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Environmental assessment of complex wastewater valorisation by polyhydroxyalkanoates production

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ABSTRACT

Polyhydroxyalkanoates (PHA) are biodegradable polymers with renewable origin that are expected to substitute conventional petrochemical plastics. However, before they are commercialized, life-cycle environmental validation is needed, to prove that there is an actual benefit with the replacement of non-renewable plastics with PHA. Nowadays, environmental evaluations assessing bioplastics production at full-scale are scarce due to the lack of data, so experimental results were used to evaluate the feasibility of PHA production employing high load wastewater. A three-stage PHA production system utilising a mixed microbial culture (MMC) was successfully operated for two years employing complex wastewater from a fish-canning industry. The results obtained were scaled-up to define and compare a circular economy scenario performance, with PHA production, with the current linear approach (i.e. effluent generation, treatment and discharge). To the best of our knowledge, this is the first time that the environmental performance of a MMC-based full-scale PHA production system using saline wastewater is evaluated. Results show an average improvement of ca. 25 % for nine out of ten studied categories if the circular economy approach is implemented. The sludge management strategy was a key factor for the environmental validation of the process, and if composting is applied instead of anaerobic digestion, the improvement is reported in eight categories. When a more conservative replacement yield of fossil-based plastic was tested, the

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circular economy approach was the preferable option in 8 out of 10 categories. The significance of the downstream process was also confirmed by this study, although it was not a barrier to show the feasibility of producing added-value bioproducts under a circular economy approach. Finally, this work proposes new process integration strategies to reduce the environmental burdens of PHA production and increase the body of knowledge on MMC-based processes, an area where LCA case studies are still scarce.

Keywords: Best available techniques; bioplastics; circular economy; industrial wastewater; life cycle assessment; mixed microbial cultures

Abbreviatures

AP	Acidification Potential
BAT	Best Available Techniques
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DAR	Depletion of Abiotic Resources
DSP	Downstream Process
EP-F	Freshwater Eutrophication Potential
EP-M	Marine Eutrophication Potential
FBR	Fed-Batch Reactor
FU	Functional Unit
GWP	Global Warming Potential
HB	Hydroxybutyrate (monomer)
HRT	Hydraulic Retention Time
HT	Human Toxicity
HV	Hydroxyvalerate (monomer)
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Inventory Assessment
LLW	Low Load Wastewater
MCW	Mussels Cooking Wastewater
ME	Marine Ecotoxicity
MMC	Mixed Microbial Cultures
ODP	Ozone Depletion Potential
PET	Polyethylene Terephthalate
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
POCP	Photochemical Oxidant Creation Potential

PP	Polypropylene
RR	Replacement Ratio
SBR	Sequencing Batch Reactor
SDS	Sodium Dodecyl Sulphate
SRT	Solids Retention Time
TAETP	Terrestrial Aquatic Ecotoxicity Potential
TSS	Total Suspended Solids
VSS	Volatile Suspended Solids
WWTP	Wastewater Treatment Plant

1. Introduction

Fish-canning industries play a significant role in the Spanish market, where the North-Western region of Galicia is the main mollusc producer of Europe (APROMAR, 2019). The production of mussels constitutes about the 80 % of the total Spanish fish-canning production, generating around 250 kt of mussels per year. This industry is an essential driving force for the region, since it is responsible for more than 100 M€ of annual income and for more than 10,000 jobs, representing between the 15 % and 40 % of the total active population living in the areas in which mussels are harvested and processed (Rey-Méndez et al., 2016).

However, the fish-canning industry activity generates high amounts of complex wastewater containing salts, organic matter, nutrients and solids, among other compounds. Moreover, the wastewater coming from the boiling of mussels (or mussels cooking wastewater, MCW) is a highly polluted effluent which treatment is challenging. In fact, the environmental concern regarding the treatment and disposal of MCW is high, and several measures (economic incentives, research projects, environmental policies…) were applied to solve the issue related to MCW, as reflected in specific legislation (Consellería de Medio Rural e Mar, 2015). These effluents constitute a threat for the industry, which is obviously dependent on the water quality of the areas where seafood is harvested. These areas, called *rías* or estuaries, are unique spaces with a high biological diversity, optimal for the farming and growth of seafood. Therefore, it is important to treat properly those industrial effluents to guarantee the environmental stability of the estuaries and the economic sustainability of this region.

Although the presence of salts, sulphate and other compounds which are characteristic of fish-canning effluents can hinder or inhibit biological activity, biological treatments (like activated sludge or anaerobic digestion) were possible in the past when specific operational strategies were applied (Palmeiro-Sánchez et al., 2013). Considering this, it is of interest to explore alternative routes for the biological treatment of these high-salinity wastewaters, and for their valorisation under the circular economy perspective.

Polyhydroxyalkanoates (PHA) are polyesters produced as intracellular storage materials by a wide range of microorganisms. The characteristic that makes these biopolymers an interesting alternative to conventional plastic is that they combine high functionality with biodegradability and non-toxicity. Due to the microbial origin of PHA, 40 – 48 % of the total production costs are related to the employed feedstock (Rodriguez-Perez et al., 2018), while the remaining costs correspond to the energy employed to maintain sterile conditions for the microorganisms culture, and the downstream process (DSP) for PHA extraction (Fernández-Dacosta et al., 2015). The use of waste streams, such as industrial wastewater, and non-sterile mixed microbial cultures (MMC) would not only reduce the cost of the final product, but also improve the environmental performance of the process (Yadav et al., 2020). Furthermore, the research for new materials that can substitute conventional plastics is essential for accomplishing the ambitious objectives targeted by the European Commission (European Commission, 2018). Moreover, the production of bioplastics employing wastewater is of great interest, especially in coastal areas, because of the link between plastic pollution and the destruction of the marine ecosystems, which directly impact not only the environment, but also the local economy (Conejo-Watt and Luisetti, 2019)[2].

