



# Degradation behavior of polyphenols in model aqueous extraction system based on mechanical and sonochemical effects induced by ultrasound

Pengxu Wang<sup>a</sup>, Chuanxiang Cheng<sup>a</sup>, Yaqin Ma<sup>a,b,\*</sup>, Meng Jia<sup>a</sup>

<sup>a</sup> Citrus Research Institute, Southwest University Chongqing 400712, People's Republic of China

<sup>b</sup> National Engineering Research Center for Citrus, Chongqing 400712, People's Republic of China

## ARTICLE INFO

### Keywords:

Polyphenols  
Degradation  
Sonochemical effects  
Mechanical effects  
Ultrasound  
Extraction

## ABSTRACT

In this study, the temporal and spatial variation of mechanical effects (ME) and sonochemical effects (SE), the degradation behavior of polyphenols as well as the correlation coefficients were comprehensively analyzed. The ME and SE showed inverse dependence along with the axial direction of transducer. Higher irradiation distance (50 mm) enhanced the ME but inhibited the generation of hydroxyl radicals (8.29  $\mu\text{mol/L}$ ). Rutin and cyanidin-3-glucoside, compared with thermal degradation (70°C, 6.41%, and 11.45%), were more susceptible to free radical degradation due to the boost of SE at low temperature (10°C, 20.23%, and 34.41%). The concentration of hydroxyl radicals at 70°C (18.38  $\mu\text{mol/L}$ ) was about 5.77 times lower than that at 10°C (3.22  $\mu\text{mol/L}$ ). No significant differences in the ME were observed for a wide range of temperatures (10–70°C). The impacts of increasing duty cycle on further promoting the ME and SE were limited. The concentration of hydroxyl radicals (0–23.37  $\mu\text{mol/L}$ ) increased linearly with sonication time (0–45 min) and the degradation of caffeic acid only occurred on a time scale (25 min). The free radical scavenger can minimize the degradation of polyphenols by inhibiting the hydroxyl radicals (23.37  $\mu\text{mol/L}$  without t-BuOH; 12.17  $\mu\text{mol/L}$  with t-BuOH). The above results showed that the degradation of polyphenols attacked by hydroxyl radicals presented a dose-response relationship. The correlation between the hydroxyl radicals and polyphenols as well as the mechanical effects and extraction yield indicated that the stability of polyphenols exposed to ultrasonic field depended on the structure-radical scavenging activity relationship and the extraction may be accompanied by the degradation.

## 1. Introduction

Stemming from the discovery of cavitation effects, ultrasound has been applied to various fields including homogenization, emulsification, catalytic reaction, and enhanced extraction. Based on the bubble dynamics and nature, the effects of collapsing cavitation bubbles were classified into sonochemical effects (SE) and mechanical effects (ME). It is widely accepted that high-energy ME such as shock waves, acoustic streaming, and microjets usually intensify the extraction process by inducing severe collisions among the plant particles and several irreparable damages near and onto the surfaces of raw materials to accelerate the disintegration and fragmentation of localized tissues [1,2]. A recent study revealed the importance of microjets produced by asymmetrical collapse of bubbles in removing the solvent stagnant layer and promoting the release of cellular contents [3].

Generally, ME dominate at low-frequency ultrasound due to the inverse dependence of ME and SE on the ultrasonic frequency [4]. Therefore, low-frequency ultrasound is usually recommended for

extraction since it has very weak SE on the quality and stability of final products and this is a cardinal precondition for the development of ultrasound-assisted extraction towards the industrial-scale application [5]. Many authors also reported that there was no significant decrease in the yield of bio-compounds whatever the parameters were used during extraction [6–8]. However, in some cases, a remarkable decrease or degradation for chlorogenic acid and protocatechuic acid has been observed [9]. Qiao et al. [10] found that only caffeic acid and sinapic acid were degraded during studying the stability of seven phenolic acids under ultrasound field. Also, Katsampa et al. [11] noticed that quercetin was partially degraded or oxidized to quercetin adduct during the extraction of phenolic compounds from onion solid wastes at 37 kHz. The mechanism of degradation was usually attributed to hydroxyl radical due to the pyrolysis of water molecules inside cavitation bubble [12,13]. In the case of an ultrasound of 20 kHz, each bubble can be regarded as an electrochemical cell, then approximate  $7.2705 \times 10^3$  active bubbles were created per second per liter in the liquid and  $3.09 \times 10^{12}$  mol  $\cdot$  OH radicals were released by each bubble in the final

\* Corresponding author at: Citrus Research Institute, Southwest University Chongqing 400712, People's Republic of China.

E-mail address: [myaya211@cric.cn](mailto:myaya211@cric.cn) (Y. Ma).

<https://doi.org/10.1016/j.seppur.2020.116967>

Received 5 November 2019; Received in revised form 14 March 2020; Accepted 17 March 2020

Available online 29 April 2020

1383-5866/© 2020 Elsevier B.V. All rights reserved.

phase of collapse [14]. Ultimately, the hydroxyl radicals, diffused from inside bubble into bulk solvent, as nonspecific oxidizing species may result in a decrease in yield or deterioration in quality for bio-compounds [15]. Nevertheless, the publication data concerning the degradation of phenolics under ultrasonic field were controversial [10,16,17]. The evidence about the degradation caused by  $\cdot\text{OH}$  radicals under low-frequency ultrasound is very limited.

As mentioned above, ME have positive effects but SE have negative effects on the extraction process. Thus, the final extraction yield and efficiency are not only overwhelmingly dependent on ME but also SE, which in turn depends upon various parameters. Accordingly, it is important to understand the parameters dependence of ME and SE due to the sensitivity of ultrasonic system for working parameters so that desirable extraction process can be achieved. Previously, the optimization and impacts of operational parameters on extraction efficiency as well as the application of hybrid techniques such as the combination of ultrasound with microwave or supercritical liquid have been excellently explored [18–20]. To our best knowledge, parametric and phenomenological study about the mechanical effects and sonochemical effects were never investigated simultaneously and the contradictions about the degradation of polyphenols under ultrasonic field have not been addressed. Driven by these doubts, the cause-effect-relationship among operating parameters, mechanical effects, sonochemical effects and bio-compounds should be preferentially solved.

With the vigorous advocacy of green chemistry concept in recent years [21], ultrasound-assisted aqueous extraction (UAE) has been applied to the extraction of polyphenols by virtue of its advantages of high reproducibility, lower energy consumption and environment-friendly solvent [18,22]. Therefore, water was chosen as a solvent. Polyphenols, as a source of food preservatives, antioxidants and medicines, are ubiquitous in the fruits and vegetables. According to the number of aromatic rings and types of carbon skeleton, they are principally divided into non-flavonoids and flavonoids (C6-C3-C6) [23]. Thus, caffeic acid as a non-flavonoid, rutin and cyanidin-3-glucoside (cy-3-glu) as a flavonoid were chosen as target compounds based on their different thermal sensitivity and free radical scavenging activity (Fig. 1) [10,24,25]. In most of UAE studies, ultrasonic parameters such as temperature, sonication time and duty cycle were commonly optimized to achieve higher yields [19,20,26]. For probe-type ultrasound equipment, irradiation distance as an important technical parameter was often neglected. Thus, these parameters were selected and investigated. In addition, degradation kinetics was developed, and correlations among ultrasound parameters,  $\cdot\text{OH}$  radicals, and three polyphenols, and correlations between extraction yield and ME were calculated to quantify the impacts of ultrasound. The aim of this study was to evaluate and understand the impacts of ME and SE on the extraction and degradation to purposefully maximize the extraction yield and minimize the degradation during UAE.

## 2. Materials and methods

### 2.1. Chemicals, reagents and plant materials

Caffeic acid (purity  $\geq 98.0\%$ ) was purchased from ANPLE Laboratory Technologies Inc. Rutin (purity  $\geq 98.0\%$ ) and potassium iodide (purity  $\geq 99.5\%$ ) were purchased from Aladdin Biochemical Technology Co., Ltd. Cyanidin-3-glucoside (purity  $\geq 99.10\%$ ) was purchased from Chengdu MUST Biotechnology Co., Ltd. Tert-butyl alcohol (purity  $\geq 99.5\%$ ) was purchased from Shanghai Macklin Biochemical Co., Ltd. Polyethylene oxide (molecular weight 900000, PEO 900000) was purchased from Acros Organics. Methanol and acetonitrile (purity  $\geq 99.9$ ) were purchased from Sigma-Aldrich Co., Ltd. Acetic acid, phosphoric acid, ethanol, sodium hydroxide, sodium carbonate, sodium nitrite, aluminum nitrate and Folin-Ciocalteu phenol reagent were obtained from Chengdu Kelong Chemical Reagent Factory (Analytical Grade). Blood orange peels (*Citrus sinensis* L. Osbeck) were dried for 72 h at  $40^\circ\text{C}$  and powered to obtain a particle size of  $250\ \mu\text{m}$ .

### 2.2. Model extraction system

#### 2.2.1. Instrument and protocol

This study adopted an ultrasonic equipment equipped with a probe attached to a titanium horn microtip of 15 mm diameter (JY98-IIIN, Ningbo Scientz Biotechnology Co. Ningbo, China). Detailed parameters of the ultrasonic equipment were as follows: output power of 120 W, frequency of  $20 \pm 0.5\ \text{kHz}$ . To eliminate the interaction effect of three polyphenols in solution, the model system of 10 mg/L caffeic acid, 10 mg/L rutin, and 5 mg/L cy-3-glu were prepared separately by using Milli-Q water ( $18.5\ \text{M}\Omega$ ). Before experiments, the model solution was injected into a double-jacket reactor, which allowed us to keep the liquid temperature constant by using a thermostatic bath (adjustable temperature at  $0\text{--}100^\circ\text{C}$ ) (SDC-6, Ningbo Scientz Biotechnology Co. Ningbo, China), and then the ultrasonic probe was immersed into the reactor. The temperature was measured by using a thermocouple with a diameter of 5 mm. After that, the samples could be irradiated by ultrasound. All samples after treatment were filtered by  $0.45\ \mu\text{m}$  filter membrane and analyzed by High-Performance Liquid Chromatography.

