Enhancement of biogas production from digested sludge with removal of H2S using airlift bioreactor

MAHAMOOD K.H. AL-MASHHADANI, STEPHEN J. WILKINSON, WILLIAM B ZIMMERMAN*

Department of Chemical and Biological Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom
E-mail: w.zimmerman@shef.ac.uk

Abstract:
This paper addresses further anaerobic digestion of already digested sludge by processing in an airlift bioreactor. Anaerobic digestion is commonly used for nutrient and energy recovery from biomass. It is used to breakdown organic matter into methane(CH₄), carbon dioxide (CO₂), hydrogen sulphate (H₂S), and digested sludge, which is used for fertilizer, through four biodegradation stages. The rate of gas generation through mesophilic anaerobic digestion is generally higher, yet, the remaining dissolved gases in a digested sludge have a pejorative effect on the environment when they are eventually released, as well as causing operational difficulties. Moreover, the generation of biogas continuously in an already digested sludge increases cavitation phenomena and the accompanying pump load. Removal of these gases is investigated by a bubbling system. An airlift bioreactor (ALR) is used as anaerobic digester in the present research to remove produced methane, carbon dioxide and hydrogen sulphate (H₂S) from digested sludge, consequently, reducing pathogens and odour as well as improvement digested sludge for fertilizer. ALRs have many valuable benefits in comparison with stirred tanks for instance: there are no moving parts inside the reactor, low cost of installation and maintenance, and low energy required. In addition, using an airlift reactor enhances the mixing efficiency. The process preferable to agitation as in conventional stirred tanks on power consumption grounds. The experimental data shows that the cumulative methane production of airlift anaerobic digester about 29% more than the observed in the conventional anaerobic digester. Through 170 hours of processing, there is a significantly greater removal of carbon dioxide and hydrogen sulphate in airlift digester over a conventional digester.
Introduction:

An anaerobic digester is a processing unit in a wastewater treatment plant where organic matter is broken down via anaerobic bacteria in the absence of oxygen. The biodegradation of organic matter in an anaerobic digester takes place through four steps. The first step is a hydrolysis stage which converts the complex organic matter into a simple state. The second step is the acidogenesis stage. In this stage, the product of the first stage converts into volatile fatty acids. Volatile fatty acids (VFA) are converted into acetate in the third step by acetotogenic stage. Finally, the acetate and carbon dioxide with hydrogen produced in the second step converts into methane and carbon dioxide in the methanogenesis stage. Each stage is mediated by a specific type of bacteria. Each bacteria requires a specific environment. Methanogenic bacteria are more sensitive to change of operating conditions. However, there are general operating conditions, such as temperature, pH, Carbon-nitrogen ratio, and ammonia etc, appropriate for all the bacterial consortia [1].

The hydraulic retention time of a mesophilic anaerobic digester is approximately 20 days. Then the sludge discharges as effluent. The digested sludge (effluent) contains organic matters (biodegradable), anaerobic bacteria and some dissolved gases, for instance carbon dioxide (CO₂) and hydrogen sulphate (H₂S). The presence of these dissolved gases has a negative impact on the piping and the downstream processing units. Corrosion is one potential problem in piping metals. In addition, the generation of biogas continuously in digested sludge during transfer creates a gas-liquid mixture. Even if a small phase fraction of gas, it degrades the performance of pumps due to cavitation phenomena.

This paper aims to utilize an airlift bioreactor as an anaerobic digester to complete a biodegradation of organic matter and to generate methane from already digested sludge. The second aim is to reduce pathogens and odour by removal H₂S from digested sludge as well as to prevent corrosion of pipelines, which is caused by excessive levels of dissolved CO₂ and H₂S. A tertiary aim is to reduce pumping requirements by reduction of the cavitation phenomena internal to pumps due to the level of dissolved gases.

