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Assessing of the most appropriate biotechnological strategy on the recovery of antioxidants from beet wastes by applying the life cycle assessment (LCA) methodology



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ABSTRACT

The valorization of agro-industrial waste streams and residues for the production of antioxidant compounds is a good strategy for circular economy approaches. However, to demonstrate its suitability and operational feasibility, it is necessary to develop environmental assessments to ensure the effectiveness of the production strategy. In this sense, a large-scale simulation has been developed, obtaining ten different scenarios in which both leaves and steam residues are used as process inputs, and five different extraction techniques are applied, both conventional: Soxhlet and maceration, and emerging technologies: ultrasonic assisted extraction (UAE), supercritical fluid extraction (SFE) and pressurized liquid extraction, (PLE). Environmental results have shown that SFE and PLE technologies have the lowest environmental burdens, while UAE has the worst profile due to high energy demand. Electricity could be considered as the main hotspot with the highest impact, followed by steam requirements and the use of extraction solvent. To improve the environmental profile, sensitivity analyses were performed, considering the use of renewable resources for the production of the energy requirements and the selection of the extraction solvent. Although significant improvements were obtained when electricity and steam production is based on hydropower and waste incineration, the environmental profile did not improve when considering ethanol: water mixture or hexane for extraction. Future research should focus on reducing energy requirements and optimizing the solvent dosage for the extraction process.

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1. Introduction

Demand for agricultural products by 2050 is expected to increase by 50% compared to current levels (Ramírez-Pulido et al., 2021), which is likely to lead to higher amounts of waste and side streams. Agricultural residues are the sum of crop losses, material unacceptable for market or consumption, industrial side streams, and food waste from consumers and services (Fritsch et al., 2017). It is estimated that one third of all food produced along the food chain is managed as waste (Bedoić et al., 2019), amounting to more than 1.3 billion tons per year (Gustavsson et al., 2011). In this sense, significant efforts have been made in the development of valorization strategies for food residues and waste aiming at closing the loop to produce high value-added compounds (Sepúlveda et al., 2018). Although the most widespread uses of these secondary streams are animal feed or biofuel production, they could potentially be used as resources for the

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Table 1 – Main process conditions, yields and antioxidant capacities of the scenarios proposed (Battistella Lasta et al., 2019; Lasta et al., 2019).

Scenario	Process conditions	Yield and antioxidant capacity
So_L	Solvent: ethanol Ratio: 1:30 (w/v) Process time: 8 h Room temperature	Yield: 21% (w/w) TPC: 47 mg GAE/g extract EC ₅₀ : 302 µg/mL TEAC: 586 µmol Trolox/g extract PR: 182 µg/mL
So_S	Solvent: ethanol Ratio: 1:30 (g:mL solvent) Process time: 8 h Room temperature	Yield: 9% (w/w) TPC: 55 mg GAE/g extract EC ₅₀ : 59.4 g/mL TEAC: 730 µmol Trolox/g extract PR: 63 µg/mL
M_L	Solvent: ethanol Ratio: 1:5 (w/v) Process time: 96 h Room temperature	Yield 1.6% (w/w) TPC: 21.3 mg GAE/g extract EC ₅₀ : 139 g/mL TEAC: 254 µmol Trolox/g extract PR: 259 µg/mL
M_S	Solvent: ethanol Ratio: 1:5 (w/v) Process time: 96 h Room temperature	Yield 5% (w/w) TPC: 22 mg GAE/g extract EC ₅₀ : 518 g/mL TEAC: 11 µmol Trolox/g extract PR: 163 µg/mL
-	: L, beet leaves; S, beet s nd M, maceration.	stalk residues, So, Soxhlet ex-

extraction of bioactive compounds and antioxidants, used as functional and natural additives in the food, cosmetic and pharmaceutical sectors (Akao, 2018).

Vegetables are outstanding sources of bioactive compounds and antioxidants. One of the antioxidant compounds that are predominant in vegetables, such as beet, are phenolics and betalains. The most abundant phenolic compound in beet is gallic acid, with health benefits, including anti-inflammatory, antioxidant and metabolic functions (Baião et al., 2020). However, other compounds may also be present: chlorogenic and syringic acids, quercetin, *p*-hydroxybenzoic and *p*-coumaric acids (Singh et al., 2019). As for betalains, their presence in beet is remarkable (Sigwela et al., 2021) and are considered one of the ten most potent natural antioxidants (Carrillo et al., 2017) and the most effective inhibitor of lipid peroxidation (Singh et al., 2019). In addition, betalains also have potent anticancer, antibacterial and anti-inflammatory properties, making them potential bioactive compounds (Fu et al., 2020).

The thermotolerance and thermodynamic stability of these compounds must be taken into account when developing a strategy for the extraction and recovery of antioxidant compounds from beet residues and secondary streams. Conventional extraction methods, such as Soxhlet and maceration, are widespread; however, environmental awareness has led to the search for new extraction technologies with better environmental profile and efficiency, named as "green emerging technologies". In this manuscript, ultrasound assisted extraction (UAE), supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) have been selected as green methods for the extraction of antioxidants from beet residues, as both have shown promising results in terms of yield and process productivity (Nirmal et al., 2021). Despite the interest in the extraction and recovery of bioactive compounds and antioxidants from agricultural residues, most research has been conducted at laboratory scale. On the other hand, when looking for a new biotechnological route to be implemented, it is important to demonstrate its technical feasibility, as well as to estimate its environmental burdens, i.e., how this new approach could "help the environment" with the recovery and use of these waste streams, whether it could be considered as a sustainability approach and how much the environmental burdens are being reduced.

