Synergistic effect of probe sonication and ionic liquid for extraction of phenolic acids from oak galls

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ABSTRACT

Phenolic acids of oak gall were extracted using ultrasonic-probe assisted extraction (UPAE) method in the presence of ionic liquid. It was compared with classical ultrasonic-bath assisted extraction (CUBAE) and conventional aqueous extraction (CAE) method, with and without the presence of ionic liquid. Remarkably, the UPAE method yielded two-fold higher extraction yield with the presence of ionic liquid, resulting 481.04 mg/g for gallic acids (GA) and 2287.90 mg/g for tannic acids (TA), while a decreased value of 130.36 mg/g for GA and 1556.26 mg/g for TA were resulted with the absence of ionic liquid. Intensification process resulted the highest yield of 497.34 mg/g and 2430.48 mg/g for GA and TA, respectively, extracted at temperature 50 °C with sonication intensity of 8.66 W/cm^2 and 10% duty cycle, diluted in ionic liquid, 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide, [Bmim][Tf$_2$N] at concentration of 0.10 M with sample-to-solvent ratio 1:10 for 8 h. Peleg's model successfully predicted the UPAE process confirming that extraction capacity is the controlling factor in extracting phenolic acids. Hence, it can be concluded that UPAE method and ionic liquid have synergistic effect as it effectively enhanced the extraction efficiency to increase the bioactive constituents yield.

1. Introduction

Oak galls (*Quercus* sp.) or known as Manjakani, has been used for centuries in several Asian countries and widely known for its therapeutic benefits. It has been used traditionally in postpartum care and treatment of various ailments [1]. The genus is belongs to the Fagaceae family which has more than 45 species, usually found in Greece, Asia Minor and Iran [2]. Oak galls extract contains high numbers of bioactive constituents such as phenolic acids including gallic acids (GA), tannic acids (TA) and ellagic acids along with flavonoids such as quercetin with main constituents of TA and GA in the oak galls [3]. Previous researchers have identified a number of pharmacological activities of these phenolic acids including anti-bacterial [3], anti-inflammatory [4] and anti-oxidant activity [5,6]. The phenolic acids are widely known for their antioxidants activities and it has been reported that they have higher antioxidant activity as compared to vitamin C and E towards the reactive oxygen species [7,8].

The phenolic acids was extracted from its plant material using various types of organic solvents including methanol, ethanol, acetone and aqueous mixture [9]. Previous report claimed that methanol yielded the highest yield of phenolic compounds from *Bauhinia vahlii* at

48.7 g/100 g extract, followed by acetone and chloroform extracts [10]. Meanwhile, another past study obtained a maximum yield of phenolic compounds at 33.67% in 50% aqueous mixture of acetone and water extracted from *Limnophila aromatica* [11]. However, these organic solvents are known to have high toxicity, which leads to an increasing need to study a new promising alternative to substitute these conventional solvents. Recently, ionic liquids which known for its unique physical-chemical properties, have shown tremendous performance on the phenolic compounds extraction processes and demonstrating high capability to dissolve all fractions from plant materials [12]. The ionic liquids are very promising to replace many organic solvents as their high polarity and selectivity implies an efficient way to yielded out high percentage of phenolic compounds.

Conventional assisted extraction (CAE) techniques were widely used to extract phenolic compounds. Nonetheless, the process was inefficient and maximum amount of phenolic contents obtained was very low. Besides using large amounts of solvents and huge loss of phenolic compounds during the extraction process, the solid-solvent contact to reach equilibrium is longer [13–15]. These days, several green and innovative extraction techniques such as supercritical fluid extraction [16], microwave assisted extraction [17], pressurized hot solvent

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extraction [18] and ultrasound-assisted extraction [19] have been used for the extraction of phenolic compounds from plant materials to substitute the conventional method. Among all these methods, ultrasound-assisted extraction (UAE) is highly efficient as it utilize acoustic cavitation to disrupt the plant tissues, breaking down cell membrane and decrease the mass transfer limitations [20]. This green technique has also attracted much attention as it was found to contribute in reducing the extraction time, extraction temperature, energy input, consumption of organic solvents, and eventually enhanced the chemical kinetics, solubility and experimental reproducibility [21]. Furthermore, this green and innovative aspect of ultrasonic system has also been previously reported by Chemat et al. [22,23] that highlighted the potential and reliable sonication process in food processing industry due to its role in environment sustainability. On top of that, UAE has been previously introduced in the extraction of polyphenols [24], flavonoids [25], alkaloid [26], anthocyanins [27], natural pigments [28] and other bioactive compounds [29,30].

