BIOCHEMICAL METHANE POTENTIAL TESTS OF DIFFERENT AUTOCLAVED AND MICROWAVED LIGNOCELLULOSIC ORGANIC FRACTIONS OF MUNICIPAL SOLID WASTE

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Introduction

The Organic Fraction of Municipal Solid Wastes (OFMSW) contains a high content of lignocellulosic fiber that is not readily digestible. Plant fiber of yard waste typically comprises around 30% hemicellulose, 45% cellulose, and 25% lignin on a dry weight basis (Bobleter, 1994). The encasing of cellulose and hemicellulose in lignin may considerably restrict anaerobic digestion (AD).

Pretreatments of OFMSW can be used to solubilize organic matter prior to AD in order to improve the overall AD process in terms of faster rates and degree of OFMSW degradation, thus increasing methane production.

The aim of this research was to enhance the anaerobic biodegradability of two synthetic OFMSW with different lignocellulosic content (M1 and M2) by assessing microwaving (MW) and autoclaving (A).
Introduction

Literature review on Microwave (MW) and Autoclave (A) pre-treatments

**MW:**
- Electromagnetic radiation operating at **2450 MHz** frequency (Beszédes et al., 2008, Appels et al., 2013);
- **Power** = ranging between 440-500 W (Elagroudy and El Gohary, 2013, Rani et al., 2013) – 1250 W (Coelho et al., 2011);
- **Temperature** = 30°C (Kuglarz et al., 2013) – 175°C (Marin et al., 2010);
- **Time** = 1-10 min. (Rani et al., 2013) - 40 min. (Marin et al., 2010, Shariari et al., 2012).

**A:**
- Hydrothermal treatment, water is used as reagent at increased temperature and pressure (Tampio et al., 2014);
- **Pressure** = 1 bar (Heerah et al., 2008) – 28.7 bars (Wilson and Novak, 2009);
- **Temperature** = 95°C (Heerah et al. 2008) – 220°C (Wilson and Novak, 2009);
- **Time** = 15-30 min. (Marchesi et al., 2013) – 2 hours (Wilson and Novak, 2009);
Materials and methods

Substrates

M1 and M2 OFMSW were characterized by different contents of fir sawdust, grass, carrot, cabbage, spinach, cooked meat, raw meat and cooked pasta.

To reduce the particle size to 3 mm diameter each fraction was placed in a food processor and sift with a strainer. Tap water was added to M1 and M2 leading to 2 mashes to guarantee a total solids content suitable for a digester technology (wet technology).

Each fraction had a known proteins, carbohydrates, lipids and fibers content. The mean proteins, carbohydrates, lipids and fibers content expressed in % for M1 and M2 is here presented.
Materials and methods

Microwave (MW) and Autoclave (A) pre-treatments

**MW:**
- Commercial domestic microwave oven (2450 MHz frequency, 850 W);
- Temperature = 96 °C;
- Sample = 500 g;
- Time = 4 minutes.

**A:**
- Conventional pressure cooker heated by a hot plate operating at 400 W;
- Temperature/pressure = 134°C and 2 bars;
- Sample = 1700 g;
- Time = 15 minutes to lead the mixtures from atmospheric to operating conditions followed by 30 minutes of heating at constant conditions.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M1_MW</th>
<th>M1_A</th>
<th>M2</th>
<th>M2_MW</th>
<th>M2_A</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS [%]</td>
<td>9.2 ± 0.1</td>
<td>9.1 ± 0.1</td>
<td>11.1 ± 0.0</td>
<td>10.0 ± 0.1</td>
<td>8.6 ± 0.4</td>
<td>11.9 ± 0.1</td>
</tr>
<tr>
<td>TVS [%]</td>
<td>96.5 ± 0.1</td>
<td>96.6 ± 0.1</td>
<td>96.9 ± 0.1</td>
<td>97.8 ± 0.1</td>
<td>97.6 ± 0.0</td>
<td>97.8 ± 0.1</td>
</tr>
<tr>
<td>pH</td>
<td>3.8 ± 0.1</td>
<td>3.5 ± 0.0</td>
<td>3.5 ± 0.0</td>
<td>4.2 ± 0.2</td>
<td>3.7 ± 0.2</td>
<td>3.5 ± 0.1</td>
</tr>
</tbody>
</table>
**Materials and methods**

