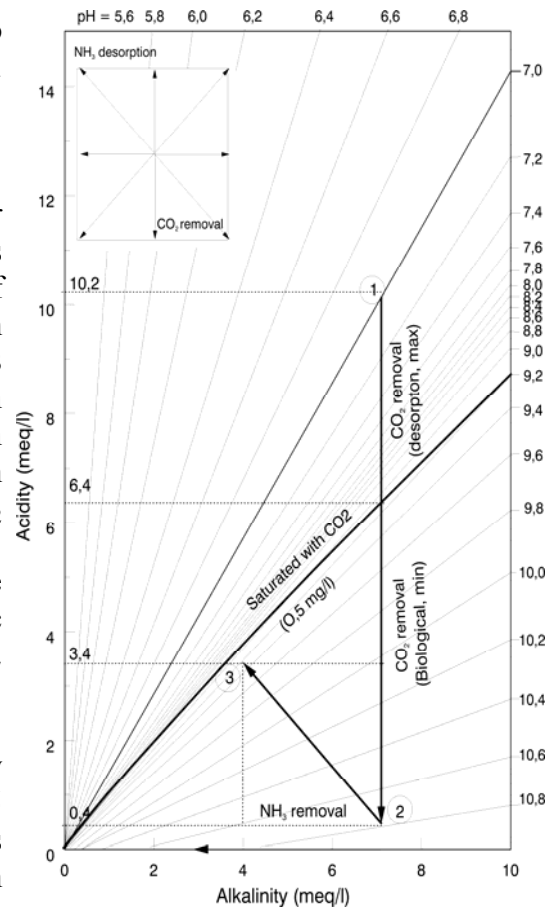


Figure 1: Deffeyes diagram for 25 °C
($\text{pK}_1 = 6,33$; $\text{pK}_2 = 10,33$)

EXPERIMENTAL INVESTIGATION

The desorption constant of carbon dioxide and ammonium can be calculated from determinations of the rate of desorption in batch ponds. In the experimental investigation plastic cylindrical tanks with different heights were used as models for batch polishing ponds. Depths of 20, 40 and 60 cm were investigated, since it had been established in earlier experiments that higher depths resulted in a slow increase of pH.

Experiment 1: CO₂ desorption

CO₂ desorption kinetics was determined both for water and polishing pond (PP) effluent. The PP was being fed with UASB effluent and operating at a hydraulic retention time (HRT) of 3 days. Three ponds were used: one being filled with water and the other two with pond effluent. In the pond with water the carbonic species concentration was increased by adding NaHCO₃ at 0,64 g.L⁻¹ and the pH was decreased with HCl. The ponds with effluent were operated until the concentration of DO was at saturation level (DO = 7,5 mg/L) and then pH was also reduced to a value of 6,2. The first and second ponds were gently stirred by a vertical axis, so as to obtain uniform values of the pH and temperature. To evaluate the influence of the agitation, the third pond was only stirred just before measurements of pH, temperature and dissolved oxygen. Experiments were continued until pH in one of the ponds remained at a near constant value. During the experiment in ponds 2 and 3 photosynthesis was controlled by blocking sunlight part of the day, so that there was no or little biological CO₂ removal and any change of the concentration was attributable to physical removal.

CO₂ concentration was calculated as a function of time from the total carbonic species concentration, which itself was determined as half of the sum of alkalinity and acidity. Alkalinity determinations were carried out by standard titrimetric tests and acidity was calculated from the values of pH and alkalinity by using the Deffeyes diagram. Eqs (1 and 2) show that the sum of alkalinity and acidity is equal to half the total carbonic species concentration:

$$C_{\text{tot}} = (\text{Ac} + \text{Alk})/2 \quad (8)$$

Desorption rate constant for CO₂ was determined by using Ckicks law:

$$\begin{aligned} \text{Rd}_{\text{CO}_2} &= K_{\text{CO}_2}([\text{CO}_2]_s - [\text{CO}_2]_{\text{liq}}) \text{ or} \\ K_{\text{CO}_2} &= \text{Rd}_{\text{CO}_2}/([\text{CO}_2]_s - [\text{CO}_2]_{\text{liq}}) \end{aligned} \quad (9)$$

where

Rd_{CO₂}: observed rate of change of the CO₂ concentration (mmol/L/d);

K_{CO₂}: desorption constant (d⁻¹);

[CO₂]_{liq}: CO₂ concentration in the liquid phase (mmol.L⁻¹);

[CO₂]_s: saturated CO₂ concentration (0,01 mmol.L⁻¹, Loewenthal and Marais 1976) .

