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Abstract

Enhancing the environmental performance of production processes is currently a major issue. To propose efficient processes both in terms of productivity and environmental impacts, it is necessary to develop multi-objective optimization tools. Such an approach was developed in this study for an ultrasound-assisted extraction process, aiming at valorizing antioxidant polyphenols from downgraded beetroot seeds (agri-food by-product). Environmental impacts of the process (assessed using LCA), as well as classical productivity indicators (extraction yield, antioxidant activity of the extract, energy consumption) were all predicted in function of the varied process parameters (extraction time, solvent composition, solvent/beetroot seeds ratio, ultrasound power density). The proposed multi-criteria optimization tool allowed to predict optimal operating conditions in function of specific constraints, such as maximization of extraction yield and/or minimization of extraction time, energy consumption and/or environmental impacts. Maximal polyphenols concentration (2.8 g.L-1 GAE) and antioxidant activity (16.6 mM TEAC) were obtained after 120 min with 65% ethanol in the solvent, ultrasound power density of 667 W.L-1, and ratio of 5 mL.g-1. Ultrasounds assistance allowed extraction yield enhancement (up to 60%) of and process duration decrease (8 times), without degrading environmental performance. The original proposed methodology could easily be adapted for multi-criteria optimization of other processes.

Keywords

multi-objective optimization; environmental impacts; LCA; ultrasound-assisted extraction; antioxidant; by-product

1. Introduction

In climate change context and necessity to reduce environmental impacts, sustainability is the new aspect to be included in process engineering in addition to productivity and economic ones (Allen and Shonnard, 2001). Life Cycle Assessment (LCA), a standardized and recognized methodology, is a useful tool to evaluate as accurately as possible environmental impacts of processes, taking into account all life cycle steps (Curran, 2013; Jolliet et al., 2015).

In extraction field, it is a common practice to call “green processes” those that are innovative and eco-friendlier in the way they allow the reduction of time, energy, water and organic solvent consumptions, such as ultrasound-, microwave-, and electrically-assisted extractions, the extractions using ohmic, infrared or ultraviolet heating and those using pressurized fluids (Chemat et al., 2017a; Chemat and Cravotto, 2017; Chemat et al., 2020). The use of ultrasounds (US) has different effects on plant matrix that can lead to an increase in molecules extraction: fragmentation, detexturation, sonoporation, etc… (Chemat et al., 2017b; Khadraoui et al., 2018). Fragmentation of particles can be noticed with the naked eye and clearly impact extraction by increasing exchange area and consequently mass transfer. The sonoporation is a well-known effect of US and allow a permeability of cells’ membranes by breaking them due to shear forces generated locally at the collapse of cavitation bubbles (Khayamian et al., 2018; Lentacker et al., 2014). Ultrasound-assisted extraction (UAE) technology was successfully used for extraction of various valuable compounds, such as antioxidant polyphenols (Chemat et al., 2017b).

These valuable molecules could be useful as natural preservatives in food and cosmetic industries (Gutiérrez-del-Río et al., 2018) and have multiple biological benefits (Majidinia et al., 2019; Yamagata et al., 2015). Interest for natural alternatives of chemical additives is growing to meet customer demand for replacing the controversial synthetic preservatives such as butylated hydroxyanisole (BHA) (Ding et al., 2019).

To optimize UAE process, some mathematical models have been proposed (Galván D’Alessandro et al., 2014; Hadrich et al., 2017; Cissé et al., 2012). Recently, a multi-objective optimization tool was developed allowing to express extraction yield, antioxidant activity of the extracts and energy consumption as a function of main

process parameters (time, temperature, solvent nature, and US power) (Pradal et al., 2016). However, to date very few studies were reported on environmental impacts of UAE and green extractions in general. Recently, a comparative LCA on antioxidants extraction from chicory grounds, an agri-food by-product, has confirmed environmental benefits of UAE compared to conventional extraction (Vauchel et al., 2018). Indeed, in the same topic of environmental consideration, valorization of agri-food industry by-products is currently a big challenge (Cristóbal et al., 2018). Food loss and waste represent one third of global food production, that corresponds to 1.3 billion tones per years, according to the Food and Agriculture Organization of the United Nations (FAO, 2013).

The case study proposed in this work aims to bring together all these different aspects of ecodesign with valorizing an agri-food by-product using a green process such as UAE in the most sustainable conditions as possible with LCA application. The present study aimed at optimizing UAE of antioxidant phenolics from downgraded beetroot seeds, i.e. by-products resulting from the sorting step in a multinational company of sugar beet seeds production, representing about 72% of seeds (non-conform size, empty or bigerminated seeds). Due to its effects on plant matrix, UAE process appeared as a good candidate. Its efficiency was previously demonstrated for other kinds of vegetal sources or by-products with quite tough matrixes such as stems, leaves or seeds from other plants than beetroot (Mahindrakar et al., 2020; Palsikowski et al., 2020; da Silva Donadone et al., 2020). Polyphenols extraction from this kind of by-product has not yet been studied.

Classically, environmental impacts of a process are calculated a posteriori thanks to a LCA software, considering previously optimized operating conditions on the base of classical criteria like yields, quality, costs, technical constraints etc. In the framework of an eco-design approach, it is necessary to include environmental performance among considered criteria while determining optimal operating conditions. In such a way, environmental performance will be no more a consequence of prior decisions, but a criterion in its own right in decision-making process. Such kind of integration of environmental impacts in a multi-objective optimization of the process was reported by Bisinella de Faria et al. (2016) for wastewater treatment plants but, in our knowledge, never yet been used in optimization of green extraction processes.

Consequently, the objective of the present study was to propose an original multi-objective tool which combines LCA with modelling of the UAE. Indeed, in common LCA method, first step consists in choosing a production objective also called functional unit (FU). For example, FU could be a desired volume of extract with a specific content (concentration) of target molecules. And then, all the elements of the LCA are calculated in reference of this objective. In contrast, the multi-criteria optimization tool proposed in the present work makes it possible to change the functional unit after LCA inventory and calculation steps. It also allows to predict concentration and yield of extracted polyphenols, antioxidant activity of the extracts, energy consumed and 16 categories of environmental impacts for each duration of extraction, solvent composition, US power density and ratio between solid and liquid phases (in the range of studied experimental conditions).

2. Material and methods

2.1. Modelling procedure

The objective of the present work was to build a predictive model for multi-criteria optimization of a green extraction process. This multi-criteria optimization tool consists in a global model, enabling to predict several outputs as a function of the varied inputs. The approach followed to build this model relies on successive work steps: a first step of experimental data collection, then several steps of outputs modelling. The first step corresponded to the compulsory production of a data set, that was then used to fit equations of modelling steps. Production of the data set was carried out on the base of experimental design methodology, as detailed in section 2.2. Experimental design methodology was used only in the view of designing accurately assays (to minimize the number of assays, with a good distribution in the studied field), but not for modelling purpose as it is classically done with polynomial equations. In the present study, modelling was performed according to equations specifically adapted for the studied process as detailed in outputs modeling steps (sections 3.2 to 3.4). Indeed, a specificity of this study is that time was not included as a parameter of the experimental design. It was chosen to take it into account more precisely by following kinetics, which was necessary in the view of being able to optimize process duration. Hence, outputs of the

experimental design were kinetics (time series of data for each output) and not a single data as usually. Coefficients of modelling equations were adjusted by minimization of deviation between model and experimental kinetics with NRMSD (Normalized Root Mean Square Deviation) as a reliability criteria. To minimize NRMSD, Excel software was used with its Solver add-in program. The settings for the Solver were GRG Nonlinear for the resolution method with the Multistart option. Validation assays were performed to assess predictive ability of the obtained model equations.

2.2. Experimental design for data collection

Experimental design methodology was used to produce a data set enabling to study the effect of 3 operating parameters, namely ethanol content of the solvent (X_1, % vol.), extraction hydromodule (X_2, mL.g^{-1}) and ultrasonic power density (X_3, W.L^{-1}), on output kinetics (energy consumption *EC*, total polyphenols yield *TP*, and antioxidant activity *AA*). The used experimental design is detailed in Table 1. It combined a central composite design (CCD) of 18 assays (also known as Box-Wilson design), and 6 supplementary assays. The CCD (18 assays) consisted in a full factorial design (cube points), with 4 center points and 6 star points (distance of 1.68 to satisfy rotatable criteria). This kind of experimental design is one of the most popular for quadratic models enabling to identify the effects of different parameters and their interactions on a process with a minimal number of experiments [34, 35]. The three studied parameters (X_1, X_2, X_3) were varied at five levels : -1.68, -1, 0, +1, +1.68. Real values of ethanol content (X_1), hydromodule (X_2) and ultrasonic power (X_3) varied in the ranges 0 - 100 %vol., 5 - 35 mL.g^{-1} and 0 - 667 W.L^{-1}, respectively. The supplementary assays were six of the eight endpoints of a biggest cube that included the star points as faces' centers (cube with vertices at ±1.68). The two endpoints assays (+1.68, +1.68, +1.68) and (+1.68, -1.68, +1.68) were not carried out because of feasibility reasons: applying US at 667 W.L^{-1} power density with pure ethanol solvent lead to important evaporation and loss of solvent. A validation of the model was performed with an additional assay at conditions included in experimental field but different from those of experimental design points, namely X_1=64% vol., X_2=35 mL.g^{-1}, X_3=642 W.L^{-1} (corresponding coded values : +0.47, +1.68, +1.56; see Table 1).