**Solubilisation**

The solubilisation effect of the pre-treatments was calculated based on:

- soluble COD (sCOD);
- soluble Carbohydrates (sCarb);
- soluble Protein (sProt).

Analyzed **before** and **after pre-treatments**. The soluble part of each substrate was determined after centrifugation at 12000g for 30 min and subsequent filtration 0.45 μm microfiber filter paper (Marin et al., 2010, Rani et al., 2013).

The increase in the soluble fraction was calculated as given in the following equation (Rani et al., 2013) where $X$ represents soluble COD, soluble proteins and soluble carbohydrates alternately.

$$
\Delta X(\%) = \frac{(X_{\text{after pretreatment}} - X_{\text{before pretreatment}})}{X_{\text{before pretreatment}}} \times 100
$$

Methods: REG CE 152/2009 27/01/2009 ALL III MET C for proteins; MP 0431 rev 1 2003 for carbohydrates; APAT CNR IRSA 5130 Man 29 2003 for COD
Materials and methods

Specific energy, energy demand and profit of the pretreatment

The specific energy demand ($E_D$) was calculated taking into account the power ($P_D$) of the microwave/autoclave heating system as well as the exposure time ($t_D$) applied for each treatment. In order to be brief, calculations were made excluding heating losses. Specific energy (kJ/kgTVS) was calculated on the mass of treated mash ($M_{TVS}$):

$$E_D = \frac{P_D \cdot t_D}{M_{TVS}}$$

According with Kuglarz et al., (2013) specific energy profit on the pre-treatment $E_T$ (kJ/kgTVS) was calculated taking into account:

- Energy produced in the form of biogas $E_B$ after subtracting the energy generated by raw mashes;
  $$E_B = (BMP_{21 Pr.} - BMP_{21 raw}) \cdot 37 \text{kJ/dm}^3$$
- Energy produced in the form of heat $E_Q$;
- Energy demand of the pre-treatment $E_D$.

$$E_T = E_B + E_Q - E_D$$
Materials and methods

BMP$_{21}$ assays and $k_h$

- Bottles incubated in water bath at mesophilic conditions (37°C)
- Duration: 21 days
- Analysis according to the methodology of Ponsà et al (2008) and Angelidaki et al. (2009)
- Hydrolysis rate calculation $k_h$ (d$^{-1}$) according to Angelidaki et al. (2009):

$$\ln \frac{B_\infty - B}{B_\infty} = -k_h t$$

$B_\infty$ = approximated by BMP$_{21}$

$B$ = methane produced at a given time $t$
Results and discussion

Substrate solubilisation by MW and A treatments

MW and A treatments led to the solubilisation of the organic material of both the OFMSW samples:

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M1_MW</th>
<th>M1_A</th>
<th>M2</th>
<th>M2_MW</th>
<th>M2_A</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCOD [mg/l O_2]</td>
<td>19700 ± 4400</td>
<td>63000 ± 14000</td>
<td>25500 ± 5600</td>
<td>17200 ± 3800</td>
<td>41700 ± 9200</td>
<td>32200 ± 7100</td>
</tr>
<tr>
<td>ΔsCOD [%]</td>
<td>-</td>
<td>219.8</td>
<td>29.4</td>
<td>-</td>
<td>142.4</td>
<td>87.2</td>
</tr>
<tr>
<td>sCarb [g/100g]</td>
<td>1.17 ± 0.11</td>
<td>1.28 ± 0.12</td>
<td>1.52 ± 0.15</td>
<td>0.62 ± 0.12</td>
<td>0.73 ± 0.14</td>
<td>0.84 ± 0.16</td>
</tr>
<tr>
<td>ΔsCarb [%]</td>
<td>-</td>
<td>9.4</td>
<td>29.9</td>
<td>-</td>
<td>17.7</td>
<td>35.5</td>
</tr>
<tr>
<td>sProt [g/100g]</td>
<td>0.47 ± 0.07</td>
<td>0.46 ± 0.07</td>
<td>0.61 ± 0.08</td>
<td>0.35 ± 0.07</td>
<td>0.36 ± 0.07</td>
<td>0.43 ± 0.07</td>
</tr>
<tr>
<td>ΔsProt [%]</td>
<td>-</td>
<td>-2.1</td>
<td>29.8</td>
<td>-</td>
<td>2.9</td>
<td>22.9</td>
</tr>
</tbody>
</table>

- sCOD, sCarb and sProt were found higher for M1 substrates than M2 substrates. This feature is concurring with the OFMSWs initial composition which shows a higher content of proteins, carbohydrates and lipids for M1 OFMSW.
- An increase of sCOD was found for both treatments and both OFMSW tested samples. This trend was found particularly relevant for the MW treatment with an increase of about 219.8% for M1_MW and 142.4% for M2_MW.
- The solubilisation effect on carbohydrate and protein was mainly relevant for A treatment.
Results and discussion

BMP$_{21}$ assays and $k_h$

- Higher methane production and methane content for M1 substrates compared to M2 which is attributable to the samples composition. In agreement with Eskicioglu et al., 2007, Sólyom et al., 2011, Kuglarz et al., 2013 for MW and Marchesi et al., 2013 for A
- MW treatment led to a BMP$_{21}$ increase of 8.5% for both the tested OFMSW
- A treatment had an increase of about 1.0% for M1 and 4.4% for M2
- The increase in methane production together with the increase in sCOD is concurring with Beszédes et al., (2008) and Elagroudy and El-Gohary, (2013).
Results and discussion

**BMP\textsubscript{21} assays and \( k_h \)**

Results on the first order hydrolysis underlines what previously reported.

- \( k_h \) was found higher for M1 samples than M2 ones
- \( k_{hM1\_MW} \) was registered superior than \( k_{hM1\_A} \)
- \( k_{hM2\_A} \) was determined slightly superior than \( k_{hM2\_MW} \)
- These results underline the efficiency on the hydrolysis phase of MW on a meager lignocellulosic substrate and A on a rich lignocellulosic substrate.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M1_MW</th>
<th>M1_A</th>
<th>M2</th>
<th>M2_MW</th>
<th>M2_A</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_4 ) [%]</td>
<td>61.6 ± 0.2</td>
<td>59.9 ± 0.8</td>
<td>60.0 ± 0.9</td>
<td>58.1 ± 0.7</td>
<td>57.2 ± 0.1</td>
<td>56.2 ± 0.5</td>
<td>51.8 ± 0.3</td>
</tr>
<tr>
<td>( k_h ) [d\textsuperscript{-1}]</td>
<td>0.229</td>
<td>0.233</td>
<td>&gt; 0.226</td>
<td>&gt; 0.212</td>
<td>0.202</td>
<td>&lt; 0.204</td>
<td>-</td>
</tr>
<tr>
<td>GB\textsubscript{21} [NICH\textsubscript{4}/gTS]</td>
<td>193.9 ± 16.6</td>
<td>216.1 ± 7.7</td>
<td>208.1 ± 14.3</td>
<td>147.7 ± 8.1</td>
<td>159.2 ± 0.7</td>
<td>158.2 ± 7.8</td>
<td>197.9 ± 12.7</td>
</tr>
<tr>
<td>GB\textsubscript{21} [NICH\textsubscript{4}/gTVS]</td>
<td>267.1 ± 20.4</td>
<td>306.4 ± 13.6</td>
<td>285.1 ± 28.2</td>
<td>196.9 ± 10.8</td>
<td>216.6 ± 0.9</td>
<td>212.7 ± 7.7</td>
<td>294.7 ± 16.2</td>
</tr>
<tr>
<td>BMP\textsubscript{21} [NICH\textsubscript{4}/gTS]</td>
<td>125.0 ± 8.2</td>
<td>136.9 ± 8.4</td>
<td>126.9 ± 8.4</td>
<td>90.0 ± 3.5</td>
<td>96.1 ± 0.7</td>
<td>93.2 ± 4.4</td>
<td>103.4 ± 6.1</td>
</tr>
<tr>
<td>BMP\textsubscript{21} [NICH\textsubscript{4}/gTVS]</td>
<td>172.1 ± 9.8</td>
<td>186.7 ± 6.5</td>
<td>173.8 ± 16.6</td>
<td>119.9 ± 4.7</td>
<td>130.2 ± 0.7</td>
<td>125.2 ± 4.2</td>
<td>154.2 ± 8.0</td>
</tr>
<tr>
<td>( \Delta BMP\textsubscript{21} ) [%]</td>
<td>-</td>
<td>8.5</td>
<td>1.0</td>
<td>-</td>
<td>8.5</td>
<td>4.4</td>
<td>-</td>
</tr>
</tbody>
</table>
Results and discussion