The following parameters were selected to investigate the impacts of ultrasound by using single factor experiment including irradiation distance (distance between the horn microtip and the bottom of reactor) (10, 20, 30, 40 and 50 mm), temperature (10, 25, 40, 55 and  $70^\circ\text{C}$ ), sonication time (5, 15, 25, 35 and 45 min), and duty cycle (ON/OFF second) (1/3, 1/2, 2/2, 2/1 and 3/1). Reference conditions were as follows: irradiation distance 20 mm, temperature  $25^\circ\text{C}$ , sonication time 15 min, and duty cycle 2/2. The corresponding ultrasonic intensity under reference conditions was  $12.79\ \text{W}/\text{cm}^2$ . The liquid volume of irradiation distance was 180 mL and the others were 100 mL. The same

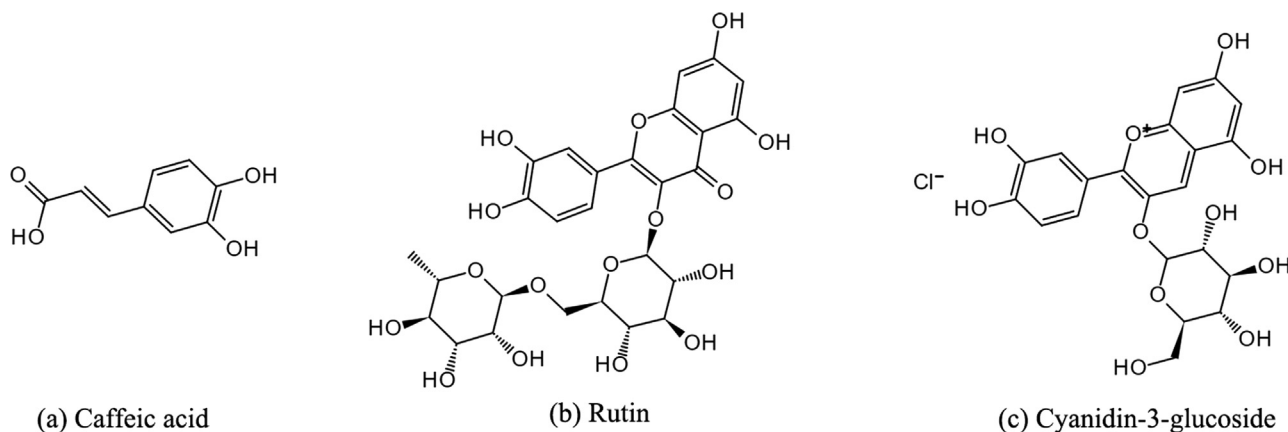


Fig. 1. Molecular structure of caffeic acid (a), rutin (b), and cyanidin-3-glucoside (c).

samples kept same condition without ultrasound as a control check (CK).

### 2.2.2. Dynamic monitoring of polyphenols

The concentrations of caffeic acid, rutin and cyanidin-3-glucoside were detected by using an Ultimate 3000 HPLC equipped with a DAD3000. Caffeic acid and rutin used a  $250 \times 4.6 \text{ mm} \times 5 \mu\text{m}$  ODS HYPERSIL C18 column (Thermo Scientific), and cyanidin-3-glucoside used a  $250 \times 4.6 \text{ mm} \times 5 \mu\text{m}$  Venusil MP C18 column. Flow rate of 1 mL/min, sample injection volume of 20  $\mu\text{L}$ , determined time of 15 min and column temperature of 30°C were set accordingly. Caffeic acid: mobile phase was 1% acetic acid/water (solvent A) and 100% methanol (solvent B) (A: B = 75:25). Rutin: mobile phase was 0.2% phosphoric acid/water (solvent A) and 100% methanol (solvent B) (A: B = 55:45). Cyanidin-3-glucoside: mobile phase was 0.5% phosphoric acid/water (solvent A) and 100% acetonitrile (solvent B) (A: B = 85:15). The detection wavelength was 320 nm, 257 nm, and 520 nm, respectively. External calibration equations of caffeic acid, rutin and cyanidin-3-glucoside were  $Y = 1.631X + 0.0416$  ( $R^2 = 0.999$ ),  $Y = 0.5524X - 0.0323$  ( $R^2 = 0.999$ ),  $Y = 0.778X - 0.0204$  ( $R^2 = 0.999$ ), respectively (Y is peak area, mAU; X is concentration of analytes, mg/L).

## 2.3. Analysis of ultrasonic effects

### 2.3.1. Quantification of mechanical effects

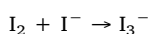
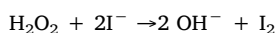
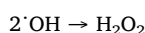
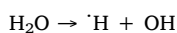
The molecular chains of polymer can be fractured by microjets, shock waves, shear forces, and hence the mechanical effects can be quantified by measuring the change in dynamic viscosity [27,28]. PEO 900000 and t-BuOH were dissolved simultaneously into water at a concentration of 3 g/L and 100 mmol/L. The dynamic viscosity before and after ultrasonic treatment measured by a viscometer (DV2T, Brookfield Engineering Labs., Inc., USA). A thermostatic bath was used to keep a constant temperature at  $25 \pm 2^\circ\text{C}$ . A lower viscosity ratio means stronger mechanical effects. The intensity of mechanical effects was calculated by using the Eq. (1)

$$V = \frac{\eta}{\eta_0} \times 100\% \quad (1)$$

where V is the viscosity ratio,  $\eta_0$  and  $\eta$  are the dynamic viscosity before and after ultrasound treatment, respectively.

### 2.3.2. Quantification of sonochemical effects

The sonochemical effects were quantified under all conditions described by Weissler [29]. Quantification of the sonochemical effects was carried out separately since phenolic compounds have the function of scavenging free radicals and affect the quantitative results. The solution of 0.1 mol/L KI was prepared to perform experiments [30]. All samples were measured by using an ultraviolet spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd, China) after ultrasound treatment. The specific reaction equations are as follows.



The calculation methods of  $\cdot\text{OH}$  radicals concentration are as follows:

$$C = \frac{2A}{\epsilon b} \times 10^6 \times 2 \quad (2)$$

where C ( $\mu\text{mol/L}$ ) is the concentration of  $\cdot\text{OH}$  radicals, A is the absorption of the KI solution after ultrasound treatment,  $\epsilon$  is the molar absorptivity of  $\text{I}_3^-$  ( $26303 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), b is the thickness of

quartz cuvette (10 mm). The value of  $10^6$  and 2 are the conversion factors.

### 2.3.3. Determination of acoustic energy

The ultrasonic intensity and acoustic energy density were measured by calorimetry [31]. The temperature rise was recorded every 30 s and measured continuously for 6 times. The value of  $dT/dt$  was obtained by regression calculation. The change in temperature was measured by using a thermocouple with a diameter of 5 mm.

$$P = \frac{dT}{dt} C_p m \quad (3)$$

$$UI = \frac{P}{S} \quad (4)$$

$$AED = \frac{P}{V} \quad (5)$$

where P is the calorimetric power (W),  $dT/dt$  is the rate of temperature rise,  $C_p$  is the specific heat capacity of water ( $4.2 \text{ J/(g} \cdot \text{K)}$ ), m is the mass of water (g), UI is the ultrasonic intensity ( $\text{W/cm}^2$ ), S is the emitting surface area of transducer ( $\text{cm}^2$ ), AED is the acoustic energy density ( $\text{W/mL}$ ) and V is the liquid volume (mL).

## 2.4. Real extraction system

The solid-liquid ratio was 1:25 g/mL. Total phenolic content was measured by Folin-Ciocalteu colorimetry [32] and the results were expressed as mg of Gallic acid equivalent per 100 g dried weight (mg/100 g DW). Total flavonoid content was detected by aluminum chloride colorimetry [33] and the results were expressed as mg of Rutin equivalent per 100 g dried weight (mg/100 g DW).

## 2.5. Analysis of degradation behavior

### 2.5.1. Determination of degradation rate

The degradation rate (D) largely reflects the stability of polyphenols impacted by sonochemical effects. A lower degradation rate indicates that the polyphenol has higher stability. The calculation method of degradation rate is as follows:

$$D = \frac{C_0 - C}{C_0} \times 100\% \quad (6)$$

where  $C_0$  is the initial concentration (mg/L), C is the concentration after ultrasound treatment (mg/L).

### 2.5.2. Modeling of degradation kinetics

The degradation kinetics of three polyphenols were developed by using an integral method under five kinetics models and the models were determined by evaluating the determination coefficient ( $R^2$ ). The half-life and rate constant for three polyphenols were calculated to evaluate the stability.

$$\text{Zero - order} \quad C_t - C_0 = -kt \quad t_{1/2} = C_0/2k \quad (7)$$

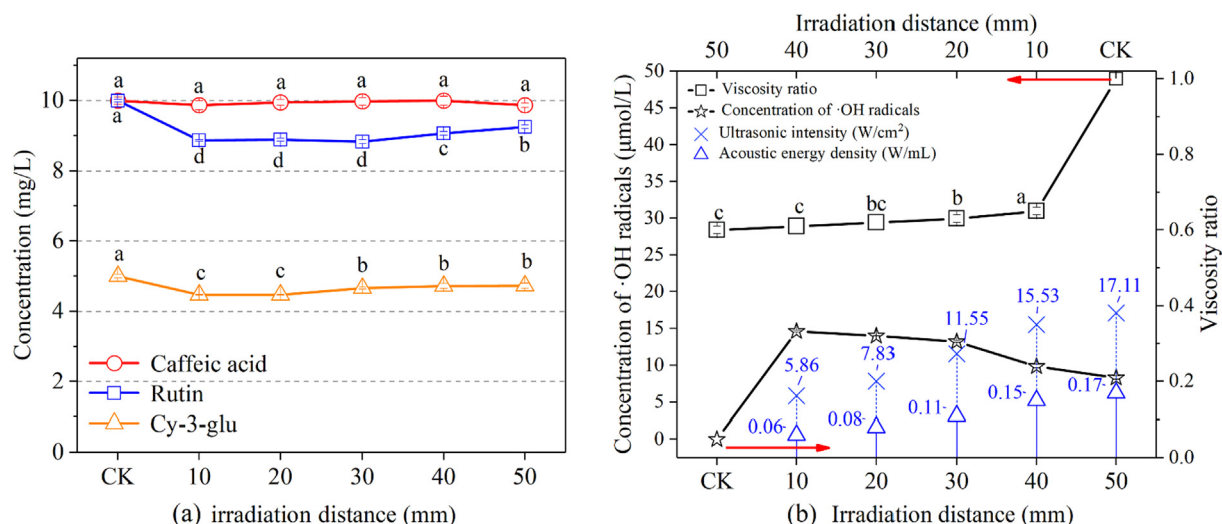
$$\text{First - order} \quad \ln C_t/C_0 = -kt \quad t_{1/2} = (\ln 2)/k \quad (8)$$

$$\text{Pseudo - first - order} \quad \ln[(C_0 - C_t)/C_0] = -kt \quad t_{1/2} = (\ln 2)/k \quad (9)$$