In this scenario, TREASURE-TECHNOSALT project[3] aims to unravel the effects of salinity over biological processes in wastewater treatment and valorisation, and biopolymer production is being technologically assessed under high salinity conditions. However, the aspects that need to be considered for biopolymer commercialization are not only related to technical issues but also to environmental concerns. Conventional plastics, which constitute a serious problem for ecosystems and human health worldwide, are dependent on oil and petrol. Therefore, new sources for plastic production are being researched and it is necessary to prove the environmental benefits of those novel alternatives compared to the non-renewable ones and to stablish criteria for their applications and safe disposal (European Commission, 2018). In this context, Life Cycle Assessment (LCA) seems to be the appropriate tool, since it has already been widely used to assess the environmental performance of different processes and products, and particularly of PHA production processes (Bengtsson et al., 2017; Fernández-Dacosta et al., 2015; Morgan-Sagastume et al., 2016). However, recent investigations pointed out the urgent need for studies in which all process stages are covered, stablishing PHA biosynthesis and extraction from waste as feedstock. This lack of research works in which the whole process is holistically studied is drawing back the scale up and commercialization of PHA (Mannina et al., 2020).

The objective of this study is then to evaluate the environmental performance of a PHA production process from high salinity wastewater using MMC and to compare it with the traditional linear economy approach (i.e. wastewater treatment and discharge). All process stages, from waste generation to product extraction and effluent discharge will be evaluated.

[2] http://www.cleanatlantic.eu/
[3] http://www.usc.es/biogroup/treasure

Therefore, the new data provided will contribute to increase the information available on full-scale MMC-based PHA production systems. To do so, lab activities carried out within the TREASURE-TECHNOSALT project will be used for the scaling-up of the process and complemented with literature sources when needed, and the environmental impacts of PHA production will be quantified. Here, a MMC-based PHA production process employing saline wastewater will be environmentally assessed for the first time.

2. Goal and scope definition

The goal of this study is to evaluate the use of high salinity wastewater as a feedstock for PHA production. To do so, a PHA production system at lab-scale was operated using MCW coming from a local industry where molluscs were boiled.

However, the production of PHA from wastes using MMC is still under development, with only a few pilot-scale plants operating worldwide (Kourmentza et al., 2017). In this scenario, the environmental evaluation of the process is challenging, since LCA results using lab-scale data do not necessarily represent the impacts associated to a full-scale process, often resulting in an overestimation of the outcomes (Moni et al., 2020). To minimise that, the present LCA is based on an up-scaling of the system from the results obtained at laboratory-scale (18 months of stable operation), where different operational conditions were tested and optimized (Roibás-Rozas et al., Unpublished Results).

2.1 Functional Unit (FU) definition and feedstock quantification

The functional unit (FU) is usually defined in terms of the system output, and this has been the case for PHA production system, in which the FU defined is normally related to the mass of biopolymer generated, being 1 kg or 1 t of PHA (or specifically polyhydroxybutyrate, PHB) the preferred option (Zarroli, 2020). Having said that, literature states that the minimum amount of biopolymer needed to make a MMC-PHA production process economically feasible is around 10^3 t PHA/year (Bengtsson et al., 2017). With the chosen substrate, MCW, and system productivity (see below), the amount of wastewater needed to guarantee the economic feasibility of the process would be approximately 1,500 m^3/day, which is a high and unrealistic flow considering the processing capacity of the region. In fact, when dealing with waste management systems, the FU might be defined in terms of the system input, that is the waste to be managed. This has been the approach taken by recent studies on PHA production when the feedstock employed was wastewater: an influent volumetric-based FU, such as the treatment of a certain amount of wastewater flow rate (Morgan-Sagastume et al., 2016). This approach might be questionable when different wastewater streams are compared, since it disregards their loads and characteristics, but not in the case where two scenarios, i.e. linear and circular economy based, are compared for the same type of wastewater as occurs in the present study. As a result, this second approach, the system input FU, is the one selected here and its quantification is described next.

As already stated, Galicia produces annually about 250 kt of mussels, of which about a 40 % is consumed fresh and the 60 % remaining is processed (i.e. boiled and canned). Furthermore, almost 70 % of the mussel rafts are located in the area of *Arousa* (Barros et al., 2009). Currently, there are ten facilities allowed to boil mussels in Galicia, nine of them in *Arousa* (Consello Regulador do Mexillón de Galicia, 2020). Consequently, it can be assumed that the mussel processing in Galicia takes place in this estuary. Among those nine, the three biggest ones are responsible for the processing of about 45 kt of mussels/year each (Mejillones Nidal, 2018), so this study focuses on these three plants (Figure 1). As the distance among boiling facilities is shorter than 10 km, it is justified to evaluate a centralized wastewater valorisation and treatment plant for a full-scale PHA production scenario.

FIGURE 1 AROUND HERE

The processing of mussels usually generates two kinds of effluents that are treated separately in the processing facility before they are discharged (Barros et al., 2009): a low-loaded wastewater stream (LLW), mainly resulting from washing operations, and a high-loaded one, from the boiling of the molluscs. The LLW only needs basic primary treatment, such as screening, before safe discharge. It is always produced, and it is out of the scope of this study. The high-loaded one, the MCW, is our target effluent due to its high carbon content and to its treatment complexity. This stream has a highly variable composition, which average values are reported in Table 1.

TABLE 1 AROUND HERE

Regarding wastewater production, a processing facility of high capacity generates about 5 m^3/t of mussels processed, of which a 6 % is considered of high load (Bello Bugallo et al., 2012). As 100 - 105 kt of mussels are assumed to be processed by the three facilities per year, the centralized full-scale plant for the valorisation and treatment of MCW would have an input flow of 85 m^3/day, considering 365 working days per year (Secretaría xeral de Calidade de Avaliación Ambiental, 2013a)[4]. This is a value significantly lower than the threshold level reported above for economic feasibility. Nevertheless, and considering the expected evolution of this novel technologies, this flow is chosen as the FU for this study, as it is the available flow of the researched feedstock in the target area. This centralized scenario will be compared with the current one, in which MCW is treated in the industrial wastewater treatment plant (WWTP) of each processing facility before being released. When the fish-canning facility is located in an industrial area, the effluents are usually disposed to the sanitation network with low requirements regarding discharge limits (Dirección Xeral de Calidade e Avaliación Ambiental, 2008a). One of the problems linked to mussels processing industry is that facilities

[4] The feedstock quantification is based on an annual production so the number of working days will neither change the annual wastewater generated or the total PHA production.

are usually located in coastal areas, away from industrial zones. Therefore, after wastewater treatment, the effluent is usually disposed directly into the estuaries through a sewage pipe, with variable discharge limits.

