Oxidation-Nitrification and Denitrification of Veal Calf Manure

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A T the ASAE International Symposium on Livestock Wastes in Ohio in 1971, Ten Have (1971) reported on aerobic decomposition of veal calf and pig liquid manure and pig urine in 35 to 1000 m^3 aeration basins and oxidation ditches.

To get a more flexible approach we started experiments in 2 to 20 liter fermentors. In this way it is much easier to investigate the influence of varying conditions and process operation on purification results. We studied the following questions:

Why is there an incomplete oxidation of ammonium and an accumulation of nitrite? Is this inherent to the procedure applied, to substrate composition or to environmental factors?

How can biological treatment be optimized to get an acceptable effluent quality regarding BOD, N and P and a small volume of surplus sludge?

THEORY OF OXIDATION-NITRIFICATION AND DENITRIFICATION

What happens when we add manure, containing BOD and ammonia (= NOD), to an aerated activated sludge suspension (Fig. 1A)? A rapid substrate respiration will occur, leading to a low level of dissolved oxygen, thus inhibiting nitrification and even bringing along denitrification of part of the nitrite or nitrate accumulated in the foregoing period. After some time the BOD cannot be met and respiration will slow down to endogenous respiration. The level of dissolved oxygen will then increase, resulting in the inhibition of denitrification and stimulating nitrification (nitrifiers use carbondioxide as a carbon source). When the latter is completed, the dissolved oxygen level will further increase and a new load may be added.

However, the "over-all" removal of nitrogen via nitrification and denitrification has certain limits. The substrate has to supply enough BOD for the denitrification if no additional BOD, as for example methanol, is added or otherwise there will be an accumulation of nitrite or nitrate. It is also known that denitrification of nitrate demands more BOD than denitrification of nitrite. Theoretically, complete denitrification demands at least 1.7 g of substrate-BOD per g

of nitrite-nitrogen and 2.9 g per g of nitrate-nitrogen. In practice complete denitrification requires about twice the theoretical amount of BOD (some BOD is used for cell synthesis). The overdose of BOD should be removed afterwards via respiration with oxygen.

It will be clear that the largest possible denitrification will be achieved when we inhibit the substrate respiration for some time after the addition of fresh substrate, which can be done by stopping the aeration. This procedure is outlined in Fig. 1B.

It may be mentioned that in certain cases nitrification and denitrification can also occur simultaneously when an oxygen gradient exists in the sludge flocs. We met this situation under certain conditions in experiments with pig manure.

For a more detailed discussion of the theory we refer to McCarthy and Haug (1971).

MATERIALS AND METHODS

Well defined liquid manure was prepared by mixing fresh urine and feces, in the ratio as excreted, sieving coarsely (0.6 mm) and storing at 4 C. Difficulties with highly variable samples, taken from manure pits, were thus eliminated. Once a day or more the activated sludge was loaded with liquid manure, after removal of effluent (further on called primary effluent) or mixed liquor. Primary effluent or mixed liquor was drawn off when ammonium-nitrogen was almost completely nitrified during aeration. As in Fig. 1B, aeration was stopped after addition of a load to denitrify nitrite and/or nitrate present in the mixed liquor. After more or less complete denitrification, aeration was resumed. More than 90 percent of the denitrification took place in the mixed liquor, since less then 10 percent of the nitrite was removed with primary effluent. This 10 percent was lost by denitrification during storage; to increase that denitrification rate some methanol was added. A "secondary denitrified" effluent could then be separated from "denitrifying sludge" by gravity settling after stirring.

Three different veal calf manures have been used. Their composition and the percentages of the components derived from the urine are shown in Table 1. Samples A, B and C were from 2, 6 and 6 weeks old calves. In case of sample B the calves had been fed with soya as part of their
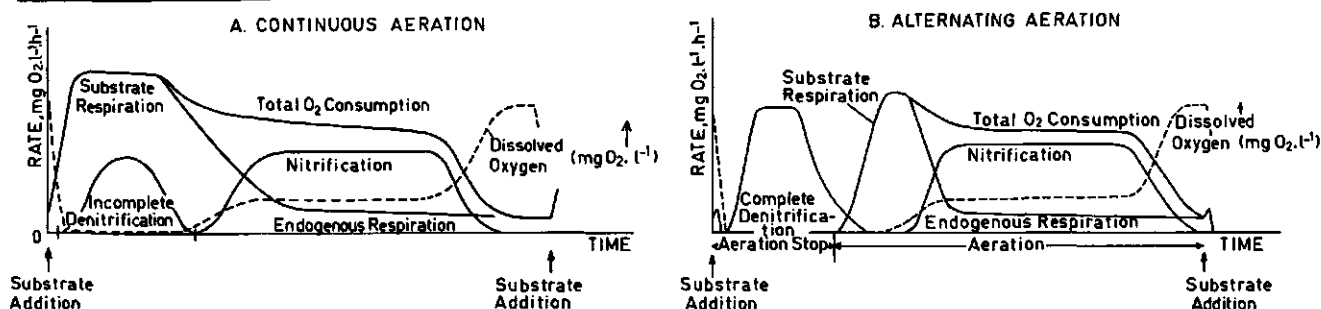
FIG. 1 Dissolved oxygen and rates of respiration, nitrification and denitrification in an activated sludge system with continuous or alternating aeration.

