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COMPETITIVE OXIDATION BETWEEN COD AND AMMONIA IN THE AEROBIC LANDFILL LEACHATE TREATMENT

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ABSTRACT

Landfill leachate is rich in nitrogen and organic compounds; their concentration varies in a large extent. This behavior makes many difficulties for designing the treatment system. In the aerobic treatment, even at maintaining high dissolved oxygen, the removal efficiency and oxidation rate of ammonia decreases in increasing initial ammonia concentration and COD in the system. There is a competitive oxidation between ammonia and COD due to lack of dissolved oxygen content inside the biomass granulars, where the reaction occurs mainly.

The diffusion flux of different species is dependent on the concentration gradient between the bulk volume and the inner space of the granulars. Inside the granulars, oxygen concentration is smallest in comparison to others..

INTRODUCTION

In the aerobic treatment of wastewaters having high N/COD ratio, such as wastewater from fish processing, slaughterhouse or municipal landfill leachate, there are two oxidation processes occurring simultaneously: oxidation of organic matters and nitrification. Each process is carried out independently by different microorganisms present in the biomass, in fraction is determined by N/COD ratio.

Both nitrifying and heterotrophic organisms use dissolved oxygen for the COD and ammonia oxidation. From this fact, one could speculate that two processes proceed independently if the dissolved oxygen is sufficiently available. In fact, in the aerobic landfill leachate treatment, the phenomenon is observed that the rate of nitrification as well as of COD removal is interdependent even in the case of high dissolved oxygen excess.

N/C ratio in landfill leachate is rather high and varies largely throughout the year, ranges from 1:6 to 1:2. This feature makes it difficult to design the leachate treatment system with a stable operating efficiency.

The investigation of the competitive oxidation of ammonia and COD is therefore necessary for a proper designing of leachate treatment system.

BACKGROUND

During aerobic treatment, the biodegradable organic matters are converted to water and carbon dioxide by heterotrophic organisms and ammonia to nitrite and nitrate by autotrophic organisms. The oxygen usage rate is approximately 1,2 kg O₂/kg COD and 4,3 kg O₂/kg NH₃-N. For the nitrification, it also requires alkalinity for the ammonia oxidation into nitrite, about 7,2 kg as CaCO₃/kg N-NH₄.

The kinetic data of ammonia oxidation are treated by first order equation:

$$C = C_0 \exp(-kt) \quad (1)$$

Where: C₀ and C the concentration of ammonia at begin and at time t, k is the kinetic constant. The k - value represents the oxidation rate of the reaction under individual conditions.

MATERIALS AND METHODS

Leachate samples were collected from the municipal landfill site in Nam Son, Hanoi. Leachate characteristics were evaluated by a set of parameters involving the treating process: COD, total Kjeldahl nitrogen (TKN), ammonia, alkalinity. During the experiment nitrite, nitrate was

determined. The analysis of parameters was implemented according APHA procedures [1]. pH meter MP - 220 and DO meter YSI 550 were used for determining pH and dissolved oxygen. Ammonia, TKN, COD vary largely, range from 123 to 561 mg/l for nH₃, 178 to 632 for TKN and 320 to 870 mg/l for COD.

A batch reactor with an effective 5 l volume was used for the aerobic experiment. Temperature was maintained at 27°C. Phosphorus was added sufficiently for the reaction. DO level was always higher than 3 mg/l (3.2 to 3.8). To achieve the different COD/N ration, sucrose was added to the leachate.

Biomass was taken from the leachate treatment system at Nam Son landfill site (operated since 18 month, continuous SBR technology, average performance 800 m³/day) with a VMLSS of 2500 mg/l.

During the experiment, pH, alkalinity, ammonia, TKN, nitrite, nitrate and COD were measured. Before aerobic treatment, landfill leachate was clarified by using PAC and polymeric flocculants.

RESULTS AND DISCUSSION

The kinetic data for ammonia oxidation with initial concentration of above 200 and 300 mg NH₃-N/l under different COD/N ratios are tabulated in tables 1 and 2 as well as presented in figures 1, 2. The kinetic constants, k and the removal yield for ammonia and COD were calculated from equation (1) and from experiment values.

Table 1. Kinetic data for ammonia oxidation with initial concentration of above 200 mg NH₃-N/l under COD/N ≈ 3, 5, 7.