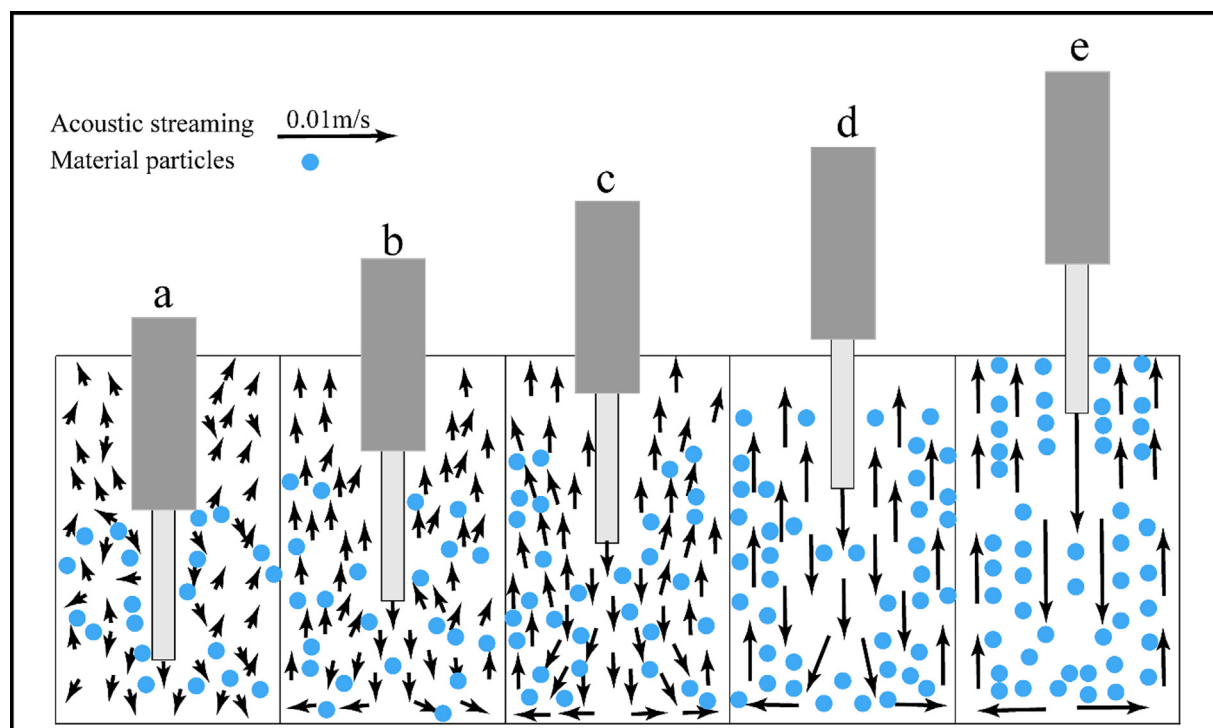
$$\text{Second - order} \quad 1/C_t - 1/C_0 = kt \quad t_{1/2} = 1/kC_0 \quad (10)$$

$$\text{Third - order} \quad 1/C_t^2 - 1/C_0^2 = kt \quad t_{1/2} = 3/2kC_0^2 \quad (11)$$

where  $C_t$  (mg/L) is the concentration after ultrasound treatment of t min,  $C_0$  (mg/L) is the initial concentration, k ( $\text{mg L}^{-1} \text{ min}^{-1}$ ) is the rate constant,  $t_{1/2}$  (min) is the half-life and t (min) is the sonication time.



**Fig. 2.** Impacts of irradiation distance (15 min, 25°C, duty cycle 2/2) on the stability of three polyphenols (a), OH radicals (sonochemical effects), viscosity ratio (mechanical effects), ultrasonic intensity (b) and acoustic energy density (b). The different letters indicate significant differences ( $P < 0.05$ ). The CK is the control check without ultrasound.



**Fig. 3.** Diagram of the impact of irradiation distance on acoustic streaming. The a, b, c, d, and e represent the different irradiation distance corresponding to 10, 20, 30, 40 and 50 mm, respectively.

## 2.6. Statistical analysis

Each sample was conducted in triplicates and all results were subjected to the analysis of variance (ANOVA) and Duncan's multiple range tests by using SPSS 22.0. Pearson correlation coefficients ( $r$ ) among ultrasound parameters, OH radicals, mechanical effects, three polyphenols, and extraction yield were calculated by using SPSS 22.0. When  $P < 0.05$ , the significant difference was considered.

## 3. Results and discussion

### 3.1. Parametric investigation in the stability of three polyphenols, sonochemical effects and mechanical effects

#### 3.1.1. Impacts of irradiation distance

Compared with ultrasonic bath system, probe-type system allows higher extraction efficiency due to the direct contact between transducers and working liquid medium [31,34]. Fig. 2 showed the impacts of irradiation distance (ID) on the stability of three polyphenols (Fig. 2a), sonochemical effects (SE) and mechanical effects (ME) (Fig. 2b). Interestingly, the variation of SE and ME along the axis direction of transducer had a similar trend. With an increase at the ID



(10–50 mm), the viscosity ratio (0.65–0.60) and the concentration of  $\cdot\text{OH}$  radicals (14.62–8.29  $\mu\text{mol/L}$ ) gradually decreased. This phenomenon indicated that ME were enhanced (lower viscosity ratio means stronger ME), while SE were weakened (higher concentration of  $\cdot\text{OH}$  radicals means stronger SE). One possible reason for the inconsistency between ME and SE might be the spatial variation in the liquid circulation patterns according to the equation of axial velocity and mixing time, respectively [35,36]:

$$v_{\text{axial}} = 2.63 \times 10^{-9} \times (I)^{1.41} \times (Z)^{-0.37} \times \left(\frac{R-r}{r}\right)^{9.4},$$
 [V axial direction (m/s); I ultrasonic intensity ( $\text{W/m}^2$ ); Z axial distance (m); R reactor radius (m); r radial distance (m)];

$$\theta_{\text{mixing time}} = 7 \times 10^6 \times d^{-0.235} \times \left[ \frac{Z^2 D^3 (D + 2Z)^{-2} d_h^{-4}}{v_h^2 g^2 \mu^{-2} \rho^2} \right],$$
 [ $\theta$  mixing time (s); d irradiation distance (m); Z liquid height (m); D reactor diameter (m);  $d_h$  horn tip diameter (m);  $v_h$  velocity of horn (m/s); g gravitational acceleration ( $\text{m/s}^2$ );  $\mu$  liquid viscosity ( $\text{N s/m}^2$ );  $\rho$  liquid density ( $\text{Kg/m}^3$ )]. From the formulas, we can conclude that an increase of ID in axial direction boost the improvement of axial velocity near the transducer (0.002–0.01 m/s) and decrease the mixing time, which enhanced acoustic streaming as well as local shear forces giving rise to the enhancement of ME (Fig. 3). The suppression of SE can be associated with rectified diffusion and bubble–bubble coalescence via Bjerknes forces within the irradiated liquid volume. The two pathways of bubble–bubble coalescence and rectified diffusion control the growth of acoustic bubble to active or inactive size and then govern the sonochemical activity. Previous study showed that growth rate of bubble can be fastened due to the existence of acoustic streaming [37]. Consequently, the enhancement of acoustic streaming accelerated the growth rate of bubble and increased the coalescence probability further inducing the bubble size to inactive range in the bulk solvent and weakening the sonochemical activity. From the perspective of spatial variation, another factor influencing ME and SE includes the components of sound waves as well as sound attenuation or sound absorption. At low ID, bubbles driven by acoustic pressure experienced asymmetric collapse near the container wall or bottom exciting high-speed jets as a source of ME. However, high ID causing partial bubbles to suspend due to the increase of ultrasonic intensity (5.86–17.11  $\text{W/cm}^2$ ) scattered or attenuated ultrasonic waves by bubble pulsations decreasing the proportion of standing and traveling waves to undermine the SE (Fig. 2b) [38]. As for polyphenols (Fig. 2a), except for caffeic acid ( $P > 0.05$ ), the amount of rutin and cy-3-glu increased slowly with the increase of ID and degradation rate reached the lowest level at 50 mm (7.50% and 5.49–6.79%,  $P > 0.05$ ). The results indicated that regulating ID can indeed reduce the degradation of polyphenols under ultrasonic field. Meanwhile, it was noteworthy that caffeic acid remained stable under all working distance, but rutin and cy-3-glu experienced significant degradation when the concentration of  $\cdot\text{OH}$  radicals exceeded the value of 8.29  $\mu\text{mol/L}$ . The anomalous phenomenon may indicate that three polyphenols have different Response Thresholds (RT) to  $\cdot\text{OH}$  radicals. According to the theory of molecular collision and transition state, the effective collision between polyphenols and  $\cdot\text{OH}$  radicals is the key to the reaction. Therefore, the instantaneous concentration and recombination rate of hydroxyl radicals as well as the activation energy of transition state will affect the final oxidation rate. Caffeic acid had a relatively higher capability against  $\cdot\text{OH}$  radicals than rutin and cy-3-glu since it has higher energy of transition state and a disposition to form stable dimer blocking the pathway of oxidation reaction. Therefore, for the extraction of low-stability natural ingredients, choosing optimum irradiation distance to enhance the ME and inhibit the generation of  $\cdot\text{OH}$  radicals is a feasible solution.

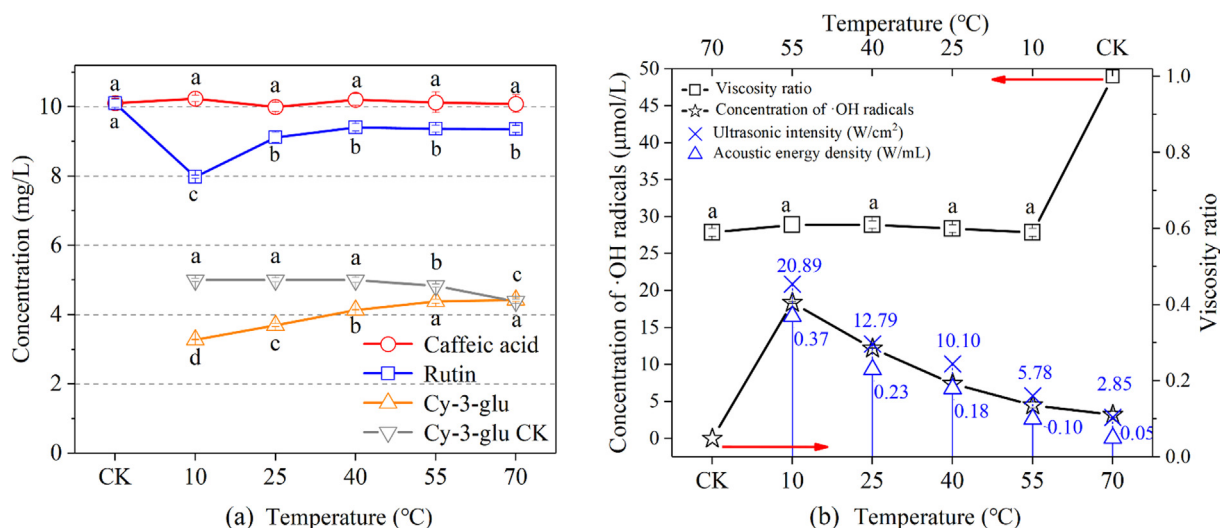
### 3.1.2. Impacts of temperature

An important factor affecting extraction yield is the operating temperature due to the thermal sensitivity of polyphenols. As shown in Fig. 4, rutin and cy-3-glu (Fig. 4a) were predicted to undergo maximum