MANAGING LIVESTOCK WASTES

TABLE 1. COMPOSITION OF THREE VEAL CALF MANURES
USED IN THE EXPERIMENTS AND PERCENTAGES OF THE
COMPONENTS CONTRIBUTED BY URINE.

Components	g per liter in sample			Percent contributed by urine to sample		
	A	B	C	A	B	C
COD	24	38	24	36	20	41
Volatile solids	12	23	11	42	24	47
Ash	12	13	12	89	64	81
Kjeldahl-N	4.4	6.0	7.4	86	74	91
NH_4-N	3.5	4.4	6.6	97	97	98
Phosphorus (P)	0.8	1.3	1.5	91	52	77

ration and therefore produced relatively more feces. As can be seen from Table 1 most of the nitrogen, phosphorus and ash, but less than half of the Chemical Oxygen Demand (COD) and volatile solids, came from the urine. Liquid manure, mixed liquor and effluent were analysed for COD, Kjeldahl-nitrogen, ammonium-nitrogen, total and volatile solids (ash) and phosphorus in every experiment; thus, material balances could be calculated. Once a day or more ammonium-, nitrite-, and nitrate-levels were estimated by color-reactions and teststrips; besides pH and redox potential were measured. Dissolved oxygen in the mixed liquor and the oxygen pressure in the air after passage through the mixed liquor were measured with temperature compensated oxygen electrodes. From the recorded value of the oxygen pressure after passage through the mixed liquor and the aeration rate, the amount of oxygen consumed could be calculated. Phosphates were separated from the effluent by flocculation with iron-aluminum-sulphate or lime, followed by settling and filtration; by adding lime to the mixed liquor more phosphate could be discharged with the surplus sludge.

The series of experiments described here was performed in a 2 liter fermentor with 1.2 liter (number 1-12) or 1.6

CONTROL OF PROCESS CONDITIONS

We tried to control the process conditions so that no bad smell was noticeable and a maximum loss of nitrogen was achieved. Air supply during aeration was amply sufficient in all cases. An aeration scheme was started with experiment 13 in which aeration was alternated with non-aeration 4-6 times per 24 hours. This appeared to be no success because the nitrification of the same load was no longer completed in 24 hours and too much BOD was lost during aeration periods, thus leading to incomplete denitrification. This schedule may be more successful, if the load is also split up, which is being investigated at the moment. Aeration rate and time, temperature and sludge concentration (estimated from analyses) are given in Table 2. Stirring rate was around 450 ppm. This rate influenced the oxygen transfer to the solution and therefore oxygen consumption and dissolved oxygen level. Thus, varying this rate occasionally was used to lengthen either the denitrification time or the nitrification time (Fig. 1B). The pH of the mixed liquor was sometimes adjusted by adding lime, if pH went below 7.0. The sludge load varied with variations in sludge level and loading. The sludge load with COD and with NOD (calculated as Kjeldahl-N times 3.4) is given in Table 3. The removal of COD and NOD in our system proved to be about 50 percent and more than 80 percent, respectively (Table 4). The average daily load with COD and NOD (Table 3) was about 2.0 and 1.2, respectively. Thus, the amount of oxygen used for the oxidation of nitrogen was about equal to the amount used for the oxidation of organic carbon. During part of experiment 15 and during experiment 16 the BOD-load was increased by addition of methanol to the mixed liquor together with the manure load. This was done to

TABLE 2. AERATION RATE, AERATION TIME, TEMPERATURE
AND ESTIMATED SLUDGE CONCENTRATION

Experiment number	Aeration rate, 1 air h^{-1}	Aeration time, Percent of time	Temperature deg C	Sludge concentration g MLVSS .1^{-1}†
1 - 5	2	85 - 94	16 - 29	5 - 12
6	2	90	14.5	7 - 13
7*	2	70	14.5	8 - 15
8	1 - 2	82	14.5	10 - 28
9 - 11	0.5 - 1	82 - 92	14.5	7 - 15
12 - 14	1	71 - 90	14.5	7 - 10
15*	1	54	14.5	6 - 7
16	1	50	14.5	6 - 7

*Transition to sample B and C, respectively
†MLVSS = Mixed Liquor Volatile Suspended Solids

TABLE 3. DAILY LOAD, SLUDGE LOAD AND VOLUME LOAD WITH
OXIDIZABLE CARBON (COD) AND NITROGEN
COMPOUNDS (NOD) FROM MANURE.

