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Published in:
Bioresource Technology

Link to article, DOI:
10.1016/j.biortech.2009.01.037

Publication date:
2009

Document Version
Early version, also known as pre-print

Link back to DTU Orbit

Citation (APA):
Hydrogen and methane production through two-stage mesophilic anaerobic digestion of olive pulp

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Abstract

The present study focused on the anaerobic biohydrogen production from olive pulp and the subsequent anaerobic treatment of the effluent for methane production under mesophilic conditions in a two-stage process. Biohydrogen production from water-diluted (1:4) olive pulp was investigated at Hydraulic Retention times (HRT) of 30 h, 14.5 h and 7.5 h while methane production from the effluent of hydrogenogenic reactor was studied at 20 d, 15 d, 10 d and 5 d HRT. In comparison with previous studies, it has been shown that the thermophilic hydrogen production process was more efficient than the mesophilic one in both hydrogen production rate and yield. The methanogenic reactor was successfully operated at 20, 15 and 10 days HRT while it failed when an HRT of 5 days was applied. Methane productivity reached the maximum value of

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1.13 ± 0.08 L/L/d at 10 days HRT whereas the methane yield increased with the HRT. The Anaerobic Digestion Model no. 1 (ADM1) was applied to the obtained experimental data from the methanogenic reactor to simulate the digester response at all HRT tested. The ability of the model to predict the experimental results was evident even in the case of the process failure, thus implying that the ADM1 could be a valuable tool for process design even in the case of a complex feedstock. In general, the two-stage anaerobic digestion proved to be a stable, reliable and effective process for energy recovery and stabilization treatment of olive pulp.

Keywords: hydrogen, mesophilic, methane, olive pulp, two-stage anaerobic digestion, ADM1, modeling
1. Introduction

One major environmental problem in the Mediterranean countries is the disposal of wastewater derived from olive oil extraction processes. The replacement of three-phase olive mills by their two-phase counterparts is a promising perspective from an environmental point of view, as the amounts of water used during the olive oil processing and thus the generated wastewater are significantly reduced. Two-phase centrifugation of milled olives results in an olive-oil containing phase and a semi-solid residue termed olive pulp (Angerosa et al., 2000; Skiadas et al., 2004). In order to secure economic viability of this option, the generated olive pulp needs to be exploited. Olive pulp is a material rich in carbohydrates and organic content and therefore suitable for biofuels production, such as hydrogen and methane. Olive pulp has been found to be an ideal substrate for mesophilic and thermophilic methane production (Gavala et al., 2005; Kalfas et al., 2006). Bio-hydrogen can also be produced in a two-stage process where hydrogen is produced in the first and methane in the subsequent stage. So far the thermophilic two-stage process (Gavala et al., 2005; Gavala et al., 2006a) as well as the mesophilic fermentative hydrogen production (Koutrouli et al., 2006) from olive pulp have been investigated. Moreover, the effluents of the abovementioned processes have been tested regarding their suitability for soil amendment with very positive results (Francioso et al., 2007).

The idea that hydrogen could replace the carbon-containing fuels came to the forefront due to the human energy dependence on fossil fuels. The pollution caused by fossil energy systems is much greater than that produced by a hydrogen energy system. Hydrogen is characterized by an abundance of applications and uses and its energy yield (122 kJ/g) is 2.75 times greater than that of fossil fuels. Biological hydrogen production processes are found to be more environmentally friendly and less energy intensive, as compared to thermochemical and electrochemical processes. Anaerobic fermentation of low cost substrates rich in carbohydrates, such as organic wastes/wastewater or agricultural residues, is one promising method to produce hydrogen.
However, fermentative hydrogen production includes the acidogenic biotransformation of organic material into by-products, such as volatile fatty acids (VFA), lactic acid and alcohols and thus results in insignificant reduction of the organic content. A very promising method for the combined energy recovery and removal of organic pollutants from wastes is the sequential anaerobic production of hydrogen and methane (Benemann et al., 2004; Ting et al., 2004; Gavala et al., 2005; Ueno et al., 2007). The basic idea is the two-stage anaerobic digestion where hydrogen and methane production can take place in two separate bioreactors in series. The two-stage anaerobic treatment process has several advantages over the conventional single-stage process, since it permits the selection and the enrichment of different bacteria in each anaerobic digester and increases the stability of the whole process by controlling the acidification phase in the first digester and hence preventing the overloading and/or the inhibition of the methanogenic population in the second digester.

