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# Impact of ultrasound on solid–liquid extraction of phenolic compounds from maritime pine sawdust waste. Kinetics, optimization and large scale experiments

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## A B S T R A C T

Maritime pine sawdust, a by-product from industry of wood transformation, has been investigated as a potential source of polyphenols which were extracted by ultrasound-assisted maceration (UAM). UAM was optimized for enhancing extraction efficiency of polyphenols and reducing time-consuming. In a first time, a preliminary study was carried out to optimize the solid/liquid ratio (6 g of dry material per mL) and the particle size (0.26 cm<sup>2</sup>) by conventional maceration (CVM). Under these conditions, the optimum conditions for polyphenols extraction by UAM, obtained by response surface methodology, were 0.67 W/cm<sup>2</sup> for the ultrasonic intensity (UI), 40 °C for the processing temperature (*T*) and 43 min for the sonication time (*t*). UAM was compared with CVM, the results showed that the quantity of polyphenols was improved by 40% (342.4 and 233.5 mg of catechin equivalent per 100 g of dry basis, respectively for UAM and CVM). A multistage cross-current extraction procedure allowed evaluating the real impact of UAM on the solid–liquid extraction enhancement. The potential industrialization of this procedure was implemented through a transition from a lab sonicated reactor (3 L) to a large scale one with 30 L volume.

### Keywords:

Ultrasonic extraction  
Maritime pine wood  
Extraction kinetics  
Maceration  
Cross current extraction  
Phenolic compounds  
Response surface methodology

## 1. Introduction

Nowadays, most of manufacturing processes in cosmetic, pharmaceutical and food industries seeks directly or indirectly to extraction of bioactive compounds from plant to replace synthetic substances. The interest in the use of plant materials as a potential source of bioactive compounds is generally focused on upgrading the large quantities of agricultural by-products generated annually and on providing for their increasing demand from food, pharmaceutical and cosmetic industries [1]. During wood industrial processing, several wastes are generated such as bark and sawdust. These by-products could be re-used to reduce their ecological impact and to obtain an economic benefit [2,3]. Among bioactive compounds, the phenolic ones are very interesting due to their several health-benefitting properties including the reduction of the risk of cardiovascular disease, neurodegenerative disorder and cancer [4,5]. Polyphenols can delay or inhibit the oxidative damage caused by free radicals such as superoxide anion radicals, hydroxyl

radicals and non free-radical species such as H<sub>2</sub>O<sub>2</sub> and singled oxygen, by inhibiting the initiation or propagation of oxidative chain reactions To be competitive and profit-making, industrials needed to define more efficient and/or intensify the conventional process of extraction, while being environmental friendly. Indeed, the traditional extraction methods including maceration, Soxhlet extraction and percolation required a long time of extraction which induces an important energy consuming, a large quantity of residual solvents and the bioactive compounds which are very sensitive to oxygen and heat can be degraded [6,7]. In recent years, a combination of organic solvent with low boiling point and steam distillation method was explored [7,8] as well as some intensified extraction methods including microwave [9,10], supercritical fluids [11], D.I.C-assisted hydrodistillation (D.I.C: Détente Instantanée Contrôlée in french) which is based on a thermomechanical extraction process [12], ultrasound assisted extraction [13,14], ionic liquid-based microwave-assisted extraction [15], ohmic-assisted hydrodistillation [16], and enzyme-assisted microwave hydro-distillation [17]. Among these numerous extraction processes, ultrasonication is reported to attack the integrity of plant cell walls resulting in the release of extractives and the most accessible polysaccharides as well as release of less extractable cell wall components [18,19]. Ultrasound also offers a mechanical effect allowing greater penetration of solvent (water) into the

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## Nomenclature

TPC	total phenolic compounds (mg catechin eq/100 g d.b)	$k_1^{\text{CVM}}$	first order kinetic constant in the 1st phase of extraction by CVM
CVM	conventional maceration	$k_2^{\text{UAM}}$	first order kinetic constant in the 2nd phase of extraction by UAM
UAM	ultrasound-assisted maceration	F	feed (dried wood waste) (g)
UI ( $=x_1$ )	ultrasonic intensity (W/cm <sup>2</sup> )	A	solute (assumed as polyphenols)
T ( $=x_2$ )	processing temperature (°C)	B	inert phase (solid)
T ( $=x_3$ )	sonication time (min)	S	solvent phase (acidified water)
C(t)	concentration of total polyphenols at time <i>t</i> (mg catechin eq/100 g d.b)	V	overflow phase (composed from A + S)
$C_\infty$	final concentration of total polyphenols <i>t</i> (mg catechin eq/100 g d.b)	L	underflow phase (composed from A + B + S)
$k_1^{\text{UAM}}$	first order kinetic constant in the 1st phase of extraction by UAM	M	ternary mixture point (composed by F + S)
$k_2^{\text{UAM}}$	First order kinetic constant in the 2nd phase of extraction by UAM		

sample matrix, increasing the contact surface area between the solid and liquid phases. As a result, heat and mass transfer are enhanced and the solute diffuses more rapidly from the solid phase into the solvent.

The recovery of value-added chemicals and bioactive compounds from maritime pine bark [20] or maritime pine needles [21] was largely studied but there are few references on wood sawdust waste which can be considered as renewable and low cost product. These types of “green” materials should be gradually in competition with their synthetic counterparts, more expensive and less environmentally friendly. In this context, this study involves three parts: the first one consisted in a preliminary study to detect the more favorable conditions for polyphenols extraction in term of particle size and solid-to-liquid ratio. The second objective of this work was to identifying optimal range of UAM extraction conditions namely the ultrasonic intensity (UI), the processing temperature (*T*) and the processing time (*t*) and to develop an effective and eco-friendly ultrasound-assisted extraction strategy for extraction of polyphenol compounds from maritime pine sawdust waste, using response surface methodology. In the third part, three concepts were investigated and compared: conventional multi-stage maceration, ultrasound assisted multi-stage maceration and a combination between them [22] in order to highlight the impact of ultrasound. Moreover, a pilot plant reactor of 30 L extraction tank was investigated at lab optimum conditions to prove that the scale up of the process is possible.

