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Role of ammonium bicarbonates in methenogenesis while co-digesting petrochemical wastewater with activated manure sludge

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Abstract

Inadequacy of nitrogenous reserve and buffering capability were acknowledged as regressive failure in former study treating petrochemical wastewater in anaerobic continuous stirred tank reactors. This study highlights the application of ammonium bicarbonate (NH_4HCO_3) as supplementation assuring nitrogenous resource and buffering requisite. To investigate the role of NH_4HCO_3 on the anaerobic degradation, a sequence of concentration up to 40 mg L^{-1} was observed. The outcome was assessed on the basis of biogas evolved. The investigation revealed that10 mg L^{-1} was the optimal without distressing methanogenesis. Likewise, mathematical calculation clarified that this optimum dosing can boost biogas yield up to 27.77% likened to control PWW degradation. Outcomes exposed an apparent commercial benefit to make the industrial application viable.

Keywords: Anaerobic digestion; Ammonium bicarbonate; Biogas yield; Petrochemical waste water

1. Introduction

Anaerobic degradation, a sustainable mechanism, has been accepted as the fundamental method of an advanced technology for environmental defense [1, 2, 3, 4]. Former works reported that PWW desires complementary substrates to withstand its critical operational parameters such as alkalinity, pH and biomass. Inquiry through the operation disclosed that those parameters had gone below acclaimed levels. Thus, after adding the organic loading rate (OLR) up to 6 kg COD $m^{-3}day^{-1}$, entire experimental process had aborted. The failure was caused by an abrupt drip of pH

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and cumulative concentration of volatile fatty acid (VFA). It is sound acknowledged that these factors are regulating to the anaerobic system, exclusively to the subtle methanogen group of microbes. Yet, the extent of organic loading at 6 kg COD $m^{-3}day^{-1}$was observed to be too squat to offset failure in anaerobic upflow fixed film reactor (UFFR) [5,6]. Consequently, deficient buffering control and interruption of microbial population balance between non-methanogen and methanogen to transform carbonaceous substance to CH_4, were recognized to be the key motivation of operational failure. To limit the level of volatile fatty acid in the process, alkalinity has to be conserved by recirculation of digested effluent [7, 8] to the digester or addition of lime and bicarbonate salt [9]. As this method has been exposed to be a capable substitute both to pollution control and to produce CH_4 as the bioenergy, interruptions while operation should be restored.

This research was commenced to offer the application of ammonium bicarbonate (NH_4HCO_3), owing to its buffering requirement in contradiction of acidity thru the treatment operation and also to conserve the microbial population balance. Hence, substantial parts will be performed by NH_4^+ as the acclaimed microbial nutrient for nitrogen and buffering capacity in an anaerobic system [9, 10]. Nevertheless, extreme NH_4HCO_3 concentrations make free ammonia toxicity particularly to the methanogen [11]. Later, the optimal dosage for NH_4HCO_3 added as supplement in anaerobic co-digestion process should be figured out.

2. Material and Methods

2.1 Preperation of substrate

The petrochemical wastewater is a complex mixture of organic pollutants can be fermented to methane, which has been analyzed to be lacking in alkalinity and nitrogenous resources. Preparation of PWW was accomplished according to a previous study by diluting the stock liquor [8]. Table 1 explains the characterization of PWW. The dilution of concentrated petroleum resulted in a consistent concentration of wastewater up to 3000 mg L^{-1} of COD, which is in the range of medium strength wastewater [12]. With a view to remove the debris the prepared sludge was initially passed through a screen. The microbial activity of the seed sludge was examined according to Najafpour's method 2006 [8].