Experiment number	Daily load		Sludge load		Volume load
	COD	NOD	COD	NOD	COD + NOD, kg $O_2.m^{-3}.day^{-1}$
	g $O_2.day^{-1}$		g $O_2.g$ MLVSS$^{-1}.day^{-1}$		
1 - 5	2.4	1.4	0.20	0.12	3.1
6	1.9	1.2	0.14	0.09	2.6
7	3.0	1.5	0.19	0.10	3.7
8	3.0	1.6	0.13	0.06	3.8
9 - 11	1.6	0.9	0.10	0.05	1.8
12 - 14	2.1	1.2	0.14	0.08	2.1
15	0.85 (0.90*)	0.9	(0.08*)	0.08	1.1
16	0.65 (1.0 *)	0.7	(0.09*)	0.07	1.1

*Addition of added methanol included

Experiment number	Removal or transformation				Discharge of nitrogen compounds	
	COD	TVS†	Kjeldahl-N	NH₄-N	with surplus sludge	with effluent
	Percent of influent				Percent of influent	
1 - 5	60	36	86	97 - 100	8 - 13	1 - 6
6	65	21	83	97	14	4
7	51	32	80	99	15	4
8	35	30	77	97	21	2
9 - 11	41	24	76	95 - 103	15 - 22	2 - 4
12 - 14	48	36	81	96 - 102	16 - 18	0 - 3
15	51(53*)	25	88	96	8	4
16	58(70*)	40	85	95	10	5

*Removal of added methanol included
†TVS = Total Volatile Solids

improve the very low BOD/N ratio in manure sample C, and thus make complete denitrification possible. We also adjusted the time during which the mixed liquor was not aerated, so that maximum use was made of the carbon compounds in the substrate for denitrification. As the denitrification time was increased we had to lower the daily load since then less time was available for nitrification and removal of the overdose of BOD. The sludge concentration was controlled by removal of mixed liquor at the end of each experiment. Because of the presence of sludge, discharged mixed liquor gave a more rapid denitrification than primary effluent; no methanol had to be added to achieve this.

RESULTS AND DISCUSSION

The effluent quality is shown in Table 5. Ammonium- and Kjeldahl-nitrogen levels were still higher than desirable, but much lower than the values given by Ten Have (1971).

Remarkably even in the primary effluent hardly any nitrate could be detected. This was in contrast with preliminary experiments at a temperature of about 30 C, where nitrate dominated. The absence of nitrate might be explained from the fact that dissolved oxygen levels were more frequently and for a longer period zero or very low due to higher loading and longer periods without aeration. Nitrification to nitrite only means a more economic use of BOD as explained under "Theory". The remainder of nitrite in the denitrified effluent was caused by too small a dose of methanol or too short a denitrification time. The effluent still had a considerable COD-value, even after chemical flocculation. It is interesting that this did not mean that the BOD₅-level too was very high. For some effluents the COD/BOD₅ ratio was determined and appeared to be about 20. For the influent this ratio was about 2. Without lime addition the phosphate levels of the effluent were high, in spite of a large decrease compared to those of the influent. The lower phosphate levels during experiments 8-14 might be explained, at least partly, from the lime additions to the mixed liquor.

Decomposition, Transformation and Discharge

Mostly somewhat more of the influent Kjeldahl-nitrogen was lost than initially present as ammonium-nitrogen. This means that part of the organic nitrogen of the influent has been ammonified and afterwards nitrified and denitrified. The transformation of ammonium-nitrogen thus almost always was more than 100 percent when related to the amount initially added.

Table 4 shows the calculated discharge of nitrogen compounds with surplus sludge and effluent; in the calculation all NH₄-N present in the mixed liquor at the end of the experiments has been included in that discharged with the effluent. Thus, the discharge of nitrogen with effluent as shown in Table 4 is less favorable than in reality. A discharge of 1 percent of influent nitrogen with the effluent seems real. The discharge of nitrogen compounds with the surplus sludge may depend both on temperature and influent composition. The larger decrease of the COD (Table 4) in the experiments 1-6 compared to 8-14 may be caused by differences in temperature, substrate and/or other conditions.

