



IDUSTRIAL SYMBIOSIS

Grant Agreement No 869318

CS meeting on "Material recovery and safe reuse" June 23, 2021

ROUTES – SMART-Plant – RES URBIS

Polyhydroxyalkanoate (PHA) recovery from sewage sludge and food waste

Mauro Majone

Department of Chemistry

Research Center for the Protection of the Environment and Cultural Heritage



Research and Innovation from 3 EU projects (FP7 and Horizon 2020)



Innovative system solutions for municipal sludge treatment and management (ROUTES),

FP7 Call: ENV.2010.3.1.1-2

GA 265156, 3 years, started May 1° 2011, 18 partners, 9 countries EU Grant: 3 364 600 € Coordinator: Giuseppe Mininni, IRSA-CNR, Italy



Scale-up of low-carbon footprint material recovery techniques

in existing wastewater treatment plants (SMART-Plant) H2020 Call: WATER-1b-2015 - Demonstration/pilot activities (IA) GA 690323, 4 years, started June 1° 2016, 29 partners, 10 countries EU Grant: 7 536 300 € Coordinator: Francesco Fatone, Technical University of Marche, Italy

www.smart-plant.eu



REsources from URban Blo-waSte (RES URBIS)

H2020 Call CIRC-05-2016: Unlocking the potential of urban organic waste (RIA) GA 730349, 3 years, started January 1° 2017, 20 partners, 8 countries. EU Grant: 2 996 688 € Coordinator: Mauro Majone, Sapienza University of Rome, Italy

www.resurbis.eu



3 projects with some common features

Focusing on "waste" streams as a renewable and largely available resource (no land, no water, no energy is needed to produce it)

Mild biotechnologies basen on **open microbial cultures** (no axenic cultures, no OGMs)

Sludge and municipal wastewater The organic fraction of municipal solid waste Park/garden waste Food-industry wastewater

A large portfolio of bioproducts with market value under investigation (e.g. cellulose, biofuels, biofertilizers, biosolvents, biomethane) and one in common: polyhydroxyalkanoate (PHA) and derived bioplastics and biocomposites

As time went on, also taking care of

✓ the whole technology chain

✓ territorial conditions

Different industrial sectors to be linked each other, each one having its own business targets, needs and specifications.

Affordable economic strategies to be tailored with respect to territorial <u>clusters</u>, i.e by taking into account present collection and management systems and where available "feedstock " is large enough

✓ <u>technical and non technical</u> <u>constraints</u> Regulatory (e.g. **"end of waste"**), environmental, and social constraints, as function of local, regional and national conditions

Why focusing on PHA?

Product related Pro's

PHA is not a single polymer but a family of copolymers with tunable composition and properties, so that, PHA can be the main constituent of several bioplastics, with a wide portfolio of applications.

Fully and quickly biodegradale



Production process Pro's

• A novel PHA production process (open microbial cultures instead of pure strains), which can better cope with large heterogeneity of the waste/wastewater feedstock,

- An upstream step, the *acidogenic fermentation*, which is both robust and tunable
- Overall, PHA production process is mostly **biological, under mild conditions and reliable**.
- Thus, an **easier integration with existing biological plants for waste and wastewater treatment**.
- Combining no-cost feedstock and novel processes, the cost of PHA can significantly decrease

Appealing: PHA is 3 times "Bio"	Applications and economics						
 Produced from renewable feestock (<u>but no food</u>) 	High market potential.						
- Produced through biological process (but no OGM)	As higher as more PHA cost decreases; but						
 Easily and "truly" biodegradable 	still higher value than biogas and compost						
and it's not recycled: it's virgin material	Already under investigation at TRL 6						

Comparison of income of PHA production with respect to biogas, as function of PHA value on the market and of biogas incentives

A) PHA
production, biogas
recovery from
downstream with
incentives
B) Biogas only



