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Nitrogen requirement for the mesophilic and thermophilic upflow anaerobic filters of a simulated papermill wastewater

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Abstract−This study determined the minimum nitrogen concentration at which the mesophilic and thermophilic upflow anaerobic filters treating a simulated papermill wastewater could operate efficiently. For this purpose, the chemical oxygen demand (COD) to nitrogen ratio in both digesters was increased in five consecutive steps, from 94 : 5 to 363 : 5. The maximum COD to nitrogen ratios that provided satisfactory operation were 283 : 5 (30 mg N/L) and 363 : 5 (23 mg N/L) for the mesophilic and thermophilic reactors, respectively. The nitrogen consumption of bacteria in the thermophilic digester was lower than that in the mesophilic digester. The operational efficiency of the thermophilic digester was higher than that of the mesophilic one regardless of the COD to nitrogen ratio.

Key words: Anaerobic Digestion, Mesophilic, Nitrogen, Thermophilic, Wastewater

INTRODUCTION

The microbial population responsible for wastewater or waste conversion and stabilization during anaerobic digestion [1] requires nitrogen, phosphate and other elements for optimum growth [2,3]. In ideal conditions a wastewater or waste should maintain a specific carbon:nitrogen:phosphorus ratio, so that each will be used during the digestion process. In the case of a nitrogen deficiency, the microbial population will be unable to produce the enzymes which are needed to utilize the carbon [2,3].

Many industrial wastewaters, such as the pulp- and paper-industry effluents, are nitrogen deficient [4,5]. Thus, for large-scale anaerobic digestion systems the reduction of supplemented nitrogen can be of considerable economic importance [2]. The phosphorus requirement is of a magnitude that has only minor economic implications compared to the nitrogen requirement [6]. Therefore, it is necessary to determine the exact nitrogen requirement for a wastewater treatment facility to avoid overloading and residuals in the final effluent. The nitrogen requirement for the digestion of an industrial wastewater may be readily calculated from the stoichiometry given by Speece [7] (Eq. (1)), while the phosphorus demand is approximately 1 : 7 to 1 : 5 that of the nitrogen demand.

$$\begin{aligned} &C_nH_aO_bN_c+(2n+c-b-9sd/20-ed/4)H_2O \\ &\quad\rightarrow(de/8)CH_4+(n-c-sd/5-de/8)CO_2 \\ &\quad\quad+(sd/20)C_5H_7O_2N+(c-sd/20)NH_4^{+}+(c-sd/20)HCO_3^{-} \qquad (1) \end{aligned}$$

where d=4n+a−2b−3c, s=fraction of waste synthesized, and $C_nH_aO_bN_c$=empirical formula of organic being digested.

The literature varies widely in the chemical oxygen demand (COD) to nitrogen ratio used, but the nitrogen to phosphorus ratio was 1 : 7 to 1:5 in most cases [8]. The theoretical minimum COD to nitrogen ratio was reported to be 350 : 7 and a value around 400 : 7 was regarded as reasonable for highly loaded anaerobic processes (i.e., 0.8-1.2 g COD/g VSS·d). For low processes (i.e., <0.5 g COD/g VSS·d), the COD to nitrogen ratio increased dramatically to 1,000 : 7 or more [6,7]. Another approach that can be followed for nitrogen requires that the reactor effluent be monitored for NH_4-N. As long as 5-10 mg/L of residual NH_4-N is detected, nitrogen should not be limiting [9,10]. However, some wastewaters apparently require 100% higher levels of residual NH_4-N [10]. It was reported that the amount of nitrogen was insufficient to sustain reactor efficiency when the reactor effluent still contained nitrogen [2]. It was also reported that the COD : nitrogen : phosphorus consumption ratio was 400 : 2.3 : 0.2, although the COD : nitrogen : phosphorus influent ratio was maintained at a ratio of 400 : 5 : 1 by adding urea and KH_2PO_4 [11]. Although a considerable amount of research has been performed on anaerobic decomposition, the comparison of the mesophilic and thermophilic anaerobic digestion in terms of the effect of COD to nitrogen ratio is lacking in the literature. This study thus determines the maximum COD to nitrogen ratios and compares the effect of COD to nitrogen ratios on the operational efficiency of the mesophilic and thermophilic upflow anaerobic filters treating a papermill wastewater.