degradation rate at the high temperature (70°C, 6.41% and 11.45%), but the higher degradation rate occurred at the lower temperature (10°C, 20.23% and 34.41%), which was enormously similar to the variation in the concentration of  $\cdot\text{OH}$  radicals (10°C 18.38  $\mu\text{mol/L}$ , 70°C 3.22  $\mu\text{mol/L}$ ) (Fig. 4b). Although the thermal stability of cy-3-glu was poor, the degradation rate still did not conform to the Arrhenius theory. Given the analysis, we could be more convinced that rutin and cy-3-glu were more prone to the free radical degradation rather than thermal degradation. Besides, caffeic acid (Fig. 4a) maintained high stability among 10 to 70 °C ( $P > 0.05$ ), which can be attributed to the fact that the peak value of  $\cdot\text{OH}$  radicals (18.38 mmol/L) was still lower than the RT of caffeic acid (about 19.64  $\mu\text{mol/L}$ ). Consistent with our results, Qiao et al. [19] also reported that caffeic acid had no suffered any degradation in the aqueous solution among –5 to 65°C, but the maximum degradation rate (12%) occurred in aqueous ethanol solution at the lower temperature (–5°C). The divergence can be explained through the theory that ethanol molecules were attacked by  $\cdot\text{OH}$  radicals to produce 1-hydroxyethyl radicals, which has been confirmed by electron paramagnetic resonance carried out by Zhang et al. [39]. The 1-hydroxyethyl radicals as a secondary carbon radical may have higher reactivity with caffeic acid than  $\cdot\text{OH}$  radicals. More interestingly, the fluctuation of temperature in the range of 10–70°C did not cause any significant change in the ME (0.59–0.61,  $P > 0.05$ ) (Fig. 4b). A similar finding was noted by Prabhu et al. [40], whose studies on cavity dynamics model from 20 to 60°C at 30 kHz indicated that operating temperature did not have any impact on the bubble lifetime ( $4.011 \times 10^{-5}$ – $4.018 \times 10^{-5}$  s) and the volume compression ratio of bubble ( $R_{\text{max}}/R_0$  262.35–262.61) that determined the physical collapse intensity. Nevertheless, for SE, the decrease of collapse peak temperature (16483.3–9973.8 K) due to the increase in the amount of vapor inside bubbles resulted in a decrease in the amount of  $\cdot\text{OH}$  radicals. Therefore, it seems that peak pressure inside bubble is responsible for ME and peak temperature inside bubble is responsible for SE. At the same time, the consistency in the trend between ultrasonic intensity and SE (Fig. 4b) indicated that in addition to the influence of temperature on liquid properties, the energy conversion efficiency was another critical factor for SE [41]. In the study of Machado et al. [8], recovered polyphenols at 60–70°C exhibited higher antioxidant activity than that at 50–60°C from pomegranate (*Punica granatum* L.) peels, but the total phenolic content decreased at the higher temperature (60°C). From the viewpoint of ultrasonic effects, this phenomenon could be explained as follows: relatively high temperature without affecting the ME not only effectively accelerated the disintegration of plant materials to promote the penetration of solvent and diffusion of functional component, but also inevitably caused the thermal degradation and free radical degradation. Inconsistent with the above results, Jovanović et al. [20] reported that the high temperature (80°C) had a positive effect on the polyphenols yield from *Thymus serpyllum* L. herb. So, we concluded that the impacts of temperature on polyphenols yield can also be associated with species of raw materials that contains different kinds of polyphenols. In the case of fine extraction of individual polyphenol, where the tolerances of polyphenols to free radicals and heat need to be considered first due to both behaviors of free radical degradation under low temperature or thermal degradation under high temperature.

### 3.1.3. Impacts of duty cycle

Duty cycle determines exposure time to the given liquid area during same duration based on the ON/OFF time and prolonging ON time will cause an increase in exposure time. Such pulse mode offers unique advantages such as relieving local temperature, extending operation life of transducer and reducing energy consumption under the premise of allowing to achieve high extraction yield [42,43]. As shown in Fig. 5, it can be noticed that the increase of duty cycle delivering more ultrasonic energy into the bulk solvent (0.05–0.34  $\text{W/mL}$ ) resulted in an increase of ultrasonic intensity (2.71–19.47  $\text{W/cm}^2$ ) (Fig. 5b), which will caused



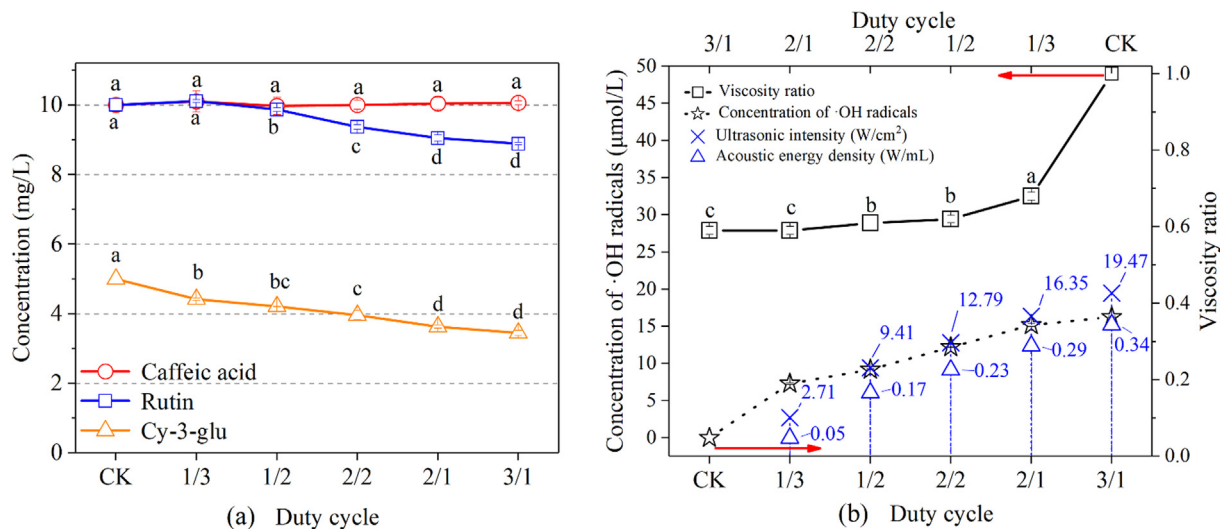
**Fig. 4.** Impacts of temperature (15 min, duty cycle 2/2, irradiation distance 20 mm) on the stability of three polyphenols (a), ·OH radicals (sonochemical effects), viscosity ratio (mechanical effects), ultrasonic intensity (b) and acoustic energy density (b). The different letters indicate significant differences ( $P < 0.05$ ). The CK is the control check without ultrasound.

an increase in the amount of active cavitation bubble per unit volume leading to the superposition of ME and SE in time and space scale. In such cases, SE (Fig. 5b) increased rapidly (7.30–15.16 μmol/L) and ME (Fig. 5b) (0.68–0.59) decreased significantly with the change of duty cycle from 1/3 to 2/1 (ON/OFF second). Therefore, relatively high duty cycle can better induce the fragmentation and destruction of raw materials, which has been confirmed by Zhao et al. [44]. They noticed an increased physical fragmentation on the microstructure of *Ganoderma lucidum* (Leyss. ex. Fr.) Karst. spores when the duty cycle changed from 1/3 to 3/1, which was consistent with the data of viscosity ratio obtained in this study (Fig. 5b). Nevertheless, further increment in duty cycle from 2/1 to 3/1 engendered an insignificant increase in the ME and SE. Exorbitant duty cycle (3/1) caused excessive formation of acoustic bubbles, which can form several bubble clouds or clusters to impede the transmission of ultrasonic energy resulting in a cavitation effect without significant rise [43]. Therefore, to a large extent, the results directly indicated that the optimization of duty cycle is so important for achieving higher extraction yield. But at the same time, it is also necessary to consider that high duty cycle will generate some

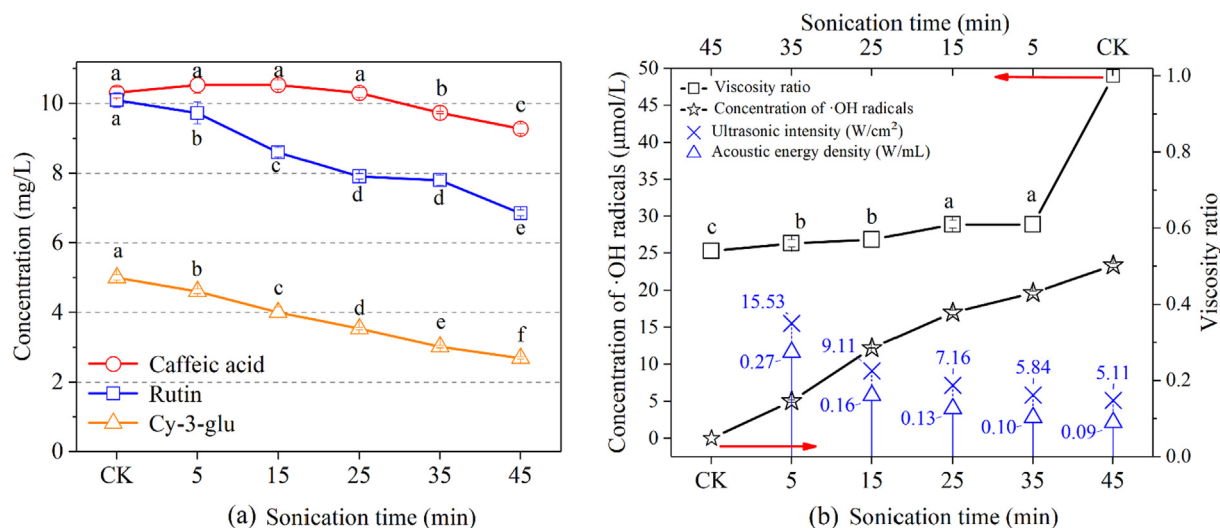
negative effects such as wear and tear effects and rapid erosion of ultrasonic transducer. Blindly increasing duty cycle may not only increase the energy consumption and equipment aging, but also induce the degradation of target compounds. In the case of cy-3-glu, the degradation rate reached 31% at 3/1 duty cycle. Although high duty cycle had no significant impact on caffeic acid (Fig. 5a) ( $P > 0.05$ ), the concentrations of rutin and cy-3-glu decreased dramatically (10–8.89 mg/L, 5–3.45 mg/L). Consistent with our results, Patil et al. [45] observed that the extraction yield of camptothecin from *Nothapodytes nimoniana* Grah. increased rapidly with the increase of duty cycle (25–75%) but decreased at 100% duty cycle. To summarize, a high duty cycle may be conducive to the extraction, but the impacts of ·OH radicals on extract cannot be ignored. The selection of duty cycle needs to be considered comprehensively according to the inherent structure of raw materials, the profile of active ingredients as well as the regulation mechanism of duty cycle on SE and ME.

