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# Supplementation of ammonium bicarbonates for the treatment of fruit cordial wastewater by anaerobic digestion process

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#### A R T I C L E I N F O

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#### ABSTRACT

Lack of nitrogenous substrate and buffering capacity have been identified as causing failure in previous work on the treatment of fruit cordial wastewater using anaerobic continuous stirred tank reactors. In this study, ammonium bicarbonate was proposed to be used as the substrate for nitrogenous and buffering resources. In order to determine the toxicity effect of the ammonium salts on the anaerobic system, a series of concentration from 0 to 40 mg L<sup>-1</sup> was tested. Biogas production was used as the indicator for NH<sup>4</sup><sub>4</sub> toxicity. The results showed no indication that methanogen was affected by the additional ammonium salt within the dosing regime. Application of the specific mathematical function ( $G = G_m^{k/t}$ ) to describe the kinetic of biogas production, suggested that the optimal concentration of ammonium bicarbonate that can be used is 10 mg L<sup>-1</sup>. This study also shows that the dosage regime up to 40 mg L<sup>-1</sup> can be used to supplement the lack of nitrogenous and buffering capacity for the anaerobic digestion process of the fruit cordial wastewater using CSTR.

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#### 1. Introduction

An experimental operation for the treatment of fruit cordial wastewater using anaerobic continuous stirred tank reactor (CSTR) has previously been carried out [1]. That study suggested that such wastewater requires supplementary substrates to sustain its critical operational parameters such as alkalinity, pH and biomass. Observation during the operation showed that those parameters had gone below recommended levels. Subsequently, after increasing the chemical oxygen demand (COD) mass loading to the level of 1.33 kg m<sup>-3</sup>, the whole experimental operation had failed. The failure was off-set by a sudden drop of pH and increasing concentration of volatile fatty acid (VFA). It is well known that these two factors are critical to the anaerobic digestion process, especially to the sensitive methanogen group of bacteria. However, the amount of COD loading at 1.33 kg  $m^{-3}$  was found to be too low to cause failure in anaerobic CSTR [2,3]. Therefore, it was concluded that inadequate buffering control and disruption of microbial population balance between non-methanogen and methanogen to

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convert carbonaceous organic to CH<sub>4</sub>, were the main causes of operational failure. Obstacles during operation should be rectified since this process has been shown to be an efficient alternative to treat such wastewater with similar characteristics and to produce CH<sub>4</sub> as the bioenergy [2,4].

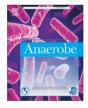
This study proposes the use of ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>), for its buffering requirement against acidity during the treatment operation and also for the microbial population. NH<sup>+</sup><sub>4</sub> will perform important roles in the anaerobic digester as the preferred bacterial nutrient for nitrogen and buffering capacity in an anaerobic digester [5]. However, high NH<sub>4</sub>HCO<sub>3</sub> concentrations cause free ammonia toxicity especially to the methanogen [5,6]. Therefore the optimal dosage for NH<sub>4</sub>HCO<sub>3</sub> used as supplement in anaerobic digestion process should be determined.

#### 2. Materials and methods

#### 2.1. Preparation of substrate

The fruit cordial wastewater in question is a purple soft drink that contains the juice of grapes, raspberries and blackcurrants, which has been analysed to be lacking in alkalinity and nitrogenous resources [1]. Preparation of fruit cordial wastewater was carried out according to a previous study by diluting the stock liquor [7]. The dilution of concentrated fruit cordial gave a consistent concentration of wastewater up to 2000 mg L<sup>-1</sup> of





Abbreviations: COD, chemical oxygen demand; CSTR, continuous stirred tank reactor; G, biogas production;  $G_{m}$ , maximum biogas production, k, specific mathematical coefficient; t, time; VFA, volatile fatty acid.

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COD, which is in the range of medium strength wastewater [8]. Fibrous matter arising from the depulping process was separated at the initial stage of production either by centrifugal process or water-pressing, and managed under solid waste management. This study was carried out to represent treatment for the unmixed wastewater without the presence of fibrous components.