An efficient extraction process of using ultrasonic based technology can be done via two types of system, which are classical ultrasonic-bath assisted extraction (CUBAE) and ultrasonic-probe assisted extraction (UPAE). Although both systems use transducer as the source for the ultrasound power [31], the CUBAE results in inconsistency due to weak intensity delivery and low power of ultrasound delivered to the sample as compared to UPAE method. Conversely, UPAE system has higher power and the transducer bonded to the probe induced a direct transfer of ultrasonic intensity to the extraction media, thus minimize the ultrasonic energy loss [32].

Although there are studies using conventional method to extract phenolic compounds from different plants, however, in this date, there are still no reports on UPAE method using ionic liquid as media for the extraction of oak galls. In recent years, the application of ionic liquid as an alternative solvents has gaining the attention of many researchers due to its remarkable and structure-dependent properties such as negligible to vapour pressure, miscibility with water or organic solvents and good extractability for the organic compounds and metal ions. Hence, these characteristic of ionic liquid make it more environmentally benign solvents compared to other traditional volatile organic solvents that has been widely used for extraction before. Furthermore, the mechanistic study related to synergistic effect between UPAE method and ionic liquid is very rare. Therefore, this work focused on UPAE process intensification in ionic liquid including sonication time, extraction methods, solid-to-solvent ratio, type of solvent and its concentration on the extraction of phenolic acids from oak galls. Mathematical Peleg's model was proposed to portray the extraction kinetics and one factor at a time (OFAT) approach was applied to optimise the condition.

2. Materials and methods

2.1. Plant materials

The oak galls were obtained from Taman Pertanian Negeri Pahang. It was first washed and air dried overnight at room temperature. Then, the gall was crushed using pestle and mortar until it become fine powder (0.5 mm) before it can be used prior to the extraction process.

2.2. Reagent and standards

Five different types of solvents were tested in this experiment. Ionic liquids of 1-Butyl-3-methylimidazolium tetrafluoroborate, [Bmim] [BF$_4$] (Sigma–Aldrich, Germany) and 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide, [Bmim][Tf$_2$N] (Sigma–Aldrich, Germany), Hexadecyltrimethylammonium bromide, CTAB (Sigma–Aldrich, Germany), methanol (Sigma–Aldrich, Germany) and deionized water. Deionized water was obtained from FKKSA Lab, UMP. Gallic acids (Merck, Germany) and tannic acids (Merck, Germany) were

used as standards for the quantification of phenolic acids. Acetonitrile (Merck, Germany) and orthophosphoric acids, 85% (Fisher Science, UK) were used as mobile phase for HPLC analysis. All reagents and standards were purchased from Nano Life Quest Sdn Bhd.

2.3. Extraction procedures

2.3.1. Conventional aqueous extraction (CAE)

9 g of powdered galls were immersed in the extraction solvent and the mixture was heated at 50 °C on a hotplate with continuous stirring for 8 h [7]. The solid-to-solvent ratio was set at 1:10 in volume of infusion, 100 ml. The beaker of mixture was covered with aluminium foil (with small holes) throughout the extraction to minimize the evaporation process.

2.3.2. Classical ultrasonic-bath assisted extraction (CUBAE)

The extraction of phenolic acids from oak galls were performed using a 2.75L Fisherbrand Scientific ultrasonic bath-type with electronic timer, quick degassing and heating [4]. An amount of 9 g powdered oak galls were immersed in the extraction solvent and the mixture was heated and sonicated for 8 h with the volume of infusion at 100 ml. This method used the same procedure as the CAE method whereby the mixture was covered with aluminium foil (with small holes) throughout the extraction to minimize the evaporation process.