Experiment 2: Ammonium desorption (NH₃)

In this experiment also ponds with three heights (0.6, 0.4 and 0.2m) were used. Again three series of batch ponds were operated one being filled with tap water and the other two with UASB effluent. The pH of water and effluent was first raised with sodium hydroxide to a value of 9 and after precipitation of calcium carbonate transferred to the ponds and ammonium chloride was added for an initial concentration of 40 mg/L. Again the rate of photosynthesis in the ponds with pond effluent was controlled so that the OD concentration was near to the saturation level and one series of ponds with UASB effluent was stirred and the other was not. The tests were stopped when the ammonium concentration became very small (< 1 mg/L). From ammonium dissociation the rate of desorption vcan be expressed as:

$$\begin{aligned} \text{Rd}_{\text{NH}_3} &= K_{\text{NH}_3}[\text{NH}_3] = K_{\text{NH}_3} N_{\text{tot}}/(K_a/[\text{H}^+] + 1) \text{ or} \\ K_{\text{NH}_3} &= \text{Rd}_{\text{NH}_3}/ N_{\text{tot}}/\{K_a/[\text{H}^+] + 1\} \end{aligned} \quad (10)$$

where:

K_a = dissociation constant of ammonium; pK_a = 0,09018 + 2729,92/T (Emerson et al, 1975).

RESULTS AND DISCUSSION

Table 1 shows the measured (pH and alkalinity) and calculated data to determine the dissociation constant K_{CO_2} . As example, the calculations are shown for pond 1 filled with tap water and oversaturated with respect to CO_2 . The following calculation steps are required to calculate de desorption constant: (1) from pH and alkalinity determine the acidity by Eq (4); (2) from alkalinity and acidity determine the total carbonic species concentration C_T by Eq (8); (3) from the change of C_T as a function of time determine the rate of change $\Delta C_T/\Delta t$; (4) from Eq (5) determine the CO_2 concentration as a function of time; (5) calculate the degree of oversaturation as a function of time, as the average of CO_2 concentration during the different intervals of measurement and the saturation concentration (0,01 mmol/L) and (6) desorption constant K_{CO_2} is the ratio between the desorption rate and the degree of oversaturation.

The average value of K_{CO_2} in the experiment (Table 1) is $0,56 d^{-1}$. The constants obtained at subsequent intervals vary considerable. This can be attributed to small experimental errors in the determination of pH and alkalinity. The result is especially sensitive with respect to pH.

Table 2 shows the average values of desorption tests with supersaturated CO_2 solutions at several depths for the three ponds. The equivalent K_{CO_2} value at a depth of 1 m is also calculated ($0,34.d^{-1}$). This value is obtained by considering that desorption is a surface limiting process and that therefore the value of the constant is inversely proportional to the depth. The results clearly show the validity of the assumption that the value of the constant is inversely proportional with the depth of the pond. The results also indicate that the values of the constant in the continuously stirred tap water and PP effluent are similar but the constant in the PP effluent without continuous stirring tends to be somewhat smaller, possibly due to stratification of the CO_2 concentration over the pond depth.

Table 1: experimental result of pH and alkalinity as functions of time in tap water, supersaturated with CO_2 and calculation procedure to determine the desorption rate constant.

