Effect of ammonia concentration and pH on anaerobic butyric acid degradation

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Introduction:

The accumulation of butyric acid is a common observation in food waste and animal manure anaerobic co-digestion (Dennehy et al., 2016; Ni et al., 2017). However, the factors that affect butyric acid anaerobic degradation have not been well studied. Excess ammonia is generally regarded as a major factor affecting volatile fatty acid degradation (Wang et al., 2022) but its impact on butyric acid degradation has not been studied. In this study, batch experiments were carried out to investigate the degradation of butyric acid and explore the inhibition degree of different ammonia species (NH_4^+, NH_3) under various total ammonia concentration (TAN, 0.18-20 g N/L) and pH (7.0-8.0) conditions. Then the recoverability of butyric acid degradation after ammonia inhibition was examined.

Materials and methods:

Batch experiments were performed using serum bottles with a working volume of 200 ml under 37℃. Butyric acid (2 g COD/L) was added as the only carbon source, and the inoculum was pre-activated anaerobic sludge. Ammonia chloride was used to provide the designed ammonia concentration in this study. The TAN levels used in inhibition experiments were 0.18, 2, 4, 8, 12, 16, 20 g N/L at pH 7.5, respectively, and labeled as R1, R2, R3, R4, R5, R6, and R7. Experiments with different pH (7.0, 7.5 and 8.0) were performed at TAN of 4 g/L, which were labeled as R8, R9, and R10, respectively. The recovery experiment was labeled R11 with TAN of 0.18 mg N/L at pH 7.5 and the inoculum was the refreshed sludge from R7. All the experiments were conducted in triplicate.

The first-order kinetic model (Eq. 1) and modified Gompertz kinetic model (Eq. 2) were used to simulate the butyric acid degradation in this study.

$$\mathrm{C} = \mathrm{C}_0 e^{-kt} + \mathrm{b} \tag{1}$$

where, C: butyric acid concentration (mg/L); *k*: the first-order degradation rate (d^{-1}); t: time (d); and C_0, b: constants.

$$C_{HBu} = C_{\max} \cdot \exp\left\{-\exp\left[\frac{\mu_m \cdot e}{C_{\max}} \cdot (\lambda - t) + 1\right]\right\} \tag{2}$$

where, C_{HBu}: butyric acid degradation concentration (mg/L); C_{max}: ultimate butyric acid degradation (mg/L); μ_m: maximum butyric acid degradation rate (mg/L/d); λ: lag phase (d).

To evaluate the inhibition degree of different ammonia species (NH_4^+, NH_3), the inhibition model (Eq. 3) was introduced. I_X ($I_{NH_4^+}$ or I_{NH_3}) represents the inhibition degree caused by NH_4^+ or NH_3. Modified Monod inhibition model can be expressed in Eq. 4 (Wang e al, 2022).

$$\mu = \mu_m \cdot I_{NH_4^+} \cdot I_{NH_3} \tag{3}$$

$$I_X = \frac{K_X{}^n}{K_X{}^n + C_X{}^n} \tag{4}$$

where μ is butyric acid degradation rate (mg/L/d); C_X is the inhibitor concentration (NH_4^+ or NH_3, mg N/L); K_X is ($K_{NH_4{}^+}$ or K_{NH_3}): the inhibitor concentration that halves the maximum butyric acid degradation rate.

Results:

The degradation rate of butyric acid was investigated under different ammonia concentrations and pH. As shown in Fig.1, the results indicated that butyric acid degradation was inhibited at TAN over 8 g N/L. Besides, when TAN concentration was at 20 g N/L, the degradation rate of butyric acid was severely inhibited and decreased to 18% from 100%. From the degradation rate of R1 and R11 in Fig.1 (a), the inhibition on butyric acid degradation at TAN of 20 g N/L was reversible. However, the lag phase of butyric acid degradation after ammonia inhibition was longer, which means that TAN of 20 g N/L inhibited the activity of butyric acid degradation bacteria.