Table 1 - Real (and coded) value of each parameter for the 24 assays of the experimental design and for validation assay

Assay	Ethanol content, X_1, % vol. (coded value)	Hydromodule, X_2, $mL.g^{-1}$ (coded value)	Ultrasonic power density, X_3, $W.L^{-1}$ (coded value)
1	20 (-1)	11 (-1)	133 (-1)
2	80 (+1)	11 (-1)	133 (-1)
3	20 (-1)	29 (+1)	133 (-1)
4	80 (+1)	29 (+1)	133 (-1)
5	20 (-1)	11 (-1)	533 (+1)
6	80 (+1)	11 (-1)	533 (+1)
7	20 (-1)	29 (+1)	533 (+1)
8	80 (+1)	29 (+1)	533 (+1)
9	0 (-1.68)	20 (0)	333 (0)
10	100 (1.68)	20 (0)	333 (0)
11	50 (0)	5 (-1.68)	333 (0)
12	50 (0)	35 (+1.68)	333 (0)
13	50 (0)	20 (0)	0 (-1.68)
14	50 (0)	20 (0)	667 (+1.68)
15	50 (0)	20 (0)	333 (0)
16	50 (0)	20 (0)	333 (0)
17	50 (0)	20 (0)	333 (0)
18	50 (0)	20 (0)	333 (0)
19	0 (-1.68)	5 (-1.68)	0 (-1.68)
20	100 (+1.68)	5 (-1.68)	0 (-1.68)
21	0 (-1.68)	35 (+1.68)	0 (-1.68)
22	100 (+1.68)	35 (+1.68)	0 (-1.68)
23	0 (-1.68)	35 (+1.68)	667 (+1.68)
24	0 (-1.68)	35 (+1.68)	667 (+1.68)
Validation	64 (+0.47)	35 (+1.68)	642 (+1.56)

2.3. Origin and pretreatment of by-product used

Beetroot seeds were kindly provided by SES Vanderhave (Belgium). This by-product does not require any treatment for preservation because of its very low moisture content (around 6.6%). Seeds' coat was very strong and to ensure a good extraction of molecules, they were crushed with a grain grinder (pieces of variable shapes and dimensions in the range 2-4 mm were obtained from the 4-6 mm diameter spherical shape seeds). Seeds contents in polyphenols and antioxidant activity were 1.7±3% g gallic acid equivalent (GAE)/100 g of seeds and 12±3% mmol Trolox equivalent (TEAC)/ 100 g of seeds (evaluated by decoction

experiments performed in triplicate with 600 mL boiling 50/50 % vol. water/ethanol, 30 g of crushed seeds, for 2 hours).

2.4. Extraction procedure

Extraction experiments were carried out with 600 mL of solvent, which was a mix of deionized water and ethanol (>99% purity) provided by VWR (France). At time zero, the required mass of crushed seeds (varying in the range 17-120 g) was added to solvent, depending on the tested extraction hydromodule (ratio solvent volume/seeds mass, varying in the range 35-5 $mL.g^{-1}$). Experiments were performed in a 0.8 L pipe contactor equipped with 8 ultrasonic transducers (Lab750 pipe processor, SinapTec, France) operating at 22 kHz. Ultrasonic power generated could be up to 400 W. Applied to 0.6 L, it corresponded to up to 667 $W.L^{-1}$ ultrasonic power density. During experiments, the mixture was agitated with a blade stirrer at a speed of 160 min^{-1} and temperature was monitored with a probe.

The initial temperature in all experiments was 24±2 °C. US assistance provoked a progressive increase in temperature. Since the operating limit of the equipment imposed not to exceed 75°C, temperature was regulated thanks to the control application of the equipment: if temperature overtook 73°C, sonication was suspended and restarted only when the temperature had dropped below 68°C. The extraction kinetics of total polyphenols (*TP*) and antioxidant activity (*AA*) were studied during two hours with sampling at 5, 10, 15, 30, 60, 90 and 120 min. Energy consumption (*EC*) was followed with an electrical consumption controller (Otio, France).

2.5. Analytical methods used for samples characterization

2.5.1. Total polyphenols

Measures of total phenolic compounds concentration's in the extracts were conducted according to Singleton et al. (1999) protocol. 7.9 mL water was added to 0.1 mL extract separated from solid residuals with 10 min centrifugation at 10 000 min^{-1} (Eppendorf Centrifuge 5804 R, Hamburg, Germany). Then, the diluted extract was mixed with 0.5 mL of Folin-Ciocalteu phenol reagent (2 N) and 1.5 mL of 200 $g.L^{-1}$ sodium carbonate solution (>99% purity, provided by Sigma-Aldrich, France). After 2 h reaction at room temperature protected against light, the mixture was analyzed. A spectrophotometer UV-1650PC (Shimadzu Europe) was

used to measure absorbance at 765 nm. Results were expressed as $mg.L^{-1}$ gallic acid equivalent (GAE) from the plot of a calibration curve of gallic acid (>98% purity, supplied by Sigma-Aldrich, France).

2.5.2. Antioxidant activity

The protocol described by Brand-Williams et al. (1995) for antioxidant activity quantification was applied. It is based on the use of a free radical: 2,2'-diphenyl-1-picrylhydrazyl (DPPH). This reagent was prepared by dissolving DPPH powder (supplied by Sigma-Aldrich, France) in methanol (>99% purity, provided by VWR, France) to get a 100 µM solution. Then 50 µL of centrifuged extract were added to 1950 µL of this DPPH methanolic solution. After exactly 30 min reaction at room temperature protected against light, samples were analyzed with the previously described spectrophotometer. Absorbance was measured at 517 nm. Results were expressed as µM Trolox equivalent (TEAC) from the plot of a calibration curve of 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) supplied by Sigma-Aldrich (France).

2.6. Life cycle assessment (LCA) methodology

Environmental impacts assessment was performed according to LCA methodology. As defined in ISO standards (ISO 14040:2006, 2006 ; ISO 14044:2006, 2006), this method is divided into four steps: goal and scope definition, life cycle inventory, life cycle impact assessment and life cycle interpretation.

2.6.1. Goal and scope definition

The purpose of this work was to propose an optimization tool enabling to vary the studied functional unit (FU) in a way to evaluate the effect of operating conditions on environmental impacts. To meet this objective, a gate-to-gate LCA focused on extraction process was performed. Boundaries of the studied system were defined as described in Fig. 1.

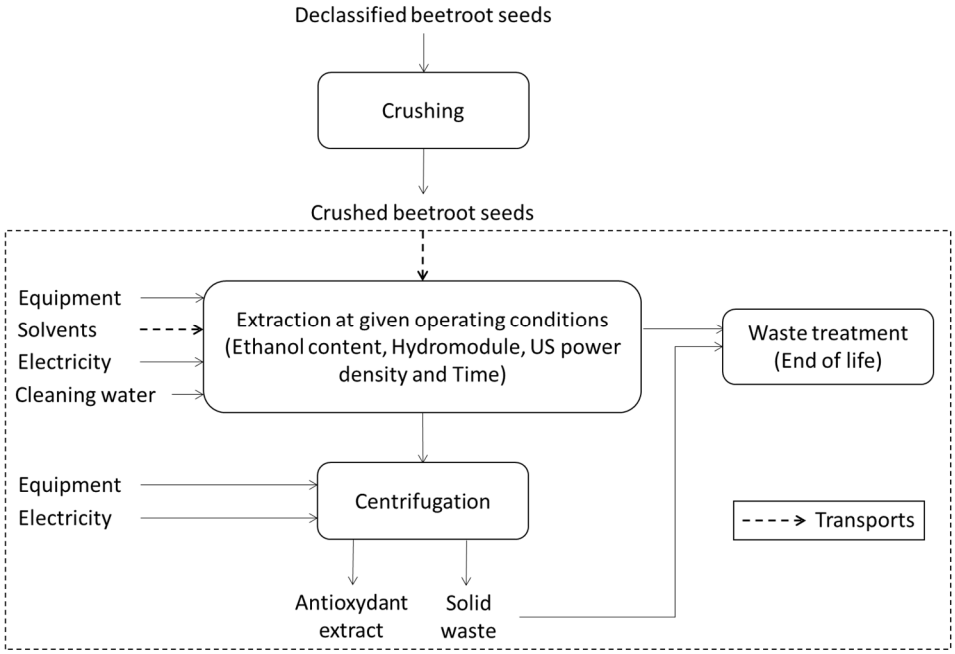

Fig. 1 - Boundaries of the studied system (dash line)

The geographical scope was France. Extraction experiments were performed in a laboratory located in the North of France; input raw materials (beetroot seeds and ethanol) were transported from the supplier's sites, respectively located at 170 and 375 km away.

2.6.2. Inventory

Assessment of environmental impacts was performed using generic data, model data and experimental data. Generic data from Ecoinvent 3 (at point of substitution, APOS) and ELCD databases were used to quantify the impacts of inputs (equipments, water, ethanol, and electricity), transport and waste treatment processes. Experimental and model data enabled to determine quantities of implemented materials and energy for a given functional unit. Five LCA stages were considered: equipment, transports, raw materials, extraction stage, and end of life. Inventory is detailed for each stage in the following paragraphs.