2.2 System boundaries and scenarios definition

The system starts with the MCW generation, so the upstream processes, i.e. the harvesting and canning of the molluscs, are left out the system boundaries. Besides, the treatment and discharge of LLW is also left out as it is a common process for all the scenarios under evaluation. The system boundaries of the present study include all the processes involved in wastewater treatment and valorisation: water line from the influent pumping to the final discharge of the effluent in the receiving water body, sludge management and disposal, and bioplastic production (extraction of the PHA from the biomass).

Sludge is produced from the MCW treatment and valorisation processes and, according to the Spanish legislation, biowaste has to be treated through anaerobic digestion or composting, encouraging administrations to promote the use of the resulting organic fertilizers in agriculture (Jefatura del Estado, 2011). A total of 19 facilities in Galicia are authorised for sludge valorisation, and only three of them work with anaerobic digestion, while the rest of them are mainly compost producers (Xunta de Galicia, 2020). Therefore, transport to the nearest of these facilities and sludge composting is considered for the conventional scenario, while anaerobic digestion at the centralized facility for the valorisation scenario is considered as the most feasible choice. However, due to the lack of information concerning the sludge characteristics, the final application of the compost and the digestate are excluded from the evaluation.

For all the stages, only the environmental impacts associated with operation have been considered in the study, while construction and decommissioning of the required infrastructures have been excluded due to lack of data.

2.2.1 Baseline scenario: the LINEAR ECONOMY approach

High strength fish-canning wastewater (like MCW) is usually treated in two stages: primary and secondary. In primary treatments, solids and oily matter are removed from the wastewater, while, in the secondary one, biological systems are usually employed to remove dissolved organic matter and nutrients. The choice of the best available technique (BAT) ensures the minimum environmental impact without compromising the economic performance of an installation. BAT selection, which is based on technical feasibility, environmental benefits and economic profitability, establishes the following treatment sequence for fish-canning effluent: first, a primary treatment (equalization, screening, sedimentation, pH adjustment, flocculation, flotation, or microfiltration) and then, a secondary treatment (aerobic or anaerobic). Therefore, the up-scaling of the linear economy scenario will be based on the treatments recommended in the BAT for fish processing (Tomczak-Wandzel et al., 2015), as it is commonly the base for WWTP design in MCW treatment (Mejillones Ría de Arosa, 2016).

For primary treatment, the use of Dissolved Air flotation systems (DAF) is widely spread due to their high efficiency and simplicity, and they are used to treat MCW (Barros et al., 2009). When coagulants are employed, its removal efficiency increases to 80 – 95 %, since the DAF unit will be able to separate not only solids, but also soluble organic compounds that can precipitate and be removed (Tomczak-Wandzel et al., 2015). In the fish-canning industry, it is recommended to operate at a pH approximately of 5 in order to decrease protein solubility. As MCW have high protein concentration, the use of this unit is justified (Figure 2), and its aim is to remove not only solids, but also organic nitrogen associated to proteins.

FIGURE 2 AROUND HERE

Concerning secondary treatment, biological processes are the preferred option (activated sludge, anaerobic digestion, granular treatments, etc.). Anaerobic digestion has been employed, but the experience has only been fully successful in facilities with low salinity wastewater (Secretaría xeral de Calidade de Avaliación Ambiental, 2013b), as the presence of sodium, ammonia and sulphate can hinder anaerobic treatments. For MCW, these ions are normally present in inhibitory concentrations, and methane production is very difficult. Despite this fact, several full-scale experiences were carried out in the past in Galician industries trying to valorise MCW anaerobically, but with unsuccessful results where the low amounts of poor quality biogas produced were permanently burned in a torch (Barros et al., 2009). Therefore, most of the industrial plants for fish-canning processing employ activated sludge processes for the wastewater secondary treatment, as it is the conventional treatment defined here. Each canning facility is supposed to have a small WWTP for the treatment of their effluents (Figure 2); so, assuming equal production capacities, the capacity of each WWTP for the linear economy scenario is supposed to be 1/3 of the total MCW generation, i.e. 28.3 m^3/day.

Sludge is thickened and stored in an industrial container. Once the container is full, it is transported to the closest industrial composting facility.

2.2.2 CIRCULAR ECONOMY approach

The valorisation scenario was designed from the knowledge acquired in previous research projects (see section 1 of the Supplementary Material (SM)) and the experimental results after two years operating a bench-scale three-stage system for PHA production employing MCW (Figure 3). For more information about the lab-scale three-stage system for PHA production, see section 2 of the SM. First, in the acidification stage, Chemical Oxygen Demand (COD) present in the MCW is transformed into Volatile Fatty Acids (VFA). The acidification reactor and its start-up is described in Fra-Vázquez et al.(2020). After biomass separation by centrifugation, VFA are fed to two reactors: a Sequencing Batch Reactor (SBR) and a Fed Batch Reactor (FBR). The SBR is an enrichment reactor for the MMC selection, while the FBR is employed to maximize PHA content in the MMC. Several operational strategies were tested throughout the experimental time (Roibás-Rozas et al., Unpublished

Results). Optimal conditions were found when a mild alkalinity addition was performed by the supplementation of 80 mg $Na(HCO_3)$/L to the MCW fed to the acidogenic reactor. The enrichment reactor operated with Modified Aerobic Dynamic Feeding, in which Feast-Famine regime was combined with a settling stage as explained by Argiz et al. (2020), who operated a reactor with the same inoculum as the one described here.

