Extraction and purification techniques for the recovery of bio-based volatile fatty acids and polyhydroxyalkanoates from organic waste: a State-of-Art

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The rapid growth of the human population implies a sharp increase in the production of waste and proper management is essential to minimize environmental degradation and promote the transition to a sustainable society. In Italy, about 154 million tons of waste were produced in 2019, registering an increase of 10.5 million tons compared to the previous year (ISPRA: Special Waste Report - Edition 2021). In this regard, innovative technologies may leverage the recovery of new products with high economic value such as energy, biofuels, water, nutrients, bio-based chemicals and materials such as volatile fatty acids (VFA) and/or PHA. To date, successful european project (eg., Smart-Plant, Resurbis, ecc) validated in relevant environment innovative technologies implemented in existing WWTP and demonstrated the high added value products recovered from municipal wastewater and organic waste. For instance, nitrogen and phosphorus-based fertilizers recovered from sludge has been applied in organic farming (e.g., OSTARA), while cellulose from sieved wastewater (Recell®) can be reused as construction material, such as asphalt and mortars.

However, the recovery and commercialization of VFAs and PHAs from waste and wastewater is, still, the "*bottleneck*" of their market. Volatile fatty acids (VFAs) are widely used chemicals and, among other applications, serve as precursors for high-value (2500 euros/ton-2100 euros/ton) fuels and chemicals (Pervez et al.,2022). Most of the global demand for VFAs is met by petrochemical routes (Riemenschneider, 2000). However, petroleum-based (cradle to grave) pathways are considered unsustainable and, therefore, recent research has focused on cradle to cradle technologies such as biological production of VFA from waste streams. The use of wastewater as fermentation feed produces broths with much lower VFA content than glucose-fed fermentation broths.

To achieve economical production of biobased VFAs, implementation of a robust VFA recovery technique is inevitable (Reyhanitash et al.,2016). To date, VFAs can be extracted through several methods: Gas stripping with absorption; Adsorption; Solvent extraction; Electrodialysis; Reverse osmosis and nanofiltration; Membrane contractor. (Atasoy et al.,2018). The challenge now will be to select cost-effective recovery methods that will result in maximum VFA recovery at minimal cost and lower carbon footprint. It must be emphasized that the decision on the selection of recovery methods will need to consider the intended application of the recovered VFA. Some of the recovery methods such as reverse osmosis and electrodialysis can be expensive due to the high energy cost, although they can recover VFA with high purity. Knowledge of how different recovery methods affect the suitability of VFA applications will aid in the selection of new methods by setting clear boundaries between recovery and/or purification of the product. Applying new protocols, modifying existing methods, and/or combining methods to recover and separate the various VFA compositions present opportunities for new research. Although traditional "thermal separation" distillation techniques are known for their high energy and cost, they have been and still are the default technique for separating VFAs from the aqueous fermentation medium (Darwish et al.,2021). However, the incentives for designing environmentally friendly, energy-efficient, and cost-effective processes have steadily increased in recent decades. Therefore, separations such as liquid-liquid extraction, adsorption, and membrane filtration are becoming attractive alternatives when they are technically feasible (Darwish et al.,2021). In addition, VFAs are known for the production of biofuels such as methane and hydrogen as well as biopolymers: polyhydroxyalkonoates (PHAs) (Domingos et al.,2017). PHAs are hydroxyalkanoic acid polyesters that are produced by various intracellular microbes as energy and carbon storage materials in response to physiological stress conditions. Poly(3-hydroxybutyrate) or PHB is the most important member of the PHAs family that has been extensively studied. The importance of PHB is mainly due to its biocompatibility, easy degradation under aerobic and/or anaerobic conditions, and release of non-toxic products during degradation. It has several promising applications in packaging, food, medical and pharmaceutical industries (Philip et al. 2007). However, 50% of the expense is related to recovery from cells (Mannina et al., 2020). Therefore, extraction and purification costs should also be reduced for successful commercialization. The challenge in extraction processes is to economically and ecologically achieve a high molecular weight with a high degree of purity of the extracted polymer (Kunasundari and Sudesh, 2011).

So far, the most studied methods for PHA recovery can be grouped into three categories: Solvent Extraction; Digestion of the NCPM; Mechanical disruption. The extraction of intracellular PHAs from cell biomass creates a major drawback in the development of a commercially viable fermentation process. This could mainly be due to several reasons such as production with high purity substrates (e.g. Glucose) and lower solubility in various classical non-toxic solvents. PHAs biopolymers are generally soluble in toxic halogenated solvents such as chloroform which are expensive or not so easy to handle due to their toxicity (Jacquel et al. 2008). While purification is commonly conducted through treatment of PHAs with hydrogen peroxide and/or ozone treatment (Muthuraj et al.,2021) making the process extraordinarily complex. Such purification allows for the production of whiter, more stable, and odorless PHAs that are aesthetically appealing to the market (Muthuraj et al.,2021). Therefore, simple, inexpensive, environmentally unburdened, and effective methods to extract and purify the biopolymer from cells are needed. As an alternative to chlorinated hydrocarbons, which are the best solvents for PHAs, many research studies address the use of green solvents, with low or no toxicity and possibly derived from biochemical conversion: ethers, esters, carbonates, and ketones. These may overcome ecological concerns, limitations involving worker safety, or strict regulations on trace solvents in commodities for particular applications. Their suitability is assessed by considering their recyclability, the need for biomass pretreatment, the recovery yield of the polymer, the quality of the extracted polymer in terms of purity and possible molecular weight reduction, as well as the cost of the process and environmental performance (Alfano et al.,2021). Certainly, international policies should break the present paradigm to develop an environmentally sustainable model that incentivizes biobased production by looking at the entire production process and the CO_2 allowances recovered from it. However, extraction and purification protocols can severely undermine the market for biobased species such as VFAs and PHAs. PHAs are biopolymers that can effectively replace conventional petrochemical plastics due to their properties. However, their large-scale production is still limited by its high production cost compared to conventional fossil fuel-based plastics, as the price of PHAs, depending on the polymer composition, ranges from 2.2 to 5.0 €/kg, which is at least three times higher than that of major petrochemical-based polymers costing less than 1.0 €/kg. (Sabapathy et al.,2020). It's been more than a decade since conventional materials. paper, wood, metals, glass and ceramics have been replaced by synthetic plastics in a number of commercial sectors, is the market ready for another revolution towards biobased materials?

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