2.6.2.1. Equipment

Equipments taken into account were those used in centrifugation and extraction steps. Centrifugation (separation of liquid extract from solid residuals) was performed with a Heraeus Multifuge FR centrifuge. For extraction, two different equipments were considered depending on usage of US assistance or not. For ultrasound assisted extractions, equipment was composed of SinapTec Lab 750 pipe reactor and generator

including 8 transducers. For classical extractions, without US assistance, a simplified extraction system only composed of a 1 L glass contactor was considered. For both systems, agitation was performed by an agitator, composed of an engine and a stirring blade.

Modelling of each equipment was carried out using generic data for materials and associated treatments, including end of life (mainly glass, stainless steel, polypropylene and its injection, electric and electronic components, electric cables, electric motor components, glass recycling and incineration, stainless steel recycling and incineration, plastics incineration, electric and electronic components treatment, used electric cable treatment).

The considered mass for each equipment was reduced on the base of a mass allocation, taking into account the duration of the process (centrifugation or extraction) according to the following calculation:

$$m_{eq,a} = \frac{m_{eq} \cdot t_u}{365 \cdot l_{eq} \cdot t_{eq,u}} \qquad (1)$$

where $m_{eq,a}$ is the allocated mass of equipment (kg), m_{eq} is the equipment mass (kg), t_u is the usage duration (h), l_{eq} the equipment lifetime (years) and $t_{eq,u}$ the average usage duration per day ($h.d^{-1}$).

2.6.2.2. Transports

Only transports for seeds and ethanol were included. Distilled water and electricity were onsite supplied. Transport was modelled with generic data on the base of mass and traveled distance. The considered masses of seeds and ethanol depended on extraction ethanol content and hydromodule parameters (X_1 and X_2). Ethanol was considered to be transported with a lorry that supplied the entire laboratory from a supplier located 375 km away. Seeds were retrieved on a site located 170 km away by car considering the quantities that were treated.

2.6.2.3. Raw materials

Seeds used being a byproduct, it was considered that their impacts are assumed by the market value product, i.e. seeds eligible for sale (Gonzalez-Garcia et al., 2018). Extraction solvent was a mix of water and ethanol, which quantities varied according to ethanol content parameter (X_1). Water was integrated with a generic data (water, deionized, from tap water). Ethanol was chosen to be issued from petrochemical origin. In fact, it was impossible to find the real origin due to the fact that chemical formulas for synthetic and bio

ethanol are exactly the same. But, according to Garcia-Garcia et al. (2019), bioethanol is reserved for beverage production while ethanol as solvent is mainly produced from ethylene hydration.

2.6.2.4. Extraction

This stage included the energy consumption during extraction and centrifugation (electric energy), the water used for cleaning of equipment and the vessel necessary for extract storage. Electricity consumption was based on French energy mix. The vessel was a simple glass bottle with a plastic cap. Cleaning water was estimated to be around 1 L for each experiment (water, deionized, from tap water). End of life of this water was considered at this step to be domestic waste water treatment.

2.6.2.5. End of life

Most of end of life treatments were included in the above detailed stages. So, this stage corresponded to the treatment of residues issued from extraction, that is to say, seeds after extraction. It was chosen to consider that this waste was thrown away like classical household waste and therefore incinerated. If the process would be extended to bigger quantities, it would be relevant to imagine another way to retreat wet seeds after extraction.

2.6.3. Life cycle impact assessment

Simapro V8.5 software and ILCD2011 midpoint method (ILCD Handbook, 2010) were used for environmental impacts assessment. This method share the impacts between 16 categories: Climate Change, Ozone depletion , Human Toxicity non-cancer effects, Human toxicity cancer effects, Particulate matter, Ionizing radiation HH, Ionizing radiation E, Photochemical ozone formation, Acidification, Terrestrial eutrophication, Freshwater eutrophication, Marine eutrophication, Freshwater eco-toxicity, Land use, Water resource depletion and Mineral, fossil & renewable resource depletion.

3. Results and discussion

The objective of the present work was to propose a multi-criteria optimization tool for a green extraction application, namely antioxidant polyphenols recovery from declassified beetroot seeds using ultrasound assisted extraction process. This multi-criteria optimization tool consists in a global model, schematically

presented in Fig. 2, enabling to predict several outputs (i.e. polyphenols extraction yield, antioxidant activity of the extract, energy consumption and 16 environmental impacts) as a function of the varied inputs (i.e. ethanol content in the solvent, extraction hydromodule, ultrasonic power density, extraction time).

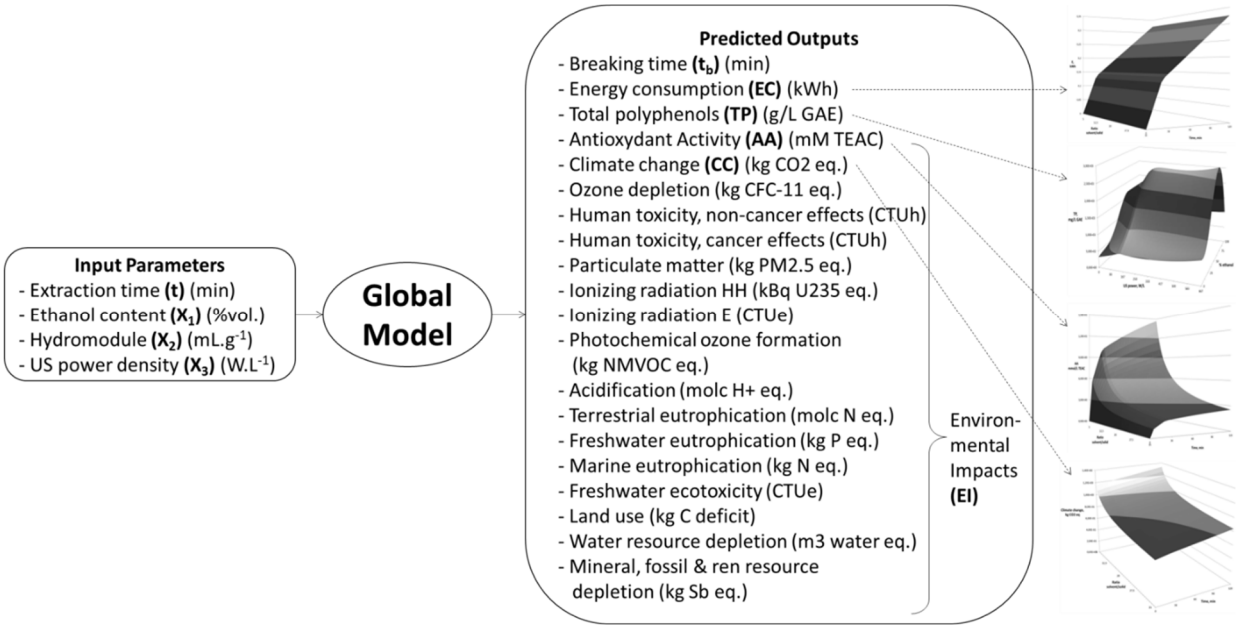

Fig. 2 - Outputs predicted by the proposed global model as a function of input parameters

As explained in section 2.1., building of this predictive model was performed following different successive work steps: (1) experimental data collection according to an experimental design; (2) modelling of energy consumption output; (3) modelling of extraction polyphenols yield and antioxidant activity outputs; (4) modelling of environmental impacts outputs (based on LCA methodology). The successive work steps are detailed below. Then possibilities offered by the obtained multi-criteria optimization tool are illustrated thanks to simulations performed for few case studies.

3.1. Data collection

For the data collection step, it was chosen to use experimental design methodology in order to have a good distribution of assays in the studied field and to minimize the number assays to perform. 24 assays were carried out following the experimental design described in *Materials and methods* part (see sections 2.1 and 2.2, and Table 1). Three input parameters were varied: ethanol content in the solvent (X_1), extraction hydromodule (X_2) and ultrasonic power density (X_3). The effect of the fourth input parameter, extraction time (t), was taken into account more precisely through kinetics following of each output, namely total

polyphenols extraction yield (*TP*), antioxidant activity of the extract (*AA*) and energy consumption (*EC*). Indeed, it seemed very important to closely follow evolution in time of extraction performance and energy consumption in the frame of a process optimization. Finally, a set of 72 kinetics (each being composed of 8 points) was collected. On the base of these experimental data, a model was developed for each studied output, as detailed below.

3.2. Modelling of energy consumption (EC) output

In the used experimental assembly, three pieces of equipment consumed energy: stirring system, UAE system and centrifuge. Centrifuge consumption did not vary with assay: for each extract 0.19 kWh were required for the 10 min centrifugation at 10,000 min^{-1}. In contrast, consumptions of stirring and UAE system were dependent on input parameters. For stirring, energy consumption only depended on extraction time input parameter (*t*) (consumed power was constant). For UAE system, US assistance was not applied continuously for all extraction assays, as temperature could not exceed 75°C in the equipment. Hence, US generation was interrupted when temperature rose above 73°C and restarted when temperature fell below 68°C, allowing to stabilize temperature around 70 C°. As example, temperature profiles are presented in Fig. 3 for assays 3 and 14 at coded values (-1, +1, -1) and (0, 0, +1.68) , corresponding to applied ultrasonic power densities of 133 and 667 $W.L^{-1}$, respectively. For 133 $W.L^{-1}$, temperature raised continuously all along the 2 h extraction experiment (continuous application of US). For 667 $W.L^{-1}$, there was a first phase until about 15-20 min where temperature raised rapidly (continuous application of US), and then a second phase where temperature was maintained at about 70°C (discontinuous application of US).

