Optimization of Primary Sludge Hydrolysis for Nutrient Removal in Wastewater Treatment Plants

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Abstract. Primary sludge biological hydrolysis may be employed to produce readily biodegradable carbon, used to enhance biological nutrient removal processes applied in wastewater treatment plants. The objective of this work was to evaluate the efficiency of primary sludge hydrolysis to produce readily biodegradable organic carbon. Lab-scale units operated, as acid digesters in order to evaluate the effect of: 1) HRT, 2) SRT, 3) temperature and 4) sludge recycle on the efficiency of primary sludge hydrolysis. Primary sludge acid digesters without recycle operating within an HRT range between 2 d – 5 d may achieve a soluble COD efficiency that ranges between 5% - 8% of influent particulate COD, at ambient temperatures. The temperature dependency of solubilization rates can be described by an Arrhenius type equation with a temperature dependence coefficient θ equal to 0.073.

Primary sludge acid digesters with sludge recycling can achieve much higher efficiencies in terms of readily biodegradable COD and VFAs production even at low HRTs of 1 day. The efficiency of acid digesters with sludge recycle in terms of soluble COD production was found to be approximately 10% of the particulate COD in the influent, at ambient temperatures.

Keywords: anaerobic sludge hydrolysis, acid digester, prefermenter, readily biodegradable COD production

1. Introduction

Anaerobic degradation processes may be divided to at least four stages: disintegration, hydrolysis, acid/acetogenesis and methanogenesis. These processes are normally catalyzed by intracellular or extracellular enzymes and act on the pool of available organic material. According to the Anaerobic Digestion model No1 (ADM1) (IWA, 2002), extracellular solubilisation which results to readily biodegradable COD production is divided into disintegration and hydrolysis. Disintegration is considered a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates, proteins and lipids. Hydrolysis of particulate carbohydrates, proteins and lipids to monosaccharides, aminoacids and long chain fatty acids (LCFA), respectively is an enzymatic process. Disintegration is mainly included to describe degradation of composite particulate material such as primary or waste activated sludge. The hydrolysis steps are to describe the degradation of well defined macromolecule substrates to each soluble monomer. All disintegration and hydrolysis kinetics are represented by first order kinetics. Digestion of soluble materials mediated by organisms is an intracellular process and results in biomass growth and decay (IWA, 2002).

In the hydrolysis phase, the volatile suspended solids, mainly consisting of proteins (approx. 30%), carbohydrates (approx. 40%) and lipids (approx. 30%), are hydrolyzed by means of extracellular enzymes to aminoacids, sugars and long chain fatty acids (LCFA) respectively. In acidogenesis phase the products from the hydrolysis are fermented into volatile acids and in subsequent acetogenesis phase LCFA as well as volatile fatty acids (VFA) except acetate are decomposed through β-oxidation (Brinch, et al., 1994). Finally, methane is produced in the last phase by means of two groups of methanogen bacteria: a) hydrogenotrophic methanogens, and b) acetoclastic or acetotrophic bacteria.

Acid phase digestion may be employed to produce soluble organic carbon to enhance biological denitrification or biological phosphorus removal (BNR). (Pitman, et al., 1992) or short-cut nitrification/denitrification process for the treatment of sludge reject water with a high NH4-N content. Maximum production of soluble organic carbon can be achieved only when methane production has been effectively suppressed. The minimum cell residence time for methane production from lipids and volatile acids at mesophilic temperatures and normal pH values of 6.8 to 7.5 is approximately 2.5 to 4 days. However some methane is produced at much shorter detention times due to utilization of hydrogen produced during fermentation of carbohydrates and proteins to volatile acids. Minimum cell residence time for hydrogen utilizing bacteria at 37°C is 19 hours. Methane production also can be suppressed by reduction of pH below the normal range of 6.8 to 7.5 required by the methanogenic phase (Eastman and Ferguson, 1981).

Guerrero et al. (1999), reported that during primary sludge digestion an initial period between 1-10 days could be observed where hydrolysis – acidification were the controlling processes and very low methane production occurred. Following this initial period, VFA accumulation
decreases and methane production becomes more important.