The present study was focused on the anaerobic biohydrogen production from olive pulp and the subsequent anaerobic treatment of the effluent for methane production under mesophilic conditions. Moreover, the Anaerobic Digestion Model no. 1 (ADM1) has been applied to the obtained experimental data from the methanogenic reactor. It has been shown that the two-stage mesophilic anaerobic digestion is a stable, reliable and effective process for energy recovery and stabilization treatment of olive pulp although thermophilic hydrogen production process was more efficient than the mesophilic one in both hydrogen production rate and yield. ADM1 could be a valuable tool for process design even in the case of a complex feedstock, yielding predictions in good agreement with the experimental results and being able to predict the digester failure due to overloading.

2. Material and methods

2.1 Analytical methods
The dissolved (dCOD) and total chemical oxygen demand (TCOD) as well as the total (TSS) and volatile (VSS) suspended solids were determined according to Standard Methods (APHA, 1995). For total and soluble (following centrifugation and filtration of the supernatant) carbohydrates determination, a coloured sugar derivative was produced through the addition of L-tryptophan, sulphuric acid and boric acid, which was subsequently measured colorimetrically at 520 nm (Josefsson, 1983). For the quantification of volatile fatty acids, acidified samples with 20% H₂SO₄ were analysed on a gas chromatograph equipped with a flame ionization detector and a capillary column with helium as carrier gas. The measurement of hydrogen and methane was carried out by gas chromatograph equipped with a thermal conductivity detector and a packed column with nitrogen as carrier gas. The method used for measurement of the produced gas volume was based on the displacement of acidified water.

2.2 Continuous experiments for biohydrogen production

A 0.5 L active volume CSTR-type digester was used for biohydrogen production under mesophilic conditions (35°C). The reactor was inoculated with a hydrogen-producing culture obtained after thermal pretreatment of anaerobic sludge and was fed with water-diluted (1:4) olive pulp. The reactor was operated at mean hydraulic retention times (HRT) of 30, 14.5 and 7.5 h until a steady state was reach at every HRT tested. The mixed liquor of the reactor was stirred periodically for 15 min, two times per hour and intermittent feeding at specific time intervals was applied corresponding to the applied HRT. The reason for using water-diluted (1:4) olive pulp was that continuous feeding of the reactor was not possible because of the high solid content of the raw olive pulp. The solids did not allow the effective operation of lab-scale experimental devices such as peristaltic pumps or stirrers. Simultaneous flow of the effluent occurred during feeding by liquid overflow, in order to maintain a constant reactor volume. Complete characterization of reactor effluent was made each time a steady state was reached.
2.3 Continuous experiments for methane production

A 3 L active volume CSTR-type digester was used for methane mesophilic production (35°C). The methanogenic reactor was inoculated with a pre-adapted anaerobic mixed culture and was fed with the effluent of the above described hydrogenogenic reactor operated at HRT 14.5 h (the effluent was collected and preserved at -20°C until it was used). The digester was operated at mean hydraulic retention times (HRT) of 20, 15, 10 and 5 d, until a steady state was reached at every HRT tested. The operational mode of the methanogenic reactor (stirring frequency, intermittent feeding, effluent discharge) was tuned similarly as in the hydrogenogenic reactor. Complete characterization of reactor effluent was made each time a steady state was reached.