## 2. Material and methods

### 2.1. Plant materials and chemicals

The maritime pine (*Pinus pinaster*) sawdust was collected from trees in southwest France (Poitou–Charentes) after wood sawmilling by Archimbaud Company (Secondigné/Belle, France). Moisture content measured by halogen Moisture Analyzer using IR radiations (Ohaus – MB 35) at 105 °C corresponded to 43% dry basis (d.b). The sawdust waste material was dried under air flow at 25 °C during 48 h to reach final moisture content around 5% (d.b). The chips were classified using different sieves to study the influence of particles size on phenolic compounds extraction. Solvents and reagents were all of analytical grade and purchased from VWR International (Darmstadt, Germany).

### 2.2. Sonication apparatus

Ultrasound-assisted extraction by maceration (UAM) experiments were performed in a sonication reactor PEX 3, Sonifier

(R.E.U.S., Contes, France) composed of a stainless jug with 23 × 13.7 cm internal dimensions and a maximal capacity of 3 L. The base of stainless jug was equipped of a transducer operating at a frequency of 25 kHz with maximum input power (output power of the generator) of 150 W (Fig. 1). The double-layered reactor allowed water to circulate using a cooling/heating system to control and regulate the medium temperature. Considering the actual input, power from the device is converted to heat which dissipated in the medium. Calorimetric measurements were performed to assess actual ultrasound dissipated power *P* (W), calculated by Eq. (1) [23].

$$P = m \cdot C_p \cdot \frac{d}{dt} \quad (1)$$

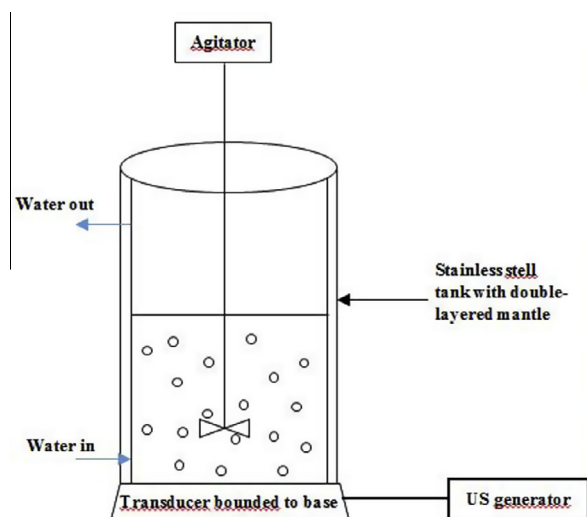
where  $C_p$  is the heat capacity of the solvent at constant pressure ( $\text{J g}^{-1} \text{°C}^{-1}$ ), *m* is the mass of solvent (g) and  $dT/dt$  is temperature rise per second ( $\text{°C s}^{-1}$ ). Then, the applied ultrasonic intensity (UI) was determined using the calculated power as shown in the Eq. (2) [24].

$$UI = \frac{4P}{\pi D^2} \quad (2)$$

where UI is the ultrasonic intensity ( $\text{W/cm}^2$ ), *P* is the ultrasound power (W) as calculated by Eq. (1) and *D* is the internal diameter (cm) of the ultrasound reactor [25].

### 2.3. Extraction procedures

All experiments (without and with sonication) were carried out with acidified water as solvent, and prepared with a phosphate buffer solution of a 50 mM adjusted to a pH of 3.8, to simulate the standard (catechin) extraction conditions. A preliminary study was performed to determine the optimal solid/liquid ratio. The solid–liquid ratio was evaluated in function of total polyphenols compounds (TPC) extracted by UAM at 40 °C during 40 min with a constant agitation at atmospheric pressure and for ultrasonic intensity of 0.764  $\text{W/cm}^2$ . Different quantities (ranged from 10 to 100 g) of dry maritime pine chips was subjected to an extraction with 1 L of the buffer solution. Samples were then pressed using a manual press and filtered with a 0.45  $\mu\text{m}$  mesh filter before analysis. A comparative study has been conducted between the conventional maceration and optimized ultrasound-assisted extractions. UAM and CVM were performed under agitation (IKA-Werk, RW 20) at atmospheric pressure in the same conditions: 60 g dried maritime pine substrate; 1 L of buffer (50 mM, pH = 3.8); 1000 RPM. CVM experiments were performed in the same reactor than that used for UAM without the sonication



**Fig. 1.** Laboratory ultrasonic device (3L) used for ultrasound-assisted extraction by maceration (UAM).

system. All experiments were carried out in triplicates (except for experimental design).

#### 2.4. Total phenolics determination

Total phenolic content was determined using Folin–Ciocalteu reagent described in literature [26]. Some modifications have been made to this method, (–) epicatechin has been used as reference. In a test tube, 200  $\mu\text{L}$  of extract were mixed with 250  $\mu\text{L}$  of Folin–Ciocalteu reagent. After 3 min of reaction, 1 mL of 10%  $\text{Na}_2\text{CO}_3$  solution has been added; all tubes are caps and agitated during 10 s. After 30 min of reaction (protected from light), the absorbance was measured using a spectrophotometer (Biochrom, libra S6) at 765 nm against a calibration curve. The results were expressed in mg of catechin equivalent per 100 g d.b. All analyses were carried out in triplicates.