Hydrolysis can be carried out in primary settling tanks, in completely mixed closed reactors or in gravity thickeners. The produced soluble organics, consisting mainly of VFA, can be elutriated from the sludge by physical or mechanical means. Sludge recycling is often employed in the case of gravity separation in order to achieve sludge retention times (SRTs) greater than hydraulic retention times (HRTs) and hence enhance “hydrolysers” population by supplying the necessary enzymes for the process. Elutriation through mechanical means is achieved more frequently by centrifugation with no sludge recycling.

The objective of this work was to evaluate the efficiency of primary sludge hydrolysis to produce readily biodegradable organic carbon. Lab-scale units operated, as acid digesters in order to evaluate the effect of: 1) HRT, 2) SRT, 3) temperature and 4) sludge recycle on the efficiency of primary sludge hydrolysis.

2. Materials and Methods

Experimental Set up and Analytical Methods

Experiments were conducted in bench scale primary sludge acid digestion systems. Each of the reactors operated at a different hydraulic retention time, submerged in a water bath for constant temperature maintenance. The anaerobic hydrolysis of primary sludge was studied at three different temperatures: 13.5, 19 and 30°C, and three different HRTs 2, 4 and 5 days. The reactors operated in a pseudo-continuous flow mechanically stirred-tank mode, without sludge recycling (HRT=SRT) or with recycle (HRT < SRT). The reactors were fed once a day with primary sludge from Psyttalia Wastewater Treatment Plant.

During all experimental periods the performance of the acid digesters units was assessed by routine measurements of temperature, pH, DO, ORP, TS, VS, total and soluble COD and NH₄-N. Total Kjeldahl Nitrogen (TKN) and volatile fatty acids (VFA) concentrations were also measured in a regular basis.

All analyses of the lab scale units were performed in accordance with Standard Methods (APHA, 2012). ORP and pH were measured daily using portable equipment (HACH, HQ40d).

Disintegration – Hydrolysis Rate Calculations

In the absence of methane production in a continuous-flow stirred-tank acid digester with constant volume V, constant inflow and outflow q, inflow dissolved and particulate constituents concentrations S_in and X_in and effluent concentrations S_i and X_i, the mass balance for the dissolved constituents is:

\[
\frac{dS_i}{dt} = qS_{in,i} - qS_i + Vr_i \Rightarrow
\]

where \( r_i \) is the rate of constituent \( i \) production due to extracellular solubilisation of \( X_i \) particulate. According to the ADM1 (IWA, 2002) and as shown by Efthathiou et al., 2003 the disintegration first order parameter effects the effluent soluble COD concentration more than the respective hydrolysis constant, as according to the model, disintegration is considered the rate limiting step for particulate COD consumption and SCOD production. Therefore the rate \( r_i \) of extracellular solubilisation that results to soluble COD production can be determined according to the following equation:

\[
r_i(T) = k_{sol}(T) \times X_i
\]

where \( X_i \) is the concentration of particulate COD (PCOD) in the reactor that may be solubilized to produce soluble COD. The various fractions of PCOD in the CSTR were determined as follows: 10% PCOD was considered to be inert, and the rest PCOD was considered to be composite particulate material and biomass that could be solubilized to produce soluble COD.

According to the ADM1 (IWA, 2002) the influence of the temperature on the kinetic expressions (disintegration, hydrolysis, etc.) is assumed to be exponential, as shown below:

\[
k_{sol}(T) = k_{sol}(35) \times \exp\{0(T-35)\} \times X_i
\]

where \( \theta \) is the temperature coefficient.

Therefore based on eq. (1), (2) and assuming steady state conditions, soluble COD in the effluent of the primary sludge acid digesters can be calculated according to the following equation:

\[
S_{sol} = S_{sol,in} + k_{sol}(T) \times X_i \times HRT
\]

Efficiency of primary sludge acid digesters

In an acid digester when methane production is negligible, solubilization of particulate organic matter in the feed results in the production of soluble COD which is present in the effluent in terms of VFA or other minor fermentation products. The efficiency of acid digesters can be expressed as a function of soluble COD in the influent and effluent or as a function of VFA in the influent and effluent as follows: (soluble COD_{inf} – solubleCOD_{eff})/COD particulate inf, according to the following equations:

\[
\frac{SolCOD_{eff} – SolCOD_{inf}}{COD particulate inf} \text{ or } \frac{VFA_{eff} – VFA_{inf}}{COD particulate inf}
\]

3. Results and Discussion

The experiments were designed to address all three parameters that according to eq. (3) effect soluble COD production in a completely mixed primary sludge acid digester. During the 1st phase of the experiments the effect of HRT and temperature on the efficiency of primary sludge hydrolysis was evaluated. The 2nd phase of the experiments aimed to evaluate the effect of increased particulate concentration (\( X_i \)), due to sludge recycle, on soluble COD production.