2.3.3. Ultrasonic-probe assisted extraction (UPAE)

The extraction was performed by ultrasonic radiation using high-intensity processor model Q700 (700 W, 20 kHz) from QSonica, Newtown, U.S.A (Fig. S1). It was armed with a replaceable flat tip ultrasonic probe, used to conduct an extraction process of phenolic acids from oak galls. The ultrasonic probe was immersed 2 cm into the extraction medium and the energy is transmitted via the probe directly into the sample [33]. In UPAE process, the ultrasound power level was varied by adjusting the amplitude setting of the sonotrode while the cumulative average ultrasound dose was diversed by adjusting the duty cycle. The sonication intensity was determined as follow,

$$I = \frac{P}{A} \tag{1}$$

where A (cm^2) is the area of the sonotrode tip (1.27 cm^2). The amplitude was set at position 1 to correspond to a power input of 11 W and 8.66 W/cm^2 sonication intensity using 10% duty cycles (a duty cycle of 10% was obtained by 1 s sonication, followed by a rest period of 9 s). The intensification process using different solvents including deionized water, CTAB, methanol, ionic liquid [Bmim][BF$_4$] and [Bmim][Tf$_2$N] at various concentration (0.05 M–0.20 M) and solid-to-solvent ratio (1:05–1:20) were done via the same procedures.

2.4. Kinetic modelling procedure

Peleg's kinetic for modelling the extraction results were widely adopted to estimate extraction rate constant, initial extraction rate and equilibrium concentration of natural compounds. In describing the phenolic acids extraction by mathematical model, Peleg's model [34] was applied in this study. The model equation describing the kinetics of extraction of materials is as follows:

$$C_t = C_0 + \frac{t}{K_1 + K_2 t} \tag{2}$$

where C_t is the concentration of GA at time t (mg/g), K_1 is Peleg's rate constant (min.g/mg), K_2 is Peleg's capacity constant (g/mg) and C_o indicted the initial concentration of GA which is zero (fresh solvent). The modified Peleg's equation which represents the concentration of target solute (GA) in extraction solvent against time can be written as follows:

$$C_t = \frac{t}{K_1 + K_2 t} \tag{3}$$

K_1 and K_2 can be obtained from the slope and intercept, respectively by plotting $1/C_t$ vs. $1/t$ graph. Then, the value of C_t can be subsequently calculated using Eq. (3) at different times to examine the fitting of the model.

2.5. High performance liquid chromatography (HPLC) analysis of phenolic compounds

The measurements of separation and determination of phenolic compounds from the oak galls were performed using a High Performance Liquid Chromatography (HPLC) system Agilent Series 1100 equipped with diode array detection (DAD) and a column Phenomenex Prodigy 5μ (250 × 4.60 mm) [8]. The wavelength for detection of gallic acid (GA) and tannic acid (TA) were set at 270 nm and 280 nm, respectively. The wavelengths were detected by fixing the flow rate of 1 ml/min with 3.0% Phosphoric acids (90%) / Acetonitrile (10%) as mobile phase, in an isocratic programme. Each sample and standard was filtered with nylon syringe filter (pore size of 0.22 μm). In preparing for the standard curve, GA and TA standard were prepared at concentration 10 ppm–60 ppm (Fig. S2).

2.6. Characterization

The functional groups of bioactive compound were identified using Fourier Transform Infrared (FT-IR) Spectrometry (Perkin Elmer Spectrum GX FTIR Spectrometry) using KBr method with a scan range 500–4000 cm^{-1}.

Scanning electron microscopy imaging was performed to visualize and characterize the morphological surface of oak galls sample particles before and after extraction process via different extraction methods. The analysis was conducted using Scanning Electron Microscope Quanta 450. Upon analysis, the samples were coated with a thin layer of platinum at room temperature before proceeding with imaging procedures.