Airlift reactors (ALR) have been used in several industrial applications for many gas-liquid contacting processes. ALRs have many advantages over stirred tanks. For instance, there are no moving parts inside the reactor, a low cost of installation and maintenance, and low energy required. In addition, it is observed that using an airlift reactor enhances the mixing efficiency the process over conventional stirred tank agitation.
Airlift reactors can be classified into two main types according to their structure:

(1) Airlift external loop reactor, in which the circulation takes place in separate conduits.

(2) Airlift internal loop reactor, the tube or plate is put to create the conduit (channel) inside a single reactor for circulation the liquid.

An airlift internal concentric loop is used in the present study, basically, comprising two regions that are separated by the inner cylinder or plat. The first region is called the riser in which the gas is sparged in the bottom zone of reactor, where the gas and liquid flow upward. The second region is called downcomer zone, in which the gas and liquid flow downward. The presence of gas in riser region and sparsity of gas in downcomer region leads to difference in mean densities of the liquid between the riser and downcomer region. This difference generates a driving force and pressure gradient necessary for circulation the liquid around the draught tube as shown in the Figure 1[2].

![Figure 1. Schematic diagram of airlift internal concentric loop](image)

Because these benefits, in addition, good mixing, long time residence, and low shear damage to cells, the airlift reactor is used as anaerobic digester in the present study.

In addition, the airlift provides contacting between liquid (sludge) and gas (nitrogen bubbles). This contact leads to reduction the partial pressure of biogas produced due to gas exchange. The low partial pressure of the products contributes to the Gibbs free energy with a negative sign, hence the reaction becomes thermodynamically favourable and provides impetus for the formation of more products [3]. Investigations that depend on the mathematical relationship
between partial pressure and Gibbs free energy are many with widespread applications. But the major results of these applications are in biological processes, particularly the production process for bio-hydrogen. This process has raised debate among researchers about controlling the partial pressure of hydrogen or carbon dioxide and its effects on the production of hydrogen. Many researchers have noted that the increase in hydrogen production could be achieved by reducing the partial pressure of hydrogen or carbon dioxide or both. The study of the effect of the reduction of the partial pressure of carbon dioxide on hydrogen production has been conducted by many researchers. Tanisho\cite{4} found that hydrogen production increased when the partial pressure of carbon dioxide decreased. Park\cite{5} demonstrated that reducing the concentration of carbon dioxide from 24.5\% into 5.3\% in the headspace caused an increase in the hydrogen yield by 43\%. Alshiyab\cite{6} indicated that there is an increase in the hydrogen yield when partial pressure of carbon dioxide is reduced. Liang\cite{7}, Mizuno\cite{8}, and Kim\cite{9}, Kraemer and Bagley\cite{10}, studied the effect of reduction in the partial pressure of hydrogen on hydrogen production. Liang\cite{7}, reported that the reduction of partial pressure of hydrogen by using silicone rubber membrane, to remove the dissolved gases, caused an increase in hydrogen yield by 15\%. Mizuno\cite{8}, found that the hydrogen yield reaches up to 68\% when its partial pressure decreases\cite{9}\cite{10}. The satisfactory results of these investigations have shown the importance of the removal of gases from biological processes and its effect on increasing production of hydrogen and increase by efficiency of the process.

Reduction of the partial pressure of gases can be achieved by different and varied means. Selection of one of these ways depends on the removal efficiency, its impact on the production and cost implications. Park\cite{5} and Alshiyab\cite{6} removed carbon dioxide by C.acetobutylicum NCIMB 133357 and KOH respectively from headspaces of the bioreactor. Tanisho\cite{4}, Mizuno\cite{8}, Kim\cite{9}, Kraemer and Bagley\cite{10}, Nath and Das\cite{11}, Hussy\cite{12}, and Kyazze\cite{13}, used the sparging gas (N\textsubscript{2}, H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4}) in bio-hydrogen production to remove the H\textsubscript{2}, CO\textsubscript{2}. Corte\cite{14} used Rhodomicrobium Vaniellii ATCC 17100 bacterium, which utilizes hydrogen and carbon dioxide, in reducing both gases and used sulfate-reduction bacteria to remove hydrogen only.