In this sense, the aim of this manuscript is to perform the process modeling of the envisioned scale-up process of different methods of antioxidant extraction from beet residues, both leaves and stems, seeking to evaluate which of them is the most efficient in terms of performance and most environmentally friendly. For this purpose, a production capacity with an input of 100 kg/batch of beet waste was considered, using the SuperPro Designer tool to simulate the process. The results of the modeling stage will provide data for the Life Cycle Inventory. Life cycle assessment (LCA) has been selected as a suitable methodology to analyze the environmental profile of the different process schemes. In addition, to evaluate the cost-effectiveness of the proposed extraction methods, the operating costs of the whole production process will also be considered.

2. Methods

2.1. Process simulation

One of the critical challenges in undertaking sustainable process design is the lack of information on full-scale process. In response to this challenge, multi-criteria assessment needs to be addressed at the early stages. It can be used to evaluate and support the decision-making process in process design, as well as to propose improvement actions. In this regard, ten antioxidant recovery scenarios have been proposed and simulated with the SuperPro Designer tool, five of them for beet root residues and the rest for beet leaf residues. Regarding conventional extraction methods, both Soxhlet and maceration, which are the most widespread (Lasta et al., 2019), have been simulated. Seeking to provide more environmentally friendly and efficient approaches, emerging technologies of UAE, SFE with CO2 and PLE have been proposed (Battistella et al., 2019). Thus, by approaching the results from a comparative point of view, not only the environmental loads, but also the antioxidant production capacity will be evaluated. For the development of the largescale simulation, laboratory-scale literature data have been used, based on the treatment of 100 kg of beet residues per batch. The most important values considered for each of the extraction methodologies strategies are shown in Table 1.

The process scheme of Soxhlet, maceration, UAE and PLE are analogous: they are based on a tray drying to reduce the water content of the beet residues (Fig. 1). Before extraction, it is necessary to cut the biomass to reduce its size. It is well known that the smaller the particle size, the higher the yield. The extraction stage has been modeled according to a stoichiometric reaction. In this stage, the operating conditions shown in Table 1 and Table 2 have been considered. Once the residence time for the extraction has been reached, the separation of the biomass is performed using microfiltration equipment, followed by solvent recovery by multi-effect evaporation, and the final formulation of the extract using

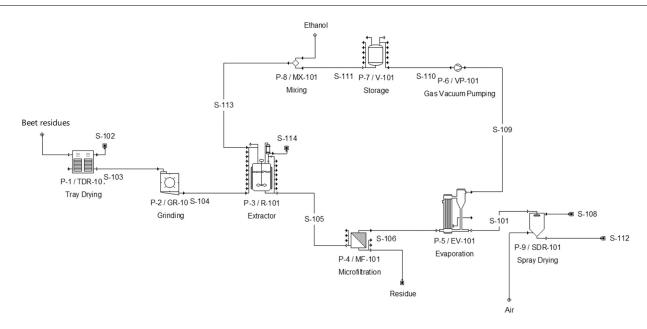


Fig. 1 - Soxhlet, maceration, UAE and PLE simulation with SuperPro Designer tool.

Table 2 – Main process conditions, yields and antioxidant capacities of the scenarios proposed (Battistella et al., 2019; Lasta et al., 2019).

Scenario	Process conditions	Yield and antioxidant capacity
UAE_L	Solvent: ethanol Ratio: 1:30 (w/v) Process time: 7 min Room temperature 500 W sonication power	Yield: 4.04% (w/w) TPC: 73 mg GAE/g extract EC ₅₀ : 139 g/mL TEAC: 275 µmol Trolox/g extract PR: 384 µg/mL
UAE_S	Solvent: ethanol Ratio: 1:30 (w/v) Process time: 7 min Room temperature 500 W sonication power	Yield: 4.7% (w/w) TPC: 33 mg GAE/g extract EC ₅₀ : 1147 g/mL TEAC: 83 µmol Trolox/g extract PR: 30 µg/mL
SFE_L	Solvent: CO ₂ + 10% ethanol:water 0.5 kg CO ₂ /h Process time: 4 h 250 bar, 40 °C	Yield: 14.45% (w/w) TPC: 11 mg GAE/g extract EC ₅₀ : 150 g/mL TEAC: 157 µmol Trolox/g extract PR: 71 µg/mL
SFE_S	Solvent: CO ₂ + 10% ethanol:water 0.5 kg CO ₂ /h Process time: 4 h 250 bar, 40 °C	Yield: 6% (w/w) TPC: 23 mg GAE/g extract EC ₅₀ : 738 g/mL TEAC: 137 µmol Trolox/g extract PR: 70 µg/mL
PLE_L	Solvent: ethanol 3 mL/min Process time: 90 min 10 MPa, 40 °C	Yield: 12.3% (w/w) TPC: 252 mg GAE/g extract EC ₅₀ : 65 g/mL TEAC: 400 µmol Trolox/g extract PR: 275 µg/mL
PLE_S	Solvent: ethanol 3 mL/min Process time: 90 min 10 MPa, 40 °C	Yield: 9.9% (w/w) TPC: N/D EC ₅₀ : 16 g/mL TEAC: 49.7 μmol Trolox/g extract PR: 18 μg/mL
Acronyms	: L, beet leaves; S, beet st	alk residues, So, Soxhlet ex-

Acronyms: L, beet leaves; S, beet stalk residues, So, Soxhlet extraction and M, maceration. spray drying equipment to obtain a powder with a purity of 95%.