FIGURE 3 AROUND HERE

Biological nitrification was inhibited in the SBR by allylthiourea addition (20 mg/L of feeding). When its addition was stopped, this biomass was able to produce nitrite during the famine period, with a nitritation rate of 30 mg NH_4^+-N consumed/g Volatile Suspended Solids·d (NH_4^+-N/(g VSS·d)). Denitritation occurred during the anoxic periods of feast, where all nitrite was consumed with no significant worsening of the enrichment performance (Fra-Vázquez et al., 2019).

In addition to the desired stream, the PHA-rich one, other streams are produced. They are unified in a single stream to be treated together and safely released to the environment. Therefore, a primary settler is required to remove solids present in this waste stream and to work as an homogenization unit to change from sequential operation to a continuous mode. Then, a biological treatment will be employed to remove nitrogen and organic matter in a conventional activated sludge system (CAS), in which aerobic nitrification and anoxic denitrification are performed in a step-fed type system with four anoxic/aerobic sections. Sludge generated in every stage of the process is treated anaerobically in a sludge digester.

The experiences carried out at lab-scale comprise only the valorisation steps, in which an effluent is generated for treatment and disposal, and PHA-rich biomass is produced for extraction. Therefore, experimental data developed in the frame of TREASURE-TECHNOSALT were employed for the up-scaling of the biological valorisation line. For the extraction and refining stage (i.e. DSP), data from USABLE PACKAGING project[5] were used. Environmental and techno-economic analysis showed that purification of PHA employing alkaline treatment with sodium dodecyl sulphate (SDS) is a promising choice for PHA extraction from MMC (Saavedra del Oso, 2020), so data from the provided inventories are used in the present study. For the selected treatment (SDS and sodium hypochlorite), 99.9 % purity was stablished according to Fernández-Dacosta et al. (2015) and an ideal recovery yield was assumed (discussed later on, see section 5.3).

Concerning the avoided product, PHA properties showed similar specifications to poly(ethylene terephthalate) (PET), poly(ethylene), poly(styrene) and poly(propylene) (PP) (Koller et al., 2013). PP is similar to PHB polymers, although when other monomers are included in the chain, like hydroxyvalerate (HV), plastic properties change (Palmeiro-Sánchez et al., 2016). Biopolymer composition in TREASURE-TECHNOSALT project was approximately 25:75 HV:HB. Recent studies show that this type of biopolymer could substitute PET for packaging applications (Melendez-Rodriguez et al., 2018) so PET is the conventional plastic selected as avoided product from the PHA production. Note that neither the use nor the end-of-life stages for both conventional and bio-based plastics are included in the present study.

Finally, the design of the anaerobic reactor for the sludge valorisation was performed according to the results obtained in the frame of PLASTICWATER[6] project, where the anaerobic digestion of sludge under brackish conditions and high ammonia and sulphate concentrations was successfully assessed (Palmeiro-Sánchez et al., 2013).

2.2.3 Mass balances and stream compositions

[5] https://www.bbi-europe.eu/projects/usable-packaging

[6] Recycling of wastewater and sludge to produce bioplastic materials (PLASTICWATER). Supported by Spanish Government (CTQ2011-22675)

Table 2 summarizes the composition of the main streams of every scenario and compares the achieved effluent with the discharge limits. As there is few information available regarding these limits in mussels boiling facilities, they were established according to the specifications imposed on a fish-canning company discharging its effluent directly to the *Arousa* estuary or *ría de Arousa* (Dirección Xeral de Calidade e Avaliación Ambiental, 2008b), which is the area where the majority of the mussels boiling facilities are located (Fig 1). More information about the design of every process unit and the mass balances performed is supplied in section 3 of SM.

TABLE 2 AROUND HERE

2.3 Life Cycle Impact Assessment: impact categories and method selection

The choice of the relevant impact categories and impact assessment methodology is essential to provide a consistent evaluation of the environmental performance of the scenarios under study. As this research has a circular economy approach, several review papers and articles were examined in order to identify the most common impact categories assessed in the different areas covered by this study: WWTP operation and management, plastic production/waste and PHA production. Here, the lack of studies regarding MMC-based PHA production is noticeable, and most research works focus on pure culture processes. Table 3 shows the result of this review. All of them will be covered in this study, paying special attention to the four first ones. For eutrophication, both freshwater and marine will be assessed (EP-F and EP-M, respectively). Besides, and considering the particularities of this study, Marine Ecotoxicity (ME) will also be considered.

TABLE 3 AROUND HERE

The Hierarchist ReCiPe 2016 Midpoint method (v1.13) has been selected to evaluate all the selected impact categories except Global Warming Potential (GWP), which was assessed by the last update of the IPCC method (v 1.03 100a). SimaPro v8.3 was used for the computational implementation of all the inventories and impact categories calculations.

3. Life Cycle Inventory

Mass balances were employed to estimate the composition and flows of every stream (section 2.2.3) and complemented with literature data when needed. Conventional treatment units were designed following wastewater treatment and chemical engineering handbooks (Coulson and Richardson, 1999; Metcalf & Eddy, 2014). Theoretical power equations (described in the section 3.3 of the SM) were used to determine the energy requirements of every stirrer, blower, centrifuge and pump. Chemicals dosage was estimated using laboratory results and literature data. Results of all the calculations are summarised in Table 4, and detailed information is given below.

TABLE 4 AROUND HERE

3.1 Inventory of the linear economy scenario

As already stated, three facilities were considered for boiling mussels. Therefore, the design was individually performed considering a third of the total flux. Then, the linear economy scenario was built up putting together the three facilities.