The current research hypothesizes that using an airlift bioreactor as anaerobic digestion will lead to increase biogas production.
Method and material

Two laboratory size airlift anaerobic digesters were used in this study. Each one has volume of 12 litres, working volume of 9 litres, while the remaining volume was used as head space as shown in the Figure 2. The diameter of this digester is 200 mm with a height of 450 mm. The draft tube diameter is 120 mm with height of 140 mm. The airlift digester was fitted with a ceramic diffuser for use in the sparging experiment. The sparging gas was nitrogen which generated by nitrogen generator (Peak scientific Ltd) with purity about 99.5%. The digesters were operated at hydrodynamic retention time (HRT) of 7 days under mesophilic conditions. Time of bubbling was one hour daily for 170 hours. Average flow rate of nitrogen is about 300 l/min. Biogas production was measured continuously by downward displacement of acidified (0.2 M HCL, pH<4) water. Concentration of CH$_4$, CO$_2$ and H$_2$S was measured by a biogas analyzer (Data gas analyzer).

Figure 2: Lab scale airlift anaerobic digestion

A proportional-integral-derivative controller (PID controller) is used to control the temperature in anaerobic digester with 35 °C in the current study. This controller attempts to reduce the error, which resulted from the different between measured temperature and a desired set-point and enable to minimize the offset. Temperature controlled system was constructed from heater with 500W and
thermocouple sensor type K with range -128 °C to 539 °C as well as controller. The block diagram and characteristics of control system is illustrated by the Figure 3 and Table 1.

The transfer function of the lab-scale batch anaerobic digestion is has the following mathematic modelling:

\[ T(s) = \frac{1}{\beta s} (Q_h - Q_w) \]

Where \( \beta = V \rho \ C_p \)

\( V = \) volume of anaerobic digestion
\( \rho = \) density of fluid
\( C_p = \) heat capacity of fluid
\( T = \) Temperature of anaerobic digestion
\( Q_h = \) heat provide by heater
\( Q_w = \) heat loss via the wall of anaerobic digester

![Figure 3. Block diagram of temperature control system which is used for airlift anaerobic digestion](image)

Table 1. Characteristics of the temperature control system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Controller</td>
<td>ON-OFF controller</td>
</tr>
<tr>
<td>Device</td>
<td>Range 0-60 Temperature</td>
</tr>
<tr>
<td></td>
<td>Resolution 0.1 Temperature</td>
</tr>
<tr>
<td></td>
<td>Accuracy ±1 Temperature</td>
</tr>
<tr>
<td>Manipulating part</td>
<td>Heater</td>
</tr>
<tr>
<td></td>
<td>Power of heater 400 Watt</td>
</tr>
<tr>
<td>Sensor</td>
<td>Type K thermocouple</td>
</tr>
</tbody>
</table>

The pH controller system used in the current study is ON/OFF relay controller. It consists of main three parts: controller, peristaltic pump and pH probe sensor. When the pH drops during the process, the pH probe sensor signals to the controller. The controller will compare this signal (received from pH sensor) with set point value. The error resulting from this
comparison will decide whether or not to actuate the ON switch of peristaltic pump to add sodium bicarbonate into the sludge. This process continues until the error becomes zero as shown in Figure 4. The low flow rate of peristaltic pump gives enough time for the spread of the solution through the sludge and reduces any eventual overshoot in pH value. The optimum pH value is between 6.8 and 7.4 which provides a suitable environment for growth of methanogenic bacteria, while other bacteria, acidogenic bacteria as an example, can grow with pH 5-6. The type of pH controller system that used in the experimental work is BL931700 pH minicontroller. The pH value was stable in the range of 6.8-7.5 using the control and monitoring system. The solution which is used to adjust with by pH control is sodium bicarbonate (NaHCO₃). It is a crystalline substance, white colour and appears in a very fine powdered form. It is an amphoteric compound because can reacted with acids and bases. Actually, using the sodium carbonate to adjust the pH in anaerobic digestion is more efficient than using any other solution for many reasons, for example: (i) no corrosion nor toxicity if used appropriately, (ii) easy handling in comparison to sodium hydroxide and calcium hydroxide, soluble in water without any difficulties; (iii) does not cause precipitation, therefore does not require maintenance or frequent cleaning, and, most importantly, (iv) does not cause big jumps in pH value even in the case of excessive doses. The big jumps in pH value not only cause inhibition of bacteria, but cause the re-dissolution of carbon dioxide to sludge again, because solubility of CO₂ increase with pH increase. Thus, this situation would cause vacuum pressure in the head space of the digester. Therefore, use of sodium bicarbonate would keep operation of anaerobic digestion with optimum conditions. The specification of the pH controller system can be illustrated in the following table:

Figure 4. Block diagram of pH control system which used in airlift anaerobic digestion
Finally, in a duplicate procedure, the two digesters were simultaneously sparged with nitrogen just in the first day to provide an anaerobic environment. Then bubbling starts with the airlift digester only. A schematic of the experimental apparatus is given in the Figure 5.

Table 2. Characteristics of the pH control system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of controller</td>
<td>On-off controller</td>
</tr>
<tr>
<td>Type of device</td>
<td>BL931700 pH minicontroller</td>
</tr>
<tr>
<td>Range of pH</td>
<td>0.00 to 14.00 pH</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.01 pH</td>
</tr>
<tr>
<td>Accuracy @ 20 °C</td>
<td>±0.02 pH</td>
</tr>
</tbody>
</table>

Manipulating part

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>Peristaltic pump</td>
</tr>
<tr>
<td>Type of pump</td>
<td>NaHCO3(0.2 M)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1 ml/min</td>
</tr>
</tbody>
</table>

Sensor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of solution</td>
<td>Double junction pH laboratory electrode</td>
</tr>
</tbody>
</table>
Sampling the digested sludge

The fresh sludge, taken from wastewater treatment plant, has physical, chemical and biological properties. These properties change for several reasons, for instance, type of wastewater, time of sampling and storage, handling and transfers from the wastewater treatment plant to the laboratory, weather conditions and seasonal variation of water treatment equipment design and operating conditions. Biologically, there are many types of anaerobic bacteria exist in the wastewater\textsuperscript{15}. Activity, type, number of these bacteria depend on the characteristics of the wastewater and weather conditions at the time of collection. This will affect strongly the production of biogas and efficiency of biodegradation of the organic matter. Since chemical and physical properties for the sewage sludge are variable, this may cause difficulties in linking the results of experiments that are carried out with different sludge batches. Therefore, the present study uses samples of same sludge, which is taken from wastewater treatment plant and distributed it into both reactors at the same time with the same operating conditions.

Many researchers \textsuperscript{16-20} do not introduce any nutrients nor trace metals into sludge in their experimental work because the sludge for anaerobic digestion is mainly composed of lipids, polysaccharides, protein and nucleic acids which are bio-degraded by anaerobic bacteria to produce the biogas and effluent, which used as fertilizer. Thus, addition of nutrients to the sludge is not necessary. Whether or not to add nutrients depends on the type of sludge.

For the successful operation of anaerobic digestion, facultative anaerobes, anaerobes including methanogenic bacteria and organic particulates should be present in the sludge. The primary clarifier provides particulates and many anaerobes including methane-produce bacteria, while the secondary clarifier provides many facultative anaerobes. In the present research, the digested sludge was collected from outlet stream of full-scale mesophilic digester from a wastewater treatment plant in Sheffield city. Digested sludge has methanogenic bacteria but with low concentration of substrates.