Time (d)	pH (-)	Alc _{HCO₃⁻} (meq/L)	Acidity (meq/L)	C _T (meq/L)	$\Delta C_T/\Delta t$ (meq/L/dia)	[CO ₂] _{liq} (mmol/L)	Supersaturation (mmol/L)	$K_{CO_2} d^{-1}$
0	6,22	5,41	19,35	12,38	-	6,97	-	-
1	6,36	5,45	15,62	10,53	1,85	5,08	6,02	0,31
2	6,78	5,23	8,96	7,09	3,44	1,87	3,46	0,99
3	6,97	5,37	7,86	6,62	0,48	1,24	1,55	0,31
4	7,26	5,15	6,36	5,76	0,86	0,61	0,92	0,94
5	7,43	5,13	5,95	5,54	0,22	0,41	0,50	0,44
6	7,61	5,15	5,69	5,42	0,12	0,27	0,33	0,36

Table 2: average values of the CO_2 desorption constant at different depths and in different environments, as well as the extrapolated values for a depth of 1 m. Temperature $\approx 26^\circ C$.

Depth	Desorption rate constant			Average	Extrapolated H = 1 m		
	Tap water stirred	PP effluent stirred	PP effluent not stirred		Tap water stirred	PP effluent stirred	PP effluent not stirred
0,6	0,56	0,58	0,57	0,5	0,336	0,348	0,342
0,4	0,88	0,85	0,81	0,8	0,352	0,34	0,324
0,2	1,77	1,65	1,59	1,8	0,354	0,33	0,318
					0,35	0,34	0,33

Table 3: average values of the NH₃ desorption constant at different depths and in different environments, as well as the extrapolated values for a depth of 1 m. Temperature ≈ 26 °C.

Depth	Desorption rate constant			Average	Extrapolated H = 1 m		
	Tap water stirred	PP effluent stirred	PP effluent not stirred		Tap water stirred	PP effluent stirred	PP effluent not stirred
0,6	0,55	0,52	0,47	0,5	0,33	0,312	0,282
0,4	0,78	0,85	0,81	0,8	0,312	0,34	0,324
0,2	1,92	1,86	1,62	1,8	0,384	0,372	0,324
					0,34	0,34	0,31

Table 3 shows the values of the desorption constant for ammonium. The same observations made for CO₂ desorption also apply for NH₃ desorption: in good approximation the value of the constant is inversely proportional to the depth and in a not continuously stirred pond the value of the constant tends to be marginally smaller. Coincidentally the values of the constants are very similar for CO₂ and NH₃ with average values of 0,34 d⁻¹ for CO₂ and 0,33 d⁻¹ for NH₃.

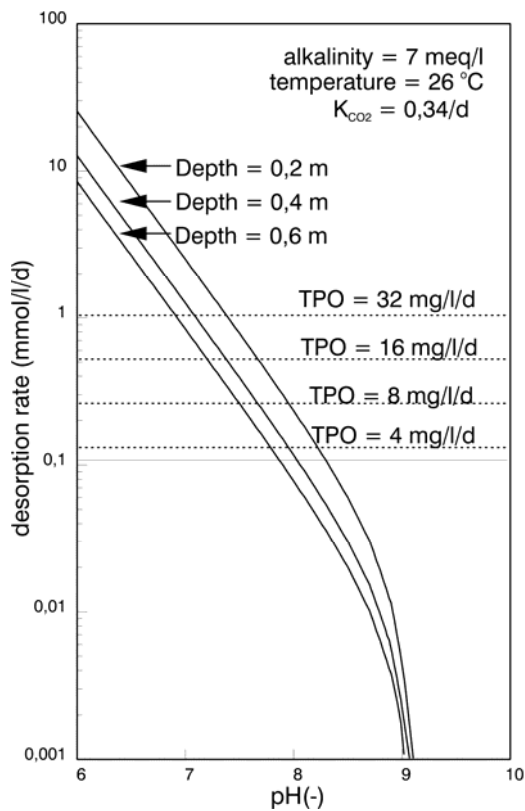


Fig. 2a CO₂ desorption rate as a function of pH for different depths.