3. Results and discussion

3.1. Identification of phenolic acids in the sample

In order to evaluate the extraction methods and operating parameters on the extraction process of oak galls, HPLC analysis was used to quantify the target compounds present in the sample. Based on Fig. 1, 12 phenolic compounds were positively identified in the oak galls extracts by HPLC. Table 1 show the extraction yield of phenolic compounds obtained from oak galls under different extraction methods namely CAE, CUBAE and UPAE methods from two to tenth hours. Total phenolic content (sum of detected phenolic content by HPLC) from oak galls extracts ranged from 150.97 to 279.79, 323.73 to 997.57 and 923.54 to 1865.96 mg/g via CAE, CUBAE and UPAE method, respectively. Tannic acid (TA), gallic acid (GA), mallic acid and ellagic acid were found as main phenolic compounds in the extracts with contents ranging from 98.86 to 179.97, 25.34 to 43.76, 9.75 to 9.42 and 7.33 to 14.15 mg/g, respectively via CAE method, 228.76 to 810.74, 42.35 to 81.56, 20.40 to 41.03 and 14.25 to 19.56 mg/g, respectively via CUBAE and 776.75 to 1556.26, 65.04 to 130.76, 37.02 to 79.28 and 16.11 to 33.44 mg/g via UPAE method.

It can be clearly seen that phenolic compounds at retention times of 3.26 min and 4.41 min namely GA and TA, respectively recorded the highest intensities. It can be assumed that these two phenolic compounds exist in large amount in the oak galls. This is in agreement with past studies reporting GA and TA to be the main constituents in oak galls at 50–70% [3]. Thus, GA and TA were used to evaluate the method selection and the process intensification of the amount of extraction

yield from the oak galls.

3.2. Method selection

Three types of extraction methods (CAE, CUBAE and UPAE) were investigated to observe the performance of the phenolic acids with extraction time ranging from one hour to tenth hours. Fig. 2A indicates that UPAE method gave the highest yield as compared to the other two methods with highest extraction yield of GA, followed by CUBAE and CAE methods with 130.76 mg/g > 81.56 mg/g > 43.76 mg/g, respectively. On the other hand, based from Fig. 2B, TA show tremendous amount of extraction yield as compared to the GA, having a same pattern with the highest value of extraction yield using UPAE system, followed by the CUBAE and CAE method with 1556.26 mg/g > 810.74 mg/g > 179.97 mg/g, respectively. CUBAE have higher extraction yield than CAE method due to the sonication effect along with the high frequency from the mechanical vibrations (sound waves) [34]. At the same amount of extraction time (eight hours), the extraction yield was observed to escalate almost two times via sonication (CUBAE) system compared to CAE method. This also indicated the decrease consumption of energy used by sonication system, making it a much greener extraction technique than CAE method [35]. The sonication produced mechanical stressing and cavitation effect and eventually led to an increase of the permeability into the plant cell [8]. Although both CUBAE and UPAE method implemented sonication effect, it can be clearly seen that the UPAE excels the CUBAE method which due to a focused and uniform power input, high localized intensity and even distribution of ultrasound [36].

Based on Table 1, all extraction methods was observed to have a steadily increased yield of phenolic compounds with the increasing time up to eight hour, before being slightly decreased with further increased in extraction time. Based on HPLC analysis, the total phenolic content of oak galls extracts were observed to decrease from 279.79 to 263.32 mg/g (5.89% degradation) via CAE method. Meanwhile, extraction via CUBAE method recorded a decreased value of total phenolic content from 997.57 to 959.45 mg/g with 3.82% of degradation. An amount of 5.96% degradation of the total phenolic content was obtained via UPAE method with decreasing value from 1865.96 to 1754.75 mg/g.

The slight decreased in extraction yield after eighth hour may due to the possible oxidation and degradation of the bioactive constituents by prolonged sonication, which facilitated the release of most of the active constituents inside the cells to the solvent during the first eight hours. Furthermore, prolonged sonication led to a decreased in diffusion area, diffusion rate, and increased diffusion distance and subsequently decreased the extraction yield of phenolic compounds [37–39].