#### 2.2. Toxicity test

The toxicity test of NH<sub>4</sub>HCO<sub>3</sub> (BDH Ltd.) on the anaerobic digestion of soft drink wastewater was done by submerging a series of air tight containers (500 mL) in a water bath at a temperature of 35 °C. These containers were connected to biogas measurement apparatus. Prior to testing by batch operation, each container was filled with 300 mL of stabilised anaerobic sludge as the seeding sludge and 100 mL of wastewater with COD concentration of 2000 mg  $L^{-1}$ . This was to simulate the non-critical COD mass loading at 0.5 kg m<sup>-3</sup>, which also avoided the seed experiencing substrate shock loading. Duplicates of five containers with an incremental series of NH<sub>4</sub>HCO<sub>3</sub> concentrations from 0 to 40 mg  $L^{-1}$ were prepared by adding concentrated stock of ammonium salt. The supplementary regime from 0 to 40 mg  $L^{-1}$  was chosen as the trial study on the optimal dosage. All containers were gently shaken every 10 min for mixing purpose and also to facilitate the release of biogas.

The optimal concentration for ammonium salt was determined according to the cumulative volumetric biogas production. It could be assumed that rapid biogas production would take place within the period of 3 h of batch operation for the same substrate [7]. Nevertheless, comparison of the maximum biogas production could indicate the toxicity of NH<sub>4</sub>HCO<sub>3</sub> especially to the methanogen in the system [6]. Composition of CH<sub>4</sub>:CO<sub>2</sub> in the previous study is at the ratio of 20:80. However the biogas production volume in this study was expected to be too low for composition analysis by gas analyser (GA94A, Geotechnical Instrument (UK), Ltd.). This study used the same methods of CO<sub>2</sub> removal by passing the biogas through a high concentration alkaline solution while measuring it by liquid displacement [1].

#### 3. Results and discussion

The previous operational failure which was instigated by the accumulation of VFA could have occurred with other limitations such as micronutrients (Fe, Ni, Cu, Co, Mg) and phosphorus [8]. Nevertheless, hypothetically the lack of micronutrients could be dismissed by the information on mineral content given on the label of this particular softdrink cordial. Meanwhile the lack of phosphorus was also not being addressed because the inoculum was taken from freshly digested sewage sludge, in which the presence of phosphorus as the micronutrient should be adequate. Meanwhile, the presence of ammoniacal nitrogen as the macronutrient in a stabilised digested sludge is also considered to be at a residual concentration after the process of denitrification is complete [8].

The other salt that could be used to supplement the lack of nitrogenous substrate is sodium nitrate. However, as for sodium nitrate, the release of  $NO_3^{-1}$  would increase the oxidation–reduction potential (ORP) of the digester. The potential ORP of the digester should be allowed to increase above -300 mV. At lower ORP methane-forming bacteria could not produce methane, for example at ORP of -300 mV [5]. While for the buffering salts, caution should be exercised in the choice of chemical used for alkalinity adjustment. Precipitation of CaCO<sub>3</sub> creates unwanted solids, and the large quantity of single cation, for example Ca, presents the potential for alkali metal toxicity.

#### 3.1. Biogas production

Fig. 1 shows the cumulative production of biogas during the toxicity test of ammonium salt on the anaerobic digestion system. It shows the typical first order reaction rate on the conversion of carbonaceous organic to biogas. It decelerates with the cessation of raw materials. Total cumulative biogas production was observed to increase when the ammonium salt was added. However, the cumulative production of biogas was observed to decline when more than 20 mg L<sup>-1</sup> of ammonium salt were added into the system. The effect of C:N ratio was not investigated during this testing. The

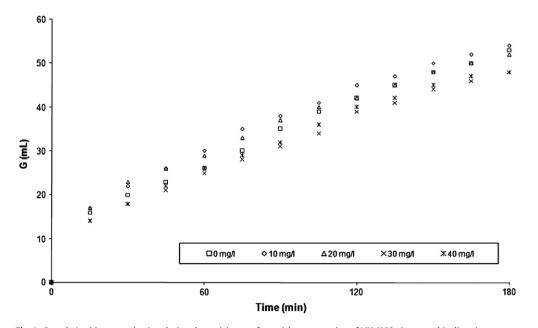


Fig. 1. Cumulative biogas production during the toxicity test for serial concentration of NH<sub>4</sub>HCO<sub>3</sub> in anaerobic digestion system.

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