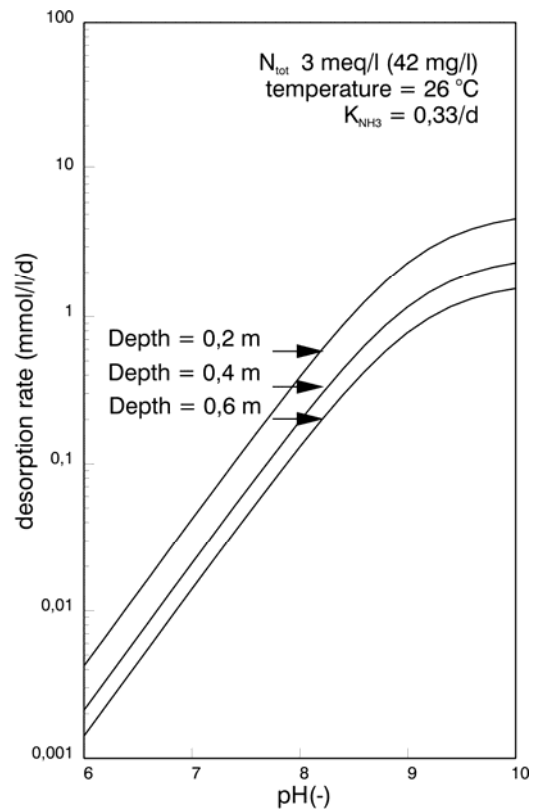


Fig. 2b NH₃ desorption rate as a function of pH for different depths.

Once desorption constants have been determined, that rate of desorption process can now be calculated for any pH for any value of the alkalinity and ammonium concentration. This has been depicted in Fig 2a and 2b for CO₂ and NH₃ respectively. In Fig 2a it can be noted that the rate of CO₂ desorption decreases rapidly as the pH increases: at a pH of 8 the rate is of the order of 0,1 mmol/L/d when compared with the extent of required removal. In Fig 1 it was concluded that for fairly typical conditions of pH, alkalinity and ammonium concentration the required CO₂ removal was about 5 mmol/L (10 meq/L). Hence a rate of 0,1 mmol/L would require a retention time of 50 days, which would be impractically long.

On the other hand in Fig 2b it can be seen that ammonium has only a relevant rate if pH is high: at a pH of 8 the rate is of the order of 0,1 mmol/L (Fig 2b) but it is very low if a removal of 3-4 meq/L is to be reached, as very often will be the case. These considerations lead to the conclusion that for ammonium removal in ponds the pH needs to be high. As the CO₂ desorption rate is low, the removal of nitrogen in ponds is only feasible if CO₂ is removed due to biological processes, in other words if the removal rate by photosynthesis is considerably higher than the production rate by oxidation of organic material. The main factors that influence the rate of biological CO₂ removal in polishing ponds are: (1) sunlight irradiation, (2) transparency of the liquid phase, (3) low concentration of organic material (4) shallow depth of the pond and (5) a high concentration of active algae. These conditions can be satisfied in regions with plentiful sunshine when the pond influent has little organic material and a low turbidity; such is the case when efficient anaerobic pre treatment is applied.

CONCLUSIONS

pH in ponds is affected basically by desorption and biological removal of CO₂ and by desorption of ammonium. CO₂ removal tends to increase the pH, ammonium removal has the opposite effect.

CO₂ and NH₃ desorption from ponds can be described as a first order process in which the desorption rate is the product of desorption constant and saturation concentration.

The desorption constant was shown to be inversely proportional to the pond depth (H) and for a temperature of 26 °C the experimental values were determined as: $K_{CO_2}=0,34/H \text{ d}^{-1}$ and $K_{NH_3}=0,33/H \text{ d}^{-1}$

In practice for nitrogen removal a high pH is required, which makes significant CO₂ desorption impossible. Nitrogen in ponds can only take place if significant CO₂ occurs, which in turn can only happen if the rate of photosynthesis is considerably higher than the rate of organic material oxidation by oxygen.

It is important to bear in mind that nitrogen removal in ponds is accompanied by transfer of ammonium to the atmosphere, which depending on the conditions may be undesirable (acid rain).

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