#### 2.5. Experimental design

The preliminary study of CVM allowed optimizing the particle size and solid/liquid ratio to reach the maximal phenolic content, while respecting the free liquid space necessary to ensure a good functioning of the conventional maceration as well as ultrasonic devices. In order to investigate the influence and the relevance of UAM processing variables on the polyphenols extraction, a response surface methodology has been used. Three independent factors namely the ultrasonic intensity (UI), the temperature ( $T$ ) and the sonication time ( $t$ ) were studied with as response the total phenolic content (TPC). The relationships between the response and process variables have been established according to a central composite design (CCD) as well as the optimal conditions of UAM process. The independent variables were coded according to Eq. (3):

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \quad i = 1, 3 \quad (3)$$

where  $x_i$  and  $X_i$  are respectively the dimensionless and the actual values of the independent variable  $i$ ,  $X_{i0}$  is the actual value of the independent variable  $i$  at the central point, and  $\Delta X_i$  is the step change of  $X_i$  corresponding to a unit variation of the dimensionless value. For the three variables, the design yielded 18 randomized experiments (to avoid effects of extraneous factors) with eight ( $2^3$ ) factorial points, six axial points (– $\alpha$  and + $\alpha$ ) to form a central

**Table 1**

Experimental and predicted data for TPC with different combinations of ultrasonic intensity ( $x_1$ ), processing temperature ( $x_2$ ) and processing time ( $x_3$ ) used in the randomized central composite design.

Run	Independent variables			TPC <sup>b</sup>	
	$x_1 = \text{UI}^a$ (W/cm <sup>2</sup> )	$x_2 = T^a$ (°C)	$x_3 = t^a$ (min)	Experimental	Predicted
1	1 (0.719)	–1 (16)	–1 (15)	264.94	262.11
2	–1 (0.431)	–1 (16)	–1 (15)	234	233.61
3	1 (0.719)	–1 (16)	1 (45)	269.76	272.63
4	–1 (0.431)	–1 (16)	1 (45)	251.53	261.28
5	1 (0.719)	1 (34)	–1 (15)	333.14	327.14
6	–1 (0.431)	1 (34)	–1 (15)	311.22	312.19
7	1 (0.719)	1 (34)	1 (45)	333.66	337.91
8	–1 (0.431)	1 (34)	1 (45)	333.46	340.11
9	– $\alpha$ (0.332)	0 (25)	0 (30)	311.78	314.65
10	+ $\alpha$ (0.764)	0 (25)	0 (30)	300.81	292.53
11	0 (0.575)	0 (25)	– $\alpha$ (5)	262.36	269.08
12	0 (0.575)	0 (25)	+ $\alpha$ (55)	313.55	301.41
13	0 (0.575)	– $\alpha$ (10)	0 (30)	237.42	233.62
14	0 (0.575)	+ $\alpha$ (40)	0 (30)	339.91	344.10
15	0 (0.575)	0 (25)	0 (30)	315.79	309.78
16	0 (0.575)	0 (25)	0 (30)	308.65	309.78
17	0 (0.575)	0 (25)	0 (30)	307.95	309.78
18	0 (0.575)	0 (25)	0 (30)	305.87	309.78
Mean absolute error for replications				3.73	

<sup>a</sup> UI: ultrasonic intensity;  $T$ : processing temperature;  $t$ : processing time.

<sup>b</sup> mg Catechin eq/100 g. db.

composite design and four center points for replications and estimation of the experimental error and to prove the suitability of the model. For the developed CDD the axial distance  $\alpha = \sqrt[4]{N}$ , with  $N$  the number of experiments in orthogonal design, i.e. the factorial design (in our case 1.68). Both the coded and actual values of the independent variables are listed in Table 1.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i<j}^2 \sum_j^3 \beta_{ij} x_i x_j \quad (4)$$

The yields in total phenolics (mg of catechin equivalent per 100 g d.b) is related to the coded independent variables  $x_i$ ,  $x_j$  according to the second order polynomial expressed by Eq. (4), with  $\beta_0$  the interception coefficient,  $\beta_i$  the linear terms,  $\beta_{ii}$  the quadratic terms,  $\beta_{ij}$  the interaction terms. The Fisher's test for analysis of variance (ANOVA) performed on experimental data permitted to estimate the statistical significance of the proposed model. Response surfaces

as represented by Fig. 4 were drawn by using the analysis design procedure of *Statgraphics Plus for Windows* software (Centurion version). The values of each variable range were chosen in function of limitations of ultrasonic apparatus (minimum and maximum power available in device). The maximal temperature and sonication time were fixed at 40 °C and 55 min respectively. Above these values, the phenolic compounds might degrade [1,3].

## 2.6. Kinetics of total phenolics extraction

The kinetics data of total phenolics extracted from maritime pine wood waste were fitted to the first-order rate equation derived from a quasi-steady model of extraction [27].

$$\left( \ln \frac{C_{\infty}}{C_{\infty} - C(t)} \right) = k_i + a \quad (5)$$

where  $C(t)$  is the concentration of total polyphenols at time  $t$ ,  $C_{\infty}$  is the final concentration of total polyphenols,  $k$  is the apparent first-order rate constant of extraction and  $a$  the semi empirical intercept. When  $\left( \ln \frac{C_{\infty}}{C_{\infty} - C(t)} \right)$  is plotted against time, the points fall on two intersecting straight lines, the first with a relatively steep slope and the second with a relatively shallow one.

## 2.7. SEM measurements

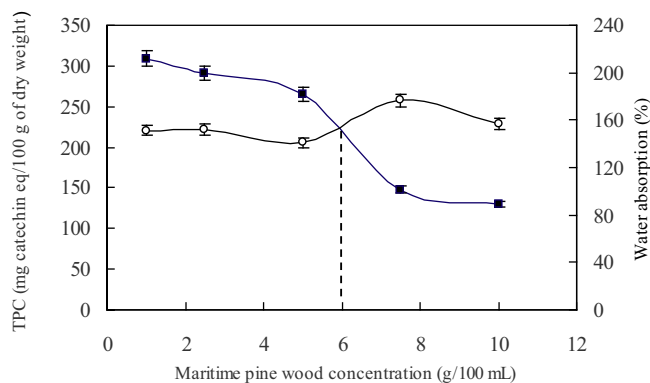
Maritime pine wood sawdust waste before and after CVM and UAM extractions have been analyzed by electronic microscopy. The microstructures were observed using an environmental SEM FEI/Philips Quanta 200 FEG (Field Effect Gun). Samples were observed under 1.5 mbar of water vapor pressure without any metallic coverage. The accelerating voltage used is 20 kV.