Fig. 3 indicates the performance analysis of different extraction methods with presence and absence of ionic liquid. Remarkably, it can be significantly observed that the UPAE method is two times much efficient than the CUBAE and eight times better than the CAE method (Fig. 3 inset). Higher extraction yield produced by UPAE system may be due to the direct delivery of ultrasonic intensity to the extraction media that was delivered through the tip of the probe [40]. The probe tip have smaller surface that could provide two-fold greater performance as compared to ultrasonic bath that have high attenuation in ultrasound delivery due to the water contained in the bath [41]. Besides, it can also be observed that the performance of each extraction methods subsequently improved with the presence of ionic liquid, [Bmim][BF$_4$]. The use of ionic liquid in extraction process improved as much as five times, four times and two times via CAE, CUBAE and UPAE methods, respectively, as compared to the extractions with the absence of ionic liquid. A literally high yield extracted from the oak galls with the application of ionic liquid is likely due to the characteristic of ionic liquid itself with long alkyl chain and complex anion making the phenolic compounds to be much soluble in it.

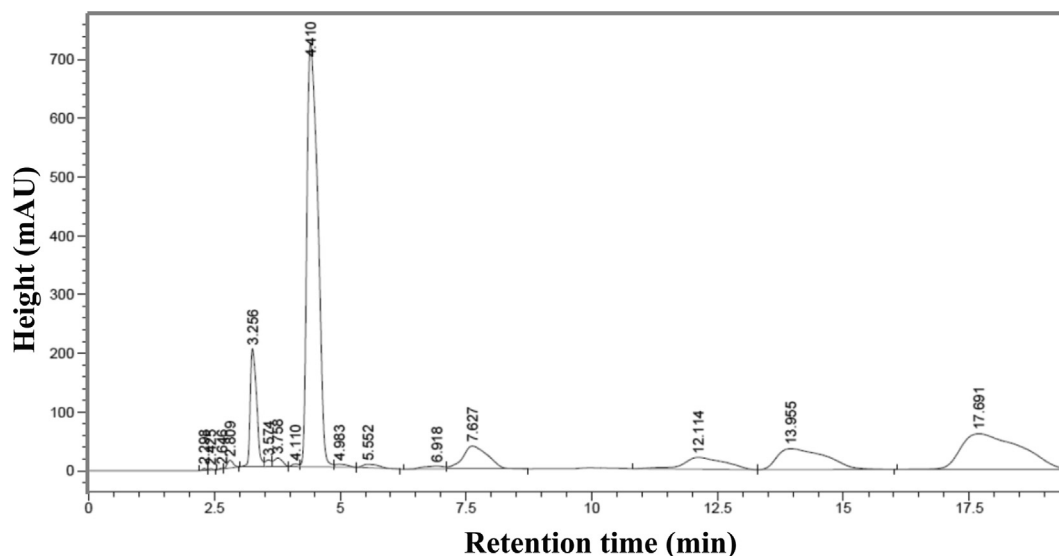The results suggest that UPAE gave highest extraction yield among

Fig. 1. HPLC chromatogram showing the phenolic compounds profile in the oak galls extract. Retention time: (3.256 min) Gallic acid, (3.574 min) Malic acid, (3.758 min) Ellagic acid, (4.110 min) Aconitic acid, (4.410 min) Tannic acid, (4.983 min) Salicylic acid, (5.552 min) Chlorogenic acid, (6.918 min) Benzoic acid, (7.727 min) Caffeic acid, (12.114 min) Myricetin, (13.955 min) Quercetin, (17.691 min) Apigenin.

other methods with the presence of ionic liquid. Therefore, UPAE process was then further intensified to maximize the extraction yield of oak galls.