### 3.1.4. Impacts of sonication time

Extraction is a time-dependent process and prolonging sonication



**Fig. 5.** Impact of duty cycle (15 min, 25°C, irradiation distance 20 mm) on the stability of three polyphenols (a), ·OH radicals (sonochemical effects), viscosity ratio (mechanical effects), ultrasonic intensity (b) and acoustic energy density (b). The different letters indicate significant differences ( $P < 0.05$ ). The CK is the control check without ultrasound.



**Fig. 6.** Impacts of sonication time (25°C, duty cycle 2/2, irradiation distance 20 mm) on the stability of three polyphenols (a), ·OH radicals (sonochemical effects), viscosity ratio (mechanical effects), ultrasonic intensity (b) and acoustic energy density (b). The different letters indicate significant differences ( $P < 0.05$ ). The CK is the control check without ultrasound.

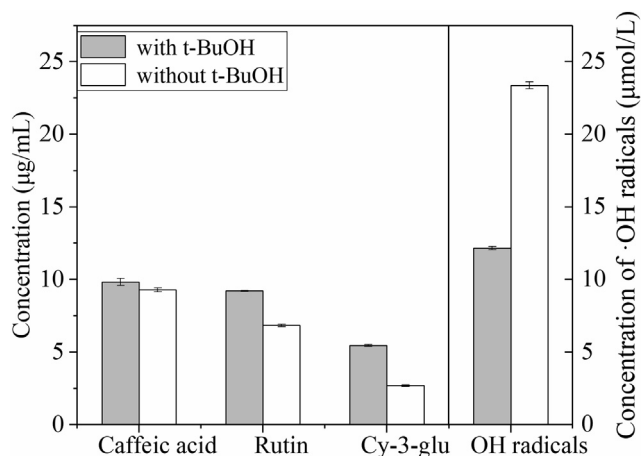
time can indeed increase extraction yield, but it also yields some negative effects on final extracts such as oxidation and polymerization [46]. As shown in Fig. 6a, increasing sonication time markedly increased the degradation of all tested polyphenols, especially rutin and cy-3-glu experienced a higher degradation rate of 31.50% and 46.29% at 45 min. The degradation rate of cy-3-glu was almost 1.5 times higher than that of rutin but caffeic acid was not degraded until 25 min (only 2.64%). Meanwhile, the relationship (Fig. 6b) between the increase in the concentration of ·OH radicals (5.02–23.37 μmol/L) and the increase in the degradation rate of three polyphenols indicated that caffeic acid had a higher RT (about 19.64 μmol/L) than rutin (about 5.02 μmol/L) and cy-3-glu (about 5.02 μmol/L). In a previous research [47], it was found that caffeic acid as a hydroxycinnamic acid experienced a decline in yield at 30°C after 40 min. Similarly, Nipornram et al. [48] also reported that the hesperidin (flavanones) yield from mandarin (*Citrus reticulata* Blanco cv. Sainampung) peels had a decreasing trend at 38.5 kHz after 35 min. One of the possible reasons could be that chain reactions were initiated when the instantaneous accumulation of hydroxyl radicals exceeded the threshold of chain reaction. To further support the free radical attack pathway for the degradation of polyphenols, the concentrations of three polyphenols (Fig. 7) were compared in the absence and presence of t-BuOH (only 100 mmol/L) after 45 min, finding that the degradation of cy-3-glu were completely

inhibited but not completely for caffeic acid and rutin (1.8%, 7.89%) due to the limited concentration of t-BuOH in the bulk solvent. The ME played a better role in breaking the molecular chain of polymer after 45 min (viscosity ratio 0.61–0.54). In other words, prolonging sonication time can effectively destroy the plant particles and promote the release of components. Consistent with our results, Khadhraoui et al. [49] using environmental scanning electron microscopy observed that the cross-sections of *Rosmarinus officinalis* L. leave were subjected to global detexturation after 60 min. Besides, from the perspective of Rayleigh-Plesset equation, bubble behavior is a complex function of frequency and power intensity. Thus, the increase of sonication time is only the superposition of ultrasonic energy field in time scale. In such context, longer sonication time is indeed conducive to the ME. However, from the viewpoint of energy, in the case of acoustic energy density (Fig. 6b), ultrasound-energy conversion efficiency gradually decreased with the increase of sonication time.

### 3.2. Correlation analysis

#### 3.2.1. Correlation between concentration of polyphenols and ·OH radicals

To further confirm the impacts of operating parameters on the stability of polyphenols is caused by different capabilities of each parameter inducing ·OH radicals, correlation coefficients were statistically analyzed. As tabulated in Table 1, high correlations were obtained between the operating parameters and the concentration of ·OH radicals (irradiation distance,  $-0.959$ ; temperature,  $-0.968$ ; duty cycle,  $0.982$ ; sonication time,  $0.998$ ). Also, high correlations also existed between ·OH radicals and rutin ( $-0.946$ ;  $-0.902$ ;  $-0.998$ ;  $-0.990$ ) as well as ·OH radicals and cy-3-glu ( $-0.876$ ;  $-0.997$ ;  $-0.996$ ;  $-0.991$ ). Microscopically, the impacts of operating parameters on SE were intricate and incomprehensible (formation, growth, oscillation, movement, and collapse of bubbles etc.), but through the yield of ·OH radical induced by SE and the stability of polyphenols, we can simplify the impacts of ultrasonic parameters on polyphenols to Dose-Response Relationship between ·OH radicals and polyphenols. Based on these results, an important conclusion can be obtained, i.e. the existence of ·OH radicals do not necessarily cause the degradation of polyphenols, only when it reaches the RT will it cause the degradation. Ashokkumar et al. [17] found that the degradation of phenol was highly dependent on ultrasound frequency and the degradation only appeared at the high frequency (358, 1062 kHz) whereas no degradation was observed at the low frequency (20 kHz) after 60 min, which may



**Fig. 7.** The concentration of three polyphenols and ·OH radicals with and without t-BuOH after 45 min sonication.

**Table 1**Correlations among each operating parameter,  $\cdot\text{OH}$  radicals, and each polyphenol after ultrasound treatment.

Correlations	Concentrations	Correlation coefficients ( <i>r</i> )							
		Irradiation distance (mm)	$\cdot\text{OH}$ ( $\mu\text{mol/L}$ )	Temperature ( $^{\circ}\text{C}$ )	$\cdot\text{OH}$ ( $\mu\text{mol/L}$ )	Duty cycle	$\cdot\text{OH}$ ( $\mu\text{mol/L}$ )	Sonication time (min)	$\cdot\text{OH}$ ( $\mu\text{mol/L}$ )
PPO	Caffeic acid (mg/L)	−0.155	0.357	−0.29	0.320	−0.08	−0.06	−0.954**	−0.917*
	Rutin (mg/L)	0.845	−0.946*	0.783	−0.902*	−0.995**	−0.998**	−0.971**	−0.990**
	Cy-3-glu (mg/L)	0.932*	−0.876*	0.963	−0.997**	−0.997**	−0.996**	−0.996**	−0.991**
COP	$\cdot\text{OH}$ ( $\mu\text{mol/L}$ )	−0.959**	–	−0.968**	–	0.998**	–	0.982**	–

PPO, the correlations between each polyphenol and each operating parameter as well as each polyphenol and  $\cdot\text{OH}$  radicals;COP, the correlations between  $\cdot\text{OH}$  radicals and each operating parameter;The significance of *r* was analyzed, \*  $P < 0.05$ ; \*\*  $P < 0.01$ .

indicate that phenol has higher RT than caffeic acid. Additionally, our study about the polyphenols stability under acoustic field in accordance with the previous data of radical-scavenging activity (RSA) that carried out by Cai et al. [24] and Rice-Evans et al. [50]. Their results about RSA (DPPH) presented the following order: caffeic acid (1.24 mM TEAC) < rutin (2.33 mM TEAC) (Cai et al.), rutin (2.4 mM TEAC) < cy-3-glu (4.4 mM TEAC) (Rice-Evans et al.). Furthermore, the degradation of polyphenols may be due to the role as free radical scavenger in bulk solvent and the stability of polyphenols is closely dependent on the structure-radical scavenging activity relationship including the electrophilicity of aromatic ring and the number or position of hydroxyl group. And presumably, the three kinds of polyphenols, as non-volatile organic compounds, mainly degraded in the gas-liquid zone of bubble and in the bulk solvent due to the diffusion process of primary radicals from inside bubble to outside bubble. Overall, through these discussions, we can more purposefully know how to reduce even eliminate the degradation that occurred during UAE.

### 3.2.2. Correlation between extraction yield and mechanical effects

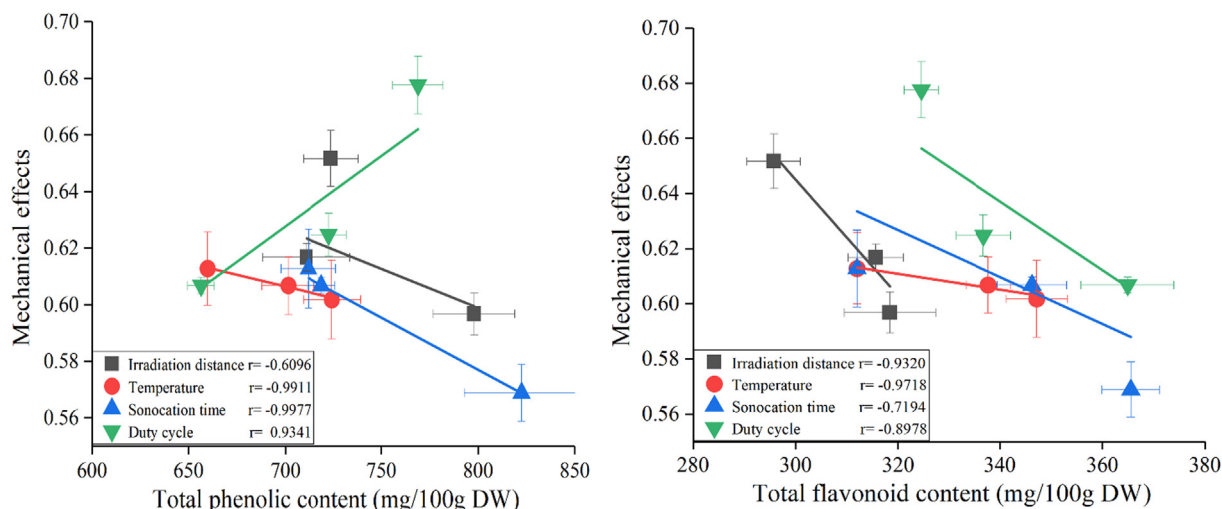
To further point out the ultrasonic parameters by affecting ME further determining the final polyphenols yield, correlations between extraction yield and ME were analyzed. As shown in Fig. 8, there were significantly negative correlations among total phenolic content (TPC), total flavonoid content (TFC) and ME for irradiation distance ( $r_{\text{TPC}} = -0.6096$ ,  $r_{\text{TFC}} = -0.9320$ ), temperature ( $r_{\text{TPC}} = -0.9911$ ,  $r_{\text{TFC}} = -0.9718$ ), sonication time ( $r_{\text{TPC}} = -0.9977$ ,  $r_{\text{TFC}} = -0.7194$ ). Evidence from the opposite characteristics in the ME and SE for irradiation distance can excellently prove the crucial role of ME during extraction. Likewise, Wang et al. [51] using a confocal laser scanning microscopy proved the importance of disintegration of fruit skin cells

induced by ME in the promotion of extraction yield. On the other hand, the data of ME relatively accurate to predict the extraction efficiency, which implied that the viscosity ratio method can be used as a tool to standardize ME induced by operating parameters to establish a database between extraction efficiency and ME, and to further promote the large-scale and standardized application of ultrasound. However, here it should be noted the inconsistency between total phenolic content and ME in the duty cycle (positive correlation). It seemed that the degradation effect induced by SE for polyphenols was stronger than the destruction effect on plant materials caused by ME at high duty cycle. In addition, how to standardize the physical properties of plant materials is particularly important for industrial-scale extraction of bioactive components.