- Design of the process units:

The DAF unit removes 85 % of solids and, with the use of coagulants at low pH, about 40 % of the COD. A volume of 1 L HCl per m^3 of wastewater is assumed to be added to lower pH to 5 (and equimolar amounts of NaOH are supplied after DAF to raise pH to neutrality). The removed COD is 80 % of coagulated proteins, eliminating approximately a 35 % of total nitrogen, and approximately 30 % of carbohydrates. After DAF unit, COD/N ratio in the wastewater is high (approximately 12), so two aerobic ponds are employed to ensure the removal of organic matter, while nitrogen is supposed to be consumed mainly due to cell growth. Mass balances were performed to determine Solids Retention Time and Hydraulic Retention Time (SRT and HRT, respectively) and the number of ponds needed to achieve discharge limits. Short SRT (5 days) guarantees avoiding nitrification in the first pond, so ammonia and COD consumption is calculated by mass balances according to the SRT. A second pond with extended aeration (SRT = 40 days) is needed to achieve COD levels according to legal requirements considering the available ammonia. Due to the long SRT in the second pond, some ammonia oxidation can take place, and it was estimated from mass balances (see Table 2).

- Direct emissions to air:

Biogenic CO_2 emissions related to COD consumption were calculated based on the emission factor reported by Campos et al. (2016): 0.08 kg CO_2/kg COD consumed. As COD/N ratio after DAF is about 12, nitrogen is consumed for biomass assimilation with no nitrification. According to the latest IPCC update for greenhouse inventories (IPCC, 2019), N_2O emissions are generally expected for aerobic systems. Depending on the stream characteristics and treatment system employed, they can vary from negligible to significant, with a emission factor range of 0.00016-0.045 kg N_2O-N/kg N in influent. In the linear economy scenario, as the main consumption of ammonia is related to cell growth, a low emission factor of 0.012 kg N_2O-N/kg N is chosen.

- Sludge production and management:

Sludge generated in DAF units usually has 4 % of solids concentration (Metcalf & Eddy, 2014). With 85 % solids removal efficiency, sludge generation is 1.8 m^3/day. Secondary sludge production was calculated according to SRT and decanters performance, producing 7.7 m^3/day of sludge with 7.43 g VSS/L. Sludge is thickened in a gravity thickener to reach a concentration of 45 g Total Suspended Solids/L (g TSS/L) (Metcalf & Eddy, 2014) and then transported to external facilities for further management. Chemically clarified supernatant is mixed with LLW, and as its contribution is less than 1.5 % of its flow (6.33 versus 430 m^3/day), the influence of this stream on the LLW treatment can be disregarded. After that, sludge is composted together with other waste streams (41 % average of sewage sludge as feedstock (TEN, 2020) was considered).

3.2 Inventory of the circular economy scenario

The centralised scenario that treats the total MCW flow (section 2.1) was up-scaled from the data obtained in the lab. Theoretical equations were used to calculate power needs, the operating time of the equipment, etc (see section 3 of the SM).

- Design of the process units:

In the valorisation line, the up-scaling was performed considering the obtained results. The effluent of the acidification reactor, which operated at SRT = HRT of 6.5 days, had 0.6 g COD_{VFA}/g COD. The SBR consumed 1.21 g COD_{VFA}/g biomass to reach 4 g VSS/L, and FBR needed 2.98 g COD_{VFA}/g biomass to achieve 41.5 % accumulation capacity. Overall, process efficiency was of 0.2 kg COD_{PHA}/kg COD_{MCW}. In the treatment line, to ensure nitrifiers growth, SRT in the step-fed CAS was set at 15 days and HRT in the anoxic volume was 58.83 m^3. Antifoaming agent (0.5 mL triethylene glycol/L feeding) was supplied in the SBR and NaOH was used for pH adjustment in the SBR and FBR (0.75 and 1 g NaOH/L, respectively), based on laboratory-scale dosages.

- Direct emissions to air:

Direct emissions of the acidogenic unit were estimated from lab measurements and literature data. Waste mixtures containing carbohydrates and proteins in acidogenic fermenters generated about 279 mL biogas/g VSS, with 47 % of CO_2 (Alibardi and Cossu, 2016). No methane was detected in several years of operation, and 2.4 % of the reactor headspace was H_2S as a consequence of the high sulphate concentrations in MCW. For this reason, ferrous oxide pellets, which are by-products of metallurgic industry, are used to remove H_2S with a ratio of 0.6 g H_2S/g pellet (Allegue and Hinge, 2014). When pellets cannot be used anymore, they are employed as raw material for roads and bricks. Fossil CO_2 is produced due to alkalinity addition, and CO_2 emissions were calculated for operational temperature and pH. For the aerobic reactors of the valorisation line, biogenic CO_2 generation due to COD consumption is 0.08 kg CO_2/kg COD (Campos et al., 2016) and due to PHA generation is 30 % (C-mol PHA/C-mol CO_2) (Jiang et al., 2011).

Regarding N_2O emissions, as nitrification and denitrification take place in the circular economy scenario, more N_2O is supposed to be generated. According to the latest IPCC update for greenhouse gas emissions (IPCC, 2019), the average value for the emission factor is 0.016 kg N_2O-N/kg N in influent for aerobic systems (as emissions for anaerobic units are not expected). This factor will be considered for the circular economy approach, assuming that nitrogen removal takes place not only in the anoxic tank of CAS but also during SBR feast.

- Sludge production and management:

Sludge is produced in the centrifuge after the acidification unit, in which most of the solids are removed and 1 m^3/day of sludge with 25 % TSS is generated (Elías, 2012). Primary settler after the valorisation line removes 55.75 % of solids and 33.96 % of COD, according to theoretical equations (Metcalf & Eddy, 2014), and produces 1.3 m^3/day of sludge with 5 % TSS. CAS unit generates sludge according to SRT and decanter performance, producing 4.0 m^3/day with 6.90 kg VSS/m^3, which is thickened in a gravity thickener to reach a final concentration of 45 g TSS/L (Metcalf & Eddy, 2014). The clarified stream from the thickener is diluted and treated together with the LLW[7], and the concentrated stream is treated together with the other high-solid streams in an anaerobic digester.