2.4 Modelling of the methanogenic step

The IWA anaerobic digestion model – ADM1 (Batstone et al., 2002) was fitted to the experimental data of the volatile fatty acid concentration obtained while the methanogenic bioreactor was operated at an HRT of 20 d. In order to obtain the appropriate kinetic data for parameter estimation, impulse disturbances were imposed to the bioreactor: each time, acetate, propionate and butyrate were spiked into the bioreactor and their concentration was monitored as it decreased to reach the original steady state value. The methodology for the parameter estimation followed is described elsewhere (Kalfas et al., 2006). Kalfas et al (2006) extended and applied the ADM1 in the case of mesophilic and thermophilic anaerobic digestion of olive pulp at a single step process. In the case studied here, the characteristics of the feed of the methanogenic bioreactor were taken into account and were broken down to its individual components as described in Kalfas et al (2006): the concentrations of the carbohydrates, proteins, lipids and inerts in the particulate phase (in gCOD/L) were 6.94, 6.31, 32.82 and 15.93 respectively, while the concentrations of the sugars, aminoacids, long chain fatty acids, inerts, acetate, propionate and butyrate in the dissolved phase (in gCOD/L) were 1.45, 0, 3.88, 6.21, 1.08, 1.13 and 2.36 respectively. The maximum uptake rate ($k_m$) and the half-saturation coefficient ($K_S$) values for all volatile fatty acid uptake processes were estimated.
simultaneously using non-linear parameter estimation. The values of the other model parameters were kept as suggested in the scientific and technical report of ADM1 (Batstone *et al.*, 2002), except of $k_m$ and $K_S$ for acetate, propionate and butyrate (estimated here) and the hydrolysis rate constants for carbohydrate, protein and lipid hydrolysis (Kalfas *et al.*, 2006).

The ADM1 was also used to predict the bioreactor response under conditions of decreased hydraulic retention time; that is, at the HRTs of 15, 10 and finally 5 d.

3. Results and discussion

3.1. Characterization of substrates

The detailed characteristics of the olive pulp and the water-diluted (1:4), olive stones-free olive pulp can be found in the study of Koutrouli *et al.*, 2006. The characteristics of the homogenised effluent from the hydrogenogenic reactor operated at HRT 14.5 h are shown in Table 1. Urea (4.2 g/L) and $K_2HPO_4$ (2 g/L) was added to the influent of the methanogenic reactor (effluent from the hydrogenogenic reactor from HRT=14.5 h) to make-up for N and P deficiency, respectively.

3.2. Continuous experiments for biohydrogen production

The characteristics of the hydrogenogenic reactor regarding hydrogen production rate and yield at HRT of 30, 14.5 and 7.5 h under steady state operation is shown in Table 2. More detailed characteristics of the various steady states can be found in the study of Koutrouli *et al.*, 2006. Also, data from a thermophilic hydrogenogenic reactor fed with olive pulp (Gavala *et al.*, 2005) are presented in the same table for comparison purposes.

One can observe that the efficiency of carbohydrates consumption in the mesophilic reactor diminished with the HRT. The hydrogen production rate increased with the HRT while the hydrogen yield decreased with the HRT. The efficiency of COD removal was quite low (4-10%) as it was anticipated for a fermentative process with no methane production. Comparison with the
thermophilic hydrogen production process showed that the latter was more efficient in both hydrogen production rate and yield. This observation is in agreement with the study of Gavala et al. (2006b), where an increased hydrogen yield from a glucose-based synthetic medium was observed under thermophilic conditions compared to that obtained under mesophilic temperature. The increased efficiency of hydrogen production under thermophilic conditions has been attributed mainly to the better performance of the hydrogenases due to their lower affinity for hydrogen at higher temperatures (Claassen et al., 1999).
3.3. Continuous experiments for methane production