### 3.3. A possible degradation behavior during UAE

#### 3.3.1. Analysis of degradation kinetics

Fig. 9 showed the degradation kinetics of three polyphenols at  $25^{\circ}\text{C}$ , respectively. Table 2 showed the determination coefficient ( $R^2$ ) of caffeic acid, rutin and cy-3-glu about  $C_t$ ,  $\ln C_t$ ,  $\ln(C_t/C_0)$ ,  $1/C_t$  and  $1/C_t^2$  against time at  $25^{\circ}\text{C}$  after ultrasonic treatment. Their degradation kinetics parameters ( $R^2$ ,  $t_{1/2}$  and  $k$ ) were tabulated in Table 3. The degradation of caffeic acid and rutin conformed to zero-order kinetics and their half-life was directly proportional to their initial concentration. In other words, caffeic acid ( $t_{1/2} = 328.9474$  min) was more stable than rutin ( $t_{1/2} = 68.5871$  min) at the same initial concentration. So, the degradation of caffeic acid was not easily observed due to the high half-life than rutin. But for cy-3-glu, it conformed to second-order kinetics at  $25^{\circ}\text{C}$  and the half-life ( $t_{1/2} = 55.5556$  min) was inversely proportional to the initial concentration. Thus, the degradation can appear in a

**Fig. 8.** Correlations between extraction yields and mechanical effects.



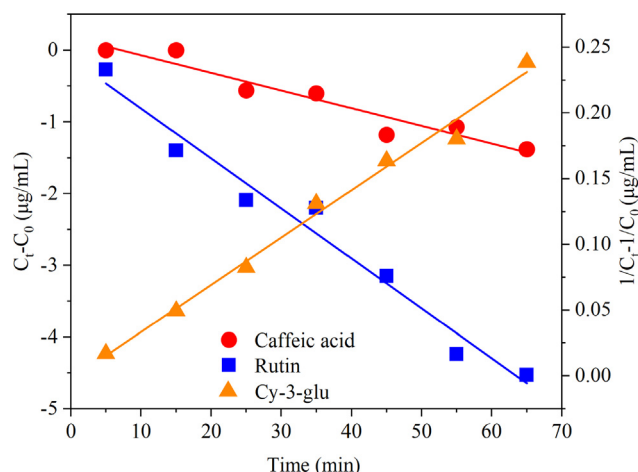


Fig. 9. Degradation kinetics curves of caffeic acid, rutin, and cyanidin-3-glucoside at 25°C under ultrasound treatment.

Table 2

The determination coefficient ( $R^2$ ) of three polyphenols of  $C_0$ ,  $\ln C_t$ ,  $\ln (C_t/C_0)$ ,  $1/C_t$  and  $1/C_t - 1/C_0$  against time at 25°C after ultrasonic treatment.

Sample	Determination coefficient ( $R^2$ )				
	Zero [ $C_t$ ]	First [ $\ln C_t$ ]	Pseudo-first [ $\ln (C_t/C_0)$ ]	Second [ $1/C_t$ ]	Third [ $1/C_t - 1/C_0$ ]
Caffeic acid	0.9308	0.879	0.9307	0.9299	0.9285
Rutin	0.9801	0.975	0.975	0.9551	0.9238
Cyanidin-3-glucoside	0.9584	0.9858	0.9858	0.9921	0.9754

$C_0$  is the initial concentration;  $C_t$  is the concentration at time  $t$ .

Table 3

Degradation kinetics parameters  $R^2$ ,  $t_{1/2}$  and  $k$  of three polyphenols at 25°C after ultrasound treatment.

Sample	Reaction order	$R^2$	$t_{1/2}$ (min)	$k$ (mg L <sup>-1</sup> min <sup>-1</sup> )
Caffeic acid	zero	0.9308	328.9474	0.0234
Rutin	zero	0.9801	68.5871	0.0706
Cy-3-glu	Second	0.9921	55.5556	0.0036

$R^2$ , determination coefficient;  $t_{1/2}$ , half-life;  $k$ , rate constant.

relatively short time. Detailed extraction and degradation process will be discussed in the next section. In addition, from the half-life results, we can conclude that rutin and cy-3-glu are more vulnerable to the attack of  $\cdot\text{OH}$  radicals. Therefore, during individual polyphenol extraction, it is necessary to formulate detailed schemes and strategies according to the stability of target compounds to reduce the occurrence of undesirable degradation products.

### 3.3.2. Interaction analysis between extraction and degradation

Generally speaking, solvent extraction can be roughly divided into washing (fast) stage and diffusion (slow) stage [3]. Two-site kinetic model is often used to describe the behavior of UAE [52]. The equation is as follows:  $C_t = C_w [1 - \exp(-k_{\text{fast}} t)] + C_d [1 - \exp(-k_{\text{slow}} t)]$ .  $k_{\text{fast}}$  and  $k_{\text{slow}}$  respectively represent the diffusion coefficients of fast extraction stage and slow extraction stage. 70–90% yields of polyphenol were extracted in the first 5–15 min and tended to achieve equilibrium after 15 min [53–55]. Therefore, given the phenomena, a possible degradation behavior during extraction was preliminarily proposed. Namely, the sonochemical degradation of polyphenols may occur in the initial stage of UAE and then accompany the remaining extraction. Fig. 10 showed a diagram of possible degradation behavior of polyphenols. When raw materials are irradiated by ultrasonic waves, mechanical

effects (microjets, shockwaves, shear forces, etc.) may first act on the raw materials promoting the swelling and fragmentation and accelerating the permeation of solvent [49]. In the washing stage, the polyphenols rush into the bulk solvent and the concentration increases rapidly, whereas the concentration of  $\cdot\text{OH}$  radicals may be at a low level ( $t = 5$  min, 5.02  $\mu\text{mol/L}$ ). Therefore, the ME of ultrasound may be dominant at this stage. It is impossible to observe the degradation with respect to experimental data and the observed results only are the apparent extraction yield. With the extension of extraction time, the polyphenols inside the materials gradually decrease and enter the solvent in the form of diffusion. At the same time, the SE is dominant and then the degradation can be observed from the experimental data. In brief, it is more conducive to the rapid development of ultrasonic industrial application after clearly understanding the control mechanism of ultrasonic parameters on the ME and SE, the texture and structure of target plant materials and the profile of bio-compounds.

## 4. Conclusion

The mechanical effects and sonochemical effects induced by acoustic cavitation have been widely applied in many fields, but how to more accurately control the occurrence of two ultrasonic effects or even to separate the two ultrasonic effects is worthy of further investigation. Current research provides some ideas from the perspective of parametric and phenomenological study. The results showed that the temperature (10–70°C) had no significant impact on the mechanical effects. Meanwhile, longer sonication time (45 min), higher irradiation distance (50 mm) can enhance the mechanical effects to promote extraction efficiency. The degradation of three polyphenols was mainly impacted by  $\cdot\text{OH}$  radicals. The application of relatively low temperature to extract heat-sensitive polyphenols may need to consider the issue of free radical degradation (cy-3-glu, decrease 46.29% at 25°C and 45 min). For high-stability polyphenols, high duty cycle and temperature can be chosen to promote the release of polyphenols from raw materials, thereby reducing the impact of sonication time. The degradation of polyphenols might occur in the initial stage of extraction, whereas the extraction held a dominant role compared with the degradation giving rise to the result that the degradation was difficult to be observed from the experimental data. In addition, attention should be focused on the dose–response relationship between free radicals and polyphenols. The functionality and safety of degradation products during aqueous extraction also need to be further examined.

## CRediT authorship contribution statement

**Pengxu Wang:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Chuanxiang Cheng:** Conceptualization, Software, Validation, Formal analysis, Investigation, Investigation, Data curation, Writing - review & editing. **Yaqin Ma:** Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Meng Jia:** Software, Investigation, Data curation, Writing - review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This study was supported by The Modern Agricultural (Citrus) Technology System of China (CARS-26-06B) and Fundamental Research Funds for the Central Universities (XDJK2019B048).

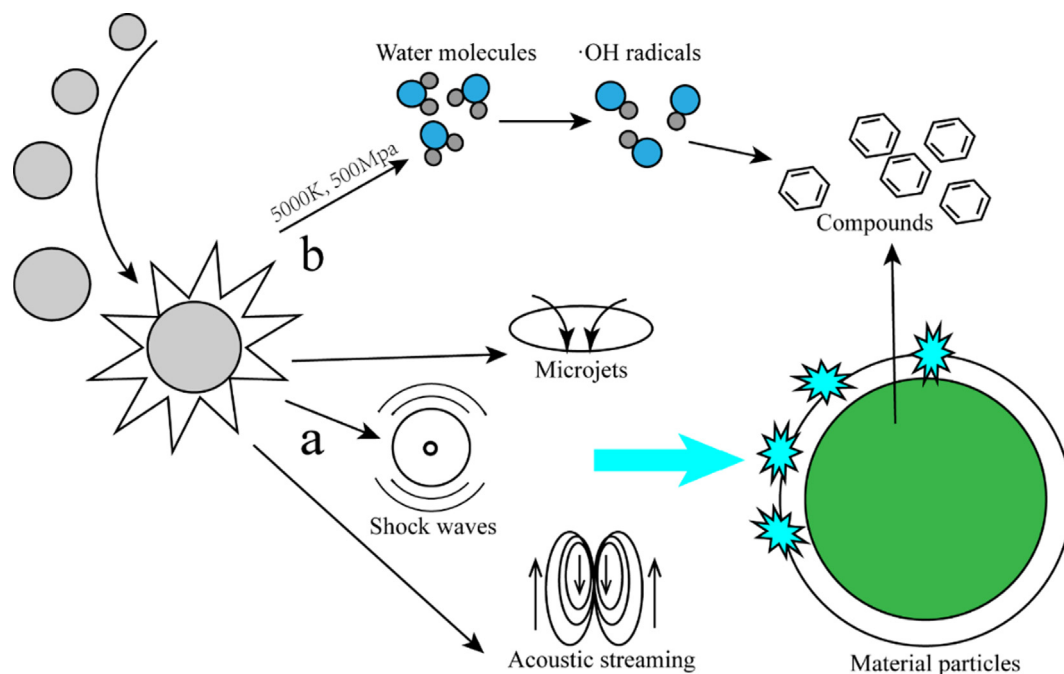


Fig. 10. A possible degradation behavior of polyphenols during ultrasound-assisted extraction.