Regarding biogas production, sludge valorisation under high concentrations of sodium, sulphate and ammonia is feasible after proper biomass acclimation and process control. Moreover, sludge digestion generated 280 L of biogas/kg VSS (with 58 % of methane) when the digester feeding composition contained 6.7 g Na^+/L and 1.5 g SO_4^{2-}/L (Palmeiro-Sánchez et al., 2013). As these conditions are similar to the ones that could be found in this digester, the obtained results will be employed for the design of the digestion unit. Finally, biogas valorisation is performed considering electric and heat efficiencies of 35 % and 45 %, respectively (Metcalf & Eddy, 2014): i.e. 133.9 kWh/day of heat energy and 104.2 kWh/day of electricity. The former was used to maintain the temperature of the digester at 38 ºC and the latter was sent to the grid and considered then as avoided product. An amount of 1.5 % of the produced biogas is leaked, while the presence of N_2, H_2S and NH_3 in the biogas is estimated in 1 %, 0.05 % and 0.01 %, respectively (Rodriguez-Verde et al., 2014). Emissions linked to biogas combustion are calculated from literature data (Paolini et al., 2018), and ferrous oxide pellets are employed for sulphide removal before valorisation.

- Downstream Process:

DSP design is indicated in Fernández-Dacosta et al., 2015 (surfactant-hypochlorite method). Wastewater generated in DSP is diluted with LLW for its safe disposal (contribution of less than 0.5 % in volume) and therefore left out the system boundaries[8].

- Energy integration:

[7] As the supernatant only represent less than 0.5% of the LLW flow (5.64 m^3 versus 1290 m^3), this addition is considered negligible and stays out the system boundaries.
[8] Same criteria than the one applied for the supernatant of thickener, with a DSP wastewater flow of 3.02 m^3/day

Following a circular economy approach, energy integration is also applied. The temperature of MCW leaving the boilers is 125 ºC, and the bioreactors in the valorisation line operate at 38 ºC and 30 ºC, for the acidogenic reactor and the SBR-FBR respectively. Currently, this heat is dissipated naturally in the facilities, so an estimation of the available heat was done (1,000 kWh/day). It can cover the heat requirements of the biological reactors (estimated to be around 500 kWh/day) as well as the heat demand of the DSP (about 100 kWh/day). Therefore, the heat contained in MCW after the boilers is enough to cover the heat used in the process units.

3.3 Background processes

Data for the processes of the background system (production of electricity, chemicals, transport, plastic materials, steam and composting process) come from the Ecoinvent v3.3 database (Weidema et al., 2013). The Spanish electricity mix has been adapted with the most recent update reported, referred to 2018 (Red Eléctrica Española, 2019). No environmental burdens are allocated to the antifoaming agent (triethylen glycol) as it is a by-product of ethylene oxidation, neither to the ferrous oxide pellets as they are considered waste from the metallurgic industry. Therefore, only the transport of these products is considered. In the case of ferrous oxide, as it is employed as a component in the production of roads and asphalt, transport to the recycling facility (asphalt producer) is also included. As the SDS used at the DSP is not available in the database, its background production process has been assimilated to the one of alkylbenzene sulfonate.

4 Life Cycle Impact Assessment

4.1 Individual environmental performance of each scenario

The contribution of the different elements to the set of impact categories for each scenario is presented in Figure 4.

FIGURE 4 AROUND HERE

For the linear economy scenario (Fig 4a), electricity has an important contribution for all the categories (between 12 – 68 %) except for EP-M. Besides, chemicals consumption (which also includes the transport from the suppliers) also has a relevant impact (13 – 87 %, except for EP-M), mainly due to hydrochloric acid production. This process affects HT, TAETP and ME, and direct emissions of chlorine impact on GWP. Composting (sludge management) process has significant effects on GWP, AP and POCP due to the expected emissions of CH_4, NH_3 and N_2O.

Behind the direct emissions label, direct emissions to air estimated in each scenario and the release to the ocean of the final effluents are included. Regarding the former, direct emissions to air also contribute to the GWP category in both scenarios, totally dominated by the N_2O release. Concerning the latter, the release of an effluent containing nitrogen (in the forms of ammonia and nitrate) is clearly impacting EP-M category for both scenarios. In the linear economy scenario, no nitrification is expected, but small amounts of nitrate can be produced in the second pond (SRT = 40 d and low COD concentration). Total nitrogen released is 23.5 mg N_T/L, which is mainly ammonia nitrogen (15.0 mg NH_4^+-N/L and 8.47 mg NO_3^--N/L). For the circular economy scenario, nitrification and denitrification are needed as further treatment to guarantee the discharge limits accomplishment, and the total nitrogen in the effluent is 18.0 mg N_T/L, distributed between ammonia (4.0 mg NH_4^+-N/L) and nitrate (14.0 mg NO_3^--N/L). Nevertheless, the implementation of innovative process approaches, like nitrogen removal by the anammox process or phosphorous recovery units, could not only mitigate negative effects in EP-M category, but also decrease the overall process impacts due to energy optimization, better effluent quality and substitution of chemical fertilizers (Morgan-Sagastume et al., 2016).

When looking at the circular economy scenario (Fig 4b), the environmental burdens are more evenly distributed among the different elements, and electricity, chemicals use, and DSP are the main contributors for most categories. The centralized characteristics of this plant, which imply the transport of the MCW by lorry to the valorisation plant (i.e. labelled transport at Fig.4b), have a non-negligible contribution in TAETP, HT and ME due to non-exhaust gasses emissions linked to the brake wear treatment, and containing several harmful particulate matter (like copper or antimony).

The environmental benefits related to the circular economy approach are dominated by the avoided production of plastic (i.e. PET). The most affected category is fossil depletion (DAR) (32 %), as the use of crude oil and natural gas is prevented. It also has non-minor benefits for many other impact categories, like POCP, AP or ME, mainly due to the avoidance of xylene formation. The energy recovered for electricity production and sent to grid also has a net credit (net negative values for sludge management at Fig 4b), although with small values due to the low load entering the digester (as most carbon in MCW is employed for PHA valorisation) and the resulting low biogas production per m^3 of MCW.

4.2 Comparison of scenarios

Figure 5 shows the comparative environmental analysis of the evaluated scenarios (absolute values per category are reported in SM, Section 4, Tables S3 and S4). The current linear economy approach shows the worst performance for all the impact categories evaluated, except for ozone depletion potential (ODP), reporting an average improvement of 24.8 % when a strategy of valorisation of the wastewater as the circular economy scenario described in the present research work is applied.