Table 1. Composition and Characteristics of PWW *Values are the mean + S.D. of the 3 determinations

Parameters	PWW
pH	6.2±0.2
BOD	7.85±0.13
COD	15.2±0.5
TOC	4.98±0.05
Total solids	0.32±0.05
Acetic acid	1.5±0.03
Phenol	0.36±0.2
Total Nitrogen	0.048±0.005
Total Phosphate	0.106±0.004

*Except pH and Acetic acid, all parameters in gL^{-1}

2. 2. Batch test of toxicity

Immersing a set of air sealed digesters (1L) in a water bath; the effect of NH_4HCO_3 on the anaerobic digestion of PWW was investigated. The operating temperature was maintained at 37° C. In order to monitor biogas generation, the digesters were linked to biogas measuring device. All digesters were seeded with 300 mL of stabilized sludge and 150 mL of PWW with COD of 3000 mg L^{-1}, before testing by batch operation. The reason behind it was to pretend non-critical COD loading [13] at 0.5 kg m^{-3} so that the shock loading to seed substrate could be avoided. An incremental set of concentrations up to 40 mg L^{-1} were prepared in duplicates of five containers via dosing of NH_4HCO_3. The supplementation dosing up to 40 mg L^{-1} was preferred to find optimal one. To ensure sufficient mixing and to assist the yield of biogas, all digesters were mildly stunned per 10 min. The optimum dosing for NH_4HCO_3 was calculated depending on the cumulative biogas yield. An assumption might be made that accelerated biogas yield would generate within 3 h of batch process for similar substrate [14]. Nonetheless, the toxicity of NH_4HCO_3 especially to the methanogen in the system could be indicated in contrast of the maximum biogas yield [11]. In the previous study Configuration of CH_4:CO_2 was at the ratio of 25:75. Even so, the biogas generation in this work was assumed to be too little for analysis by gas analyzer. Liquid displacement method was applied to measure gas generation [15].

3. Results and Discussion

Former operational breakdown that was provoked by VFA agglomeration might have happened through supplementary confines like as micronutrients (Fe, Mg, Ni, Cu, Co and P). Nonetheless, theoretically the scarcity of micronutrients might be abolished on the basis of mineral percentage. As seed sludge was collected from partially digested sewage, the content of phosphorus must be sufficient. Consequently, the lack of phosphorus was also not being addressed. For the time being, the existence of ammoniacal nitrogen as the resource macronutrient in a stabilized digested sludge is acknowledged to be at an outstanding concentration after de-nitrification process is accomplished [12]. Sodium nitrate is an alternative supplementation to meet up the want of nitrogenous resource. Still, in case of its application, the discharge of NO_3^{-1} would enhance the oxidation–reduction potential (ORP) of the reactor. The ORP potential of the reactor supposed to maintain above -300 mV. It was due to the cause that methanogenesis is deteriorated at lesser ORP [9]. In order to adjust the buffering capacity of the substrate solution, chemical selection is a rate limiting factor. Unwanted solids are created due to Precipitation of $CaCO_3$.

3.1 Biogas production

Fig. 1 illustrates the effect of NH_4HCO_3 supplementation to anaerobic co-digestion process. However, the digestion performance has been evaluated in terms of cumulative biogas generation vs. time graph. It slows through termination of raw resources. While NH_4HCO_3 dosing, total cumulative biogas generation was detected to increase. More specifically, at 10 mg/L dosing and contact time ranging from 15 to 180 min, cumulative biogas generation was enhanced. Subsequently, the cumulative biogas generation was detected to drop in case of 20, 30, 40 mgL^{-1}

dosing applied to the process. The C: N ratio was maintained fixed at within the range of 25/1 to 30/1.

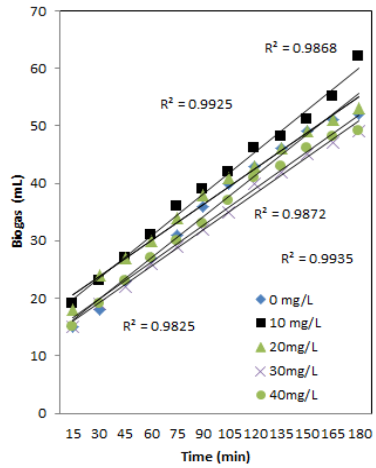

Fig. 1. Evaluation of digestion performance in terms of cumulative biogas generation vs. time graph.