## 3. Results and discussion

### 3.1. Preliminary results

#### 3.1.1. Optimization of solid/liquid ratio

To determine the optimum solid/liquid ratio, total polyphenol compounds and the liquid absorbing capacity of maritime pine wood waste chips plotted according to the concentration of the solid phase in the slurry. All extractions were performed by UAM procedure ( $UI = 0.764 \text{ W/cm}^2$ ;  $T = 40 \text{ }^{\circ}\text{C}$  and  $t = 40 \text{ min}$ ). From Fig. 2 it can be observed that the optimum ratio was about 6 g of dry material/100 mL. For concentrations greater than 7.5 g of dry material/100 mL the maritime pine wood absorbed all available liquid. During procedures of CVM and UAM a minimum of free



**Fig. 2.** Optimization of solid/liquid ratio for maritime pine chips extraction with acidified water by maceration: polyphenol concentration in the extract (TPC) (○) and water absorption (■).

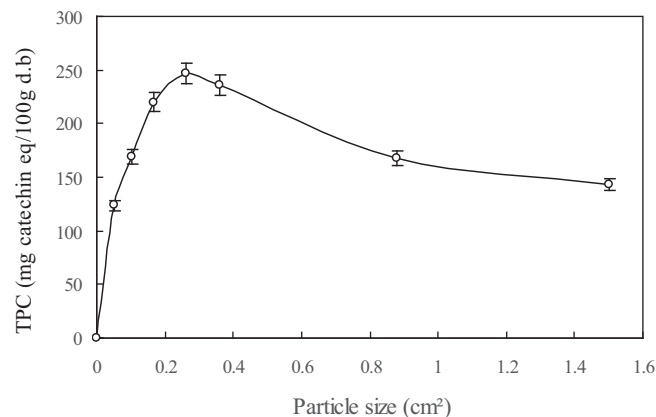
liquid is required in the extraction apparatus, therefore a compromise between a high TPC yield and a high amount of available acidified water was chosen. Pingret et al. [28] observed the same behavior when they optimized the ratio solid/liquid in ultrasound assisted procedure of polyphenol extraction from apple pomace.

#### 3.1.2. Influence of particle size

The particle size controls the mass transfer kinetics and the access of the solvent to the soluble components [29,12]. In a general way, higher extraction efficiencies can be achieved by applying smaller particle sizes, which results in an increase in mass transfer surface and in quantity of soluble fraction isolated. Fig. 3 depicts the influence of different particle sizes (0.05, 0.10, 0.17, 0.26, 0.36, 0.88 and 1.5  $\text{cm}^2$ ) on polyphenols yield extracted with a ratio solid/liquid of 6 g/100 mL of acidified water and 40 °C as processing temperature during 40 min and 0.764  $\text{W/cm}^2$  for ultrasonic intensity. An optimum is observed for a particle size of 0.26  $\text{cm}^2$  beyond which the quantity of extracted polyphenols decreased due to the recalcitrant structure of wood. This behavior can be explained by the fact that the fine particles stayed in suspension at the surface of the solvent and therefore were not subjected to the vigorous agitation and ultrasonic waves.

### 3.2. Experimental design and statistical analysis

After preliminary determination of optimum particle size (0.26  $\text{cm}^2$ ) and optimum solid/liquid ratio (6% (w/v)), three variables that could potentially affect extraction efficiency of polyphenols were studied by UAM in a central composite design, namely ultrasonic intensity (UI), temperature ( $T$ ) and sonication time ( $t$ ). UI ranged from 0.335 to 0.764  $\text{W/cm}^2$  and chosen according the limitations of the ultrasonic device. The choice of the temperature variation domain is very important in order to avoid the degradation of organic compounds and for an efficient application of ultrasound. In a general way, the polyphenols might undergoing degradation when the temperature is higher than 60 °C [30] and especially when temperature is combined with ultrasound as for UAM extraction [28]. Thus, moderate temperatures were chosen with a range of 10–40 °C. Concerning the processing time of sonication, we aimed to carry out extractions in a relatively short time to be competitive with conventional extraction methods and interesting for potential industrial applications. Moreover, after a certain time the cavitation bubbles do not continue to absorb energy to grow and collapse [31]. Thus, sonication time was varied between 5 and 55 min. The controlled variables were studied in a multivariate study with 18 experiments as shown in Table 1.



**Fig. 3.** Optimization of particle size of maritime pine chips for polyphenols extraction.

3.2.1. Results for TPC

Full coded experiments and responses obtained for each run of the central composite design are presented on Table 1. As it can be observed, responses varied greatly in function of the combination of parameters setting. TPC varied from 233.6 to 343.9 mg of catechin equivalent per 100 g d.b of maritime pine wood waste. Significance and suitability of the design were studied using an analysis of the variance (ANOVA) displayed in Table 2. The statistical significance of each effect (including interaction terms, linear and quadratic effects) was determined using Fisher test (*F-value*) and the probability *p* (*p-value*). Corresponding variables would be more significant if absolute *F-value* becomes greater and *p-value* becomes smaller depending on the confidence level. By considering a confidence level of 95%, the linear effects of the three key variables (*UI*, *T*, *t*) as well as the quadratic effects of sonication time (*t*<sup>2</sup>) and processing temperature (*T*<sup>2</sup>) were significant. For these five effects, *p-value* was largely lower than 0.05. All cross-product terms (*UI.T*; *UI.t* and *T.t*) were statistically not significant suggesting an absence of interaction between the variables. The experimental data obtained from the central composite design allowed us to determine an empirical relationship linking response studied (TPC) and key variables involved in the model (in coded units). Thus, a second order polynomial equation was obtained (Eq. (6)) where only the significant effects are shown (*p* < 0.05):

$$Y = 309.67 - 13.15UI + 68.89T + 19.21t - 14.49T^2 - 16.41t^2 \quad (6)$$

where, *Y* represents TPC (expressed in mg of catechin equivalent per 100 g of dried maritime pine chips), *UI*, *T* and *t* are expressed in coded units. The quality of the models developed was evaluated based on the correlation coefficient *R*<sup>2</sup> and also on the lack-of fit value. From ANOVA (Table 2), it can be seen that *R*<sup>2</sup> was about 97.4% and *p-value* of lack-of-fit higher than 0.05 (non-significant) suggesting that the predicted models reasonably represent the observed values within the limits of the experimental ranges used. *R*<sub>adj</sub><sup>2</sup> is a regression coefficient adjusted for the number of coefficient involved in the model; its permit comparison between models with different numbers of independent variables and allows testing the goodness-of-fit of regression coefficient. Its value (>0.94) indicates a good degree of correlation between observed and predicted data as indicated in Table 1.