- PHA value ranging between 500 and 5000 €/ton
- Either 0, 40, or 80 % of residual TVS are recovered into biogas
 Biogas yield 0.75 m³/kgTVS; electric energy 2.56 kWh/m³
- EE value: 60 €/MWh (no incentives) <u>continuous lines</u>
 246/MWh (present italian incentives, worst case) <u>dotted lines</u>

- In most conditions, PHA production offers an additional income with respect to biogas only (alternative b minus alternative a)
- Competition with biogas is negligible if PHA maintain present high cost and if biogas has no incentives
- <u>However, biogas recovery from PHA production</u> <u>residual streams is especially needed if</u> <u>incentives are high</u>

•The additional income should overcompensate the larger costs for PHA production with respect to biogas only (however, still lack of full scale data)

Income only, production costs not included



An old story: PHA is often present in activated sludge



Typical process for PHA production from MMC and organic waste stream

Pilot scale optimisation of PHA production process from urban bio-waste

Although the main steps of MMC process are largely validated at lab-scale, pilot scale experimentation is essential for several reasons

Process-related challenges

- Given the process has many steps, pilot-scale is essential to supply robust technicaleconomic data, especially because cost decrease remains a key target
- Long term experimentation with "true" waste feedstock is needed to address effects of feedstock heterogeneity
- An integrated process is required for optimal management of water/solid overflows and related energy recovery. This is also essential for making appropriate LCA
- The extraction step still requires optimization (as milder conditions as possible)

Product-related challenges

- PHA batches have to be steadily produced and delivered to investigate downstream processing, including by using industrial equipments (i.e in the range 1-100 Kg/batch).
- Same as for development of novel products, including low-purity end-uses; product samples to be checked for performance and acceptance (e.g. consumers panels).
- Contaminant migration and abatement and possible transfer into the products has to be investigated under close-to reality conditions.

Figure 1 | Schematic process flow diagram of municipal wastewater and sludge treatment in conjunction with PHA production under study in the project Routes (MAD = mesophilic anaerobic digestion). Laboratory-scale studies are conducted on BPP, PPP and PRP (La Sapienza University of Rome/AnoxKaldnes), advanced/ primary treatment and sludge fermentation (Italian Water Research Institute IRSA-CNR). Pilot-scale studies are conducted on fermentation, BPP, PPP and PRP (AnoxKaldnes/Veolia) and sludge wet oxidation for producing a VFA-rich liquid stream (3VGreen Eagle). Results from WAS fermentation, BPP, PPP are reported here.

F. Morgan-Sagastume et al. Polyhydroxyalkanoate (PHA) production from sludge and municipal wastewater treatment, Water Science & Technology, 69, 1, 177-184, 2014; <u>https://doi.org/10.2166/wst.2013.643</u>

Morgan-Sagastume, F., Valentino, F., Hjort, M. *et al.* Acclimation Process for Enhancing Polyhydroxyalkanoate Accumulation in Activated-Sludge Biomass. *Waste Biomass Valor* **10**, 1065–1082 (2019). https://doi.org/10.1007/s12649-017-0122-8

Scale-up of low-carbon footprint MAterial Recovery Techniques in existing wastewater treatment PLANTs (SMART-PLANT)

Unique Selling Point of the SMARTechs: high water quality, energy-efficiency, carbon footprint, sludge reduction and...materials recovery and reuse via SMART-Products

Horizon2020 IA

9 demo SMARTechs

SMARTechs integrated in existing WWTPs (revamped/upgraded to WRRFs)

	SMARTech n.	Integrated municipal WWTP	Key enabling process(es)	SMART-product(s)			
instream	1	Geestmerambacht (Netherlands)	Upstream dynamic fine- screen and post-processing of cellulosic sludge	Cellulosic sludge, refined clean cellulose			
	2а) єт V	Karmiel (Israel)	Mainstream polyurethane- based anaerobic biofilter	Biogas, Energy- efficient water reuse			
R	2b	Manresa (Spain)	Mainstream SCEPPHAR	Struvite, PHA			
estream	3	Cranfield (UK)	Mainstream tertiary hybrid ion exchange	Nutrients			
	4a)€TV	Carbonera (Italy)	Sidestream SCENA	P-rich sludge, VFA			
	4b	Psyttalia (Greece)	Sidestream Thermal hydrolysis – SCENA	P-rich sludge			
Sid	5	Carbonera (Italy)	Sidestream SCEPPHAR	PHA, struvite, VFA			