3.3. Process intensification

3.3.1. Effect of solvent

Fig. 4A indicated the extraction performance of phenolic acids using different solvents including water, methanol, CTAB surfactant and ionic liquid [Bmim][BF$_4$] and [Bmim][Tf$_2$N]. It can be observed that the extraction yield increased subsequently from 130.76 mg/g to 138.79 mg/g for GA and from 1556.26 mg/g to 1846.05 mg/g for TA, using water and methanol as solvents, respectively. Even though water is known for its high polarity properties as compared to other solvents, the decreased extraction yield might resulted from the less compatibility issue between the water solvent and the target compounds [42]. In contrast, the use of methanol, an organic solvent, lead to an increase of the extraction yield possibly due to the fact that phenolic compounds are more likely soluble in organic solvents, which have low polarity than water [43]. The amount of extraction yield in methanol extracted in this study is comparable with the past extraction of oak galls by Ab Rahman et al, obtaining 51.14 mg/g and 1332.88 mg/g of GA and TA, respectively [42]. Despite the promising intense increased of phenolic acids yield by substituting water to methanol as the extraction medium, it is flammable and often responsible for environmental pollution and the greenhouse effect [44].

In aiming to improve the extraction time and yield also in attempt to imply the green technology based extraction method of the oak galls, CTAB surfactant and few types of ionic liquids were used and compared as the solvents. The extraction yield using CTAB gave 161.74 mg/g of GA and 1964.72 mg/g of TA, while ionic liquids [Bmim][BF$_4$] and [Bmim][Tf$_2$N] resulted an amount of 481.39 mg/g and 497.34 mg/g for GA and 2287.90 mg/g and 2430.48 mg/g for TA, correspondingly. Although both CTAB and ionic liquid have good hydrophilicity properties and long alkyl chain which can enhance the aqueous solubility of solutes, CTAB with much longer alkyl chain could lead to an increase in the degree of steric hindrance between the solvent and target molecule. This then decreases the extraction yield compared to the solution using imidazolium-based ionic for instance, [Bmim][BF$_4$] and [Bmim][Tf$_2$N] as solvent. It can be clearly observed that [Bmim][Tf$_2$N] has greater extraction yield than [Bmim][BF$_4$]. Past study also claimed that

imidazolium-based ionic liquids performed much effectively towards the extraction of phenolic acids [44,45]. Although both ionic liquids has the same length of alkyl chain, however, Tf$_2$N$^-$ anion exhibited strongest hydrogen bonding and hydrophobic interactions with both GA and TA, hence increases their solubility in the ionic liquid and eventually maximized the extraction yield [46].

On top of that, Previous study by El-Harbawi [47] investigating the toxicity measurement of some imidazolium-based ionic liquids, namely 1-butyl-3-imidazolium hydrogen sulphate, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, [Bmim][Tf$_2$N] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide towards fish marine and freshwater fish classified a practically nontoxic liquids of the ionic liquids based on Acute Toxicity Rating Scale by Fish and Wildlife Service (FWS). This proved the safety used of the ionic liquid as solvent.

3.3.2. Effect of solvent concentration

The ionic liquid concentration is another critical parameter to be study for an efficient extraction process that will maximized the amount of target compounds. The experimental results in Fig. 4B revealed that it increased at solvent concentration 0.10 M. The extraction yield increased gradually from 489.61 mg/g to 497.34 mg/g for GA and from 2317.04 mg/g to 2430.48 mg/g for TA, at solvent's concentration of 0.05 M and 0.10 M, respectively. The increased amount of both GA and TA as the ionic liquid concentration increased might be due to the attractive electrostatic between the imidazolium cations of the ionic liquid and the hydroxyl groups of the phenolic acids [48]. The higher amount of cationic charges in the aqueous mixture leads to an enhanced electrostatic interaction between target phenolic acids and the extraction media. In addition, higher dosage or concentration of the extraction solvent offers a large number of active sites and a large surface area for the sorption of target phenolic acids, and eventually improved the extraction yield [49]. As the ionic liquid aqueous solution concentration increased, along with the implementation of UPAE method, it was easier to disrupt cellulose structure and facilitate dissolving the solute in cell, thus promoting extraction efficiency of the phenolic compounds. Significantly, the result suggested that both ionic liquid and UPAE method has synergistic effect that subsequently enhanced the extraction yield. Nevertheless, as the concentration was further increased, the extraction yield starts deescalated rapidly to 357.70 mg/g and 311.59 mg/g for GA and 2307.36 mg/g and 2252.65 mg/g for TA, at

Table 1
Extraction yields of phenolic compounds identified by HPLC in oak galls extracts obtained from different extraction methods namely CAE, CUBAE and UPAE at extraction time of 2–10 h.