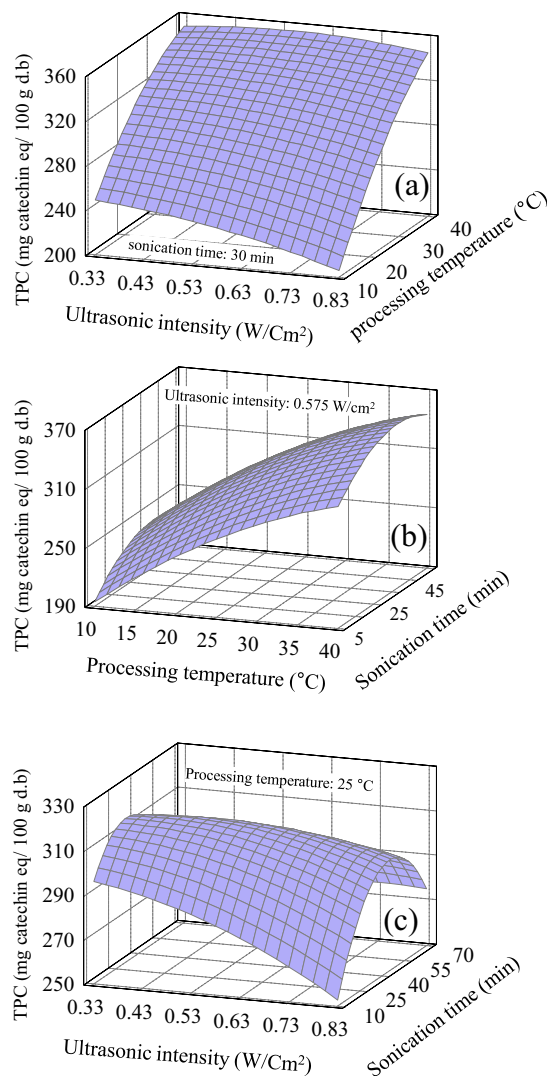
3.2.2. Optimization for TPC

Three-dimensional profiles of multiple non-linear regression model was employed to illustrate the linear and quadratic effects as well as the interaction effects on the extracted TPC. Fig. 4

**Table 2**  
 Analysis of variance (ANOVA) showing the effect of the three independent variables as linear, quadratic and cross products terms on TPC.

Source	Sum of square	Df	Mean squares	F-ratio	P-value
UI: ultrasonic intensity	590.47	1	590.47	31.63	0.0111
T: temperature	17662.10	1	17662.10	946.02	0.0001
t: sonication time	1261.19	1	1261.19	67.55	0.0038
UI <sup>2</sup>	60.54	1	60.54	3.24	0.2525
UI.T	91.80	1	91.80	4.92	0.1133
UI.t	147.06	1	147.06	7.88	0.0675
T <sup>2</sup>	388.64	1	388.64	20.82	0.0094
T.t	0.031	1	0.031	0.00	0.9699
t <sup>2</sup>	952.03	1	952.03	50.99	0.0066
Lack-of-fit	494.12	5	98.82	5.29	0.0956
Pure error	56.01	3			

*R*<sup>2</sup> = 0.974; *R*<sub>adj</sub><sup>2</sup> (adjusted for Df) = 0.945.



**Fig. 4.** Optimization of ultrasound-assisted maritime pine sawdust extraction by water: TPC investigation in the multivariate study: (a) TPC as a function of ultrasonic intensity and sonication time, (b) TPC as a function of ultrasonic intensity and temperature, and (c) TPC as a function of temperature and sonication time.

highlights TPC behavior in function of two variables. In each plot, the third one is fixed at its central value ("0"). The most influential effects are the linear terms of processing temperature (*T*) and sonication time (*t*). It is clearly showed that the TPC yield increase linearly as temperature and sonication time increased. The ultrasonic intensity (*UI*) also exerted a significant negative linear effect (Fig. 4a and c) but with a less predominant influence as indicated by *p-values* of ANOVA analysis (Table 2). The sonication time displayed a strong quadratic effect (*p* = 0.0057) clearly visible in Fig. 4c in which the yield of TPC systematically increased until a certain value after which a decreasing was observed. For the central value of processing temperature (25 °C) and ultrasonic intensity (0.575 W/cm<sup>2</sup>), the yield in TPC varied between 290 and 306 mg catechin eq/100 g d.b when the sonication time increased from 15 to 45 min with a maximum of 312.5 mg catechin eq/100 g d.b at 40 min. This quadratic effect of sonication time was also pointed out by [32,33,3] for isolation of polyphenols from arecanut, sugar beet molasses and spruce wood bark respectively. The processing temperature also exerted a significant quadratic effect (*p* = 0.0197) but it was less predominant as that of sonication time as indicated by Fig. 4a and b in which the surface curvature is

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less visible than that of Fig 4c. According to Zhang et al. [34] this quadratic effect may be attributed to the fact that higher concentration of chemical species is present in the cavitation bubbles due to the higher vapor pressure at higher operating temperature which results in much higher amounts of free radicals in the liquid leading to higher degradation rate. Optimal settings for TPC maximization were 0.67 W/cm<sup>2</sup> for ultrasonic intensity, 40 °C for processing temperature and 43 min for sonication time. The optimum TPC yield predicted by the model (348.5 mg of catechin equivalent per 100 g d.b) was confirmed experimentally using the optimized operating conditions in Section 3.3 where the yield obtained for a sonication time of 43 min was about 342.4 mg of catechin equivalent per 100 g d.b.