COD/N	Time (h)	pH	Alkalinity (mg CaCO ₃ /l)	NH ₄ ⁺ (mgN/l)	TKN (mgN/l)	COD (mgO ₂ /l)
3:1	DV	8,3	1595	203	214	622
	1	8,3	1455	177	-	578
	2	8,4	1320	159	-	556
	3	8,5	1150	126	-	547
	4	8,5	995	105	-	531
	5	8,5	860	83	-	510
	6	8,6	700	61	-	497
	7	8,6	580	47	67	486
Yield (%)				76,8		21,9
5:1	DV	8,1	1575	204	319	1032
	1	8,1	1495	184	-	915
	2	8,2	1385	163	-	838
	3	8,2	1270	145	-	760
	4	8,2	1140	127	-	689
	5	8,3	1026	109	-	640
	6	8,3	905	95	-	604
	7	8,4	805	80	64	576
Yield (%)				60,8		44,2
7:1	DV	8,1	1580	196	207	1387
	1	8,1	1510	186	-	1250
	2	8,2	1430	174	-	1122
	3	8,2	1330	156	-	994
	4	8,2	1235	141	-	875
	5	8,2	1130	127	-	736
	6	8,3	1025	113	-	670
	7	8,3	895	97	41	602
Yield (%)				50,5		56,6

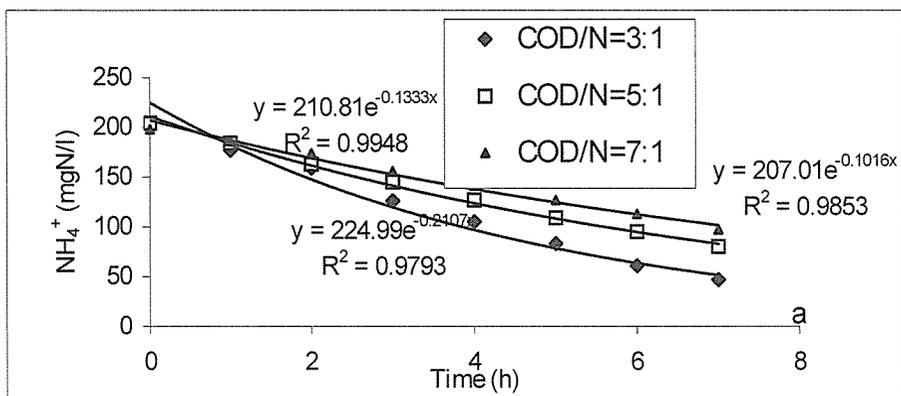


Figure 1. The influence of COD concentration on the ammonia oxidation (initial concentration ~ 200 mg NH₃-N/l)

Table 2. Kinetic data for ammonia oxidation with initial concentration of above 300 mg NH₃-N/l under COD/N ≈ 3, 4, 5.

COD/N	Time (h)	pH	Alkalinity (mg CaCO ₃ /l)	NH ₄ ⁺ (mgN/l)	TKN (mgN/l)	COD (mgO ₂ /l)
3:1	DV	8,4	2120	298	312	901
	1	8,4	1995	273	-	837
	2	8,5	1820	245	-	757
	3	8,5	1675	215	-	653
	4	8,5	1530	187	-	576
	5	8,6	1370	159	-	544
	6	8,6	1225	135	-	536
	7	8,6	1110	106	57	518
Yield (%)				64,4		42,5
4:1	DV	8,5	2115	302	306	1260
	1	8,6	2050	285	-	1172
	2	8,6	1980	268	-	1020
	3	8,6	1915	255	-	875
	4	8,6	1820	236	-	736
	5	8,7	1720	210	-	676
	6	8,7	1630	188	-	608
	7	8,7	1530	165	42	554
Yield (%)				45,4		56,0
5:1	DV	8,6	2120	296	301	1590
	1	8,6	2075	288	-	1365
	2	8,6	2010	275	-	1135
	3	8,6	1955	259	-	974
	4	8,7	1870	241	-	860
	5	8,7	1795	227	-	784
	6	8,7	1715	212	-	655
	7	8,8	1620	192	23	602
Yield (%)				35,6		62,1

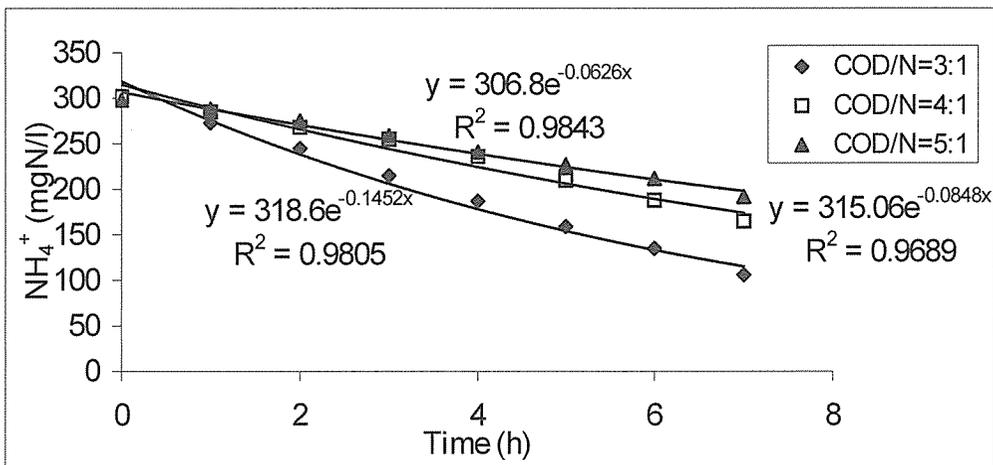


Figure 2. The influence of COD concentration on the ammonia oxidation (initial concentration ~ 300 mg NH₃-N/l)