The characteristics of the methanogenic reactor at HRT of 20, 15, 10 and 5 d, under steady state operation, are shown in Table 3. The percentage of dissolved COD removal was approximately 53%, 45% and 45% during operation of digester at HRT=20 d and HRT=15 d, 10 d respectively. The concentration of volatile fatty acids increased as organic load increased during HRT reduction. The reactor performance was unstable at HRT=5 h and resulted in an increase in volatile fatty acids concentration, decrease in methane and biogas productivity and pH value. Therefore, based on biogas and methane productivity (1.69 ± 0.07 L/L/d and 1.13 ± 0.08 L/L/d, respectively) the optimal HRT seems to be at 10 d. However, in terms of methane yield expressed in L/kg COD added, the optimal HRT seems to be at 20 d (0.16 L methane/kg COD added). If all organic matter fed is anaerobically biodegradable and assumed to be converted to methane, then 0.35 L methane per kg COD added are expected to be produced. In this way, the experimentally determined yield compared with the maximum (0.35), indicates the biodegradable portion of the COD introduced in the bioreactor. In comparison with the one stage mesophilic anaerobic digestion of olive pulp, the observed yield is similar with the one calculate by Kalfas 2007 (0.17 L/kg COD added), but lower than the one calculated based on the results of Borja et al (2002) who studied the anaerobic digestion of olive pulp under a wide range of conditions. In the case where Borja et al (2002) applied a dilution of 1:2.5, resulting in a COD concentration of 81.1 g/l at HRTs of 25, 16.6, 12.5, 10 d, they reported a specific methane production of 0.845, 1.230, 1.545 and 1.375 L/L/d respectively. The calculated yields based on these results are 0.26, 0.25, 0.24 and 0.17 L/kg COD added respectively. The yield decreased towards decreasing the HRT in the study of Borja et al, as observed in the present study as well. The higher yields in Borja et al (2002) could be attributed to the fact that the olive pulp contained more dissolved COD (37.5 g/L) than the olive pulp used in the present study (16.9 g/L), as well as, that the anaerobic bioreactor Borja et al (2002) used, allowed for biomass retention (and, therefore, accumulation).
On the other hand, the application of ADM1, which considers the COD and carbon balances of all components involved in the process, makes the evaluation of the process performance more reliable. As long as the feed characteristics and the operating conditions have been fully determined, the ADM1 can be used to simulate the process. Previously, the ADM1 had been applied for the anaerobic digestion of olive pulp under mesophilic and thermophilic conditions by Kalfas et al (2006) who assumed that the solids retention time in the bioreactors was equal to the hydraulic retention time. This was not the case here, since it was found out that the concentration of the solids inside the reactor was slightly higher than in the effluent. The solids retention time was calculated (Table 3) by dividing the solids concentration inside the bioreactor with the solids removal rate through the effluent and it was taken into account in the model.

The values of the kinetic parameters involved in the uptake rates of the volatile fatty acids, estimated after the model fitting, are listed in Table 4. They are also compared with the ADM parameter values estimated by Kalfas et al (2006) who modelled the anaerobic digestion of olive pulp, as well as with the parameter values suggested in the scientific and technical report of ADM1 by Batstone et al. (2002) who applied the model in the case of the anaerobic digestion of sludge. It is obvious that the parameter values estimated here are close to the one used in Batstone et al. (2002) except from the ones involved in the propionate uptake where the maximum specific uptake rate and the saturation constants are one order of magnitude lower. Since propionic acid degraders comprise a sensitive group of acetogenic bacteria, it seems that a component of the olive pulp has inhibited this group of bacteria. The values estimated for all volatile fatty acids were similar with those reported in Kalfas et al (2006), verifying the model validity for feeding media based on olive pulp (raw olive pulp in the case of Kalfas et al, 2006 and acidified olive pulp in the present study).

The quality of fitness can be evaluated in Figure 1 where the volatile fatty acid concentration is shown during the kinetic experiments performed in the bioreactor. It is worthy to mention that the residuals calculated as the difference between the experimental and model values followed a normal
distribution indicating that they are only related with the experimental measurements and not with false model structure or false experiment design.