MATERIALS AND METHODS

1. Digesters

Two identical anaerobic filters were constructed from glass columns (7.1 cm diameter×60 cm) with external water jackets. Distribution plates with a series of concentric holes (0.5 cm diameter) were located 5.5 cm from the bottom to distribute the feed evenly. Each filter was packed with Raschig rings (1.2 cm diameter×1.2 cm). Water was circulated through the jackets to maintain temperatures at 35 °C and 55 °C for the mesophilic and thermophilic digesters, respectively. The working volume (i.e., the total liquid volume of the packed reactors) was 1.55 and 1.52 L for the thermophilic and mesophilic reactors, respectively. Both reactors had been acclimated to simulated starch and papermill wastewaters in series in a previous study which had lasted for 557 days. The simulated paper-

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mill wastewater was used in this study. The wastewater was prepared by passing surface sized, shredded paper through a pulper (Wennbergs, Sweden) and filtering the resultant suspension. The wastewater was supplemented with urea and dipotassium hydrogen phosphate (K_2HPO_4) to balance the nitrogen and phosphorus. Additional COD was provided by adding soluble starch. The COD to nitrogen ratio in both digesters was increased in five consecutive phases, from 94 : 5 to 363 : 5, by reducing nitrogen and phosphorus concentrations (Table 1). The hydraulic retention time was maintained at 12.3±0.3 d with an organic loading rate of 3.34±0.01 g COD/L·d in both digesters. The pH in the effluent of the mesophilic and thermophilic digesters was sustained at 7.3±0.1 and 7.4±0.2, respectively.

2. Analytical Methods

The COD was measured according to the Standard Methods [12]. The composition of the biogas was measured by gas chromatography (Pye Unicam, Model 104) as described previously [13]. The volatile fatty acids (VFAs) were measured by gas chromatography (Cambridge, Model Ai) by using a D-BFFAP megabore column (30 m×0.536 mm ID). Ammonium nitrogen was measured with the Model 95-12 Ammonia Electrode (Orion). All statistical analyses were done with the Analysis ToolPak (Anova: Single Factor) at the 5% level using Microsoft Excel.

RESULTS AND DISCUSSION

1. Soluble Chemical Oxygen Demand Removal

The effluent soluble COD (SCOD) concentrations of the mesophilic digester were clearly higher than those of the thermophilic one over all phases (Fig. 1 and Table 2). The COD to nitrogen ratio in mesophilic digester was increased to 283 : 5 without any fluctuation. However, after the phase was changed from IV to V in the mesophilic digester, SCOD increased up to 586 mg/L and nitrogen consumption decreased from 29 to 22 mg/L (Table 3). Nitrogen concentrations in the effluent of the mesophilic digester were not significantly different at the 5% confidence level between Phases IV and V.

Table 1. Experimental conditions

Phase	I	II	III	IV	V
COD : N : P	94 : 5 : 1	165 : 5 : 1	237 : 5 : 1	283 : 5 : 1	363 : 5 : 1

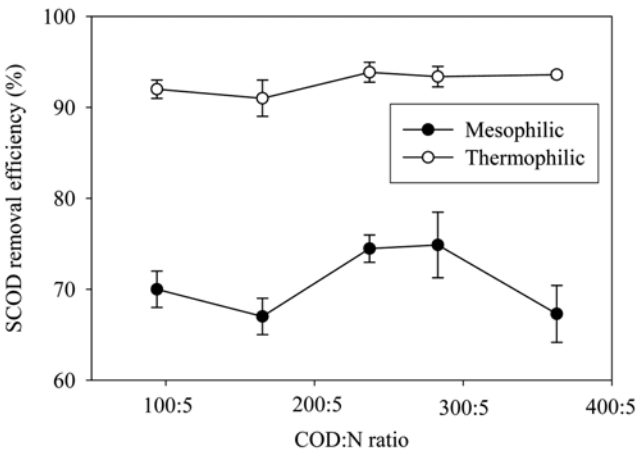

Fig. 1. SCOD removal efficiencies in the mesophilic and thermophilic digesters with various COD to nitrogen ratios.