The values from tables 1, 2 show that within 7 hours reaction the removal yields for ammonia were achieved 76.8%, 60.8% and 50.5% corresponding with COD/N ratios 3:1, 5:1 and 7:1. For initial ammonia concentration of above 300 mg NH₃-N, the value obtained were 64.4%, 45.4% and 35.6% corresponding with COD/N 3:1, 4:1 and 5:1.

For low ammonia concentration range the removal yield is higher than that in higher range. The reason for this fact is the F/M ratio (food/microorganisms) increases with decreasing initial ammonia concentration (biomass remained unchanged).

For higher COD/N ratios, the ammonia removal yield was lowering with a higher rate for high ammonia level. For example, for ammonia concentration range 200 mg NH₃-N/l and 300 mg NH₃-N/l the removal efficiency decrease from 76.8% to 60.8% and from 64.4% to 35.6% when COD/N increase from 3:1 to 5:1.

In general, the ammonia removal decreases with increasing of both initial concentration and COD content in the system treated.

All reactions were accomplished at the same time (7 hours), the decline of ammonia removal efficiency is attributed to the lowering reaction rate, namely to the kinetic constants. Kinetic constants were obtained from experiment date (concentration versus time) by using equation (1). Although the mechanism of the biological process is rather complex, the reaction is assumed as pseudo first equation by maintaining other variables approximately unchanged. The kinetic constants obtained are presented in table 3.

Table 3. Kinetic constants under different experiment conditions.

Initial ammonia concentration			
~ 200 mg NH ₃ -N/l		~ 300 mg NH ₃ -N/l	
COD/N ratio	k (h ⁻¹)	COD/N ratio	k (h ⁻¹)
3:1	0.2107	3:1	0.1452
5:1	0.1333	4:1	0.0848
7:1	0.1016	5:1	0.0626

The assumption of first order equation is acceptable due the high values of the correlation factor (about 0.98). The decline of the kinetic constants has the same trend as the ammonia removal efficiency under individual conditions.

From the results it could be concluded that both oxidation rate as well as the removing efficiency of ammonia are lowering at high initial ammonia concentration and COD content in the system.

One could therefore state that there are competitive oxidation between COD and ammonia.

Principally, two oxidation processes proceed independently, only one parameter, DO, is involved in both reactions. In all experiment, DO is maintained at high level (3.2 to 3.8 mg/l), it is sufficient for each reaction proceeded a lonely.

This phenomenon could be explained as following: DO content measured is the value in the bulk volume. The autotrophic and heterotrophic organisms are distributed inhomogeneous throughout the whole reaction volume but rather homogeneous within the granulars. The oxidation of both components are occurring on the outer surface and within the granular where the reaction within the granular contributes mainly due to high specific areas of the biomass granulars, in comparison to the outer surface [2]. The DO concentration influenced directly on the oxidation process is therefore the DO level within the granulars, but not the value measured in the bulk volume. The difference between DO measured and inside the granulars is determined by diffusion process.

The diffusion flux of each component is dependent on the concentration gradient, on the nature of diffusing species and other operating parameters.

In comparison to ammonia and COD diffusion fluxes, the DO flux is the smallest due to the lowest concentration gradient. In the other words, the DO content within the granulars is the lowest and that of COD is highest. From researches and practical experiences, the oxidation rate of ammonia is much less than that of COD, so COD consumes dissolved oxygen within granular faster than ammonia [3].

The influence of COD content on the oxidation of ammonia could be explained in summary: the oxidation of both components are occurring mainly within the biomass granulars where the DO is insufficient for the reactions due to small, diffusion flux and COD takes DO faster than ammonia. This fact is of importance for designing treatment system for wastewaters having variable nutrient and COD concentration.

CONCLUSION

The investigation of aerobic landfill leachate having variable ammonia and COD concentrations showed that:

1. There is a competitive oxidation between COD and ammonia in the system even at high DO level.
2. Ammonia removal efficiency and the rate of oxidation are decreased with increasing initial ammonia and COD concentrations.
3. This phenomenon could be explained by the lack of DO within the granulars due to limited diffusion flux and the ammonia oxidation rate is lower than that of COD.
4. This fact is of importance for designing the treatment system for wastewaters having variable nitrogen and COD contents.
5. To limit the competitive oxidation between two components, the measures of increasing DO diffusion flux can be applied.
6. Acknowledgment of financial support: Ministry of Natural Resources and Environment, Vietnam Academy of Science and Technology.

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