The ADM1 was then used to predict the performance of the methanogenic bioreactor under different operating conditions, without any other modification or parameter estimation. The ADM1 simulation of the methane production against the respective experimental data is shown in figure 2. It is obvious that the model was able to satisfactorily predict the experimental data over a wide range of operating conditions both at steady state and dynamic transitions. Additionally, ADM1 was able to predict the failure of the process at the HRT of 5 d. These results demonstrate that in cases of very complex wastes such as the acidified olive pulp, ADM1 can be used as a valuable tool for adequate process simulation and design.
4. Conclusions

The present study focused on the anaerobic biohydrogen production from olive pulp and the subsequent anaerobic treatment of the effluent for methane production under mesophilic conditions. In comparison with previous studies, it has been shown that the thermophilic hydrogen production process was more efficient than the mesophilic one in both hydrogen production rate and yield. The methanogenic reactor was successfully operated at 20, 15 and 10 days HRT while it failed when an HRT of 5 days was applied. Methane productivity reached the maximum value of $1.13 \pm 0.08$ L/L/d at 10 days HRT whereas the methane yield increased with the HRT as it was anticipated. The application of the Anaerobic Digestion Model no. 1 to the obtained experimental data from the methanogenic reactor at all HRT tested was successful, since the model was able to predict the bioreactor response even in the case of the process failure. Therefore, the ADM1 could be a valuable tool for process design even in the case of a complex feedstock. In general, the two-stage anaerobic digestion proved to be a stable, reliable and effective process for energy recovery and stabilization treatment of olive pulp.

Acknowledgement

The authors wish to thank the Commission of the European Communities for the financial support of this work under Grant No QLK5-CT-2002-02344 (Acronym: BIOTROLL).

References


Skiadas, I.V., Gavala, H.N., Lyberatos, G., Pistikopoulos, E., Ciavatta, C. And Ahring, B.K., 2004. Integrated biological treatment and agricultural reuse of olive mill effluents with the concurrent recovery of energy sources (BIOTROLL). (In Proceedings of the 10th World Congress of Anaerobic Digestion, Montreal, Canada, 29 August-2 September)


Table 1. Characteristics of the homogenised effluent from the hydrogenogenic reactor operated at 14.5 h HRT

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.37 ± 0.03</td>
</tr>
<tr>
<td>TSS (g/L)</td>
<td>39.4 ± 2.7</td>
</tr>
<tr>
<td>VSS (g/L)</td>
<td>38.0 ± 2.4</td>
</tr>
<tr>
<td>Total COD (g/L)</td>
<td>79 ± 2.5</td>
</tr>
<tr>
<td>Dissolved COD (g/L)</td>
<td>16.9 ± 0.4</td>
</tr>
<tr>
<td>Soluble carbohydrates (g/L)</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>Acetic acid (g/L)</td>
<td>1.01 ± 0.14</td>
</tr>
<tr>
<td>Propionic acid (g/L)</td>
<td>0.75 ± 0.05</td>
</tr>
<tr>
<td>Butyric acid (g/L)</td>
<td>1.30 ± 0.09</td>
</tr>
<tr>
<td>Valeric acid (g/L)</td>
<td>0.032 ± 0.002</td>
</tr>
</tbody>
</table>
Table 2. Characteristics of the hydrogenogenic reactor under steady state operation

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Mesophilic (35°C)</th>
<th>Thermophilic (55°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT (h)</td>
<td>30</td>
<td>14.5</td>
</tr>
<tr>
<td>Flow rate (mL/d)</td>
<td>383</td>
<td>827</td>
</tr>
<tr>
<td>Loading rate (g TS/d)</td>
<td>21.5</td>
<td>46.3</td>
</tr>
</tbody>
</table>

**Characteristics at steady state**

<table>
<thead>
<tr>
<th></th>
<th>Mesophilic (35°C)</th>
<th>Thermophilic (55°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5 ± 0.1</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>Efficiency of COD removal (%)</td>
<td>9.1 ± 0.9</td>
<td>10.2 ± 1.1</td>
</tr>
<tr>
<td>Efficiency of soluble carbohydrates consumption (%)</td>
<td>90.1 ± 1.1</td>
<td>65.2 ± 1.8</td>
</tr>
<tr>
<td>Biogas production rate (mL/d)</td>
<td>490 ± 54</td>
<td>737 ± 82</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>26.4 ± 1.7</td>
<td>26.7 ± 1.4</td>
</tr>
<tr>
<td>Hydrogen production rate (mL/d)</td>
<td>130 ± 0.4</td>
<td>196 ± 24</td>
</tr>
<tr>
<td>Hydrogen yield (mole/kg TS olive pulp)</td>
<td>0.19</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*NC* Not calculated
Table 3. Characteristics of the methanogenic reactor under steady state operation