SMARTechs integrated in existing WWTPs (revamped/upgraded to WRRFs)

SMARTech2b and Downstream SMARTech B - Manresa WWTP (Spain)

SMARTech 4a and SMARTech 5 Carbonera WWTP (Italy)

Sidestream S.C.E.P.P.H.A.R.: Short-Cut Enhanced Phosphorus and PHA recovery (Smartech 5)

Supported by the Horizon 2020 Framework Programme of the European Union

www.smart-plant.eu

Conca et al. Long-term validation of polyhydroxyalkanoates production potential from the sidestream of municipal wastewater treatment plant at pilot scale Chemical Engineering Journal, 390, 124627, 2020, https://doi.org/10.1016/j.cej.2020.124627

Sidestream SCEPPHAR pilot scale (Smartech 5): TRL 5

Pilot plant potential recoveries: 0.7-0.8 kgPHA/day; up to 300 gStruvite/day)

Full scale final projection: PHA 1-1,2 kg per PE per YearStruvite 0,2-0,4 kg PE per Year

STA POLICE

RESources from URban Blo-waSte RES URBIS

EN Horizon 2020 Work Programme 2016 - 2017 CIRC-05-2016: Unlocking the potential of urban organic waste Research and Innovation Actions (RIA)

> 3-year project, Jan 2017 – Dec 2019 20 partners, 8 countries around 3 M€ EU support

Project coordinator: M. Majone Research Centre for Protection of Environment and Cultural Heritage University of Rome "La Sapienza", Italy Website: www.resurbis.eu

PROVINCIA AUTONOMA

DI TRENTO

Bioinicia

CIRC-05-2016: Unlocking the potential of urban organic waste

In a Circular Economy perspective, turning waste into a resource is an essential part of increasing resource efficiency and closing the loop

More than 70% of Europeans live in cities and urban areas, and produce huge amount of organic waste (**including sludge from wastewater treatment**)

Challenges from the Call which RES URBIS aims at answering to

Can different organic waste streams of urban origin combined into a common valorization chain?

Can <u>bio-based products</u> be obtained from organic waste of urban origin, with a <u>higher economic value than compost and biogas</u>?

Can both targets be fullfilled togheter?

Can the new technological solutions be integrated in the present waste management systems

"End of waste" criteria: where and how

The definition of "end of waste" criteria is a key step along any way a waste is transformed into a product

"End-of-waste" status

Article 6 of the Directive 2008/98/EC, as amended by the new Waste Directive (Brussels, 27 April 2018 (OR. en) 2015/0275 (COD) PE-CONS 11/18)

1. Member states shall take appropriate measures to ensure that waste which has undergone a recycling or other recovery operation is considered to have ceased to be waste if it complies with the following conditions:

- (a) the substance or object is to be used for specific purposes;
- (b) a market or demand exists for such a substance or object;

(c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and

(d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

Analysis of contaminants in PHA samples

As function of:

- Feedstock
 - Stabilization method
- Before/after extraction
- Extraction mehod

Inorganic elements, including toxic metals >40

Astolfi ML. et al., Chemosphere, 259, 127472, 2020 https://doi.org/10.1016/j.chemosphere.2020.127472.