Several differences can be distinguished in the simulation of the SFE scenarios (Fig. 2). The extraction is based on the use of pressurized CO₂, which is subsequently recovered by flash evaporation. As for the latter drying process, spray drying is not considered due to the low moisture content of the extract, so drum drying equipment is used.

The facility operates 330 days per year with 30 days for maintenance activities. Thus, the amount of antioxidant produced depends on the yields and batch times required for each of the proposed extraction schemes. In this regard, the capacity and the amount of the product for each scenario are shown in Table 3. The detailed capacities of process equipment are included in Table 4.

2.2. Environmental assessment

LCA methodology has been used to assess the environmental loads of the extraction alternatives, with the aim of identifying the most promising valorization route under an environmental point of view. The data required for the life cycle inventories have been obtained by process simulation with the SuperPro Designer software. In order to improve the impact results, the main hotspots of the process will be identified, with the development of the subsequent sensitivity analysis.

2.2.1. Definition of the LCA

The functional unit (FU) selected for the evaluation was the production of 1 g of antioxidant extract, with a purity of 95%, in line with other related studies for the extraction of polyphenols (Barjoveanu et al., 2020). The production capacity of the simulated facilities is identical for all scenarios: 100 kg beet residues/batch. As for the system boundaries, a "cradle to gate" approach has been considered, covering all stages between the extraction of inputs and consumables and the production of the final product, including emissions and waste streams. Regarding the calculation methodologies used to carry out the environmental profiles, two have been

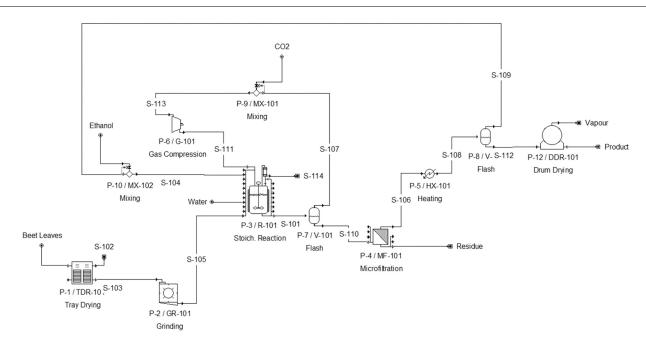


Fig. 2 - SFE simulation with SuperPro Designer tool.

Table 3 – Batch time, number of batches per year and antioxidant production capacity for each of the scenarios under assessment.

Scenario	Batch time (h)	Number of batches per year	Antioxidant production (kg/year)
So_L	18.55	913	1620.51
So_S	18.55	913	696.16
M_L	106.31	82	12.81
M_S	106.31	82	39.77
UAE_L	11.12	1319	452.60
UAE_S	11.12	1319	526.44
SFE_L	15.00	1318	1964.65
SFE_S	15.00	1318	818.55
PLE_L	12.50	1318	1397.96
PLE_S	12.50	1318	1126.57

selected: CML-IA Baseline V3.05/EU25 for midpoint impact categories as depicted in Table 5 and ReCiPe 2016 EndPoint (H) V1.03 World (2010) H/H for endpoint impact categories:

Human Health (HH), Ecosystem Quality (EQ) and Resource Scarcity (RS), which are reported as a single score for the sum of the three.

2.2.2. Life cycle inventories

The overall balance of mass and energy components required within the antioxidant production process are presented in Table 1-10 in the Supplementary Material. All data provided refer to the selected FU: 1g of antioxidant-rich powder. The simulation of the production process has been developed according to laboratory data, so the transport activities have not been considered within the environmental assessment, assuming that the process is delocalized. For the selection of the database, it is necessary to use a database that provides all secondary data corresponding to the background activities of all inputs, such as solvent or beet residues, utilities (i.e., steam and cooling water), and waste streams such as exhausted biomass and the gas stream from the drying stages. In this regard, the Ecoinvent V3.2 database has been selected.

Table 4 – Detailed capacity of process equipment.										
Equipment	Capacity									
	So_L	So_S	M_L	M_S	UAE_L	UAE_S	SFE_L	SFE_S	PLE_L	PLE_S
Compressor (kW)	-	-	-	-	-	-	0.07	0.07	-	-
Drum dryer (m ²)	-	-	-	-	-	-	0.02	0.02	-	-
Flash drum (L)	-	-	-	-	-	-	1.80	0.33	-	-
Grinder (kg/h)	1.24	1.24	0.11	0.11	1.78	1.78	1.78	1.78	1.78	1.78
Microfilter (m ²)	3,13	3.15	0.59	0.59	3.16	3.16	0.03	0.02	1.90	1.90
Mixer (kg/h)	27.42	27.61	0.40	0.40	40.01	39.99	0.51	0.51	23.20	23.20
Multi-effect evaporator (m ²)	0.02	0.02	0.01	0.01	0.02	0.02	-	-	0.01	0.01
Tank (L)	256.82	259.36	49.54	49.54	260.41	260.27	-	-	157.94	158.34
Spray dryer (L)	19.31	171.48	0.28	0.28	173.22	172.99	-	-	72.34	71.13
Extractor (L)	347.45	349.95	66.24	66.24	350.98	350.85	11.67	11.67	211.57	211.57
Tray dryer (m²)	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	6.08
Vacuum pump (kW)	1.87	2.13	0.03	0.03	3.10	3.09	-	-	1.88	1.88

 Table 5 – CML-IA Baseline impact categories considered for the environmental assessment of the proposed extraction scenarios.