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>HRT (d)</th>
<th>SRT (d)</th>
<th>Flow rate (mL/d)</th>
<th>Organic loading rate (g totalCOD/L/d)</th>
<th>Organic loading rate (g dissolvedCOD/L/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>17</td>
<td>300</td>
<td>5.26</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11</td>
<td>600</td>
<td>7.9</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.5</td>
<td></td>
<td>15.8</td>
<td>3.40</td>
</tr>
</tbody>
</table>

**Characteristics at steady state**

<table>
<thead>
<tr>
<th></th>
<th>Biogas productivity (L/L/d)</th>
<th>Methane (%)</th>
<th>Methane productivity (L/L/d)</th>
<th>Methane yield (L/kg COD added)</th>
<th>Volatile fatty acids (mg/L)</th>
<th>pH</th>
<th>Dissolved COD (g/L)</th>
<th>TSS (g/L)</th>
<th>VSS (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.96 ± 0.05</td>
<td>66 ± 2</td>
<td>0.64 ± 0.05</td>
<td>0.16</td>
<td>488 ± 83</td>
<td>7.62 ± 0.05</td>
<td>8.0 ± 0.6</td>
<td>43.8 ± 1.5</td>
<td>39.9 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>1.22 ± 0.04</td>
<td>65 ± 2</td>
<td>0.79 ± 0.05</td>
<td>0.15</td>
<td>925 ± 75</td>
<td>7.59 ± 0.02</td>
<td>9.3 ± 0.3</td>
<td>43.4 ± 0.7</td>
<td>38.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1.69 ± 0.07</td>
<td>67 ± 2</td>
<td>1.13 ± 0.08</td>
<td>0.14</td>
<td>1992 ± 91</td>
<td>7.51 ± 0.02</td>
<td>9.4 ± 0.5</td>
<td>42.8 ± 1.4</td>
<td>38.5 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>0.82*</td>
<td>25*</td>
<td>0.21*</td>
<td>-</td>
<td>8713*</td>
<td>6.58*</td>
<td>19.8*</td>
<td>58.5*</td>
<td>51.7*</td>
</tr>
</tbody>
</table>

* The values of the parameters recorded in this operating condition do not correspond to steady state operation, since the bioreactor was in transition to the washout steady state.
Table 4. Parameter values of the ADM1 as estimated here and as suggested in Batstone et al. (2002)

<table>
<thead>
<tr>
<th></th>
<th>Acetic acid</th>
<th>Propionic acid</th>
<th>Butyric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td></td>
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</tr>
<tr>
<td>$k_m^{(1)}$</td>
<td>8.34 ± 1.02</td>
<td>2.02 ± 0.07</td>
<td>15.55 ± 2.59</td>
</tr>
<tr>
<td>$K_s^{(2)}$</td>
<td>0.96 ± 0.21</td>
<td>0.03 ± 0.01</td>
<td>0.20 ± 0.09</td>
</tr>
<tr>
<td>Kalfas et al.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2006)</td>
<td>9.99±1.2</td>
<td>3.50±0.32</td>
<td>20.61±3.90</td>
</tr>
<tr>
<td>$k_m^{(1)}$</td>
<td>0.31±0.09</td>
<td>0.06±0.03</td>
<td>0.12±0.14</td>
</tr>
<tr>
<td>$K_s^{(2)}$</td>
<td>3.50±0.32</td>
<td>20.61±3.90</td>
<td></td>
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<tr>
<td>Batstone et al. (2002)</td>
<td>8</td>
<td>0.15</td>
<td>0.1</td>
</tr>
</tbody>
</table>

$^{(1)}$Units: (gCOD/gCOD/d)

$^{(2)}$Units: (gCOD/L)

± error calculated at 95% confidence level
Figure 1. Volatile fatty acid concentration during the impulse disturbances of a methanogenic bioreactor treating the acidified olive pulp
Figure 2. Methane production rate during the anaerobic digestion of the acidified olive pulp