Extraction methods	Extraction time (hr)	Phenolic compounds (mg/g)											
		Gallic acid	Malic acid	Ellagic acid	Aconitic acid	Tannic acid	Salicylic acid	Chlorogenic acid	Benzoic acid	Caffeic acid	Myricetin	Quercetin	Apigenin
CAE	2	25.34	9.75	7.33	4.31	98.86	0.61	4.04	0.23	0.50	–	–	–
	4	29.52	15.01	9.41	4.85	123.13	0.83	4.28	0.23	0.57	–	0.03	–
	6	32.54	15.78	10.02	7.06	133.13	0.88	5.23	0.61	1.34	0.05	0.10	–
	8	43.76	19.42	14.15	9.70	179.97	1.14	8.57	0.85	2.01	0.06	0.16	–
	10	42.08	18.11	13.80	8.22	170.84	0.92	7.11	0.81	1.22	0.06	0.15	–
CUBAE	2	42.35	20.40	14.25	8.75	228.76	1.05	5.67	0.97	1.40	0.05	0.08	–
	4	50.98	33.27	14.57	9.04	443.75	2.34	7.90	1.55	2.79	0.08	0.17	–
	6	58.88	33.83	15.41	10.57	594.36	2.90	8.02	2.21	3.12	0.08	0.35	0.01
	8	81.56	41.03	19.56	17.92	810.74	6.09	10.43	3.80	5.53	0.12	0.76	0.03
	10	78.34	37.62	15.89	10.50	794.30	4.85	8.91	3.25	5.04	0.12	0.60	0.03
UPAE	2	65.04	37.02	16.11	10.23	776.75	3.69	8.13	2.45	3.56	0.09	0.47	–
	4	108.57	60.10	27.55	14.50	1427.36	5.06	10.55	4.11	4.80	0.15	0.81	0.03
	6	117.46	60.49	28.00	14.84	1456.12	5.70	13.80	5.50	7.27	0.38	1.92	0.05
	8	130.76	79.28	33.44	20.37	1556.26	6.61	17.23	7.54	10.07	0.55	3.76	0.09
	10	127.67	66.38	28.75	16.32	1472.84	6.02	16.31	7.20	9.69	0.47	3.03	0.07

0.15 M and 0.20 M, respectively. Excessive [Bmim][Tf$_2$N] concentration can led to the increase of the solution viscosity, and it will increase the mass transfer limitation of target component and then decreased the extraction efficiency [50]. Hence, based on the results, solvent's concentration of 1.0 M was selected as the optimum condition for further intensification process.

3.3.3. Effect of solid-to-solvent ratio

In investigating the effect of solid-to-solvent ratio on the phenolic acids extraction yield, experiments were performed at different ratios over the range 1:05 to 1:20 obtaining results as shown in Fig. 5. It can be seen that an increased ratio from 1:05 to 1:10, increased the extraction yield from 432.58 mg/g to 497.34 mg/g for GA and 2283.69 mg/g to 2430.48 mg/g for TA. A high solid-to-solvent ratio up to 1:10 was found to be favourable in extraction of phenolic acids. That was consistent with mass transfer principle where the driving force for mass transfer is the concentration gradient between the interior of the plant cells and the external solvent [48] which eventually promote a faster extraction rate. Nonetheless, the extraction yield slightly decreased as the ratio is further increased to 1:20. This indicated the viscosity of ionic liquid affected the mass transfer of the target phenolic acids [51]. Similar observations were reported before on total phenolic and flavonoid from *Aquilaria crassna* young leaves, where the results increased significantly with the increased of solid-to-solvent ratio from 1:10 to 1:20, and decreases as the ratio was further increased to 1:80 [51].