Effect of HRT: Three lab-scale primary sludge acid digesters operated at HRTs equal to 2, 4 and 5 days and constant temperature of 19 – 21°C, in order to evaluate the effect of HRT on the efficiency of primary sludge
solubilization. The reactors operated in a pseudo-
continuous flow mechanically stirred-tank mode, without
sludge recycling (HRT=SRRT). The star-up of each acid
digester lasted for approximately one month. Following
achievement of steady state conditions the acid digesters
operated for approximately another two months to collect
all necessary data. The results of the steady state operation
of the acid digesters for the three HRTs are summarized in
Table 1, while the results of their efficiency in terms of
soluble COD and VFAs production is shown in Figures 1-
2.

As shown in Figures 1 and 2, within the range of
temperatures, pH and residence times studied, increasing
residence, results in a significant increase in effluent
soluble COD. The efficiency of acid digesters in terms of
soluble COD production equals 5%, 6% and 7.9% of the
particulate COD in the influent for HRTs of 2 d, 4 d and 5 d
respectively. In addition VFAs production is also increased
both as absolute value and as percent of effluent soluble
COD. As shown in Table 1 VFAs production equals to 56,
94.7 and 126 mg COD/VFA / g VS, for HRTs of 2 d, 4 d and 5 d
respectively. Approximately 80% of the soluble COD in the
effluent is VFAs. The distribution of VFAs, illustrated in Figure 2, was similar in all HRTs studied and
on average equals 44.5% acetate, 37% propionate, 15%
butyrate and 3.5% isobutyrate. However it should be
underlined that due to the relatively low pH in the acid
digesters that was consistently below 6.1 and the relatively
low average operating temperature that ranged between 19
– 21°C the methanogenesis obtained even at HRT of 5 d,
was practically negligible. Methanogenesis was estimated
according to the difference between TCOD in the influent
and effluent sludge samples. The difference between
influent and effluent TCOD concentration was practically
zero and therefore methane production was considered
negligible. As shown by the ADM1 (IWA, 2002) a higher
methanogenesis should be expected if operating at higher
pH values and temperatures or HRTs. Therefore based on
the results presented in this study it appears that the
optimum HRT is approximately 4 d for pH and
temperatures do not exceed 6 and 21oC respectively. For
higher pHs or temperatures optimum HRTs should be
lower than 4d in order to maintain methanogenesis to a
minimum.

Effect of temperature: In order to evaluate the effect of
temperature on the solubilization rate of particulate organic
matter in primary sludge, lab-scale primary sludge acid
digesters operated at a constant HRT of 2 d. Each of
the reactors was submerged in a water bath for constant
temperature maintenance. The anaerobic hydrolysis of
primary sludge was studied at three different temperatures:
13.5, 18.5 and 30°C. The total disintegration and
hydrolysis rate for each temperature was calculated
according to eq. (3). The average values for disintegration
and hydrolysis first order parameters equal to 0.023, 0.034,
0.074 d−1 estimated at various temperatures are shown in
Table 2.

The temperature dependency of the solubilisation of
particulate matter was evaluated using Arrhenius
relationship (Figures 3) as follows:

\[
k_{\text{sol}}(T) = A \times \exp \left[-\frac{E_a}{R \times T}\right]
\]

where \(k_{\text{sol}}(T)\) is the solubilization rate (d−1), \(A\) is a
frequency factor (d−1), \(E_a\) is the activation energy of the
process (J mol−1), \(R\) is the ideal gas constant (8.314 J mol−1
K−1) and \(T\) is the temperature (K). In Figure 3, primary
sludge hydrolysis data from a previous study (Efstathiou
et al, 2003) are also presented that are in very good
agreement with the present study. Both studies show that
from the slope of the straight line the activation energy was
calculated equal to 52.96 KJ mol−1 for the solubilization
rate. These values are very close to the ones reported by
Veeken and Hamelers (1999) for the hydrolysis of organic
waste (64 KJ mol−1). The temperature dependence
coefficient \(0\) for disintegration and hydrolysis was 0.073,
which is higher than the value of 0.054 proposed by
Ferreiro et al., (2003) for primary sludge hydrolysis.