## References

- [1] F. Chemat, N. Rombaut, A.G. Sicaire, A. Meullemiestre, A.S. Fabiano-Tixier, M. Abert-Vian, Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review, *Ultrason. Sonochem.* 34 (2017) 540–560, <https://doi.org/10.1016/j.ulsonch.2016.06.035>.
- [2] M. Toma, M. Vinatoru, L. Paniwnyk, T.J. Mason, Investigation of the effects of ultrasound on vegetal tissues during solvent extraction, *Ultrason. Sonochem.* 8 (2001) 137–142, [https://doi.org/10.1016/S1350-4177\(00\)00033-X](https://doi.org/10.1016/S1350-4177(00)00033-X).
- [3] I.A. Saleh, M. Vinatoru, T.J. Mason, N.S. Abdel-Azim, E.A. Aboutabl, F.M. Hammouda, A possible general mechanism for ultrasound-assisted extraction (UAE) suggested from the results of UAE of chlorogenic acid from *Cynara scolymus* L. (artichoke) leaves, *Ultrason. Sonochem.* 31 (2016) 330–336, <https://doi.org/10.1016/j.ulsonch.2016.01.002>.
- [4] T.J. Mason, A.J. Cobley, J.E. Graves, D. Morgan, New evidence for the inverse dependence of mechanical and chemical effects on the frequency of ultrasound, *Ultrason. Sonochem.* 18 (2011) 226–230, <https://doi.org/10.1016/j.ulsonch.2010.05.008>.
- [5] Y. Tao, D.W. Sun, Enhancement of food processes by ultrasound: a review, *Crit. Rev. Food Sci. Nutr.* 55 (2015) 570–594, <https://doi.org/10.1080/10408398.2012.667849>.
- [6] A. Golmohamadi, G. Möller, J. Powers, C. Nindo, Effect of ultrasound frequency on antioxidant activity, total phenolic and anthocyanin content of red raspberry puree, *Ultrason. Sonochem.* 20 (2013) 1316–1323, <https://doi.org/10.1016/j.ulsonch.2013.01.020>.
- [7] K. Papoutsis, P. Pristijono, J.B. Golding, C.E. Stathopoulos, M.C. Bowyer, C.J. Scarlett, Q.V. Vuong, Screening the effect of four ultrasound-assisted extraction parameters on hesperidin and phenolic acid content of aqueous citrus pomace extracts, *Food Biosci.* 21 (2018) 20–26, <https://doi.org/10.1016/j.fbio.2017.11.001>.
- [8] A.P.D.F. Machado, B.R. Sumere, C. Mekaru, J. Martinez, R.M.N. Bezerra, M.A. Rostagno, Extraction of polyphenols and antioxidants from pomegranate peel using ultrasound: influence of temperature, frequency and operation mode, *Int. J. Food Sci. Technol.* (2019) 1–10, <https://doi.org/10.1111/ijfs.14194>.
- [9] N.A. Al-Dhabi, K. Ponmurugan, P. Maran Jeganathan, Development and validation of ultrasound-assisted solid-liquid extraction of phenolic compounds from waste spent coffee grounds, *Ultrason. Sonochem.* 34 (2017) 206–213, <https://doi.org/10.1016/j.ulsonch.2016.05.005>.
- [10] L. Qiao, X. Ye, Y. Sun, J. Ying, Y. Shen, J. Chen, Sonochemical effects on free phenolic acids under ultrasound treatment in a model system, *Ultrason. Sonochem.* 20 (2013) 1017–1025, <https://doi.org/10.1016/j.ulsonch.2012.12.007>.
- [11] P. Katsampa, E. Valsamedou, S. Grigorakis, D.P. Makris, A green ultrasound-assisted extraction method for the recovery of antioxidant polyphenols and pigments from onion solid wastes using Box-Behnken experimental design and kinetics, *Ind. Crops Prod.* 77 (2015) 535–543, <https://doi.org/10.1016/j.indcrop.2015.09.039>.
- [12] B.K. Tiwari, C.P. O'Donnell, A. Patras, P.J. Cullen, Anthocyanin and ascorbic acid degradation in sonicated strawberry juice, *J. Agric. Food Chem.* 56 (2008) 10071–10077, <https://doi.org/10.1021/jf801824v>.
- [13] J. Liao, B. Qu, D. Liu, N. Zheng, New method to enhance the extraction yield of rutin from *Sophora japonica* using a novel ultrasonic extraction system by determining optimum ultrasonic frequency, *Ultrason. Sonochem.* (2015), <https://doi.org/10.1016/j.ulsonch.2015.05.005>.
- [14] S. Merouani, H. Ferkous, O. Hamdaoui, Y. Rezgui, M. Guemini, A method for predicting the number of active bubbles in sonochemical reactors, *Ultrason. Sonochem.* 22 (2015) 51–58, <https://doi.org/10.1016/j.ulsonch.2014.07.015>.
- [15] Y.Q. Ma, X.Q. Ye, Z.X. Fang, J.C. Chen, G.H. Xu, D.H. Liu, Phenolic compounds and antioxidant activity of extracts from ultrasonic treatment of satsuma mandarin (*Citrus unshiu* Marc.) peels, *J. Agric. Food Chem.* (2008), <https://doi.org/10.1021/jf072474o>.
- [16] Q.A. Zhang, H. Shen, X.H. Fan, Y. Shen, X. Wang, Y. Song, Changes of gallic acid mediated by ultrasound in a model extraction solution, *Ultrason. Sonochem.* 22 (2015) 149–154, <https://doi.org/10.1016/j.ulsonch.2014.06.010>.
- [17] M. Ashokkumar, D. Sunarti, S. Kentish, R. Mawson, L. Simons, K. Vilku, C. (Kees) Versteeg, Modification of food ingredients by ultrasound to improve functionality: A preliminary study on a model system, *Innov. Food Sci. Emerg. Technol.* 9 (2008) 155–160, <https://doi.org/10.1016/j.ifset.2007.05.005>.
- [18] Q. Ma, X.D. Fan, X.C. Liu, T.Q. Qiu, J.G. Jiang, Ultrasound-enhanced subcritical water extraction of essential oils from *Kaempferia galangal* L. and their comparative antioxidant activities, *Sep. Purif. Technol.* (2015), <https://doi.org/10.1016/j.seppur.2015.06.013>.
- [19] J. Živković, K. Šavikin, T. Janković, N. Čujić, N. Menković, Optimization of ultrasound-assisted extraction of polyphenolic compounds from pomegranate peel using response surface methodology, *Sep. Purif. Technol.* (2018), <https://doi.org/10.1016/j.seppur.2017.11.032>.
- [20] A.A. Jovanović, V.B. Đorđević, G.M. Zdunić, D.S. Pljevljakušić, K.P. Šavikin, D.M. Godevac, B.M. Bugarski, Optimization of the extraction process of polyphenols from *Thymus serpyllum* L. herb using maceration, heat- and ultrasound-assisted techniques, *Sep. Purif. Technol.* (2017), <https://doi.org/10.1016/j.seppur.2017.01.055>.
- [21] F. Chemat, M. Abert-Vian, A.S. Fabiano-Tixier, J. Strube, L. Uhlenbrock, V. Gunjevic, G. Cravotto, Green extraction of natural products. Origins, current status, and future challenges, *TrAC, Trends Anal. Chem.* 118 (2019) 248–263, <https://doi.org/10.1016/j.trac.2019.05.037>.
- [22] D. Pingret, A.S. Fabiano-Tixier, C. Le Bourvellec, C.M.G.C. Renard, F. Chemat, Lab and pilot-scale ultrasound-assisted water extraction of polyphenols from apple pomace, *J. Food Eng.* 111 (2012) 73–81, <https://doi.org/10.1016/j.jfoodeng.2012.01.026>.
- [23] S. de Pascual-Teresa, M.N. Clifford, Advances in polyphenol research: a journal of agricultural and food chemistry virtual Issue, *J. Agric. Food Chem.* 65 (2017) 8093–8095, <https://doi.org/10.1021/acs.jafc.7b04055>.
- [24] Y. Cai, M. Sun, J. Xing, Q. Luo, H. Corke, Structure – radical scavenging activity relationships of phenolic compounds from traditional Chinese medicinal plants, 78 (2006) 2872–2888, <https://doi.org/10.1016/j.lfs.2005.11.004>.
- [25] G.L. Yao, X.H. Ma, X.Y. Cao, J. Chen, Effects of power ultrasound on stability of cyanidin-3-glucoside obtained from blueberry, *Molecules* 21 (2016), <https://doi.org/10.3390/molecules21111564>.
- [26] L. Galvan D'Alessandro, K. Kriaa, I. Nikov, K. Dimitrov, Ultrasound assisted extraction of polyphenols from black chokeberry, *Sep. Purif. Technol.* (2012), <https://doi.org/10.1016/j.seppur.2012.03.024>.
- [27] V.S. Sutkar, P.R. Gogate, Design aspects of sonochemical reactors: Techniques for understanding cavitation activity distribution and effect of operating parameters,