### 3.3. Comparison of CVM and UAM polyphenols extraction kinetics

In order to evaluate the impact of ultrasound on extraction of polyphenols, a kinetic comparative study was performed between UAM in optimized conditions and CVM in the conditions described in Section 2.3 (the same conditions except sonication). On Fig. 5, it can be clearly seen that UAM extraction permits to greatly improve the TPC yield by more than 40% (233.5 and 342.4 mg of catechin equivalent per 100 g d.b for CVM and UAM as a maximum of polyphenols extraction, respectively). The kinetic of extraction was clearly improved, which could be explained by ultrasonic cavitation since it is the only variable modified between both experiments. For the two techniques, extraction of polyphenols occurred in two distinct kinetic steps as testified by the rupture of the slope in the linear plots drawn in Fig. 6. The first step between 0 and

15 min and the second one between 15 and 50 min. The calculations of the first order kinetic constants indicated that it was slightly higher for UAM in the first step (0.1085 and 0.1270 min<sup>-1</sup>, with R<sup>2</sup> of 0.996 and 0.992 respectively for CVM and UAM).

During the second step the first-order kinetic rate constants were similar (0.0678 and 0.0687 min<sup>-1</sup>, with R<sup>2</sup> of 0.966 and 0.977 for CVM and UAM, respectively). Since the difference between the first-order kinetic constants for both fast and slow periods were not significant it can be concluded that ultrasound treatment did not modify the extraction kinetics, even though the yield of polyphenols extracted by UAM was largely more important than that obtained for CVM. This finding was also quoted by some authors [35–36] who attributed it to the ultrasonic cavitation phenomenon which is responsible of modifications on the plant material inducing disruption of the cells, due to the burst of the cavitation bubble on the surface of the matrix.

### 3.4. Large scale ultrasound-assisted extraction

Ultrasound-assisted extraction provides numerous advantages for an industrial application compared to conventional maceration which requires a long extraction time and/or energy consuming [37,38]. For this purpose, a study was performed in a 30 L extraction tank (Fig. 7) from R.E.U.S company. The reactor is composed of a quadruple output of ultrasound at 25 kHz and a power of 4 × 200 Watts. UAM Polyphenols extraction was carried out in the optimum conditions obtained from the previous experiments at laboratory scale and defined by the response surface methodology results. TPC yield obtained by UAM extraction at a pilot scale was of 308.7 mg of catechin equivalent per 100 g d.b. Despite that this results was lower than that obtained at lab scale (342.4 mg of catechin equivalent per 100 g d.b) it remains 32% higher than the maximum TPC yield (233.5 mg of catechin equivalent per 100 g d.b) obtained by CVM polyphenols extraction. This result shows that extraction assisted by ultrasound is promising technique that can be considered at industrial scale, especially when the solvent employed is water (a green environmental solvent). It can reduce the energy consumption while improving the final yield [39]. Thus, the valorization of the industrial wood byproducts such as maritime pine using a green solvent (as acidified water) and a rapid extraction method as UAM is a real advantage from environmental and industrial points of view.

### 3.5. Multistage cross-current extraction

#### 3.5.1. Experimental results

Three concepts of multistage cross-current extraction (Fig. 8) were implemented. Firstly, three stage of conventional maceration (CVM) were compared to three stages of ultrasound-assisted (UAM) extraction (Fig. 8a and b), in the same conditions: T = 40 °C, t = 3 × 14 min, constant agitation, solvent: acidified water at pH = 3.8 (renewed in each stage). In the 3rd configuration, the influence of ultrasound was quantified by using the first stage of UAM as a pretreatment for the two further stages of CVM (Fig 8c). UAM experiments were carried out in optimized settings obtained from the second order polynomial equation for TPC and CVM in the conditions defined in Section 2.3. Fig. 9 depicts the TPC results obtained (expressed in mg of catechin equivalent per 100 g d.b for CVM, UAM and combination of UAM and CVM, respectively). This result confirmed the previous extraction kinetics obtained in Section 3.3 which asserted the presence of two distinct phases, a rapid period (about 15 min) followed by a slow period for which the rate coefficient was two times lower. It can

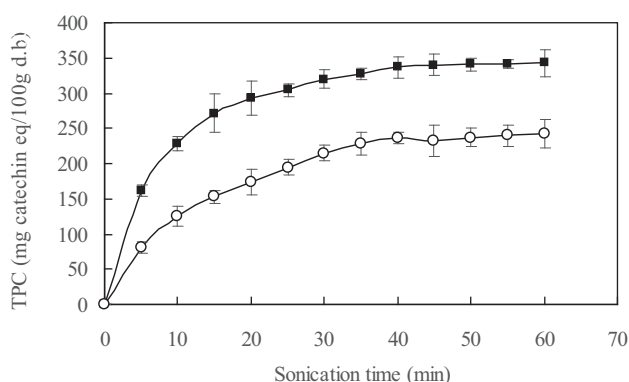


Fig. 5. Comparison between conventional maceration (CVM ○) and ultrasound-assisted maceration (UAM ■).

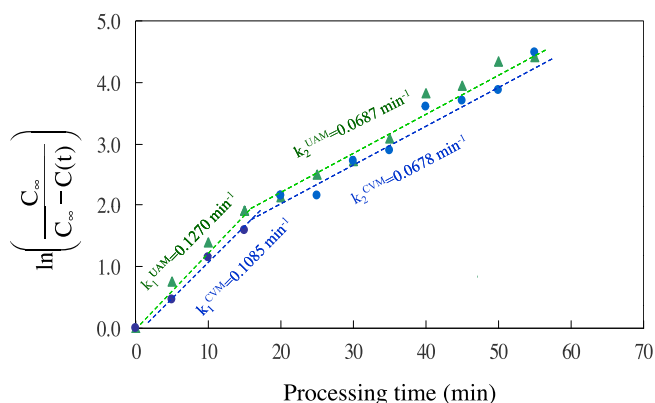


Fig. 6. First-order plots for the two stages of polyphenols extraction by CVM (●) and UAM (▲) and the respective semi-empirical factors  $k_i$ .