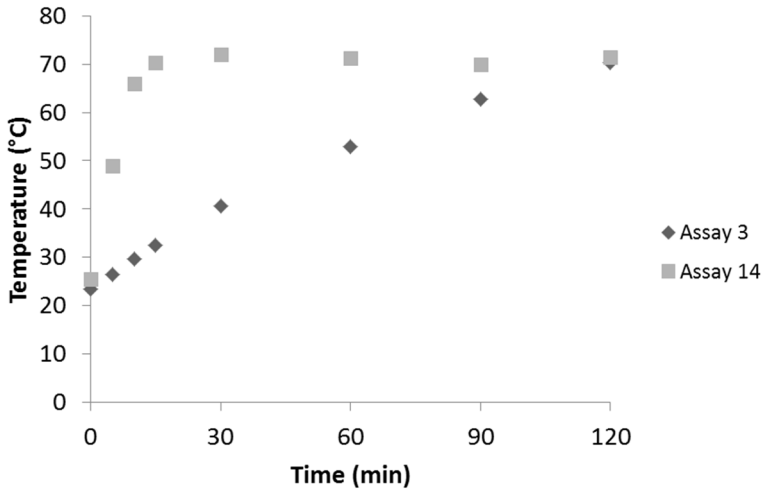

Fig. 3 - Temperature kinetics for assays 3 and 14 at coded values (-1, +1, -1) and (0, 0, +1.68), corresponding to applied US power densities of 133 and 667 W.L^{-1}, respectively

These different phases with continuous or discontinuous application of US made modelling more complex. So, before modelling energy consumption output, it was necessary to determine the breaking time t_b, i.e. the time when US generation switch from continuous to discontinuous mode. In fact, breaking time depended on operating conditions. It was calculated from the first thermodynamic law:

$$P \cdot t_b = m \cdot Cp \cdot \Delta T \qquad (2)$$

with ΔT the temperature variation between initial room temperature and the fixed temperature cutoff threshold (73°C), Cp the calorific capacity of the solvent (dependent of ethanol content in the solvent X_1), m the mass of solvent (also dependent of X_1) and P the power received by the solvent.

P depended on ultrasonic power density (X_3) and on the efficiency of heat transmission to the solvent y, which itself depended on X_1 and X_3. y was expressed as a second order polynomial function of X_1 and X_3.

Then, t_b was described with the following equation:

$$t_b = V \cdot \left(\mu_w + X_1 \cdot (\rho_e - \rho_w)\right) \cdot \left(Cp_w + X_1 \cdot (Cp_e - Cp_w)\right) \cdot \Delta T \cdot \left(\frac{1}{y \cdot X_3}\right) \qquad (3)$$

with V the volume of solvent, ρ_e and ρ_w the densities of ethanol and water respectively, Cp_e and Cp_w the calorific capacities of ethanol and water respectively.

Values of polynomial coefficients for y equation were determined on the base of EC experimental data (set of 24 EC experimental kinetics, corresponding to the 24 assays described in Table 1) and minimization of deviation between prediction and experimental values with normalized root mean square deviation (NRMSD). NRMSD appeared indeed as a suitable criteria since minimization of deviation had to be performed with kinetics (series of 8 data).

Equation for energy consumption (EC) in function of time (t) was built with three terms, one for the stirrer, another one for the continuous US generation before t_b and the last one for the discontinuous US generation after t_b, according to the following equation:

$$EC = P_s \cdot t + \begin{cases} P_{us} \cdot t & if\ t \le t_b \\ P_{us} \cdot t_b + P_{us}^* \cdot (t - t_b) & if\ t > t_b \end{cases} \qquad (4)$$

with $P_{us} = V \cdot X_3$

$$P_{us}^{*} = V \cdot (0.058 - 0.011 \cdot X_3 + 0.0081 \cdot {X_3}^2)$$

with P_s the electric power consumed by the stirrer, t the time, t_b the breaking time defined above, P_{us} the power consumed for US generation in continuous mode and P_{us}^{*} the power consumed for US generation in discontinuous mode. P_{us}^{*} was expressed as a second order polynomial function of X_3. Values of polynomial coefficients were determined by minimization of deviation (NRMSD) between prediction and experimental values for *EC* (24 *EC* experimental kinetics).

A validation experiment was performed (see Table 1) with monitoring of *EC*. The NRMSD between the whole experimental and model kinetics was 1.39%. This value was satisfactory considering the average NRMSD of the model for the 24 assays (2.47%) and included between the maximal (4.64%) and minimal (1.11%) values. Hence, validation results proved the model ability to predict *EC* output in the studied experimental field (t = 0-120 min, X_1 = 0-100% vol., X_2 = 5-35 mL.g^{-1}, and X_3 = 0-667 W.L^{-1}).

3.3. Modelling of total polyphenols (TP) and antioxidant activity (AA) outputs

As expected, all total polyphenols (*TP*) and antioxidant activity (*AA*) data were in close accordance in the studied domain. Hence, modelling of *TP* and *AA* outputs in function of input parameters was performed using the same structure of equation.

In previous studies, a methodology was developed to model extraction kinetics, consisting in combining a standard extraction model based on mass transfer (Peleg model) and experimental design tool (Galván D'Alessandro et al., 2014; Pradal et al., 2016). Parameters of Peleg model were expressed as second order polynomial functions of varied input parameters, and polynomial coefficients values were adjusted thanks to the experimental design data. This methodology enabled to obtain accurate modelling of extraction kinetics, and consequently reliable predictions of extraction performance evolution in time, which is crucial in the frame of a process optimization. The same methodology was used in the present study to model *TP* and *AA* outputs. Peleg (1988) model is relatively simple and often used to fit extraction kinetics, including in UAE cases (Galván D'Alessandro et al., 2014; Hadrich et al., 2017). However, it was not adapted for the studied case of UAE applied to beetroot seeds. Actually, two distinct steps could clearly be distinguished on

experimental *TP* and *AA* kinetics in the present study. Firstly, a very quick extraction of a relatively high amount of polyphenols and then a slower kinetics until equilibrium was reached. Among several tested models, the most suitable appeared to be the one proposed by Patricelli et al. (1979). This model involves two simultaneous extraction steps with different kinetics, mathematically traduced by two exponential expressions. The faster step, called "washing" of the vegetable matrix, describes the quasi-instantaneous transfer of biomolecules from vegetal matrix to solvent when they are put in contact. This corresponds to biomolecules which are close to the vegetal matrix surface and immediately leave the matrix to the liquid phase due to their affinity with the solvent. Patricelli coefficients *A* and K_1 describe this extraction step (in Eq. 5). The slower step, called "diffusion", describes the transfer of less directly reachable biomolecules, which could be facilitated by stirring, heating or other assistance (Patricelli et al., 1979). Patricelli coefficients *B* and K_2 describe this extraction step (in Eq. 5).

In the same way as for *EC* equation (Eq. 4), Patricelli equation had to be adapted for describing *TP* and *AA* outputs, considering the particularity of the existing breaking time t_b in the studied process (continuous US application phase before t_b, and discontinuous US application phase after t_b). It was chosen to differentiate diffusion step expression of Patricelli equation for each phase (before and after t_b), considering that temperature profile was different in each phase (continuous increase before t_b, maintained constant after t_b). Hence, in the proposed adapted Patricelli equation, diffusion step coefficients should account both for diffusion phenomena and temperature effect (respectively two other coefficients were added: *C* and K_3). Finally, *TP* and *AA* outputs were modelled according to the modified Patricelli equation given in Eq.5 (with differentiated expressions for diffusion step before and after t_b):

$$\left.\begin{matrix} TP \\ or \\ AA \end{matrix}\right\} = \frac{1}{X_2} \cdot \left(A \cdot \left(1 - e^{(-K_1 \cdot t)}\right) + \begin{cases} B \cdot \left(1 - e^{(-K_2 \cdot t)}\right) & if\ t \leq t_b \\ C \cdot \left(1 - e^{(-K_3 \cdot (t - t_b))}\right) + D & if\ t > t_b \end{cases} \right) \quad (5)$$

with $D = B \cdot \left(1 - e^{(-K_2 \cdot t_b)}\right)$

where *t* is the extraction time (min), *TP* is the total polyphenols concentration (g.L^{-1} GAE) and *AA* is the antioxidant activity (mM TEAC). *A*, *B*, *C*, K_1, K_2 and K_3 are coefficients of the three steps: washing (*A*, K_1), diffusion for continuous US generation phase (*B*, K_2) and diffusion for discontinuous US generation phase (*C*,

K_3). These coefficients were expressed as second order polynomial functions of input parameters (ethanol content X_1, hydromodule X_2 and US power density X_3). Coefficients of these polynomial equations were determined on the base of the experimental data set (24 *TP* experimental kinetics and 24 *AA* experimental kinetics) and minimization of deviation between prediction and experimental values for *TP* and *AA* with NRMSD criteria. The obtained expressions are given in Table 2.