However, the detailed data revealed that the maximum biogas generation took place while 10 mg L^{-1} of NH_4HCO_3 was applied. It can be studied from previous work, the CH_4 yield form the petroleum wastewater COD added ranged between 0.37–0.43 [5]. During the current work, CH_4 yield was calculated assuming similar substrate digestion. The maximum CH_4 yield from this study could be equal to 60 mL, as listed in Table 2. From Fig. 1 it is obvious that the data collected during digester operation is consistent enough having regression co-efficient value of 0.9925, 0.9868, 0.9825, 0.9872 and 0.9935.

Table 2. Results of NH_4HCO_3 dosing to anaerobic digestion system in terms of Cumulative biogas generation

Contact time (min)	Mean cumulative biogas generation (mL)				
	NH4HCO3 dosing (mg/L)				
	0	10	20	30	40
16	15	19	18	15	15
30	18	23	24	19	19
45	23	27	27	22	23
60	27	31	30	26	27
75	31	36	34	29	30
90	36	39	38	32	33
120	40	42	41	35	37
105	43	46	43	40	41
135	46	48	46	42	43
150	49	51	49	45	46
165	51	55	51	47	48
180	54	62	53	49	49

3. 2. Calculation

For the calculation of % increase in biogas yield the following formula was employed:
% increase in biogas yield = (A – B) / B X 100
Where, A = Biogas yield at dosing 10 mg/L
B = Biogas yield at dosing 0 mg/L (control)
For example, at contact time of 16 min, % increase in biogas yield = (19 -15) / 15 X 100 = 26.67 %.

Fig. 2 is actually a comparison of effectiveness of NH_4HCO_3 dosing with control PWW digestion. The obvious effect of 10 mg/L NH_4HCO_3 dosing has been demonstrated along with contact time ranging between 15 to 180 min. From contact time vs. % increase in biogas yield curve it can be stated that the maximum enhancement in biogas yield is 27.77% at contact time of 30 min. It might be due to the fast reaction took place at that specific environmental condition. It has been studied, for the transformation of carbonaceous materials in to CH_4 during the anaerobic digestion system, sustaining methanogenesis was the key operational process. H_2 and CO_2 will be used by Hydrogenotropic methanogens while acetic acid and CO_2 will be used by acetoclastic methanogens to give CH_4 as eventual outcome [16]. The volatile fatty acid (VFA) accumulation is suggested to be avoided employing supplementation of strong bases and co-digestion with other wastes [17]. This strategy provides appropriate C/N ratio and strong buffering capacity to pH change. As a result methanogenesis occurs with great stability leading to enhanced CH_4 generation. It can be concluded from Fig. 2 that 10 mg/L NH_4HCO_3 dosing can provide up to 27.77% enhanced biogas yield compared to control PWW digestion.

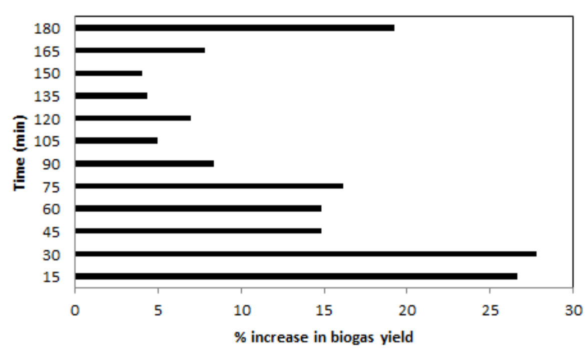

Fig. 2. Determinations of % increase in biogas yield compared to control PWW digestion.

4. Conclusions

The influence of unlike concentration of NH_4HCO_3 on efficiency and stability of anaerobic co-digestion was studied. The conclusions are projected here:

- This work discloses that the NH_4HCO_3 might speed up the anaerobic digestion of PWW.
- 10 mg L^{-1} of NH_4HCO_3 concentration was found to be the optimal for the substrate compared to the enhanced concentrations up to 40 mg L^{-1}.
- The usefulness of NH_4HCO_3 application was also clarified by formula.
- In relation to the calculation, 10 mg L^{-1} NH_4HCO_3 concentration can offer up to 27.77% enhanced biogas yield than control PWW digestion. This attainment can apparently add some financial advantage to make the treatment policy more feasible for industrial application.

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