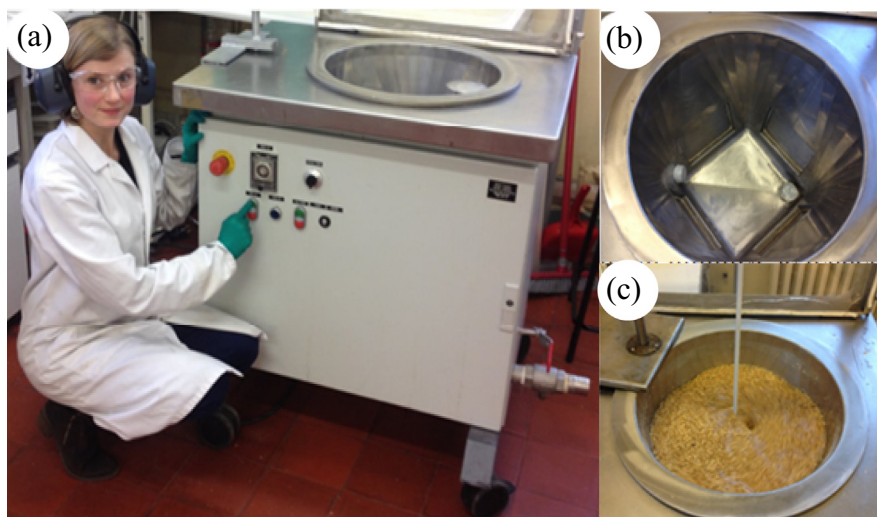


Fig. 7. Large scale ultrasound apparatus (a), inside view of apparatus (b), UAM for polyphenol extraction from maritime pine sawdust (c).

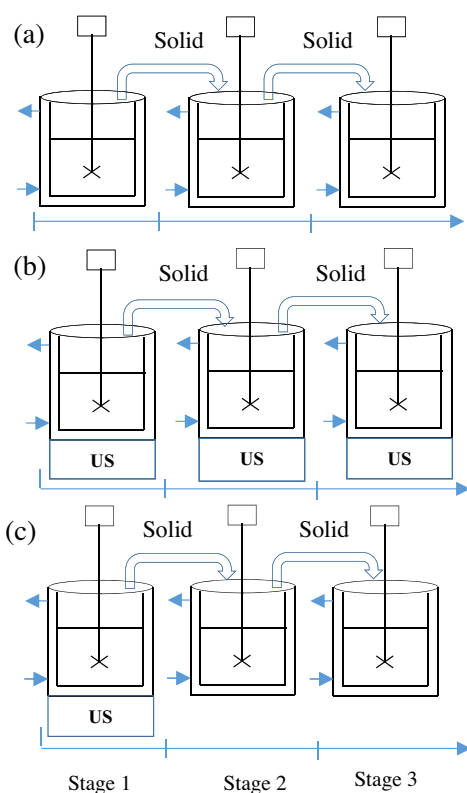


Fig. 8. Multistage cross-current extraction; (a) multistage conventional maceration, (b) multistage maceration, ultrasound-assisted, (c) multistage extraction combination of (a) and (b).

be also observed on Fig. 8 that a pretreatment of maritime pine wood waste material by ultrasound followed by two stages of conventional maceration leads to reach a similar TPC yield to that obtained for three stages of UAM (313.3 and 333.6 mg of catechin equivalent per 100 g d.b for UAM and CVM mixed extraction and multistage of UAM, respectively). Thus ultrasounds appeared to be more effective during the first minutes of extraction and their effect decreases over time. Thus, from an environmental and industrial point of view, this result is particularly interesting since it would not need to change an existing extraction installation, only a pretreatment of the wood sawdust waste by UAM is sufficient.

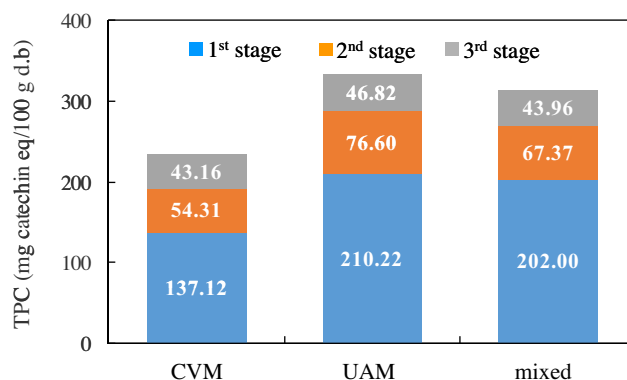


Fig. 9. TPC yields in multi-stage cross-current extraction conventional, under ultrasound and mixed.

### 3.5.2. Theoretical considerations on solid-liquid multistage cross-current extraction

In brief, solid/liquid extraction is the separation of a solid solute (solute, A) from a mixture of insoluble solids (inert, B) by dissolving it in a liquid phase (solvent, S). In most cases, the diffusion intra-particle soluble component(s) controls the extraction rate. Therefore the process is often called as diffusion extraction. The extraction process can be dissociated by four major steps: (1) solvent diffusion within the solid matrix; (2) internal solute dissolution in the solvent; (3) solute diffusion in the solvent within the solid and its migration towards the surface; (4) external transfer (by diffusion, but more generally by convection or agitation, etc.) of the solute from the surface of the solid to the external environment [40]. The transfer of the researched active molecules to the outside environment is accomplished by solvent diffusion into the solid, which is mainly the result of a concentration gradient of solute between the inner solution near the solid phase (more concentrated) and the liquid phase (less concentrated). At the end of the operation, the system reaches equilibrium and the diffusion is close to zero. In the case of a multistage cross-current extraction performed in this study (Fig. 8), at the end of each stage, the liquid phase constituting the extract (A + S) is recovered and the solvent (S) is renewed, thus the diffusion continues until the complete exhaustion of solid phase. At the end, the solid exhausted, named inert (B) did not contain or a little bit of solute