 Acronym
 Impact category
 Acronym
 Impact category

 AD
 Abiotic Depletion
 MET
 Marine Aquatic Ecotoxicity

AD	Abiotic Depletion	MET	Marine Aquatic Ecotoxicity
ADF	Abiotic Depletion-Fossil Fuels	TET	Terrestrial Ecotoxicity
GWP	Global Warming Potential	PO	Photochemical Oxidation
ODP	Ozone Layer Depletion	AC	Acidification
HT	Human Toxicity	EP	Eutrophication
FET	Freshwater Aquatic Ecotoxicity		

Table 6 – Characterization values of the scenarios assessed for the extraction of antioxidant compounds from beet residues valorization.

	Unit	S_L	S_S	M_L	M_S	UAE_L	UAE_S	SFE_L	SFE_S	PLE_L
AD	mg Sb eq	0.05	0.09	0.16	0.07	0.77	0.75	0.07	0.09	0.06
ADF	MJ	1.96	4.66	4.77	1.7	15.24	14.07	2.23	2.48	0.75
GWP	kg CO ₂ eq	0.09	0.2	0.3	0.11	0.9	0.85	0.11	0.13	0.06
ODP	mg CFC-11 eq	0.01	0.01	0.03	0.01	0.08	0.08	0.01	0.01	0.01
HT	kg 1.4-DB eq	0.02	0.03	0.04	0.02	0.25	0.24	0.02	0.03	0.02
FET	kg 1.4-DB eq	0.02	0.03	0.03	0.02	0.31	0.31	0.02	0.03	0.02
MET	kg 1.4-DB eq	59.4	91.7	102	56.9	1004	992.5	77.14	93.47	75.94
TET	mg 1.4-DB eq	16.5	11.8	-213	-54.5	569.6	576.6	15.51	13.54	19.37
PO	g C ₂ H ₄ eq	3.65	8.71	1.05	1	19.64	16.88	2.49	3.03	0.01
AC	g SO ₂ eq	0.33	0.66	1.1	0.42	3.58	3.43	0.41	0.49	0.27
EP	g PO4 ²⁻ eq	0.17	0.31	0.52	0.22	2.27	2.21	0.22	0.27	0.18

2.2.3. Sensitivity analysis

To improve the environmental profiles and impact results obtained for the scenarios proposed, sensitivity analyses will be conducted for the main hot spots identified. For the scenarios in which energy requirements are the main hotspots, the use of renewable resources will be proposed, for those in which the solvent is one of the main contributors to the environmental profile, the use of other efficient extractive agents will be evaluated, as is the case of the ethanol:water mixture or hexane (Chemat et al., 2020).

3. Results

In order to evaluate which of the extraction procedures is the best alternative, from an environmental point of view, an analysis of the profiles obtained for each of the proposed scenarios has been developed. With this evaluation, it has been possible to identify the main contributors to the impact values, i.e., hotspots, where improvements actions should be considered to reduce environmental impacts.

3.1. Environmental profile of Soxhlet extraction scenarios

The environmental profile of antioxidant production using leaf and stem residues, applying Soxhlet extraction technology, is illustrated in Fig. 3. The acronyms L and S represent leaves and stems, respectively. As can be seen, the difference between using leaves or stems as input resources is not so significant, as this variation depends directly on the extraction yield value, with no other difference in the process scheme. Three main hotspots could be identified in the environmental profile obtained. The one that stands out the most is electricity, being the largest contributor in the impact categories related to toxicity (HT, FET, MET and TET), while in the case of abiotic depletion (AD and ADF) and global warming potential (GWP) it is the solvent used: ethanol, that entails the greatest impact. In the case of steam requirements, it ranks third among the hotspots, with the largest contribution in the ODP impact category.

On the other hand, the environmental contribution of beet waste in the TET impact category is remarkable. The negative value can be considered as an environmental credit and is justified based on the strategy of valorization of beet waste as a resource to produce antioxidants, which avoids the equivalent external process to produce a similar amount of the target product.

Process emissions have their environmental contribution in the OP category, with a value close to 100%, which is attributed to ethanol emissions. Although the negative impact of VOCs on the atmosphere is well known, it is important to mention that ethanol is classified as a category B compound, indicating a low hazard.

3.2. Environmental profile of maceration extraction scenarios

The environmental results of the maceration extraction scenarios are shown in Fig. 4. As observed for Soxhlet extraction, the use of leaves or stems does not imply significant contribution differences in the environmental profile obtained. However, there are significant differences with

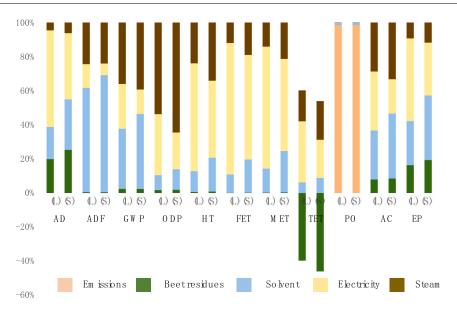


Fig. 3 – Environmental impacts of Soxhlet extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

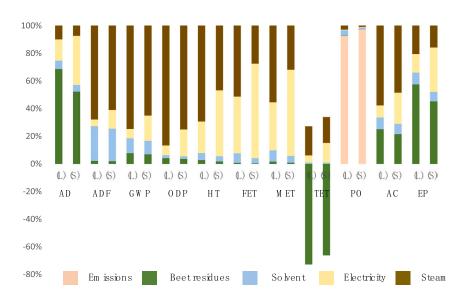


Fig. 4 – Environmental impacts of maceration extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

respect to the energy needs. While in Soxhlet scenario it was electricity the main hotspot, in maceration one the impact of steam is the one that stands out the most.