Table 2. Performance of the mesophilic and thermophilic digesters at various COD to nitrogen ratios

Phase	Digester	SCOD (mg/L)	Methane content (%)	Methane yield (L CH_4/g COD_{rm})
I	Meso.	531±44	76±1.1	0.25±0.02
	Thermo.	152±18	75±1.3	0.23±0.02
II	Meso.	556±39	76±1.4	0.26±0.03
	Thermo.	158±32	74±0.8	0.26±0.02
III	Meso.	453±36	77±0.5	0.23±0.01
	Thermo.	107±19	74±1.0	0.25±0.01
IV	Meso.	430±51	77±0.8	0.23±0.02
	Thermo.	114±19	73±0.7	0.27±0.01
V	Meso.	549±54	75±0.2	0.23±0.01
	Thermo.	106±6	72±1.4	0.29±0.02

Table 3. Nitrogen concentrations in the influent and effluent of the mesophilic and thermophilic digesters

Phase	Digester	Influent conc. of nitrogen (mg N/L)	Effluent conc. of nitrogen (mg N/L)	Nitrogen consumption (mg N/L)
I	Meso.	95	59±1.6	36
	Thermo.		62±4.1	33
II	Meso.	51	21±4.0	30
	Thermo.		24±2.6	27
III	Meso.	37	7.1±0.8	30
	Thermo.		11±1.4	26
IV	Meso.	30	1.3±1.0	29
	Thermo.		10±3.8	20
V	Meso.	23	1.4±0.6	22
	Thermo.		4.7±1.7	18

On the other hand, the effluent SCOD concentrations in Phases III-V of the thermophilic digester were lower at the 5% confidence level than those in Phases I and II (Fig. 1 and Table 2). In the thermophilic digester, the COD to nitrogen ratio in the papermill wastewater was increased to 363 : 5 without any fluctuation. Nitrogen concentration in the effluent of the thermophilic digester decreased to 4.7±1.7 mg/L (Table 3). It has been suggested nitrogen should not be limiting as long as 5-10 mg/L of residual NH_4-N is detected [9,10]. Therefore, the maximum COD to nitrogen ratio for the papermill wastewater in the thermophilic digester should be about 363 to 5 in this study.

2. Biogas Production

The biogas productions in Phases I-III were lower at the 5% confidence level than those in the other phases in the thermophilic digester. On the other hand, in the mesophilic digester, the biogas production was not significantly different at the 5% confidence level among phases, except for Phase V. After the phase was changed from IV to V in the mesophilic digester, the biogas production decreased to 0.65 L/L·d (Fig. 2) and nitrogen consumption decreased (Table 3).

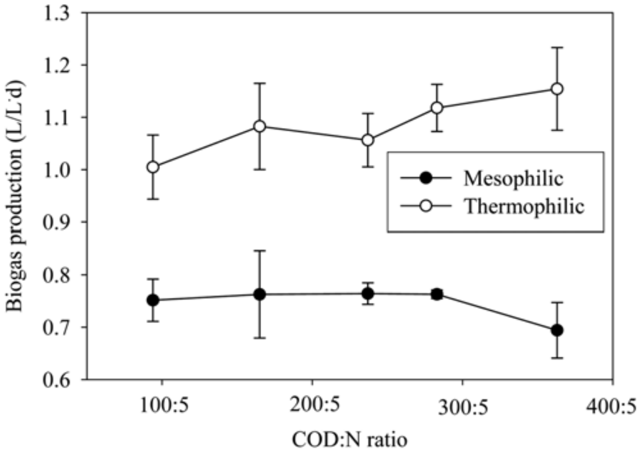

Fig. 2. Biogas productions in the mesophilic and thermophilic digesters with various COD to nitrogen ratios.