Specific energy demand and profit of the pretreatment

Analyzing the specific energy balance, no energy profit were registered for all treatments.

- This was mainly due to the low increase in biogas production compared to raw substrate digestion.
- The amount of energy produced in the form of biogas ($E_B$) and heat ($E_Q$) was not enough to level the treatment energy demand ($E_D$).
- Even if with negative results, MW showed better energetic response than A.
- Previous studies showed relevant increase in total energy (Kuglarz et al., 2013) leading to the conclusion that further investigations with different pre-treatment conditions are necessary to examine the feasibility of such pre-treatments on lignocellulosic OFMSW.

<table>
<thead>
<tr>
<th></th>
<th>$E_B$ [kJ/kgTVS]</th>
<th>$E_Q$ [kJ/kgTVS]</th>
<th>$E_D$ [kJ/kgTVS]</th>
<th>$E_T$ [kJ/kgTVS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1_MW</td>
<td>540.2</td>
<td>2580.6</td>
<td>-1324.3</td>
<td></td>
</tr>
<tr>
<td>M1_A</td>
<td>62.9</td>
<td>4200.0</td>
<td>-2658.5</td>
<td></td>
</tr>
<tr>
<td>M2_MW</td>
<td>410.7</td>
<td>2415.5</td>
<td>-1352.3</td>
<td></td>
</tr>
<tr>
<td>M2_A</td>
<td>225.7</td>
<td>3931.3</td>
<td>-2349.3</td>
<td></td>
</tr>
</tbody>
</table>

Under lab. scale conditions
Conclusions

1. **M1** substrates resulted in a higher GB$_{21}$, BMP$_{21}$, k$_h$, mean methane content and soluble fractions compared to **M2**. This is attributable to the OFMSW composition which is characterized by a low lignocellulosic content than **M2**.

2. **MW** was found to be an efficient treatment for both the tested OFMSW

3. **A** was more efficient for a richer lignocellulosic substrate (**M2**).

4. k$_h$ analysis showed a better impact on the hydrolysis phase for **MW** on a meager lignocellulosic substrate (**M1**) and for **A** on a richer lignocellulosic substrate (**M2**).

5. **No energy profit** was registered for any tested pretreatment due to the low increase on biogas production. Even if with negative results, **MW** showed better energetic response than **A**.

Further investigations with different treatment conditions and lignocellulosic contents are required to better probe the pre-treatment efficiency on the anaerobic digestion of OFMSW.
Thank you for your attention!

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