Results and discussion

Figure 6 shows that during 170 hours, the cumulative methane production from the airlift anaerobic digester was about 29 \% higher than observed in the conventional anaerobic digester. A large amount of methane obtained from airlift anaerobic digester occurred during the sparging nitrogen for one hour daily as shown as in the Figure 7. This indicates that the biogas produced by biological process is remaining in digested sludge due to characteristics
of sludge that prevents biogas rising. Therefore any contact with gas bubbles will strip immediately due to difference of concentration between them. Poor solubility of methane gas enhances gas stripped from digested sludge. One hour daily to refresh the digested sludge led to increase methane production due to decrease of the partial pressure of methane and other gases. Therefore, the overall Gibbs free energy became more negative, hence the reaction becomes thermodynamically favourable and moves towards the formation of more products. However, due to the use of digested sludge in this experiment, the substrate composition was slight compared with methanogenic bacteria. Thus, during the hydraulic retention time, the production of methane was decreased per day as illustrated in the Figure 7. That reduction occurred in both digesters.

![Figure 6. Methane production digester with and without fine bubble](image)

![Figure 7. Methane production per day before and after one hour nitrogen sparging in airlift digester.](image)
The essential ingredient in the biological medium is water with a composition of 90-95% depending on the type of bioprocess. For instance, water content in sludge is around 95%, while 5% consists of micro-organisms, organic matters, elements and suspended solids. Micro-organisms feed on the organic matter and elements to produce gases by metabolic processes. Carbon dioxide, methane, and hydrogen are highest composition gases produced from fermentation process. The ability of these gases to stay in the liquid phase is related to their relatively solubility, see Table 3.

Table 3. Solubility of biogas

<table>
<thead>
<tr>
<th>Substance</th>
<th>Solubility</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.45</td>
<td>g gas/kg water</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0215</td>
<td>g gas/kg water</td>
</tr>
<tr>
<td>H₂</td>
<td>0.00155</td>
<td>g gas/kg water</td>
</tr>
</tbody>
</table>

It can be seen that CO₂ is relatively high solubility compare with CH₄ and H₂. Thus, it will be stay in the liquid phase longer as dissolved aqueous gas (CO₂(aq))

\[ CO₂(g) ⇌ CO₂(aq) \]  \hspace{1cm} (1)

Figure 8 shows the pathway of biogas produced from bacteria. Released carbon dioxide reacts with water to produce carbonic acid.

\[ CO₂(aq) + H₂O(l) ⇌ H₂CO₃(l) \] \hspace{1cm} (2)

Figure 8. Conversion processes in anaerobic process

Kinetically, the conversion to carbonic acid is very slow, just 0.2% of carbon dioxide converts to carbonic acid and its ions, while 99.8% of the carbon dioxide remains as dissolved gas as shown below:

\[ Kh = \frac{[H₂CO₃]}{[CO₂(aq)]} \] \hspace{1cm} (3)
Carbonic acid is a diprotic acid, thus it contains two hydrogen atoms ionisable in water and dissociates into bicarbonate and carbonate ions:

\[ H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad (4) \]

\[ HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (5) \]

From the above equations, it can be noted that the presence of dissolved carbon dioxide in liquid phase will produce a hydrogen ion that would lead to the lowering of the pH. However, the pH observed in airlift anaerobic digestion and conventional anaerobic digester is approximately stabilized during the experimental work, except that a slight change in the airlift digester was observed during sparging of nitrogen as shown in Figure 9. This means that the carbonic acid produced from dissolved carbon dioxide is treated immediately by ammonia produced from biodegradation of protein. The low solubility of the methane contributes to transfer it from the liquid phase to the gas phase. While most of carbon dioxide remains in the sludge as "dissolved gas" until providing the suitable opportunity to transfer. Therefore; a driving force for this transfer is created when nitrogen is sparged. Figure 10 shows the production of carbon dioxide from anaerobic digester with and without nitrogen sparging. The figure shows that the bubbling system in anaerobic digestion contributes to increasing the carbon dioxide in biogas production. The efficiency was 350% with bubbling system more than with the control digester. Experimentally, the complex characteristics of the sludge has played important role in stripping of all gases.