The use of steam produced from non-renewable resources could be considered, as it is observed that GWP, ADF and ODP are the most affected categories, which is directly related to the use of fossil fuels and CO_2 emissions. To improve the profile, the possibility of obtaining steam from renewable resources would be desirable. This option will be considered when developing the sensitivity assessment.

As observed in Fig. 4, the solvent contribution is not as significant as in the Soxhlet one. The reason is based on the solute:solvent ratio required for the maceration extraction: 1:5, much lower in contrast to that of Soxhlet: 1:30. This lower solvent consumption leads to a minor contribution to the environmental profile.

Moreover, as far as beet residues are concerned, their contribution is higher in the AD, AC and EP categories. This can be explained in terms of the yield value, which is much lower compared to Soxhlet extraction, meaning that, to produce the same amount of antioxidant, i.e., 1g, a higher amount of beet residues is required, so their contribution to the environmental profile will also be higher. Accordingly, production capacity and overall process yield are key factors in the search for improved environmental profiles and in the selection of the most environmentally suitable alternative.

3.3. Environmental profile of ultrasound assisted extraction (UAE) scenarios

The outcomes of the UAE process do not provide the highest yields (Table 1), but as for the PLE process, it entails the best

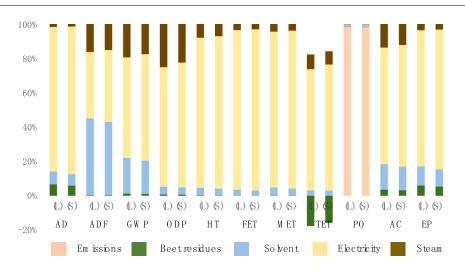


Fig. 5 – Environmental impacts of UAE scenarios expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

antioxidant results in terms of TPC, TEAC and PR values. The EC_{50} value, which represents the effective concentration of the extract to achieve 50% of the antioxidant potential, should be as low as possible for a better antioxidant potential, and quite small values are obtained when developing the UAE technology. Another fact to consider is the extraction time of the UAE process, only 7 min are required for the extraction of the antioxidant compounds. This small residence time allows for a significantly higher number of batches per year, which will increase the annual production capacity of the facilities.

The environmental profile of the UAE scenarios developed for leaves and stems is illustrated in Fig. 5. As expected, the impact of electricity requirements is the one that stands out, mainly in all impact categories, as UAE is a highly energy demanding technology. The best way to reduce its impact would be to apply renewable resources to produce electricity, instead of using fossil resources. In addition to electricity, the impact on the use of solvents is also appreciable in the ADF category. The reason for this impact contribution is the result of the background activities associated with the production of the solvent, which is based on the use of fossil resources and non-renewable materials.

3.4. Environmental profile of supercritical fluid extraction (SFE) scenarios

Carbon dioxide, along with ethanol and water, is the main solvent used in SFE, which requires a pressure of 250 bar and a residence time of 4 h. As in the previous profiles, the contribution of electricity requirements remains significant, being the main hotspot in most impact categories, except for ADF, GWP and ODP, where the contribution of steam is also significant (Fig. 6).

Comparing the SFE environmental profile with the previous ones assessed, two main differences can be identified.

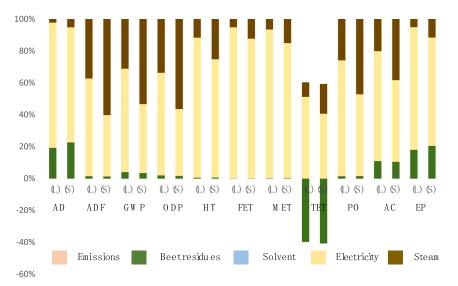


Fig. 6 – Environmental impacts of SFE scenarios expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

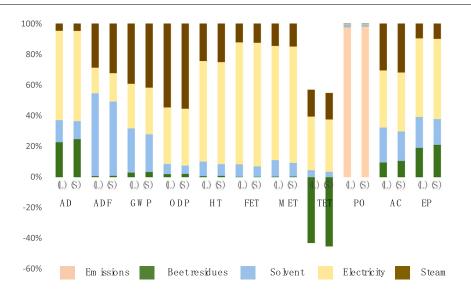


Fig. 7 – Environmental impacts of PLE scenarios expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

First, the lack of emissions impact, due to the use of CO_2 as the main solvent, which is mostly recycled to the process, avoiding on-site emissions from the process and solvent inputs. Secondly, as the amount of ethanol used in the SFE is very low, the output of ethanol in the waste and secondary streams is also small, which implies that the environmental contribution of these is not substantial.

On the other hand, it can also be seen that, when comparing the environmental contribution of the components when leaves or stems are used as the main input, the differences are greater than in the previous scenarios. This fact could be explained by the yield results obtained for each of them, while the yield for leaves amounts to 14.45%, the values decrease to 6% for stems.