The first-order model and modified Gompertz model were used to simulate butyric acid degradation. The kinetic parameters were summarized in Table 1. The results indicated that the modified Gompertz model fitted better than the first-order model. The simulated λ values showed that the lag phase of butyric acid degradation was extended with the ammonia concentration increasing.

As shown in Fig.2, the actual ΔG of butyric acid oxidation was in the range of -50 ~ -250 KJ/mol, indicating that the butyric acid degradation was thermodynamically spontaneous at different ammonia concentrations. The ratio of $I_{NH_4^+} / I_{NH_3}$ was to evaluate individual contributions of NH_4^+ and NH_3 to the ammonia inhibition. The ratio <1 means that NH_4^+ makes more contribution to the inhibition. As shown in Fig.2 (b), the ration <1 indicated that NH_4^+ made more contributions to the ammonia inhibition at TAN ≥ 2 g N/L.

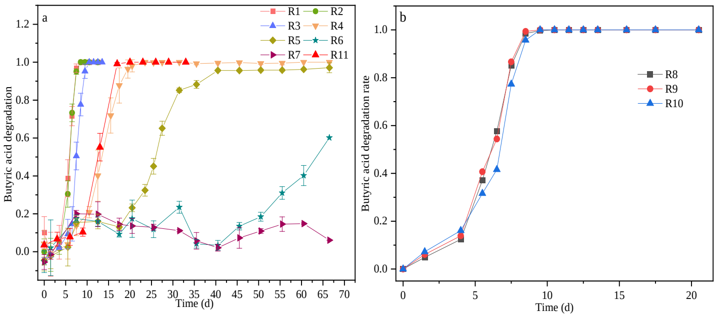

Fig. 1 Butyric acid degradation rate under different ammonia concentrations (a) and pH (b).

Table 1. Kinetic parameters of butyric acid degradation

No.	First-order model				Modified Gompertz model			
	C_0	k	B	Adj.R^2	C_{max}	μ_m	λ	Adj.R^2
R1	3910.200	0.286	-48.236	0.8734	2229.691	973.399	4.630	0.9929
R2	3913.737	0.275	-51.887	0.8501	2224.040	1125.812	4.889	0.9983
R3	3695.583	0.188	-92.453	0.8386	2251.013	796.561	6.049	0.9914
R4	3232.293	0.092	-149.281	0.8674	2215.592	258.906	8.668	0.9889
R5	3.735×10^3	2.144×10^{-2}	-1163	0.8816	2180.327	132.555	16.614	0.9598
R6	-2.711	-0.0913	1979.807	0.8289	5.211×10^7	5.272×10^4	565.470	0.5990
R7	416.990	0.4365	1905.401	0.2328	374.378	403.476	1.288	0.467

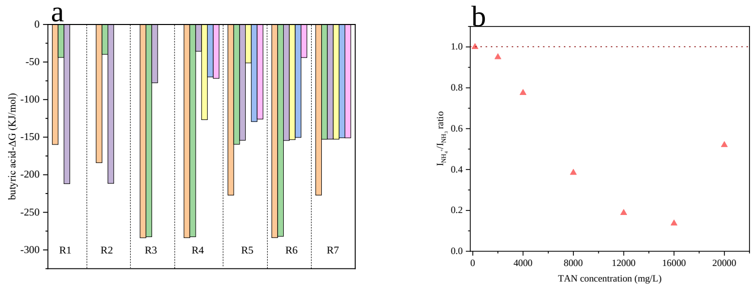

Fig. 2 Actual ΔG of butyric acid (a) and ration of $I_{NH_4^+} / I_{NH_3}$ (b) under different ammonia concentrations

Conclusion:

The study verified that the butyric acid degradation rate was inhibited at TAN ≥ 8 g N/L and the lag phase of butyric acid degradation was extended with ammonia concentration increasing. NH_4^+ made more contribution to the inhibition than NH_3 at TAN of 2-20 g N/L. Butyric acid degradation was thermodynamically spontaneous in different ammonia concentration. A long HRT strategy is suggested to reduce butyric acid accumulation when treating food waste and animal manure via anaerobic digestion.

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