Figure 9. pH of airlift digester and conventional digester
Figure 10. Carbon dioxide produced from airlift digester with and without nitrogen bubbling

The same thing happens with H$_2$S. The high solubility of hydrogen sulphate contributes to remaining in the sludge as H$_2$S(aq). When H$_2$S dissolves in sludge, the pH, also, would drop due to releasing a hydrogen ion and forming a weak acid. Indeed, the behaviour of the solubility of hydrogen sulfide is very similar to carbon dioxide because both gases form a diprotic acid in water as showing in following reactions.

$$H_2S(g) \leftrightarrow H_2S(aq) \quad (6)$$

$$H_2S(aq) \leftrightarrow HS^-(aq) + H^+ \quad (7)$$

$$HS^-(aq) \leftrightarrow S^{2-}(aq) + H^+ \quad (8)$$

Sulfate dissolved with a high concentration, can inhibit generation of biogas produced from the anaerobic digestion of wastewater. The most important reasons leading to this inhibition is that the sulfate dissolved in wastewater encourages growth of the sulfate-reducing bacteria which consume the acetic acid and hydrogen that are consumed by methanogenic bacteria to produce the biogas as well $^{[21]}$. This competition between the sulfate-reducing bacteria and the methane-producing bacteria for the consumption of the hydrogen and acetic acid can be illustrated thermodynamically through the following equation.

Methanogensis:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (9) \quad \Delta G = -135 \text{ kJ}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (10) \quad \Delta G = -28.5 \text{ kJ}$$
Sulfate reduction

\[
\begin{align*}
\text{SO}_4^{2-} + 4\text{H}_2 & \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^- & (11) \quad \Delta G = -154 \text{ kJ} \\
\text{SO}_4^{2-} + \text{CH}_3\text{COOH} & \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- & (12) \quad \Delta G = -43 \text{ kJ}
\end{align*}
\]

From above equations, it can be seen that the sulfate-reduction reactions have greater thermodynamic driving force than methanogenesis, therefore methane production is inversely related to sulfate concentration. Therefore, H₂S has a negative impact on the methane production bacteria as mentioned Karhadkar\textsuperscript{[22]}. He also suggested that the concentration of H₂S can be taken as an indicator of inhibition of methanogenic bacteria.

A removal of dissolved H₂S from sludge is necessary to prevent inhibition of methanogenic bacteria and reduce odour from digested sludge. Normally, the removal of CO₂ and H₂S take place by biogas generated (CH₄ and CO₂) or by contact with head space in the top of sludge. But this is insufficient to remove the dissolved gases. Mixing of the digested sludge provides intimate contact between sludge and bubbles of biogas or headspace. However, the characteristics of digested sludge require high energy to make it. Using an airlift digester with low energy requirement helps to remove most of hydrogen sulphate generated. Figure 11 shows the hydrogen sulphide removal from digested sludge during nitrogen bubbling. The figure indicates that with one hour of nitrogen sparging with fine bubbles, there is a stark increase in the removal of hydrogen sulphate compared to a conventional digester.

![Figure 11. Hydrogen sulphate produced from anaerobic digestion with and without nitrogen sparging.](image)

The benefits of the airlift bioreactor are illustrated through the above results. Low energy, good mixing, and enhancement of stripping gases are the most important of the
characteristics of airlift bioreactor that were utilized in this study. More methane and more stripping of carbon dioxide and hydrogen sulphate were obtained from this utilization.

CONCLUSIONS

Anaerobic digestion for processing the already digested sludge in an airlift bioreactor is investigated in this paper. The results show that the cumulative methane production of airlift anaerobic digester is about 29% more than observed in conventional anaerobic digestion. Greater removal of the dissolved gases (CO₂ and H₂S) compared to a conventional digester was observed through 170 hours of processing. More methane, CO₂ and H₂S were obtained during nitrogen sparging.

ACKNOWLEDGMENT

W.Z. would like to acknowledge support from the EPSRC (Grant No. EP/I019790/1). W.Z. would like to acknowledge the Royal Society for a Brian Mercer Innovation award and the Royal Academy of Engineering for an industrial secondment with AECOM Design Build. MKHaM would like to thank the Iraqi Ministry of Education for a doctoral scholarship.

References