Table 2 - Polynomial expressions for *A*, *B*, *C*, K_1, K_2 and K_3 coefficients included in *TP* and *AA* equations (Eq. 5) and corresponding NRMSD values

Coefficient	for *TP*	for *AA*
A	$3.44-0.0354X_1+0.318X_2-0.597X_1^2$	$22.0-0.652X_1+1.01X_2-5.31X_1^2$
K_1	$3.30+0.821X_1+0.817X_3$	$4.44+0.824X_1+1.37X_3$
B	$15.9-0.712X_1+0.943X_2+2.80X_3+0.586X_2X_3-3.21X_1^2$	$115-5.83X_1+6.50X_2+16.1X_3+3.05X_2X_3-25.6X_1^2$
K_2	$0.0106+0.00740X_1+0.00441X_3+0.000968X_2X_3+0.00262X_1^2$	$0.00968+0.00650X_1+0.00457X_3+0.00168X_2X_3+0.00164X_1^2$
C	$6.79-1.06X_1+0.923X_3+0.0984X_1X_2-0.700X_1X_3-1.35X_1^2$	$52.3-3.22X_1+1.20X_3+4.97X_1X_2-4.60X_1X_3-11.1X_1^2$
K_3	$0.0117+0.0149X_1+0.00272X_2-0.00189X_3-0.00149X_2X_3+0.00636X_1^2$	$0.00802+0.00908X_1+0.000573X_2-0.00164X_3-0.000134X_2X_3+0.00389X_1^2$
Average NRMSD (min; max), %	5.22 (0.98; 13.5)	8.02 (1.50; 18.3)
NRMSD for validation assay, %	5.86	8.31

Results obtained for *TP* and *AA* during validation experiment were compared to model predictions for the corresponding conditions. As mentioned in Table 2, NRMSD value for *TP* was 5.86%, which was satisfactory considering the average NRMSD (5.22%) and variation range for the whole experimental set (0.98-13.5%). NRMSD value for *AA* gave also satisfaction with a value of 8.31% close to the average value of 8.02% and included in the variation range 1.50-18.3%. Validation results proved the model ability to predict *TP* and *AA* outputs in the studied experimental field (t = 0-120 min, X_1 = 0-100% vol., X_2 = 5-35 mL.g^{-1}, and X_3 = 0-667 W.L^{-1}).

It has to be mentioned that the presented model (Eq. 5) corresponds to *TP* and *AA* outputs expressed as concentrations (in g.L^{-1} GAE and mM TEAC, respectively), but similar expressions have been obtained for *TP*

and *AA* outputs expressed as yields (in $mg.g^{-1}$ GAE and $\mu mol.g^{-1}$ TEAC, respectively), simply by multiplying the expression by the hydromodule X_2.

3.4. Modelling of environmental impacts (EI) outputs

Modelling approach in the present work aimed at being able to predict also *EI* of the studied process in function of input parameters (i.e. operating conditions).

During the inventory work, it appeared that *EI* of each life cycle stage (equipments, transports, raw materials, extraction, end of life, as described in section 2.6.2) could be determined with quite simple equations in function of input parameters (t, X_1, X_2, X_3). The model obtained for *EI* of the whole life cycle is presented in Eq. 6.

$$EI = \overbrace{\left(A_{eq} \cdot t + B_{eq}\right)}^{equipments} + \overbrace{\left(A_t \cdot X_1 + \frac{B_t}{X_2}\right)}^{transports} + \overbrace{\left(A_{rm} \cdot X_1 + B_{rm}\right)}^{raw\ materials} + \overbrace{\left(A_{ex} \cdot EC + B_{ex}\right)}^{extraction} + \overbrace{\frac{A_{eof}}{X_2}}^{end\ of\ life} \quad (6)$$

Impacts relative to equipments stage were a linear function of t (mass allocation depending on extraction duration). Coefficients A_{eq} and B_{eq} were differentiated for extraction performed without or with US assistance (simple glass reactor or UAE system). For transports stage, impacts depended on transported quantities of beetroot seeds and ethanol, i.e. X_1 and X_2 input parameters. Impacts relative to raw materials stage and extraction stage were linear functions of X_1 (ethanol quantity) and *EC* (energy consumption during extraction), respectively, *EC* depending itself of t and X_3 (Eq. 4). For end of life stage, impacts depended on the quantity of beetroot seeds treated at the end of the extraction process, i.e. X_2.

Values of all coefficients (A_{eq}, B_{eq}, A_t, B_t, A_{rm}, B_{rm}, A_{ex}, B_{ex}, A_{eof}) were determined for each of the 16 *EI* categories. They were recovered by varying the parameters of the parametric LCA conceived with the LCA software. In this way, a set of inputs (t, X_1, X_2 and EC) and corresponding outputs (the 16 categories EI) was available to calculate and adjust the parameters using NRMSD tool.

3.5. Global model for ultrasound assisted extraction: a multi-criteria optimization tool

Finally, combining all equations presented above (Eqs. 3-6), a multi-parametric global model was obtained. This multi-criteria optimization tool enables predicting numerous outputs (t_b, *EC*, *TP*, *AA* and 16 *EI*) in function of input operating parameters (t, X_1, X_2, X_3), as described in Fig. 2. The predicted outputs enable to

have a global vision on the whole studied domain of the extraction process performances which can be expressed in terms of extraction yield or concentration of *TP* or *AA* of the extract, *EC* and *EI*, as illustrated with examples of 3D graphs in Figs. 4 and 5.

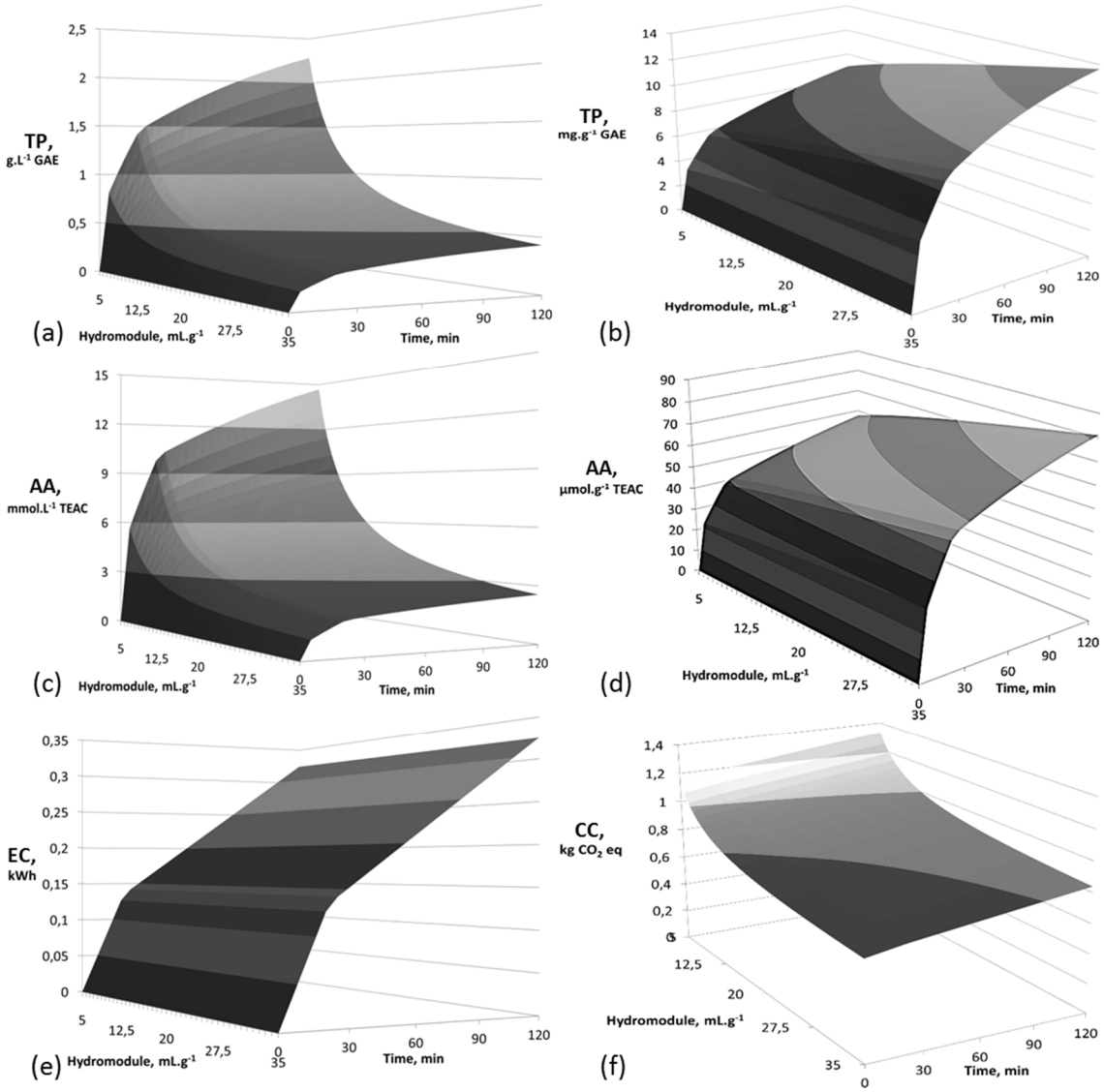

Fig. 4 – Predicted evolution of *TP* concentration (a), *TP* yield (b), *AA* concentration (c), *AA* yield (d), *EC* (e) and *CC* (f) in function of hydromodule and time (for X_1 = 50% vol. and X_3 = 532 W.L^{-1})