Oxygen Consumption

The rate of oxygen consumption was higher at the higher temperatures. The oxygen consumed per kg of manure has been calculated from direct measurements and indirectly from material balances. From the theory the "overall" decrease of COD plus NOD should be equal to the oxygen consumed. The decrease of NOD is calculated as 1.7 times the nitrogen loss. In Table 6 the amount of oxygen consumed is compared with the calculated amount for some experiments; the agreement is good. From the values in Table 6 it can be calculated that 42, 49 and 84 percent, respectively, of the oxygen used for the oxidation of carbon compounds, from the samples A, B and C, is delivered by nitrite during denitrification. However, with sample C methanol was also added to the mixed liquor. If the oxidation of methanol is not included in the calculation for sample C, then 45 percent of the carbon oxidation took place by denitrification, which fits in rather well with the values of 42 and 49 percent. These percentages again show that denitrification demands an overdose of BOD. This can also be seen from the ratio of COD-removal and nitrogen

TABLE 5. EFFLUENT QUALITY OF SECONDARY
(DENITRIFIED) EFFLUENT

Experiment number	COD, g O₂.l⁻¹	Kjeldahl-N	NH₄-N	NO₂-N	P
		mg.l⁻¹			
1 - 5	1.5 - 2.3	70 - 220	35 - 70	2 - 20	220 - 380
5	1.2	100	40	25	150
7	2.2	190	100	5	280
8	1.7	100	50	30	25
9 - 11	1.5	100	85	0 - 10	15 - 120
12 - 14	1.8 - 2.2	60 - 140	10 - 25	0 - 40	40
15	1.6	40	35	0	35
16	2.4	130	30	5	70

TABLE 6. COMPARISON OF CALCULATED AND MEASURED OVER-ALL OXYGEN CONSUMPTION: RATIO BETWEEN DECREASE OF COD AND NITROGEN LOSS.

Experiment number	Decrease of COD + Decrease of NOD		= Calculated O_2-consumption	Measured O_2-consumption	Decrease of COD / Nitrogen loss g O_2/g N_2
	"overall" values expressed as g O_2/kg veal calf manure				
1 - 5	15.5	6.5	22.0	21.5 ± 2	4.1
6	14.5	6.0	20.5	22 ± 2	4.0
7	18.5	7.5	26.0	---	4.2
8	13.5	7.5	21.0	24 ± 2	3.1
9 - 11	16.0	8.0	24.0	—	3.3
12 - 14	17.5	9.0	26.5	—	3.3
15	12.0	11.0	23.0	—	1.9(2.1*)
16	13.0	11.0	24.0	—	2.1(3.7*)

*Removal of added methanol included

loss (Table 6); during the experiments 15 and 16 with manure sample C, this ratio had to be increased by methanol addition, to get complete denitrification.

CONTINUATION OF THE PROJECT

We are now automating the procedure, in order to investigate the results with more frequent loading split up over 24 hours. Experiments with larger scale plants have recently been started in The Netherlands in Wageningen. Efforts will be made to improve the effluent quality still more. Parallel, experiments with pig manure are also going on. Because of the higher BOD to nitrogen ratio in that substrate, the overdose of nitrogen is eliminated by simultaneous nitrification and denitrification. Our aim here is to produce biomass for animal feed combined with an acceptable effluent.

CONCLUSIONS

1 The nitrite accumulations found in practice during aerobic treatment of veal calf manure are caused by incomplete denitrification, during the time that dissolved oxygen is zero (Fig. 1A). Because of continued aeration after loading, maximum use of BOD for denitrification is not made (Fig. 1A vs. 1B). Over-aeration will lead to high dissolved oxygen levels and a high redox potential, further inhibiting denitrification. However, even with an optimal process, the BOD/N ratio of the manure may be too low for complete denitrification without addition of e.g. methanol.

2 The nitrite accumulation, accompanied by a low pH will inhibit further nitrification. This explains the accumulation of ammonia.

3 For optimal biological treatment, oxidation-nitrification should be alternated with denitrification, in such a way that in each cycle the added ammonia is fully nitrified and nitrite is kept below 500 mg/l NO_2 by denitrification. Thus, per cycle about 150 mg of ammonifiable nitrogen can be added per liter mixed liquor. How long aeration must be stopped per cycle will depend on the denitrification rate at the particular temperature and substrate composition. The pH should preferably be kept between 7 and 8, e.g. by adding lime.

4 Nitrification should be limited to nitrite formation in the case of wastes with a low BOD/N ratio; this can be done by working at low dissolved oxygen levels and a redox potential (E_{cal}) below + 100 mV. In this way complete denitrification can be achieved with the smallest amount of BOD.

References

1 McCarthy, P. L. and R. T Haug. 1971. Nitrogen removal from wastewaters by biological nitrification and denitrification p. 215-232. In: G. Sykes and F. A. Skinner (eds.), Microbial aspects of pollution. Soc. Appl. Bacteriol. Symp. Ser. 1. Academic Press, New York.

2 Ten Have, P. 1971. Aerobic biological breakdown of farm waste, p. 275-278. In: Livestock waste management and pollution abatement. Proc. Int. Symp. Livestock Wastes. ASAE, St. Joseph, Mich. 49085.