3.5. Environmental profile of pressurized liquid extraction (PLE) scenarios

When selecting an extraction alternative, it is not only the environmental profile that must be taken into account, but also the characteristics of the product obtained, in this case, its properties and antioxidant capacity. It is in the case of PLE where the best values of antioxidant capacity of the extracted product are obtained, according to the data included in Tables 1 and 2. In this case, the environmental contribution of the solvent, ethanol with a flow rate of 9 mL/min, is observable in mainly all the impact categories, being ADF and GWP the most relevant. The fact that this chemical compound is produced by using fossil resources and nonrenewable compounds is the main reason for this contribution. One possibility to reduce its environmental impact would be related to the use of bioethanol produced by renewable resources. Considering the operation conditions: 40°C, 10 MPa and incubation time of 90 min, energy requirements lead to the largest environmental contribution. In the case of ODP, the use of steam as a heat source has the greatest influence, representing approximately 50% of the total impact. On the other hand, the release of residues and side streams with a residual content of solvent also affects the PO impact category, even though most of the ethanol is recycled to the extractor after the separation and evaporation stages. The use of beet residues to produce antioxidants leads to environmental benefits in the TET impact category, reducing the impact by approximately 50%. In order to achieve a better environmental profile, with a lower contribution of electricity consumption, it would be desirable to optimize the extraction process and reducing the residence time as well as using renewable energy sources.

3.6. Best extraction alternative?

For identifying the best alternative for the valorization of beet wastes as inputs for the extraction of antioxidants, several aspects will be considered: the yields of antioxidant recovery, the production capacity, and the environmental impacts. The PLE technology is the one that obtains the best antioxidant capacity values, reaching a value of 65 and 16 g/L for leaves and stems, respectively. It is also with this extraction method that, together with SFE and Soxhlet, the highest production capacity is achieved, with more than 1000 kg/year of antioxidant. Regarding environmental values, there is one technology that could be identified as having the greatest contribution to environmental impact (Table 4): UAE. Even though in terms of production and antioxidant capacities the results are promising, the high energy demand for the extraction process implies an environmental impact. Significant improvements, in terms of energy consumption, are necessary if better environmental results are to be achieved for this scenario.

Although there are no major differences when comparing the remaining alternative extraction process scenarios, two of them can be identified as having the lowest environmental

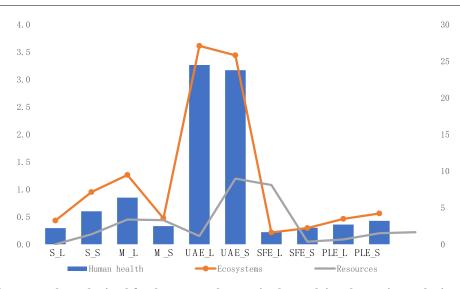


Fig. 8 - Single score values obtained for the assessed scenarios by applying the ReCiPe EndPoint methodology.

impact and, therefore, can be considered the most efficient in environmental terms. This is the case of the SFE and PLE technologies, whose impact values are quite similar, although certain differences are observed. The most significant variations are observed in the ADF impact category, where the impact value of SFE is 1.48 times and 1.29 times higher for leaves and stems, respectively, in TET, the impact of the PLE scenario being almost 9 points higher for the valorization of beet stems, and in the PO category, where the impact value of SFE is up to 3 times higher (Table 4).

The characterization of the scenarios considering the ReCiPe Endpoint methodology, to achieve a single score value encompassing the three main damage categories; human health, resource scarcity and ecosystem quality, have shown similar trends with respect to the previous environmental assessment (Fig. 8). The UAE scenarios have the highest environmental single score value, significantly higher compared to the other extraction technologies. On the other hand, certain differences could be identified when comparing leaves and stems as renewable resources for the extraction of antioxidant compounds, with the use of stems having the highest environmental impact in all the proposed scenarios, except for the maceration scenarios, where the use of leaves entails the highest impact. Looking for the best extraction alternative, both SFE and PLE could be defined as the most promising, since their environmental impact values are the lowest.

3.7. Sensitivity analysis for better environmental profiles

With the aim of improving the environmental profiles of the scenarios presented, sensitivity analyses have been performed focusing on the main hotspots identified for each of the alternatives evaluated. As the main hotspot is electricity, the substitution of fossil resources by hydroelectric power is an option to consider. To evaluate the improvements of the sensitivity scenarios, the normalization values of the baseline CML methodology have been used, obtaining a score that is the result of the sum of all the impact categories that were included in the baseline environmental profiles (Fig. 9). The best results were obtained for the SFE and UAE technologies, as expected, since they have the highest electricity demand. However, significant improvements were also obtained in the other scenarios, with reduction values between 26% and 64%.

In addition to electricity, other hotspots have also been identified. In the case of maceration, PLE and SFE technologies, the use of steam also has an important environmental contribution of the profiles. Heat would be obtained from waste resources, by incineration, which have a heat capacity of 12 MJ/kg of incinerated biowaste. Among the three technologies, it was the maceration the one with the highest impact contribution of steam, so the improvement of environmental impacts is also the highest for this alternative, reaching reduction values of 52% for the valorization of beet leaves and 30% for beet stems. In the case of PLE, the reduction is analogous for these types of waste, with a reduction of 12%, but, for SFE, a reduction of 18% in impacts has been obtained when considering beet stems as a resource for the extraction of antioxidants, while only 8% when using beet leaves.