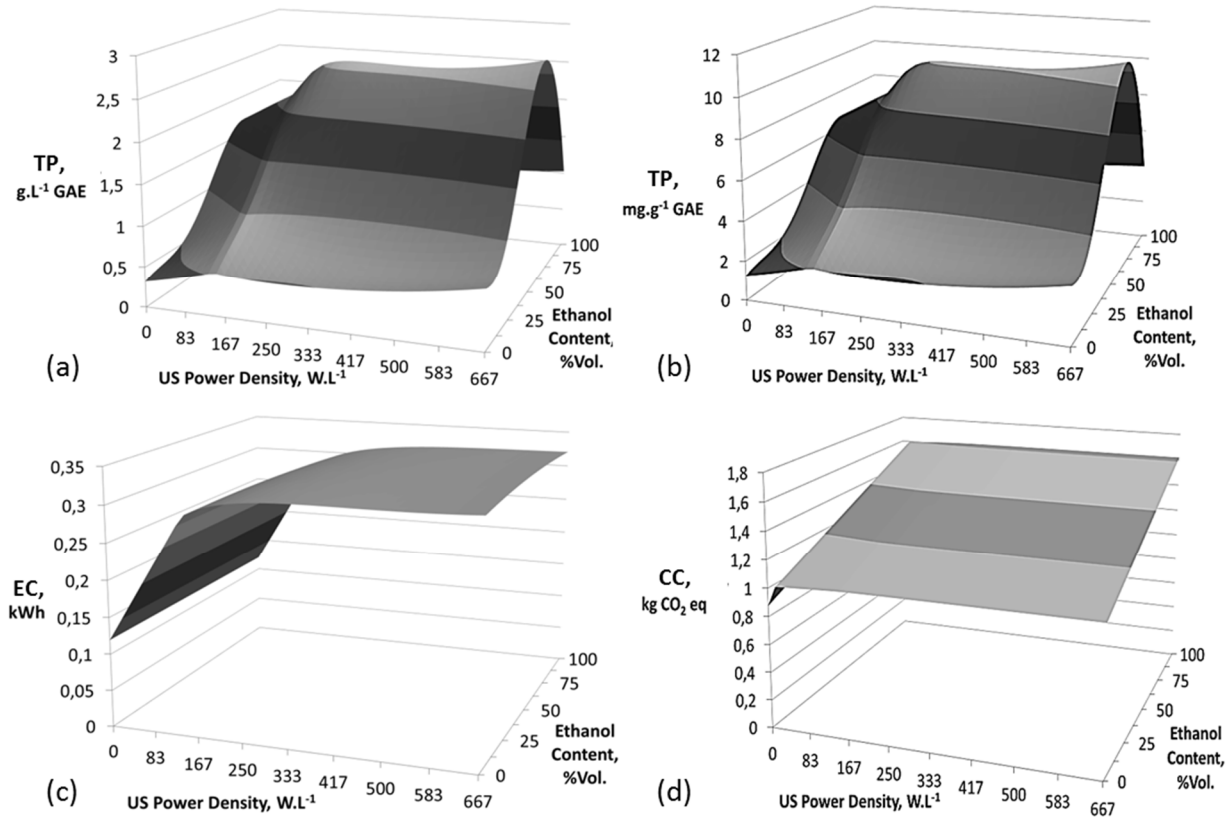

Fig. 5 – Predicted evolution of *TP* concentration (a) and yield (b), *EC* (c) and *CC* (d) in function of US power density and ethanol content in the solvent (for t = 120 min and X_2 = 5 mL.g^{-1})

Here, it was chosen to present climate change among the 16 predicted *EI* outputs as an example as one of the most popular and most known among *EIs*. All these predicted outputs make it possible to have a full and detailed comprehension of the influence of input operating parameters, and to make informed decisions concerning the way the extraction process should be conducted in function of the fixed objectives and constraints.

Analyzing these 3D graphs enables to understand the effect of input parameters on the different outputs, and consequently identify leads for optimization of the process. Firstly, it has to be noticed that *TP* and *AA* outputs on Fig. 4 were in close accordance (be that in concentration or yield) confirming the narrow relationship between the amount of phenolic compounds and antioxidant activity of the extracts often observed for other vegetal extracts. Hence, to simplify, only one of these outputs (*TP*) was presented on the following figures.

Time input parameter (*t*) had of course an influence on all outputs. Important increases of *TP* and *AA* occurred at the beginning of the extraction process, then kinetics slowed down, and *TP* and *AA* values tended more or less rapidly to a maximum depending on hydromodule value (X_2) (Fig. 4a,b,c,d). For example, on Fig. 4a, equilibrium was almost reached at about 30 min for a hydromodule of 35, whereas it was still visibly increasing at 120 min for a hydromodule of 5. These observations are in accordance with major trends generally observed in other studies on vegetal sources with quite tough matrixes (Mahindrakar et al., 2020; Palsikowski et al., 2020; da Silva Donadone et al., 2020). Fig. 4e illustrates the linear dependence of *EC* on time with a break in the slope occurring at about 20 min in the presented example (for $X_3 = 532$ W.L^{-1}), which corresponded to the switch to discontinuous sonication. The slight increase of climate change (*CC*) with time (Fig. 4f) was linked to equipments and extraction life cycle stages (equipments mass allocation and energy consumption, respectively), as described in Eq. 6.

Obviously, hydromodule input parameter (X_2) influenced *TP* and *AA* outputs: the highest concentrations were obtained with the lowest hydromodule, whereas the highest yields were obtained with the highest hydromodule (Fig. 4a,b,c,d). This was also observed by Mahindrakar et al. (2020) in their study of UAE of phenolics from seeds of another plant. Varying hydromodule had some effect on *CC*, via beetroot seeds quantities impacting transports and end of life cycle stages (Fig. 4f), and no effect at all on *EC* (Fig. 4e).

As observed on Fig. 5a,b, *TP* output was strongly dependent of ethanol content input parameter (X_1). These results are in line with expectations, considering that polyphenolic compounds generally have higher affinities with ethanol-water mixtures, than with pure water or pure ethanol (Naczk and Shahidi, 2006). The optimum was around 65% vol. ethanol for both *TP* yield and concentration outputs. No variation of *EC* was observed in function of ethanol content (Fig. 5c), and *CC* logically increased when more ethanol was used (via transports and raw materials life cycle stages) (Fig. 5d).

CC output was not impacted by US power density (Fig. 5d), except for the case without US assistance ($X_3 = 0$ W.L^{-1}) because of the equipment difference (a simpler equipment was considered for extractions without US assistance). The influence of US assistance on polyphenols recovery can be observed on Fig. 5a,b. Globally, increasing US power density had a positive impact on *TP*, but it was observed that the increase of *TP* was

amplified for US power densities above 130 W.L^{-1}, and then slowed down for US power densities above about 200 W.L^{-1} (at these extraction conditions: 120 min and a hydromodule of 5 mL.g^{-1}). One can suggest that rather important power density (over 130 W.L^{-1}) is necessary to impact considerably the relatively solid beetroot seeds and, therefore, accelerate TP extraction. Then, the increase in power densities over about 200 W.L^{-1} led to a slow raise in polyphenols extraction because of the big part of discontinuous mode of extraction at these conditions (short cycles of sonication). The shift from continuous to discontinuous mode corresponding to breaking time is easily seen in Figs. 5c and 6b presenting *EC*. The trend of US power effect was very specific in this study (due to continuous and discontinuous mode shift), but the observed general positive impact of US power increase was in accordance with other studies with quite tough vegetal matrixes (Mahindrakar et al., 2020; Palsikowski et al., 2020; da Silva Donadone et al., 2020).