The pattern of methane production in the mesophilic and thermophilic digesters followed that of biogas production, which means that COD to nitrogen ratio was successfully increased in both digesters without adversely affecting methanogenic bacteria. The methane contents in biogas were not discernibly different among the phases in both digesters, but the methane contents in the mesophilic digester were higher at the 5% confidence level than those in the thermophilic one over all phases (Table 2). On the other hand, there was no discernible trend or relationship between or within the mesophilic and thermophilic digesters in terms of the methane yield (Table 2).

3. Total Volatile Fatty Acid in the Effluent

Butyric acid as well as acetic and propionic acids was detected in the mesophilic digester, while butyric acid was not detected in the thermophilic digester [13]. The total VFA (TVFA) in Phases III, IV, and V was lower at the 5% confidence level than those in Phases I and II in the mesophilic digester (Fig. 3). In the thermophilic digester, the TVFA of Phase I was higher at the 5% confidence level than that of the other phases.

4. Nitrogen Consumption

The nitrogen concentration in the mesophilic and thermophilic digesters was successfully reduced to 30 and 23 mg N/L, respectively. From the results of Phase V in the mesophilic digester, the influent concentration of nitrogen, 23 mg N/L, was insufficient to sustain reactor efficiency even though the reactor effluent still contained nitrogen [2].

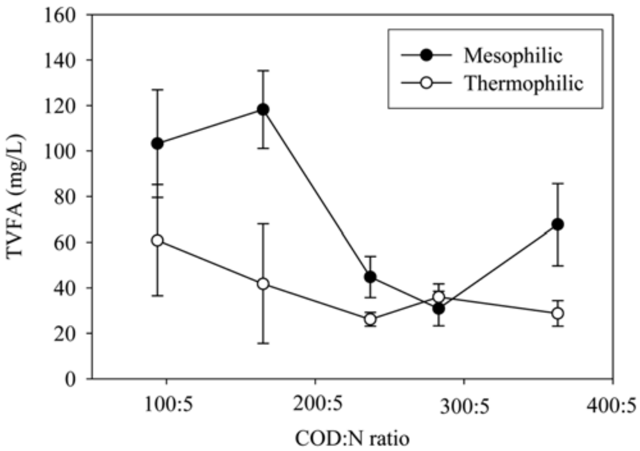

Fig. 3. Total volatile fatty acids in the mesophilic and thermophilic digesters with various COD to nitrogen ratios.

The nitrogen concentration in the effluent was not significantly different at the 5% confidence level between the digesters in Phases I and II. However, in Phases III-V, the nitrogen concentration in the effluent of the thermophilic digester was higher at the 5% confidence level than that of the mesophilic one. Therefore, it could be assumed that the nitrogen consumption of thermophilic anaerobes is lower than that of mesophilic ones, which might be partly explained by the report that the cellular carbon to nitrogen ratio of nutrient-sufficient *Scenedesmus* sp. increases with temperature [14].

After the phase was changed from IV to V in the mesophilic digester, the SCOD removal efficiency decreased (Fig. 1), biogas production decreased (Fig. 2), and nitrogen consumption decreased from 29 to 22 mg/L (Table 3). However, the nitrogen concentrations in the effluent of the mesophilic digester were not significantly different at the 5% confidence level between Phases IV and V, as mentioned earlier.

It must be noted that nitrogen must be available in sufficient quantity to ensure that the digester population can operate unimpeded. It must also be stressed that this study was performed on reactors where the existing population had already stabilized [2].

CONCLUSIONS

The operational efficiency of a thermophilic digester was higher than that of a mesophilic one, regardless of the COD to nitrogen ratio in the papermill wastewater treatment. The COD to nitrogen ratios in this study were successfully increased to 283 : 5 and 363 : 5 in the mesophilic and thermophilic digesters, respectively. The nitrogen consumption of thermophilic anaerobes was also lower than that of mesophilic ones. Therefore, the thermophilic digester should be more economical in terms of nitrogen supplementation. For large-scale anaerobic digestion systems, the reduction of supplemented nitrogen can be of considerable economic importance.

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