Finally, in the case of PLE and Soxhlet technologies, it has also been identified that the solvent used is an important environmental contributor on the profile. In the case of PLE, the use of hexane instead of ethanol has also been tested, obtaining also good results in the antioxidant values of the extracted compounds. Thus, ethanol was replaced by hexane to evaluate whether the environmental profile could be improved, but only a reduction of 4% and 3% was obtained for beet leaves and stems, respectively. Similarly with Soxhlet, the use of an ethanol:water mixture also provides good extraction yields, but impact reductions of less than 5% have been obtained, concluding that there is not much difference between the profiles.

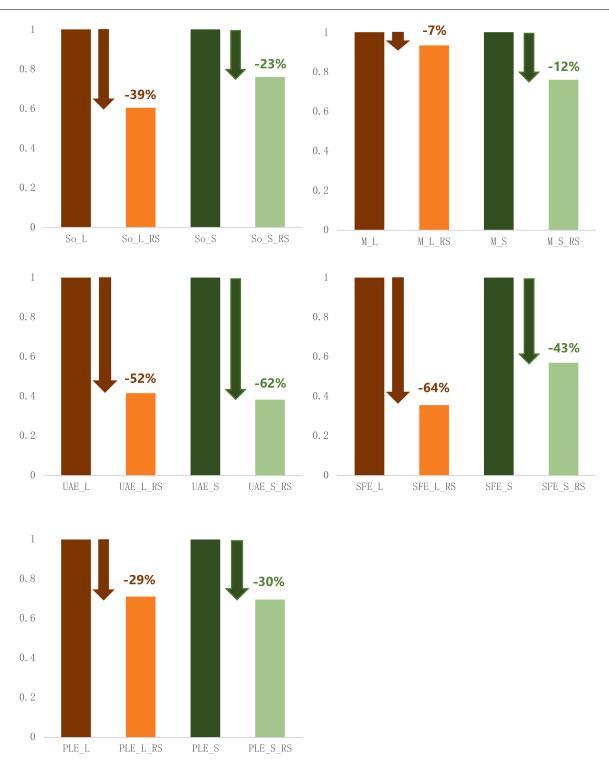


Fig. 9 – Sensitivity analysis based on the use of alternative source for electricity requirements. Acronym RS refers to the scenario of the renewable resource for electricity production.

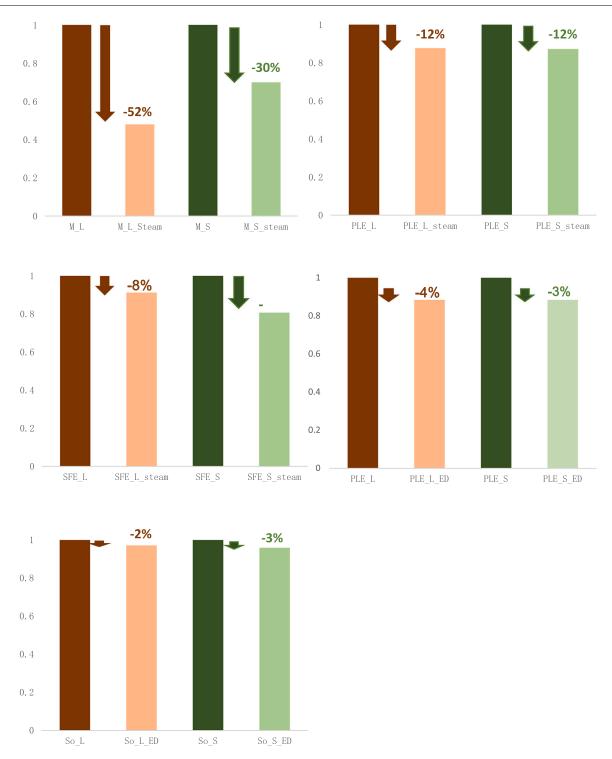


Fig. 10 – Sensitivity analysis based on the use of alternative source for steam requirements and modification on solvent characteristics. Acronyms: Steam is the scenario of the waste resource for steam production and ED to the solvent modification.

4. Discussion and conclusions

This report has been based on the evaluation and assessment of different extraction technologies for the valorization of beet wastes as resources for the extraction of antioxidants. Both beet leaves and stems have been considered as process inputs, with the use of five extraction technologies, two conventional: Soxhlet and maceration, and three green technologies; UAE, PLE and SFE. To develop the environmental assessment, the LCA methodology has been used, which requires obtaining input and output data. These values were obtained by performing a large-scale simulation of the scenarios from laboratory-scale literature data, using the SuperPro Designer tool, and considering a production capacity of 100 kg/batch of beet waste. The environmental profiles and impact values obtained have revealed that the best extraction techniques are SFE and PLE, as they have the lowest environmental load. In the case of UAE, significant improvements are needed, as huge environmental values are obtained, mainly due to the high electricity demand required for the extraction process. On the other hand, the LCA results have pointed out that the main hotspot was electricity demand, followed by steam requirements and solvent production. Thus, sensitivity analyses were performed, considering the use of renewable resources, in the case of energy needs, and modifications in the solvent. Significant improvements were obtained when hydroelectric energy is considered as a renewable resource for electricity production and when steam is obtained as a result of municipal waste incineration. However, in the case of the solvent, the use of hexane or an ethanol:water mixture does not lead to interesting improvements in the impact values obtained, so, in this case, future research work should focus on trying to reduce the solvent dosage required for the extraction step.

As a conclusion, it could be said that the results of this research confirm the potentiality of beet wastes as valuable resources for the extraction of antioxidant compounds and the validity of green technologies as extraction techniques to replace conventional ones such as maceration or Soxhlet.