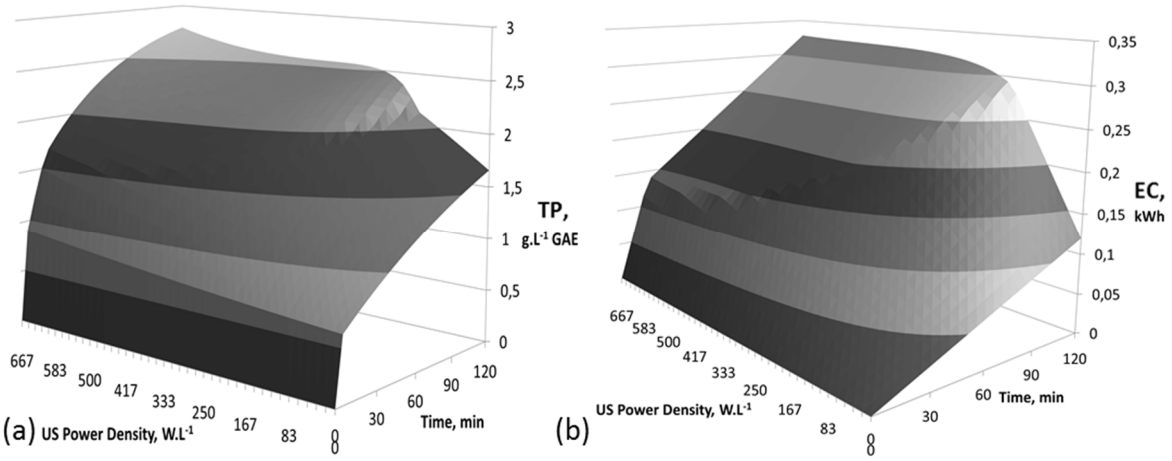

Fig. 6 – Predicted evolution of *TP* concentration (a) and *EC* (b) in function of US power density and time (for X_1 = 64% vol. and a X_2 = 5 mL.g^{-1})

Fig. 6a presents the positive effect of US power density on the kinetics of TP extraction at fixed hydromodule and fixed ethanol content in the solvent. Comparing to extraction without US assistance, concentration of polyphenols was increased by about 60% in the case of UAE. The improved extraction yields could be related to cavitation phenomena provoked by ultrasound sonication that impacts vegetal matrix such as observed by Khadraoui et al. (2018) phenomena: local erosion, shear forces, sonoporation, fragmentation, capillary effect, and detexturation. Heating of the solvent in the case of UAE also contributes to the faster mass transfer and higher solubility of the phenolics in the solvent used. Here, the noticed stronger improvement

of extraction efficiency between about 130 and 200 $W.L^{-1}$ is mainly marked for 120 min extraction time, and less and less evident for shorter extraction times (at these extraction conditions: 64 % ethanol and a hydromodule of 5 $mL.g^{-1}$). Quite better results at higher US power density could also be attributed to stronger mechanical effects, as well as to the faster heating of the solvent at these conditions. It seemed justified to favor the highest US power, as for the same results of TP recovery and energy consumption, it enabled to reduce extraction duration.

3.6. Multi-criteria optimization of the studied UAE process

Further to these general observations on input parameters effects on the process performances, simulation examples were performed to illustrate possibilities offered by the obtained multi-criteria optimization tool. Optimization target could be defined regarding extraction yield, with an objective of extracting the biggest quantity of compounds from a mass of seeds and exhaust it. Or, it could be to produce the most concentrated extract, with an objective of saving solvent and treating the largest amount of seeds. Few case studies are proposed in the following sections: firstly, a classical target of maximizing polyphenols recovery, then few examples of optimization under different specific constraints.

3.6.1. Maximization of extraction yield and antioxidant activity

Using the proposed model, it is possible to predict operating conditions (input parameters t, X_1, X_2, X_3) enabling to maximize extraction, whether in terms of total polyphenols recovery (*TP*) or antioxidant activity of the extract (*AA*), expressed as concentration or yield. Simulation results are given in Table 3, as well as predicted energy consumption (*EC*) and climate change (*CC*) (as an example of the 16 predicted *EI*) for each case.

Table 3 - Predictions of the model for maximized recovery of *TP* and *AA* (in yield and concentration)

Output	Maximum value	Extraction time, *t*, min	Ethanol content, X_1, % vol.	Hydromodule, X_2, mL.g^{-1}	Ultrasonic power density, X_3, W.L^{-1}	Energy consumption, *EC*, W.h	*Climate change*, *CC*, kg CO_2 eq
***TP* concentration, g.L^{-1} GAE**	2.8	120	64	5	667	337	1.44
***AA* concentration, mM TEAC**	16.6	120	65	5	667	337	1.45
***TP* yield, mg.g^{-1} GAE**	15.6	120	67	35	667	337	0.969
***AA* yield, µmol.g^{-1} TEAC**	98.3	120	71	35	667	337	0.996

Very similar extraction conditions allowed to maximize *TP* and *AA*, confirming once again the close relationship between these 2 parameters. Optimal ethanol content in the solvent for maximizing *TP* and *AA* recovery is in the range 65-70% vol., as noticed above on Fig. 5a,b. In agreement with expectations, results showed that the lowest hydromodule (5 mL.g^{-1}) should be privileged for maximizing *TP* and *AA* concentrations, whereas the highest hydromodule (35 mL.g^{-1}) should be privileged for maximizing *TP* and *AA* yields. In all cases, to reach these maximal amounts, it is necessary to perform the extraction during two hours and to apply the maximal US power density (667 W.L^{-1}), leading to the same *EC*. Indeed, observing Fig. 6a, the absolute maximum of *TP* concentration is obtained for the maximum extraction time and US power density values. But *TP* concentrations close to the absolute maximum could be obtained with shorter extraction durations and/or lower US power densities.

In fact, beyond a certain extracted amount, there is less and less interest in pursuing the extraction. It is possible to get values close to maximal amounts with durations and energy consumptions far much lower. Examples are presented in the next section (3.6.2).

3.6.2. Multi-criteria optimization under different constraints

In the studied application of beetroot seeds valorization, the content of targeted biomolecules (polyphenols) in the source was not very high, but in return this source was a by-product available in huge quantities. Exhausting the source and targeting a high recovery yield wouldn't correspond to the present case study.

The objective would rather be to treat high quantities of seeds and to get an extract with a given antioxidant activity for further use as a preservative in food or cosmetic fields for example.

Then, for simulations performed in this section, the target was defined as an antioxidant activity concentration in the extract. *AA* concentration target was fixed at 80% of the maximum reachable in the studied domain, in order to find out operating conditions, which could permit gains in terms of extraction duration, energy and ethanol consumptions, and environmental performance. This maximum being 16.7 mM TEAC, the target was to get an extract with an *AA* concentration of 13.4 mM TEAC. Five scenarios were simulated with different constraints: minimizing (1) energy consumption, (2) extraction time, (3) climate change impact, (4) ethanol consumption, and (5) US power density. Predictions of the model for each studied scenario are given in Table 4 and Fig. 7.

Table 4 - Predictions of the model for five scenarios with different minimization constraints (target objective: *AA* of 13.4 mM TEAC)

Scenario	1	2	3	4	5
Constraint	Minimize *EC*	Minimize *t*	Minimize *CC*	Minimize X_1	Minimize X_3
Time required, *t*, min	46	46	70	120	120
Ethanol content, X_1, % vol.	67	67	52	45	66
Hydromodule, X_2, mL.g^{-1}	5	5	5	5	5
US power density, X_3, W.L^{-1}	667	667	667	667	105
Energy consumption, *EC*, W.h	187	187	233	327	246

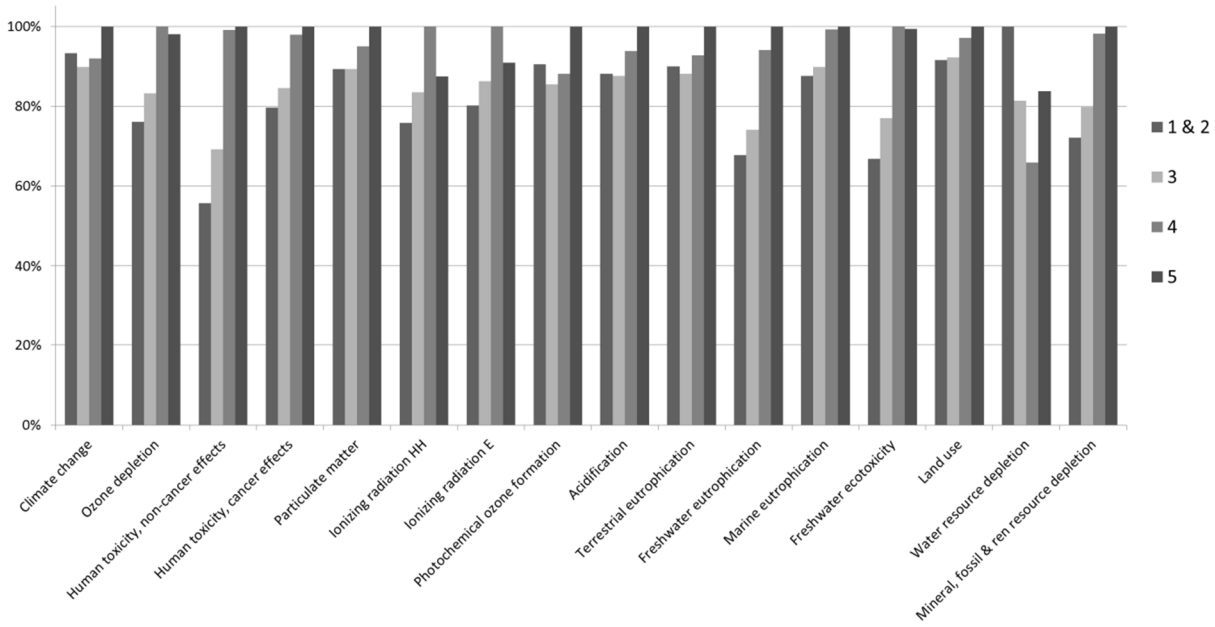

Fig. 7 - Comparison of *EI* predictions for the five scenarios presented in Table 4 (the same results were obtained for scenarios 1 & 2) (target objective: *AA* of 13.4 mM TEAC)

For all scenarios, the lowest hydromodule was of course preconized, as the target objective was to get a high *AA* concentration. Imposing a constraint of minimizing extraction duration (scenario 1) or energy consumption (scenario 2) conducted to the same prediction results: the optimal ethanol content (about 67%) and maximum US power density should be chosen. Minimizing time and energy consumption was quite positive in terms of *EI*, as 11 among the 16 *EI* were also minimized compared to the other studied scenarios (scenarios 1 and 2 were the worst only for one *EI*: Water resource depletion).

