Effect of strong base during co-digestion of petrochemical waste water and cow dung

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Abstract**—*****Inadequacy of nitrogenous resource and buffering ability were detected as reverting failure in previous work treating petrochemical wastewater (PWW) in anaerobic continuous stirred tank reactors. The aim of this study is to explore the use of ammonium bicarbonate (NH_4HCO_3) as supplementation assuring nitrogenous supply and buffering requirement. To observe the effect of strong base such as NH_4HCO_3 on the anaerobic process, a set of dosing up to 40 mg L^{-1} was examined. The outcomes were assessed in terms of biogas yield. It was observed that10 mg L^{-1} dosing was the optimal dosing without affecting methanogenesis. Furthermore, mathematical calculation explained that this optimum dosing can enhance biogas yield up to 27.77% compared to control PWW digestion. Results showed an obvious financial advantage to make the industrial application feasible.***

Index Terms— ammonium bicarbonate, Anaerobic digestion, Petrochemical wastewater, CSTR, Methane

I. Introduction

Anaerobic digestion among other treatment methods has been accepted as the key system of an advanced technology for environmental protection [1]. Earlier studies suggested that PWW craves supplementary substrates to sustain its critical operational parameters such as alkalinity, pH and biomass. Investigation during the operation flashed that those parameters had gone below recommended levels. Consequently, after increasing the organic loading rate (OLR) to the level of 6 kg COD $m^{-3}day^{-1}$, the whole experimental operation had failed. The failure was countervailed by a sudden drop of pH and increasing concentration of volatile fatty acid (VFA). It is well known that these two factors are limiting to the anaerobic digestion process, especially to the sensitive methanogen group of bacteria. However, the amount of organic loading at 6 kg COD $m^{-3}day^{-1}$was found to be too low to cause failure in anaerobic upflow fixed film reactor (UFFR) [2,3]. Thereupon, insufficient buffering control and disruption of microbial population balance between non-methanogen and methanogen to convert carbonaceous organic to CH_4, were identified to be the main reason of operational failure. To control the level of volatile fatty acid in the system, alkalinity has to be maintained by recirculation of treated effluent [4,5] to the digester or addition of lime
and bicarbonate salt [6]. As this process has been shown to be a proficient alternative both to pollution control and to produce CH4 as the bioenergy, hindrances while operation should be mend.

This study was undertaken to propose the use of ammonium bicarbonate (NH4HCO3), due to its buffering requirement against acidity throughout the treatment operation and also to maintain the microbial population balance. So, significant roles will be performed by NH4+ as the recommended bacterial nutrient for nitrogen and buffering capacity in an anaerobic digester [6]. However, excessive NH4HCO3 concentrations create free ammonia toxicity especially to the methanogen [7]. Hence, the optimal dosage for NH4HCO3 applied as supplement in anaerobic co-digestion process should be determined.

II. Materials and Methods

A. Preparation of substrate

A 100 L of PWW sample was collected in plastic containers at the point of discharge in to the main stream and from the receiving stream. 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 [5]. 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 [8]. 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 M.N.I. Siddique's method 2014 [5].

B. 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 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.

Table 1 Composition and Characteristics of PWW

Parameters	PWW
pH	6.5-8.5
BOD	8-32
COD	15-60
TOC	6-9
Total solids	0.02-0.30
Acetic acid	46.60
Phenol	0.36
Total Nitrogen	0.05-0.212
Total Phosphate	0.102-0.227
Volatile fatty acids	93-95

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

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 [9]. Nonetheless, the toxicity of NH_4HCO_3 especially to the methanogen in the system could be indicated in contrast of the maximum biogas yield [7]. 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 [10].

B. Batch test of toxicity

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 [8]. 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 [6]. 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 $CaCO_3$.

C. Biogas production

Fig. 1 illustrates the effect of NH4HCO3 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 NH4HCO3 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.

However, the detailed data revealed that the maximum biogas generation took place while 10 mg L-1 of NH4HCO3 was applied. It can be studied from previous work, the CH4 yield form the petroleum wastewater COD added ranged between 0.37–0.43 [2]. During the current work, CH4 yield was calculated assuming similar substrate digestion. The maximum CH4 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)				
	NH_4HCO_3 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

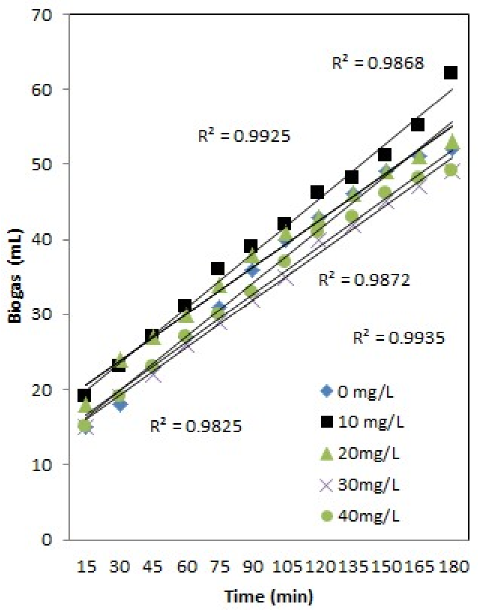

Figure 1: Evaluation of digestion performance in terms of cumulative biogas generation vs. time graph

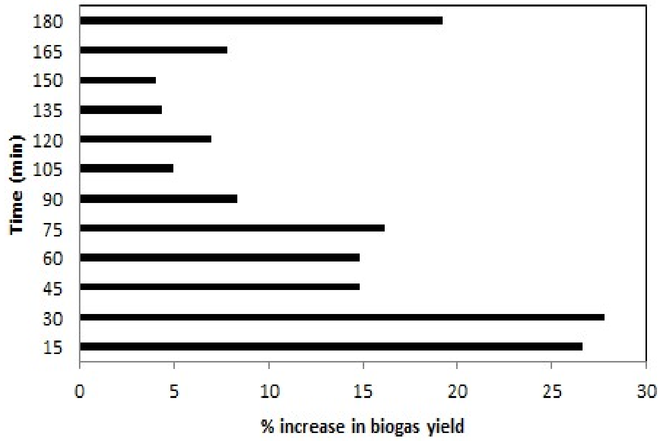

Figure 2: Effluent microbial cell concentration vs. solid retention time for co-digestion process.

For the calculation of % increase in biogas yield the following formula was employed:

% increase in biogas yield = (A – B) / B * 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 * 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 [11]. The volatile fatty acid (VFA) accumulation is suggested to be avoided employing supplementation of strong bases and co-digestion with other wastes [12]. 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.

III. CONCLUSION

This study reveals that the NH_4HCO_3 might be accelerate the anaerobic digestion of PWW. Ultimately, 10 mg L^{-1} of NH_4HCO_3 dosing was found to be the optimal dose for the substrate in comparison to the enhanced doses up to 40 mg L^{-1}. Moreover, the effectiveness of NH_4HCO_3 supplementation was also explained by formula. According to the calculation, 10 mg/L NH_4HCO_3 dosing can provide up to 27.77% enhanced biogas yield compared to control PWW digestion. This achievement can obviously add some financial advantage to make the treatment policy more feasible for industrial application.

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