Downstream processing for Polyhydroxyalkanoates from mixed microbial cultures: Study of microbial activity inhibition, polymer recovery and characterizations

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Polyhydroxyalkanoates (PHA)

**Product related Pro’s**

Family of copolymers with tunable composition

Main constituent of several bioplastics

- Biodegradable commodity film
- Packaging interlayer film
- Specialty durables (such as electronics)
- Slow C-release system for groundwater remediation

(R)-3HB

(R)-3HV

Bio-based feedstock

Bio-PE (PP/PVS), biobased PET

Bio-based feedstock and biodegradability

Biopolymers

Starch, blends, PLA, PHA

Oil-based plastics

PBAT, PBS, PCL

Biodegradability

End of note on product related pro's.
PHA production from MMC and organic waste

Organic fraction of municipal solid waste (OFMSW)

Acidogenic Fermentation

Sludge from wastewater treatment plant

Stage II (SBR): biomass selection/enrichment (ADF)

Stage III: PHA production

VFA

Solid fraction

Liquid fraction

VFA

Activated sludge

MMC

PHA-rich biomass

PHA extraction

Anaerobic Digestion

Energy

Nutrients

PHA processing

Biodegradable bioplastics

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Pilot platform
Wastewater Treatment Plant in Treviso (North-East of Italy)
Aim of the study

Optimization of a stabilization method
✓ Influence of pH ➔ $\text{H}_2\text{SO}_4$; NaOH
✓ Oxidation ➔ NaClO
✓ Excess of substrates
✓ Thermal treatments ➔ oven dried at 70°C (with or without shock at 170°C)

Innovative extraction and recovery methods
✓ Non-chlorinated solvent: ethyl acetate

Characterization of extracted polymer:
✓ GC-FID ➔ purity, recovery yield and monomeric composition
✓ Capillary viscosimetry ➔ molecular weight
✓ DSC ➔ thermal properties
Selection of PHA-producing biomass (SBR)

Operative cycle (12 h)

Feeding = 10 min
Reaction 1 = 140 min
Withdrawal = 3 min
Nitrogen feeding = 5 min

V = 1L

Organic load rate (OLR)
4.25 gCOD/L d

VFA (85% Acetic acid; 15% Propionic acid)

T = 25°C
PHA accumulation step

- Batch reactor V= 0.5L
- 6h test
- Multispike strategy (85% Acetic acid; 15% Propionic acid)

[Graph showing PHA content over time]
Stabilization tests

Two kinds of thermal treatment
Extraction and characterization

5 different batches (Pilot scale Batches 11, 15, 19, 22, 24) and 1 batch (Lab scale) thermally stabilized.

Soxhlet extraction with CHCl₃
Oxidation with NaClO

**Purity (PHA %w/w)**
- 95.3 % (CHCl₃);
- 85.2 % (NaClO);

**Recovery yield (%w/w)**
- 83.2 % (CHCl₃);
- 87.4 % (NaClO)
Non-chlorinated solvent extraction

Batch 11 thermally stabilized

Extraction in a pressurized steel reactor with Ethyl acetate (100 and 125°C) for 1h

Residues extracted with CHCl₃

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Purity (PHA %w/w)</th>
<th>Mv (g/mol)</th>
<th>% HV</th>
<th>χc %</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>92.9 ± 6.1</td>
<td>133947</td>
<td>19</td>
<td>40</td>
<td>164</td>
</tr>
<tr>
<td>Ethyl Acetate 100°C</td>
<td>75.7 ± 1.8</td>
<td>71667</td>
<td>31</td>
<td>28</td>
<td>164</td>
</tr>
<tr>
<td>Ethyl Acetate 125°C</td>
<td>100 ± 4.5</td>
<td>48880</td>
<td>20</td>
<td>36</td>
<td>163</td>
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<tr>
<td>Residue 100°C CHCl₃</td>
<td>99.5 ± 7.9</td>
<td>126250</td>
<td>12</td>
<td>48</td>
<td>167</td>
</tr>
<tr>
<td>Residue 125°C CHCl₃</td>
<td>90.7 ± 1.1</td>
<td>75000</td>
<td>25</td>
<td>31</td>
<td>161</td>
</tr>
</tbody>
</table>
Conclusions and future perspectives

- Thermal treatment applicable at pilot scale
- NaClO gave results comparable to traditional chloroform extraction
- Ethyl acetate selectively extracts shorter chains

Evaluation of the effects of thermal treatment on the polymer, in comparison with an acidification method applied at pilot scale

Optimization of Ethyl acetate extraction and use of other non-chlorinated solvents
Thanks for your attention