- Chem. Eng. J. 155 (2009) 26–36, <https://doi.org/10.1016/j.cej.2009.07.021>.
- [28] K.V.B. Tran, T. Kimura, T. Kondo, S. Koda, Quantification of frequency dependence of mechanical effects induced by ultrasound, *Ultrason. Sonochem.* 21 (2014) 716–721, <https://doi.org/10.1016/j.ultsonch.2013.08.018>.
- [29] A. Weissler, H.W. Cooper, S. Snyder, Chemical effect of ultrasonic waves - oxidation of potassium iodide solution by carbon tetrachloride, *J. Am. Chem. Soc.* 50 (1950) 1769–1775, <https://doi.org/10.1021/ja01160a102>.
- [30] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, *Ultrason. Sonochem.* 10 (2003) 149–156, [https://doi.org/10.1016/S1350-4177\(03\)00084-1](https://doi.org/10.1016/S1350-4177(03)00084-1).
- [31] B.K. Tiwari, Ultrasound: A clean, green extraction technology, *TrAC - Trends Anal. Chem.* 71 (2015) 100–109, <https://doi.org/10.1016/j.trac.2015.04.013>.
- [32] COLORIMETRY OF TOTAL PHENOLICS WITH PHOSPHOMOLYBDIC-PHOSPHOTUNGSTIC ACID REAGENTS, *Am. J. Enol. Vitic.* (1965).
- [33] C.C. Chang, M.H. Yang, H.M. Wen, J.C. Chern, Estimation of total flavonoid content in propolis by two complementary colorimetric methods, *J. Food Drug Anal.* (2002).
- [34] Z. Piñeiro, R.F. Guerrero, M.I. Fernández-Marín, E. Cantos-Villar, M. Palma, Ultrasound-assisted extraction of stilbenoids from grape stems, *J. Agric. Food Chem.* (2013), <https://doi.org/10.1021/jf4030129>.
- [35] A. Kumar, T. Kumaresan, A.B. Pandit, J.B. Joshi, Characterization of flow phenomena induced by ultrasonic horn, *Chem. Eng. Sci.* (2006), <https://doi.org/10.1016/j.ces.2006.08.038>.
- [36] N.P. Vichare, P.R. Gogate, V.Y. Dindore, A.B. Pandit, Mixing time analysis of a sonochemical reactor, *Ultrason. Sonochem.* (2001), [https://doi.org/10.1016/S1350-4177\(99\)00046-2](https://doi.org/10.1016/S1350-4177(99)00046-2).
- [37] R.K. Gould, Rectified diffusion in the presence of, and absence of, acoustic streaming, *J. Acoust. Soc. Am.* (1974), <https://doi.org/10.1121/1.1903506>.
- [38] M. Ashokkumar, F. Cavaliere, F. Chemat, K. Okitsu, A. Sambandam, K. Yasui, B. Zisu, Handbook of ultrasonics and sonochemistry (2016), <https://doi.org/10.1007/978-981-287-278-4>.
- [39] Y. Song, Y. Shen, Q.-A. Zhang, X. Fan, J.F.G. Martín, X. Wang, Free radical generation induced by ultrasound in red wine and model wine: An EPR spin-trapping study, *Ultrason. Sonochem.* 27 (2015) 96–101, <https://doi.org/10.1016/j.ultsonch.2015.05.003>.
- [40] A.V. Prabhu, P.R. Gogate, A.B. Pandit, Optimization of multiple-frequency sonochemical reactors, *Chem. Eng. Sci.* 59 (2004) 4991–4998, <https://doi.org/10.1016/j.ces.2004.09.033>.
- [41] M.W.A. Kuijpers, M.F. Kemmere, J.T.F. Keurentjes, Calorimetric study of the energy efficiency for ultrasound-induced radical formation, *Ultrasonics* 40 (2002) 675–678, [https://doi.org/10.1016/S0041-624X\(02\)00197-X](https://doi.org/10.1016/S0041-624X(02)00197-X).
- [42] M. Kazemi, R. Karim, H. Mirhosseini, A. Abdul Hamid, Optimization of pulsed ultrasound-assisted technique for extraction of phenolics from pomegranate peel of Malas variety: Punicalagin and hydroxybenzoic acids, *Food Chem.* 206 (2016) 156–166, <https://doi.org/10.1016/j.foodchem.2016.03.017>.
- [43] S.V. Sancheti, P.R. Gogate, A review of engineering aspects of intensification of chemical synthesis using ultrasound, *Ultrason. Sonochem.* 36 (2017) 527–543, <https://doi.org/10.1016/j.ultsonch.2016.08.009>.
- [44] D. Zhao, M. Chang, J. Li, W. Suen, J. Huang, Investigation of Ice-assisted sonication on the microstructure and chemical quality of *Ganoderma lucidum* spores, 79 (2014), <https://doi.org/10.1111/1750-3841.12681>.
- [45] D.M. Patil, K.G. Akamanchi, Ultrasound-assisted rapid extraction and kinetic modelling of influential factors: extraction of camptothecin from *Nothapodytes nimmoniana* plant, *Ultrason. Sonochem.* 37 (2017) 582–591, <https://doi.org/10.1016/j.ultsonch.2017.02.015>.
- [46] W. Qu, R. Masoud Sehemu, Y. Feng, S.Q. Shi, J. Wang, H. Ma, C. Venkatasamy, Sonochemical effect of flat sweep frequency and pulsed ultrasound (FSFP) treatment on stability of phenolic acids in a model system, *Ultrason. Sonochem.* 39 (2017) 707–715, <https://doi.org/10.1016/j.ultsonch.2017.05.034>.
- [47] Y.Q. Ma, J.C. Chen, D.H. Liu, X.Q. Ye, Simultaneous extraction of phenolic compounds of citrus peel extracts: effect of ultrasound, *Ultrason. Sonochem.* 16 (2009) 57–62, <https://doi.org/10.1016/j.ultsonch.2008.04.012>.
- [48] S. Nipornram, W. Tochampa, P. Rattanatraiwong, R. Singanusong, Optimization of low power ultrasound-assisted extraction of phenolic compounds from mandarin (*Citrus reticulata* Blanco cv. Sainampung) peel, *Food Chem.* 241 (2018) 338–345, <https://doi.org/10.1016/j.foodchem.2017.08.114>.
- [49] B. Khadhraoui, M. Turk, A.S. Fabiano-Tixier, E. Petitcolas, P. Robinet, R. Imbert, M. El Maâtaoui, F. Chemat, Histo-cytochemistry and scanning electron microscopy for studying spatial and temporal extraction of metabolites induced by ultrasound. Towards chain detexturation mechanism, *Ultrason. Sonochem.* 42 (2018) 482–492, <https://doi.org/10.1016/j.ultsonch.2017.11.029>.
- [50] C.A. Rice-Evans, N.J. Miller, G. Paganga, Structure-antioxidant activity relationships of flavonoids and phenolic acids, *Free Radic. Biol. Med.* 20 (1996) 933–956, [https://doi.org/10.1016/0891-5849\(95\)02227-9](https://doi.org/10.1016/0891-5849(95)02227-9).
- [51] L. Wang, N. Boussetta, N. Lebovka, C. Lefebvre, E. Vorobiev, Correlations between disintegration degree of fruit skin cells induced by ultrasound and efficiency of bio-compounds extraction, *Ultrason. Sonochem.* 52 (2019) 280–285, <https://doi.org/10.1016/j.ultsonch.2018.11.026>.
- [52] Y. Tao, Z. Zhang, D.W. Sun, Kinetic modeling of ultrasound-assisted extraction of phenolic compounds from grape marc: Influence of acoustic energy density and temperature, *Ultrason. Sonochem.* 21 (2014) 1461–1469, <https://doi.org/10.1016/j.ultsonch.2014.01.029>.
- [53] C. Chen, L. Wang, R. Wang, X. Luo, Y. Li, J. Li, Y. Li, Z. Chen, Ultrasound-assisted extraction from defatted oat (*Avena sativa* L.) bran to simultaneously enhance phenolic compounds and  $\beta$ -glucan contents: compositional and kinetic studies, *J. Food Eng.* 222 (2018) 1–10, <https://doi.org/10.1016/j.jfoodeng.2017.11.002>.
- [54] B. He, L. Zhang, X. Yue, J. Liang, J. Jiang, X. Gao, P. Yue, Optimization of Ultrasound-Assisted Extraction of phenolic compounds and anthocyanins from blueberry (*Vaccinium ashei*) wine pomace, 204 (2016) 70–76, <https://doi.org/10.1016/j.foodchem.2016.02.094>.
- [55] W. Setyaningsih, I.E. Saputro, C.A. Carrera, M. Palma, Optimisation of an ultrasound-assisted extraction method for the simultaneous determination of phenolics in rice grains, *Food Chem.* 288 (2019) 221–227, <https://doi.org/10.1016/j.foodchem.2019.02.107>.

报告编号: 202108-58

# 检索报告

项目名称: 论文被 SCI 收录情况

委托人: 西南大学柑桔研究所      马亚琴

日期: 2021 年 08 月 17 日

认证单位: 教育部科技查新工作站 N08



二〇二〇年制





检索项目名称	委托人提交论文被 SCI 收录情况			
查新机构	名称	教育部科技查新工作站 N08	邮 编	400715
	地 址	重庆市北碚区西南大学图书馆	电 话	023-68253283
委托文献目录	<p><b>Degradation behavior of polyphenols in model aqueous extraction system based on mechanical and sonochemical effects induced by ultrasound</b></p> <p><b>Wang, PX; Cheng, CX; (...); Jia, M</b></p> <p>Sep 15 2020   SEPARATION AND PURIFICATION TECHNOLOGY 247</p> <p>等 4 篇</p>			
检索的数据库范围	<p>1. Science Citation Index Expanded (SCIE) -1900 年至今</p> <p>2. 中科院期刊分区数据在线平台升级版</p> <p>3. 中科院期刊分区数据在线平台基础版</p>			
检索要点	论文被 SCI 收录, 影响因子, 中科院分区情况			
检索结论	<p>经检索, 委托人提交的 4 篇论文被 SCI 收录, 影响因子、分区等检索结果详细情况见附件 1 和附件 2。</p> <div style="display: flex; justify-content: space-between; align-items: center;"> <div style="text-align: center;">  <p>检索人 (签名): 周剑</p> </div> <div style="text-align: right;"> <p>职称: 研究馆员</p> <p>教育部科技查新工作站 N08</p> <p>2021 年 08 月 17 日</p> </div> </div>			
备注	1、影响因子及分区为最新的影响因子和分区。			

附件 1: SCI 收录情况

序号	题名	检索号	影响因子	中科院类别 分区		出版时间	语种
1	Degradation behavior of polyphenols in model aqueous extraction system based on mechanical and sonochemical effects induced by ultrasound Wang, PX; Cheng, CX; (...); Jia, M Sep 15 2020   SEPARATION AND PURIFICATION TECHNOLOGY 247	000536142200014	IF <sub>2020</sub> =7.312	中科院类别升级版		2020	英文
				大类	工程技术		
				小类	ENGINEERING, CHEMICAL 工程: 化工		
2	Comparison of the effects of novel processing technologies and conventional thermal pasteurisation on the nutritional quality and aroma of Mandarin (Citrus unshiu) juice Cheng, CX; Jia, M; (...); Ma, YQ Aug 2020   INNOVATIVE FOOD SCIENCE & EMERGING TECHNOLOGIES 64	000564512100007	IF <sub>2020</sub> =5.916	中科院类别升级版		2020	英文
				大类	农林科学		
				小类	E FOOD SCIENCE & TECHNOLOGY 食品科技		
3	Evaluation of the effect of ultrasonic variables at locally ultrasonic field on yield of hesperidin from penggan (Citrus reticulata) peels Ma, YQ; Ye, XQ; (...); Han, Z Mar 2015   LWT-FOOD SCIENCE AND TECHNOLOGY 60 (2), pp.1088-1094	000347740800004	IF <sub>2015</sub> =2.711	中科院类别基础版		2015	英文
				大类	工程技术		
				小类	E FOOD SCIENCE & TECHNOLOGY 食品科技		
4	Considering solubility disparity and acoustic-cavitation susceptibility of neoteric solvents to accurately predict sono-recovery yield of value-added compounds Wang, PX; Ma, YQ; (...); Jia, M Dec 1 2021   SEPARATION AND PURIFICATION TECHNOLOGY 276	000681684300001	IF <sub>2020</sub> =7.312	中科院类别升级版		2020	英文
				大类	工程技术		
				小类	ENGINEERING, CHEMICAL 工程: 化工		