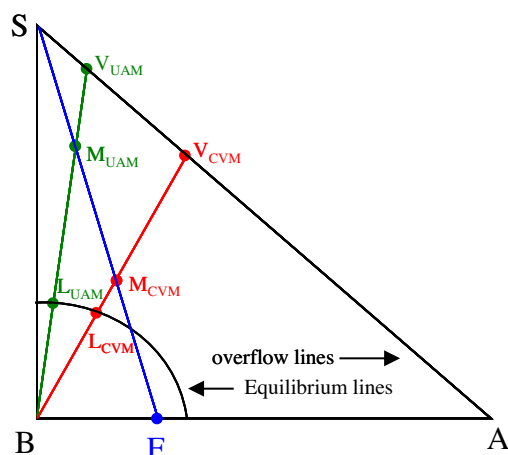
[41], and the system reaches equilibrium and the diffusion is close to zero. In the case of a multistage cross-current extraction (Fig. 10), at the end of each stage, the liquid phase constituting the extract (A + S) is recovered and the solvent (S) is renewed, thus the diffusion continues until the complete exhaustion of solid phase. In order to understand the extraction process, a diagram phase was constructed for classical maceration and ultrasound-assisted extraction (Fig. 11). Each extraction by cross-current (Fig. 11) of polyphenols from maritime pine constitutes one stage (both phases are in thermodynamic equilibrium). The overflow (V = A + S) was recovered and then quantified in mg of catechin equivalent per 100 g of d.b. and the underflow (L = A + B + S) composed of impoverished solid in solute and inert with a little bit of solvent was recovered to undergo another stage of extraction with renewed solvent. Equilibrium of extraction is represented by a right-angled triangle (Fig. 11), where each top of triangle is associated to a pure substance, S (100% of solvent), A (100% of solute) and B (100% of inert). Each side of triangle represents a binary mixture and each point inside the triangle is a ternary mixture. The material balance of first stage is expressed as:  $F + S = L_1 + V_1 = M$ . The quantity of feed ( $F = A + B$ ) and solvent (S) were fixed, thus the point M can be placed on the phase triangle according to Eq. (7):

$$\begin{aligned} F \cdot \overline{FM} &= S \cdot \overline{SM} \\ FS = \overline{FM} + \overline{SM} &\Rightarrow \overline{FM} = F + S \cdot \frac{\overline{SM}}{\overline{FS}} \end{aligned} \quad (7)$$

During the conventional solid-liquid extraction,  $V_{CVM}$  (overflow) is in equilibrium with  $L_{CVM}$  (underflow) and are located on the same equilibrium line than M and B. On the other side, during ultrasound-assisted extraction,  $V_{UAM}$  (S + A) is more concentrated, richer in solute (210.2 mg of catechin equivalent per 100 g d.b as indicated in Fig. 9). The conventional equilibrium (B,  $L_{CVM}$ ,  $M_{CVM}$ ,  $V_{CVM}$ ) is modified and replaced by a new equilibrium (B,  $L_{UAM}$ ,  $M_{UAM}$ ,  $V_{UAM}$ ). The effect of ultrasound on the plant matrix appears to enhance the solvent enrichment in solute during the first minutes of extraction.

### 3.6. Impact of ultrasound on microstructure

In order to investigate the effects of ultrasonic waves on the solid matrix, scanning electron microscopy (SEM) analysis was performed on untreated wood (Fig. 11a), after CVM (Fig. 11b) and after UAM (Fig. 11c). The raw material owned small uniform pores, around 5  $\mu\text{m}$  of diameter. After CVM, a slight expansion of pores was observed (around 20  $\mu\text{m}$  of diameter) allowing a conventional



**Fig. 10.** Diagram phase of conventional (CVM) and ultrasound-assisted extraction (UAM).



**Fig. 11.** Maritime pine sawdust observed by SEM; (a) raw material, (b) after maceration, (c) after ultrasound-assisted extraction.

diffusion during maceration. For the samples that underwent UAM process, the cell walls were damaged and a perforation was observed allowing easy entry of the solvent into cellular channels [19]. This damage is probably due to exploding and cavitation mechanism of microbubbles generated by ultrasounds which induce fragmentation and surface erosion. Some authors [42,43] disserted about a mechanism that involves a more severe thermal stress due to rapid temperature rise and high localized pressures induced cavities into the cellular matrix compared to conventional extraction methods. However, increase in extraction yields as obtained in Sections 3.3 and 3.4 cannot be simply explained by the abrasive effects or by the turbulence created by ultrasonic waves. The experimental observations noted by Santos et al. [44] suggested that the intensification of mass transport is also due to physical effects on the surface of the particles. They showed that the mass transfer coefficient increase when the solid matrix is exposed to such disturbances.

#### 4. Conclusion

This work presented the enhancement and the industrial potential of ultrasound-assisted extraction in the field of the valorization of by-products. Considering the fact that polyphenols are the most common extracted targets in industrial production, a multivariate study allowed defining optimal parameters of ultrasound-assisted maceration (UAM), to maximize extraction of total phenolics from maritime pine sawdust waste. In comparison with conventional maceration (CVM), UAM showed an increase of more than 30% in total phenolic content after 40 min with a green environmental solvent (water). This increasing was assessed by large scale experiments that confirmed that UAM have a potential to extract natural products with better yields than conventional techniques not only at a lab-scale but also at a pilot-plant scale, thus showing the industrial potential applicability of ultrasound. The multistage cross-current extraction study showed that the first minutes of ultrasound are the most efficient. So, a simple pretreatment (few minutes) of plant material below a conventional extraction is enough. Also, this process can be considered as an improvement for the polyphenol extraction since it allows the reduction of processing time and saving energy.

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