FIGURE 5 AROUND HERE

The DSP is behind the worse performance of the circular economy scenario for ODP due to the chemical intensity of that stage (in particular the hypochlorite production is the main contributor for this category). Additionally, the use of sodium hydroxide for pH control in this scenario has also negative effects on ODP. Possible improvements and approaches for this issue will be discussed in section 5.3.

5 Discussion

5.1 Results obtained versus available literature

To the best of the author´s knowledge, only few papers have evaluated the environmental performance of MMC-based PHA production (Bengtsson et al., 2017; Fernández-Dacosta et al., 2015; Gurieff and Lant, 2007; Morgan-Sagastume et al., 2016; Vega et al., 2019), showing the scarcity of original data for the environmental validation of bio-based products and biorefineries. Moreover, conflicting conclusions have been reported (Hottle et al., 2013; Yates and Barlow, 2013), showing better environmental performances for GWP when PHA is compared to PE (Gurieff and Lant, 2007), but generally worse when compared to PET (Fernández-Dacosta et al., 2015).

Even when the impact assessment method and the categories selected are different in each reference, some comparisons can be done between the results reported here and values available in the literature. For example, Fernández-Dacosta et al. (2015) estimated a production of 2.06 kg CO_2-eq/kg biopolymer, while 3.51 kg CO_2-eq/kg biopolymer was found for the present study, being in the current literature range for MMC-based PHA. Although no absolute values were reported, Morgan-Sagastume et al. (2016) found impact reductions for GWP, AP, EP and POCP considering a volumetric unit of feedstock as FU. Their reduction values are higher than the ones found in the present study, although in their case DSP was out of the system boundaries.

Results suggest that the environmental and economic performance of PHA production can be highly enhanced if it is integrated in existing plants (WWTP, biodiesel plants, hydrogen production factories) adapting to seasonal and operational variations (Rodriguez-Perez et al., 2018), or combining the production of several by-products, as biogas or compost (Morgan-Sagastume et al., 2016; Vega et al., 2019). The present research work has assessed the potential environmental benefits of PHA production from boiling mussel wastewater combing real data from 2-year lab-scale operation and literature, responding to the urgent need of performing new studies that can help to understand the implications of the integration of PHA production processes in WWTP.

5.2 Benefits of process integration strategies

Energy consumption and DSP were identified in the past as bottlenecks for environmental and economic validation of PHA production (Fernández-Dacosta et al., 2015; Gurieff and Lant, 2007; López-Abelairas et al., 2015). Moreover, Fernández-Dacosta et al. (2015) pointed out the non-negligible impacts related to heating (through steam) in the fermenter unit to maintain adequate temperature for biological reactions, and identified DSP as the main contributor to GWP category and energy consumption (60 % of GWP impacts and 72 % of non-renewable energy use).

In this respect, process integration was applied in this study through the use of MCW excess energy in the DSP and for reactors heating, and through anaerobic digestion of the waste sludge. Therefore, no heat was supplied to maintain process temperature neither in the bioreactors nor in the DSP, saving approximately 500 kWh/day and 100 kWh/day, respectively.

Regarding DSP, energy consumption includes electricity and cooling energy (as heating energy is avoided, Table 4). It accounts for 54 % of the total energy consumed in the plant, while process integration saved about 15 % of the DSP needs, showing that an integral approach could improve process feasibility (environmentally, but also economically). There are only a few pilot-scale plants operating worldwide for PHA production from waste stocks (Mannina et al., 2020), and studies up-scaling PHA production with waste feedstocks are still scarce. Therefore, actual integration proposals are not yet specific and well defined, so potential environmental benefits arising from process integration and energy optimization are being disregarded from the assessment. This result shows a whole new path for the validation and for the technical, economic and environmental optimization of bio-based products, although case-by-case studies might be needed.

Concerning anaerobic digestion, although heat provided by the exhaust gases is enough to maintain the digester temperature, the effect of anaerobic digestion in the overall process performance is low, as most of the carbon present in MCW is employed for PHA production. However, the implementation of anaerobic digestion avoids the release of harming emissions linked to composting and generates electricity, enhancing the overall environmental performance.

Moving to another topic, the results obtained also confirm the environmental benefits of the combined production of PHA and biogas as reported by other authors, such as Vega et al. (2019), who assessed the environmental performance of centralized biorefineries to produce PHA and biogas using a mixture of cow manure and grape marc. This is linked to the idea of second generation biorefineries, in which several resource recovery methods are combined and different feedstocks can be treated, that is coming along as the future of bio-based products (Dietrich et al., 2017). Although some potential improvement strategies were not included in the present study due to uncertainties, they are mentioned here. First, the use of waste non-PHA biomass coming from the DSP was excluded from the environmental evaluation, although it contains carbon that could be used to improve biogas production. Second, the anaerobic digester could be eventually transformed into a secondary VFA provider, improving system productivity, and enhancing the plant capacity. Finally, the co-digestion of sludge and other wastes coming from local industries could stimulate biogas production and increase the economic and environmental benefits of the anaerobic digestion unit.

Finally, a centralized strategy was more beneficial than the current non-centralized approach, although the transport stage had relevant impacts that need to be considered before the centralized strategy is implemented (Figure 4b). Otherwise, the environmental benefit from the biorefinery process could be offset by the impacts of transportation (Vega et al., 2019).

5.3 Sensitivity analysis

Figure 5 reported a better environmental performance for the circular economy scenario, as its relative impacts are lower. In order to assess the robustness of those results, two decisions are evaluated here: the alternative defined for sludge management and the final PHA:PET equivalence (including extraction efficiency and replacement ratio).