Effect of sludge recycle: Sludge recycling in primary
sludge acid digesters may be employed in a WWTP if
the acid digester is followed by a gravity thickener of primary
sludge. Applying sludge recycling achieves sludge
retention times (SRTs) greater than hydraulic retention
times (HRTs) and enhances acid digestion efficiency by
recycling necessary extracellular enzymes and by
increasing particulate COD concentration in the reactor.

In order to evaluate the effect of sludge recycling, three
lab-scale primary sludge acid digesters operated at a
constant SRT of 4 d, in a pseudo-continuous flow
mechanically stirred-tank mode. Two digesters operated
with sludge recycle and HRTs equal to 1 d and 2 d,
respectively. The third digester operated without recycle
and thus HRT was equal to 4 d. All reactors operated at a
constant temperature between 21 – 23°C and were fed once
da day with primary sludge from Psyttalia Wastewater
Treatment Plant.

The results of the steady state operation of the three acid
digesters are summarized in Table 2. Their efficiency in
terms of soluble COD production is shown in Figure 4.
The data illustrate that sludge recycling significantly
increases the efficiency of primary sludge hydrolysis and
soluble COD production. The efficiency of acid digesters,
in terms of soluble COD production, equals to approximately 9.5 – 10% of the particulate COD in the
influent for the two acid digesters with recycle whereas for
the system without recycle is equal to 6%. The higher
efficiency of the two digesters with recycle is even more
evident if one calculates soluble COD production per m³
of reactor per day. Soluble COD production for digest 1 and
2 with recycle equals to 2.64 kg COD_{sol}/m³-d and 1.26 kg
COD_{sol}/m³-d, respectively whereas for the digester 3
without recycle is limited to 0.42 kg COD_{sol}/m³-d. Similar,
higher efficiencies are obtained for VFA production. It
should be underlined also that no significant difference in
the efficiency between the two digesters with recycle was
observed. Therefore the digester with the lower HRT (HRT
= 1 d) appears the most cost effective solution for primary
sludge hydrolysis for readily biodegradable COD
production.
Table 1: Primary sludge acid digesters operating with no recycle at various HRTs and effluent values (average values ±standard deviation).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent HRT = 2 d</th>
<th>Effluent HRT = 4 d</th>
<th>Effluent HRT = 5 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.35±0.21</td>
<td>6.2±0.2</td>
<td>5.9±0.2</td>
<td>7.87±0.3</td>
</tr>
<tr>
<td>T (°C)</td>
<td>18.7±2.2</td>
<td>21±1.7</td>
<td>21.2±1.5</td>
<td></td>
</tr>
<tr>
<td>TS (g L⁻¹)</td>
<td>21.5±9.8</td>
<td>17.6±8.8</td>
<td>17.6±6.6</td>
<td>25.0±4.7</td>
</tr>
<tr>
<td>VS (g L⁻¹)</td>
<td>15.1±7.0</td>
<td>12.9±6.5</td>
<td>12.8±4.9</td>
<td>16.4±5.6</td>
</tr>
<tr>
<td>COD total (g L⁻¹)</td>
<td>29.0±14.7</td>
<td>23.5±0.07</td>
<td>28.0±10.3</td>
<td>34.0±7.7</td>
</tr>
<tr>
<td>COD sol (g L⁻¹)</td>
<td>1.61±0.81</td>
<td>2.40±1.20</td>
<td>3.5±1.0</td>
<td>4.4±0.7</td>
</tr>
<tr>
<td>NH₄-N (mg L⁻¹)</td>
<td>111±30</td>
<td>201±114</td>
<td>233±50</td>
<td>298±57</td>
</tr>
<tr>
<td>Redox (mV)</td>
<td>-198±18</td>
<td>-206±26</td>
<td>-171±26</td>
<td></td>
</tr>
<tr>
<td>VFA (mg COD L⁻¹)</td>
<td>1114±576</td>
<td>1854±926</td>
<td>2694±816</td>
<td>3880±616</td>
</tr>
<tr>
<td>Sol COD production (mg CODsol/ g VS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>72.5</td>
<td>116</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>Sol COD production (%) (CODsol/ COD partic&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>5.0</td>
<td>6.0</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>VFA production (mg COD&lt;sub&gt;VFA&lt;/sub&gt;/ g VS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>56</td>
<td>94.7</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>NH₄-N production (mg NH₄-N increase/ gVS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>7.1</td>
<td>9.0</td>
<td>9.3</td>
<td></td>
</tr>
</tbody>
</table>