Polycyclic aromatic hydrocarbons (PAHs) 16 compounds

Cavaliere C. et al., Molecules 2021, 26, 539. https://doi.org/10.3390/molecules26030539

Polychlorinated biphenyls (PCBs) 21 compounds

Riccardi C. et al. Polymers 2020, 12, 659. https://doi.org/10.3390/polym12030659

H																He		
L	i	Be											В	С	N	0	F	Ne
Na	а	Mg											AL	Si	Ρ	S	CI	Ar
K		Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
R	b	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
C	s	Ba	La	Hf	Ta	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
F	r	Ra	Ac															
					Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
					Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Summary from analytical results

- The PHA content of contaminants is generally low, i.e in the range between ppb and a few ppm, but for alkaline and alkaline earth metals (which are of little environmental or health concern)
- The **type of feedstock** affects the contaminant contents:
 - PHA from fruit waste has lower content than PHA from the mixture of organic fraction of municipal waste and sludge from wastewater treatment.
 - commercial PHAs derived from crops have lower concentrations of heavy metals than waste-based PHA, but similar concentrations of PAH and PCB.
- **PHA extraction** also affects the contaminant contents: acid stabilization and extraction with aqueous inorganic extractants generally brings to lower contents than thermal stabilization and extraction with either hypochlorite or chloroform.
- Although a specific regulation does not exist yet, all tested PHA types meet present regulatory standards and guidelines for similar conditions and materials (e.g. limits for Cd and PAH in plastic materials based on REACH regulation, including toys; limits for PCB in Recycling Plastics from Shredder Residue, based on EPA guidelines).
- From reliminary results (to be confirmed) waste-based PHA slightly exceed the limits for heavy metals set by the EU Directive n. 10/2011 on PHA-based plastic materials and articles to come into contact with food. Thus, based on available results so far, the use of waste-based PHA in direct contact with food cannot be suggested.
- On the other hand, in migration tests, the PHA samples obtained under the best operating conditions complied with the EU limits for the safety of toys and on plastic materials intended for contact with refrigerated or frozen food (10/2011).

A tentative proposal for an EoW national decree on PHA

Directive 2018/851 (art 6) states that End of Waste for a given material can be determined case by case when a specific EU regulation is absent.

The specific Decree at National level, should be based on the following points:

- 1. Definition of the waste type (with indication of the European Catalogue Code) and its characteristics including the acceptability definitions/standards
- 2. Technical parameters in terms of characteristics and definition of limits of the resulting "new" material / substance
- 3. Definition of the specific use and markets for the new waste-derived material

In the case of PHA production from urban organic waste these three points can be clearly defined:

- a) Proposed organic waste for PHA production are typically the **organic fraction from municipal solid waste and/or the sludge from municipal wastewater treatment**, whose quantity and characteristics are typically well defined at territorial level. Based on local conditions, food processing waste can be also included.
- b) Characteristics of obtained PHA can be easily determined (monomer composition, purity, ashes), and PHA meet regulatory standards or guidelines for the allowable presence of relevant contaminants as well. Exemption/compliance for REACH/ECHA regulation has to be checked case by case as well as compliance with CLP regulation has to be warranted
- c) There is a clear market demand for bioplastics in several sectors and a first estimation of at least 1 million ton per year worldwide can be considered. Because all market segments are well ruled, there's a general provision that PHA use complies with existing regulations, guidelines and technical specification for the respective sector.

Perception and awareness of consumers towards bioplastics from waste/sludge

Thanks to Ivan Russo

G. Moretto et al. Water Research https://doi.org/10.1016/j.watres.2019.115371

A few remarks

How to transform wastewater/waste treatment plants into biorefineries as part of the development strategies of the circular bioeconomy

✓ Availability of supply of sufficient "raw material", stable, and not in competition with more noble uses.

✓ Simple and robust technologies to deal with the intrinsic variability of the raw material and at the same time to guarantee the reliability of bioproducts.

 \checkmark Integration of new technologies with existing plants.

 Rethinking and adaptation of the legislation in the light of technological developments (e.g. overcoming the dichotomy between wastewater and waste in specific cases).
 Rapid implementation of the regulatory and authorization aspects (eg "end of waste"),

starting from the early development stage of the new technologies.Management of the possible contradiction between the circularity of waste and non-

contaminants.

✓ Bio-products with real market value

✓Adequate connection between the different industrial sectors and business models (revenues/tariffs/taxes and incentives if any)

✓ Effective and proven sustainability of bioproducts (LCA, "end of life")

 \checkmark Awareness, motivation and satisfaction on a social level