Regarding the former, two new situations were modelled: anaerobic digestion without energy recovery and composting. The circular economy scenario is still a favourable alternative, even when no energy is recovered in the digester, compared to the current scenario (Figure 6) for eight of the ten categories, being only DAR the impact category that changes balance when no electricity is recovered (i.e. circular worse than linear based scenario), as the digester energy needs (basically stirring) are no longer covered by the biogas production. Direct emissions from the composting process and the removal of the benefits associated to energy recovery identified this alternative as the worse one, being the circular based scenario no longer the better option for DAR.

FIGURE 6 AROUND HERE

Concerning the latter, a replacement ratio (RR) PHA:PET of 1:1 was considered as no better approximation was available. That ratio is dependent of the yield strength and the density of the materials, and a recent study suggested that its value is of 0.93:1, i.e. 1 kg of PHA would replace 0.93 kg of conventional PET in the plastic market (Vega et al., 2019). Besides, ideal DSP efficiency was considered, that is to say, all the PHA entering the DSP process is effectively extracted during the process. However, this efficiency is hard to estimate and is dependent of several factors, such as the specific MMC used or the PHA content of the resultant stream (Mannina et al., 2019). Averaging the results reported by (Fernández-Dacosta et al., 2015) for PHA recovery yields using diverse DSP strategies, a value of 77.17 % is obtained. Combining this value with the RR of 0.93, a replacement yield PHA:PET of 0.72:1 (i.e. 0.72 kg of PET production is avoided by each kg of PHA extracted from the Circular Economy based Scenario) was applied and results are displayed in Figure 7.

FIGURE 7 AROUND HERE

The circular economy approach is still preferable to the non-centralized linear economy current scenario, as average improvements of 25 % were found for all categories except DAR and ODP. Not surprisingly, the worsening in fossil depletion category is linked to the lower amount of avoided product (PET), being this lower the environmental benefits of the circular economy approach are no longer present.

On the other hand, DSP is responsible for about 50 % of the impacts in the categories that do not show any improvement compared to the circular economy scenario (DAR and ODP). The significance of the DSP is not new (Gurieff and Lant, 2007; López-Abelairas et al., 2015). Due to this fact, new research works are stepping forward towards new eco-friendly and cost-effective extraction techniques, like the ones based on switchable anionic surfactants (Mannina et al., 2019). The implementation of these new techniques could improve even more the overall environmental response of the process and decrease the negative effects reported for ODP category. Moreover, the DSP was included in the present study as new results covering the whole PHA production process are demanded by the scientific community. However, the answer to solve the DSP question may be linked to the creation of regional networks in which WWTPs are high PHA-content biomass suppliers where the biopolymer is extracted in centralized facilities (Morgan-Sagastume et al., 2016).

5.4 Future outlook

PHA production from MCW is still under development and optimization and, at present, the overall process conversion is relatively low (0.2 g COD_{PHA}/g COD fed). Increasing this process yield would increase environmental and economic benefits, and strategies such as the combination of several substrates for PHA production (wastewater from other industries, VFA coming from sludge management…) are potential ways to improve this efficiency (Rodriguez-Perez et al., 2018).

The present research work focuses on one single type of wastewater, the MCW. However, as stated in section 1, Galicia is responsible for about 80 % of the Spanish fish-canning production. Once the production of MMC-based PHA under high salinity is validated from a technical and environmental point of view, the possibilities are huge. One single fish-canning facility can produce about 3,300 m^3 of wastewater per day (Dirección Xeral de Calidade e Avaliación Ambiental, 2008a), so assuming 6 % of high strength effluent each facility could produce about 50 m^3/day of a PHA-rich stream (containing 380 kg PHA) on-site. Supposing 300 working days per year, and knowing that 7 of the top ten fish-canning companies (in production and incomes) are located in Galicia (Eleconomista.es, 2018), the annual regional potential is of 911 t PHA/year, which is near the minimum value reported by Bengtsson et al. (2017) for economic feasibility. Four of these fish-canning plants are separated less than 25 km, although the longest distance among facilities is of 100 km. Therefore, DSP can be centralised for an optimized environmental and economic performance of bio-based products, opening an unexplored scenario where technical, economic and environmental issues need to be studied.

Finally, one challenge that is being faced by plastics and bioplastics industry is related to end of life options (Geyer et al., 2017). Due to the lack of information, this study has excluded them. Recent research works point out that mechanical recycling is preferable to composting, incineration or landfilling for bio-based materials (Changwichan et al., 2018). However, the effects of plastic litter in the water bodies, especially in the ocean, are still unknown, and the actual effects of plastic pollution worldwide are uncertain. Initiatives such as Plastic Leak Project[9] or MarILCA[10] will allow for better metrics to account for plastic leakage and to integrate potential environmental impacts of marine litter, especially plastic, in LCA results.

6 Conclusions

The renewable origin of bio-based plastics does not convert them automatically in an environmentally sustainable products and, even when is clear that they are promising materials, the environmental assessments comparing conventional plastics and bioplastics do not always show explicit benefits.

This study presents a detailed analysis of the environmental performance of PHA production from industrial wastewater, an area in which the LCA studies are still scarce. The current linear economy approach for mussel cooking wastewater management (generation – treatment – discharge) was compared with a circular economy approach, where PHA is

[9] https://quantis-intl.com/strategy/collaborative-initiatives/plastic-leak-project/
[10] http://marilca.org/

produced and wastewater is safely treated and discharged. A better environmental performance was reported for nine out of the ten impact categories under evaluation, which reflects the potential benefits of this novel approach. Process optimization through innovative systems (like anammox reactors for nitrogen removal) come along as preferred choices to improve overall performance (effluent quality and energy optimization).

The potential of bioplastics production processes is huge, although case-by-case studies are needed, evaluating the local industries and waste streams availability, as well as PHA and biogas yield for every feedstock. This study showed that the feasibility of producing added-value bioproducts under a circular economy approach is linked to the integral vision of the process, where all streams are valorised, and energy use is optimized. Finally, the potential of Galician region for bioplastics production was estimated near 1 kt PHA/year, near the threshold value for economic feasibility. Accordingly, centralized extraction facilities employing novel extraction protocols could be the key for the environmental validation and the economic viability of these products, stepping towards high-scale PHA production from mixed microbial cultures.

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