Scenario 3 aimed at reducing *CC*, but focusing efforts on only this impact has limits. As it was observed, comparing scenarios 1 and 3 (Fig. 7), reducing *CC* was responsible for increasing ten of the fifteen other *EI*, while counterbalancing it with an interesting diminution among the remaining five. In this case, the way to reduce *CC* was reducing ethanol percentage in the solvent, which resulted in an increase in extraction duration (about 50%) and therefore *EC* (about 25% increase).

Observing *EI* predictions (Fig. 7) for scenario 4, it clearly appeared that minimization of ethanol percentage in the solvent had a negative effect on most of impacts. Indeed, the less ethanol was used in the solvent, the longer was the time needed and the higher was the energy consumption to reach the fixed *AA* target (*t* and *EC* values for scenario 4 were the highest in Table 4). Because of the polarity of the solvent, polyphenols

have a really better affinity to solvent with around 65% vol. ethanol in which they were extracted faster and in higher quantities.

Results obtained for scenario 5 showed that reducing US power density (from 667 to 105 $W.L^{-1}$, compared to scenario 1) led to important increases of time (more than twice) and energy consumption (about 30%) for nearly the same ethanol consumption. Then, it corresponded to the worst scenario for 11 *EI*, as observed on Fig. 7. Indeed, applying maximum US power density of 667 $W.L^{-1}$, the limit temperature was reached very rapidly (less than 20 min as seen in Fig. 3), and then the system did not consume a lot of energy during the discontinuous US generation phase. So, reducing US power density in the view of lowering energy consumption appeared to be counterproductive.

All studied scenarios tended to show that US assistance was favorable in terms of extraction duration, energy consumption and environmental impacts. It should also be underlined that the maximal *AA* in the case of conventional extraction was 10.3 mM TEAC, while UAE allowed to attain 16.7 mM TEAC (more than 60% increase due to sonication). It was also interesting to compare UAE and conventional extraction for a value which is attainable by both methods. Fig. 8 and Table 5 present prediction results for conventional extraction process performed in a simple glass reactor without US assistance (scenario 1) and UAE performed in the more complex equipment (scenario 2).

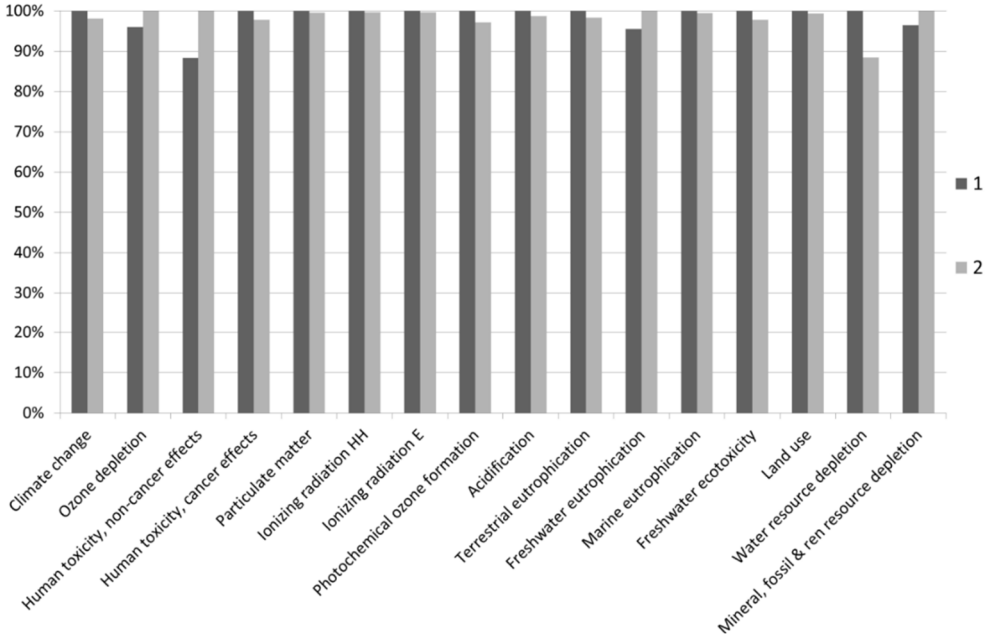

Fig. 8 - Comparison of *EI* predictions for a conventional extraction process (scenario 1) and a UAE process (scenario 2) (target objective: *AA* of 10.3 mM TEAC)

Table 5 - Predictions of the model for a conventional extraction process (scenario 1) and a UAE process (scenario 2) (target objective: *AA* of 10.3 mM TEAC)

Scenario	1	2
Time required, *t*, min	120	15
Ethanol content, X_1, % vol.	71	65
Hydromodule, X_2, mL.g^{-1}	5	5
US power density, X_3, W.L^{-1}	0	667
Energy consumption, *EC*, W.h	120	113

Results in Fig. 8 show quite similar impacts of the 2 scenarios to obtain this target (10.3 mM TEAC) since differences higher than 10% were observed for 2 impacts only: 12% lower impact for *Human toxicity, non-cancer effects* for scenario 1, and 12% lower impact for *Water depletion* for scenario 2. Considering inherent uncertainties in LCA results, it is difficult to conclude on an effective difference of *EI* between these two scenarios. For example, it is generally considered that assessment of climate change presents a deviation of about 10% (Jolliet et al., 2010). However, results showed that the use of US technology, despite much more sophisticated equipment, did not led to negative effects for *EI*, while having positive effects for extraction time, energy and ethanol consumptions (Table 5). The most striking advantage of UAE compared to conventional extraction was a huge reduction of extraction duration (divided by a factor 8). This also permitted to slightly reduce ethanol use and energy consumption, despite the use of sonication.

4. Conclusions

The tool presented above is original and innovative in its approach of LCA, as calculation of environmental impacts is included in the multi-criteria model built for process optimization. It allows the functional unit (FU) to be modified after the inventory step of LCA, and so offers the possibility to interpret results at different FUs and with different constraints. It allows, therefore, a better knowledge of extraction process

and help to consider its productivity criteria (antioxidant activity, extraction yield and concentration) together with energy considerations and environmental impacts at each operating condition. All these predicted outputs make it possible to have a full and detailed comprehension of the influence of input operating parameters, and to make informed decisions concerning the way the extraction process should be conducted in function of the fixed objectives and constraints. As next step, it would be relevant to combine this tool with a weighting method to assign different degrees of importance to outputs.

The proposed modelling procedure could be applied to other systems or processes, as far as process kinetics can be modelled. Indeed, to obtain an efficient predictive tool, it is necessary to accurately model kinetics of criteria of interest for the optimization of the studied process. Then sufficiently numerous assays must be conducted and equations adapted to the studied system must be used. In the present study, quite complex equations and 24 assays were required because of the studied system complexity (solid-liquid extraction with variation of temperature in time, discontinuous application of US…). Proposed modification of Patricelli model allowed a good description of extraction kinetics, especially for the cases when extraction temperature was not constant. The number of assays could be reduced and simpler equations could be used in the case of less complex systems and processes (more easily modellable kinetics).

The experimental data and the proposed modelling tool have clearly demonstrated the positive effect of ultrasound assistance on polyphenols extraction from beetroot seeds. At the end of extraction (after 2 h) the extraction yield, polyphenols concentration and antioxidant activity were about 60% higher than in the case of conventional extraction. Ultrasound assistance also led to a significant reduction in extraction duration, energy consumption and environmental impacts (for the same target yield, concentration or antioxidant activity).

The present work also proposed a way to valorize an agri-food by-product. Even if polyphenols content in beetroot seeds is not very high (less than 2%), this by-product is available in a quite high quantity and UAE allows to obtain concentrated extracts with high antioxidant activity, reducing also the wastes of beetroot seeds.

Finally, the proposed in present study valorization of agri-food wastes as by-products using UAE is closely related to the Principles of the Green Extraction of Natural Products (Chemat et al., 2019): it complies with principles n°2 (privilege alternative solvents and principally water and agro-solvents), n°3 (reduction of energy consumption and environmental impacts using innovative technologies), and n°4 (production of co-products instead of waste).

Funding sources

This work has been carried out in the framework of Alibiotech project financed by European Union, French State and the French Region of Hauts-de-France. The partial financial participation by University of Lille is gratefully appreciated.

Abbreviations

AA: Antioxidant Activity

CC: Climate Change

CCD: Central Composite Design

EC: Energy Consumption

EI: Environmental Impacts

FU: Functional Unit

GAE: Gallic Acid Equivalent

LCA: Life Cycle Assessment

LCI: Life Cycle Inventory

NRMSD: Normalized Root Mean Squared Deviation

TEAC: Trolox Equivalent Antioxidant Capacity

TP: Total Polyphenols

UAE: Ultrasound Assisted Extraction

US: Ultrasound

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