CRediT authorship contribution statement

A. Arias: Methodology, Formal analysis, Investigation, Writing – original draft. G. Feijoo: Writing – review & editing.
M.T. Moreira: Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ana Arias reports financial support was provided by Spain Ministry of Science and Innovation.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fbp.2022.08.003.

References

- Akao, S., 2018. Nitrogen, phosphorus, and antioxidant contents in crop residues for potential cascade utilization. Waste Biomass Valoriz. 9, 1535–1542. https://doi.org/10.1007/S12649–017-9929–6/.
- Baião, D., dos S., da Silva, D.V.T., Paschoalin, V.M.F., 2020. Beetroot, a remarkable vegetable: its nitrate and phytochemical contents can be adjusted in novel formulations to benefit health and support cardiovascular disease therapies.

Antioxidants 9 (2020) 960 9, 960. https://doi.org/10.3390/ ANTIOX9100960.

- Barjoveanu, G., Pătrăuțanu, O.-A., Teodosiu, C., Volf, I., 2020. Life cycle assessment of polyphenols extraction processes from waste biomass. Sci. Rep. 101 10 (2020) 1–12. https://doi.org/10. 1038/s41598–020-70587-w.
- Battistella Lasta, H.F., Lentz, L., Gonçalves Rodrigues, L.G., Mezzomo, N., Vitali, L., Salvador Ferreira, S.R., 2019.
 Pressurized liquid extraction applied for the recovery of phenolic compounds from beetroot waste. Biocatal. Agric.
 Biotechnol. 21. https://doi.org/10.1016/J.BCAB.2019.101353
- Bedoić, R., Ćosić, B., Duić, N., 2019. Technical potential and geographic distribution of agricultural residues, co-products and by-products in the European Union. Sci. Total Environ. 686, 568–579. https://doi.org/10.1016/J.SCITOTENV.2019.05.219
- Carrillo, C., Rey, R., Hendrickx, M., María Del Mar Cavia, Alonso-Torre, S., 2017. Antioxidant capacity of beetroot: traditional vs novel approaches. Plant Foods Hum. Nutr. 72, 266–273. https:// doi.org/10.1007/s11130-017-0617-2
- Chemat, F., Abert Vian, M., Fabiano-Tixier, A.S., Nutrizio, M., Režek Jambrak, A., Munekata, P.E.S., Lorenzo, J.M., Barba, F.J., Binello, A., Cravotto, G., 2020. A review of sustainable and intensified techniques for extraction of food and natural products. Green Chem. 22, 2325–2353. https://doi.org/10.1039/ C9GC03878G
- Fritsch, C., Staebler, A., Happel, A., Angel Cubero Márquez, M., Aguiló-Aguayo, I., Abadias, M., Gallur, M., Maria Cigognini, I., Montanari, A., Jose López, M., Suárez-Estrella, F., Brunton, N., Luengo, E., Sisti, L., Ferri, M., Belotti, G., 2017. Processing, valorization and application of bio-waste derived compounds from potato, tomato, olive and cereals: a review. Sustainability 9, 1492. https://doi.org/10.3390/su9081492
- Fu, Y., Shi, J., Xie, S.Y., Zhang, T.Y., Soladoye, O.P., Aluko, R.E., 2020. Red beetroot betalains: perspectives on extraction, processing, and potential health benefits. J. Agric. Food Chem. 68, 11595–11611. https://doi.org/10.1021/ACS.JAFC.0C04241
- Gustavsson, J., Cederberg, C., Sonesson, U., Van Otterdijk, R., Meybeck, A., Rome, F., 2011. Cutting food waste to feed the world global food lossess and food waste. Interpack.
- Lasta, H.F.B., Lentz, L., Mezzomo, N., Ferreira, S.R.S., 2019.
 Supercritical CO₂ to recover extracts enriched in antioxidant compounds from beetroot aerial parts. Biocatal. Agric.
 Biotechnol. 19, 101169. https://doi.org/10.1016/J.BCAB.2019.
 101169
- Nirmal, N.P., Mereddy, R., Maqsood, S., 2021. Recent developments in emerging technologies for beetroot pigment extraction and its food applications. Food Chem. 356. https://doi.org/ 10.1016/J.FOODCHEM.2021.129611
- Ramírez-Pulido, B., Bas-Bellver, C., Betoret, N., Barrera, C., Seguí, L., 2021. Valorization of vegetable fresh-processing residues as functional powdered ingredients. A review on the potential impact of pretreatments and drying methods on bioactive compounds and their bioaccessibility. Front. Sustain. Food Syst. 5, 82. https://doi.org/10.3389/FSUFS.2021.654313/
- Sepúlveda, L., Romaní, A., Aguilar, C.N., Teixeira, J., 2018. Valorization of pineapple waste for the extraction of bioactive compounds and glycosides using autohydrolysis. Innov. Food Sci. Emerg. Technol. 47, 38–45. https://doi.org/10.1016/j.ifset. 2018.01.012
- Sigwela, V., De Wit, M., Du Toit, A., Osthoff, G., Hugo, A., 2021. Bioactive betalain extracts from cactus pear fruit pulp, beetroot tubers, and Amaranth leaves. Molecules 26 (16), 5012. https://doi.org/10.3390/molecules26
- Singh, N., Singh, A., Masih, D., 2019. Red beetroot: a source of natural colourant and antioxidants: a review. J. Pharmacogn. Phytochem. 8, 162–166.