1. influent data are average values that cover all the period of the experiments of all three digesters

Table 2: Primary sludge acid digesters operating at constant SRT equal to 4 d with and without recycle - influent and effluent values (average values ±standard deviation).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Digester 1 with recycle</th>
<th>Digester 2 with recycle</th>
<th>Digester 3 without recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT (d)</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>pH</td>
<td>5.96±0.31</td>
<td>6.14±0.25</td>
<td>5.9±0.2</td>
</tr>
<tr>
<td>T (°C)</td>
<td>23±1.5</td>
<td>21±2.5</td>
<td>21±1.7</td>
</tr>
<tr>
<td>Influent TS (g L⁻¹)</td>
<td>21.4±8.4</td>
<td>20.0±13.3</td>
<td>20.9±10.6</td>
</tr>
<tr>
<td>Influent VS (g L⁻¹)</td>
<td>15.3±6.1</td>
<td>14.7±9.3</td>
<td>14.6±7.7</td>
</tr>
<tr>
<td>Influent COD total (g L⁻¹)</td>
<td>26.5±12.2</td>
<td>28.1±16.3</td>
<td>29.8±16.3</td>
</tr>
<tr>
<td>Influent COD sol (g L⁻¹)</td>
<td>1.55±0.64</td>
<td>1.37±1.0</td>
<td>1.63±1.0</td>
</tr>
<tr>
<td>Reactor TS (g L⁻¹)</td>
<td>37.0±6.8</td>
<td>20.0±13.3</td>
<td>17.1±6.6</td>
</tr>
<tr>
<td>Reactor VS (g L⁻¹)</td>
<td>25.8±5.3</td>
<td>14.7±9.3</td>
<td>12.8±4.9</td>
</tr>
<tr>
<td>Reactor COD total (g L⁻¹)</td>
<td>50.2±11.3</td>
<td>37.0±11.3</td>
<td>28.0±10.3</td>
</tr>
<tr>
<td>Reactor COD sol (g L⁻¹)</td>
<td>4.20±1.24</td>
<td>3.91±1.22</td>
<td>3.3±1.0</td>
</tr>
<tr>
<td>Effluent NH₄-N (mg L⁻¹)</td>
<td>235±50</td>
<td>202±42</td>
<td>233±50</td>
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</tr>
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<td>Sol COD production (mg CODsol/ g VS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>173</td>
<td>170</td>
<td>116</td>
</tr>
<tr>
<td>Sol COD production (%) (CODsol/ COD partic&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>10.0</td>
<td>9.5</td>
<td>6.0</td>
</tr>
<tr>
<td>VFA production (mg COD&lt;sub&gt;VFA&lt;/sub&gt;/ g VS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>125</td>
<td>111</td>
<td>94.7</td>
</tr>
<tr>
<td>NH₄-N production (mg NH₄-N increase/ gVS&lt;sub&gt;int&lt;/sub&gt;)</td>
<td>7.2</td>
<td>7.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Figure 1: Effect of HRT on soluble COD production

Figure 2: Effect of HRT on VFAs production and distribution

Figure 3: Effect of temperature on solubilization rate: Arrhenius plot with corresponding activation energy calculation.

Figure 4: Effect of sludge recycling on primary sludge solubilization in acid digesters.

4. Conclusions

According to the results presented, primary sludge acid digesters without recycle operating within an HRT range between 2 d – 5 d may achieve a soluble COD efficiency that ranges between 5% - 8% of influent particulate COD, at ambient temperatures. The temperature dependency of solubilization rates can be described by an Arrhenius type equation with a temperature dependence coefficient θ equal to 0.073. Primary sludge acid digesters with sludge recycling can achieve much higher efficiencies in terms of readily biodegradable COD and VFAs production even at low HRTs of 1 day. The efficiency of acid digesters with sludge recycle in terms of soluble COD production was found to be approximately 10% of the particulate COD in the influent, at ambient temperatures.

Acknowledgment
This work was partially funded by Joint Venture AKTOR SA – ATHENA SA.

References