3.4. Kinetic analysis

The data on the kinetics of phenolic acids according to Peleg's model was discussed on different type of solvent, solvent's concentration and solid-to-solvent ratio. The parameters obtained from the Peleg's are model constants K_1 and K_2, which related to extraction rate at the beginning process and the maximum phenolic acids concentration during the extraction process, respectively, coefficient of determination (R^2) and the root mean squared deviation (RMSD). The RMSD is frequently used to measure the differences between values predicted by a model and the values actually observed while R^2 is a statistic that will give the information about the goodness of fit of a model.

The calculated parameters of Peleg's model (constants K_1 and K_2), along with the RMSD and R^2 are shown in Table 2, comparing different type of solvent namely, water, methanol, CTAB surfactant also [Bmim][BF$_4$] and [Bmim][Tf$_2$N] ionic liquids. It can be seen that the K_2 values are decreasing as the solvents improved from water to the ionic liquids. The smallest K_2 value was found for ionic liquid [Bmim][Tf$_2$N] solvent, indicating a maximum phenolic acids concentration as compared to other solvents. On top of that, a good R^2 values were high in all experiment data set (0.77–0.98), implying an excellent linearity $R^2 \approx 1$ of the model while the RMSD were in range from 1.88 to 10.53 mg/g, represent a reasonable and acceptable agreement between the experimental and calculated data.

On the other hand, the kinetics on different solvent's concentration was summarized in Table 3. Based on all four analysed solvent's concentration, the K_1 and K_2 constants both decreases as the concentration increase up to 0.10 M. However, the constants start to increases as the solvent's concentration further increased to 0.20 M. This shows that 0.10 M is the optimum solvent concentration as it implied a higher initial extraction rate and maximum phenolic acids yield compared to other concentrations. In addition, a literally high R^2 values (0.94–0.96) for all concentrations and RMSD values ranging from 3.42 to 3.50 mg/g depicts a good fitting of phenolic acids concentration predicted by the model with the experimental value [35].

As visualized in Table 4, the Peleg's parameters on different solid-to-solvent ratio were demonstrated to be the same pattern, as K_1 and K_2 constants were observed to be decreases as the ratio increase to 1:10,
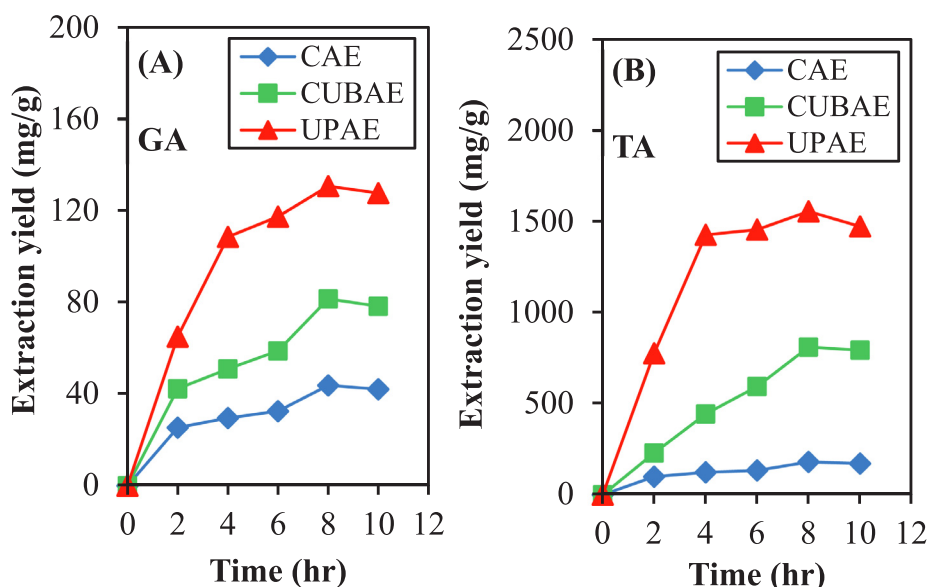
Fig. 2. Extraction yield under different extraction methods of (A) Gallic Acid, (B) Tannic acid from oak galls [temperature 50 °C; solid-to-solvent ratio 1:10; solvent water; duty cycle 10%]
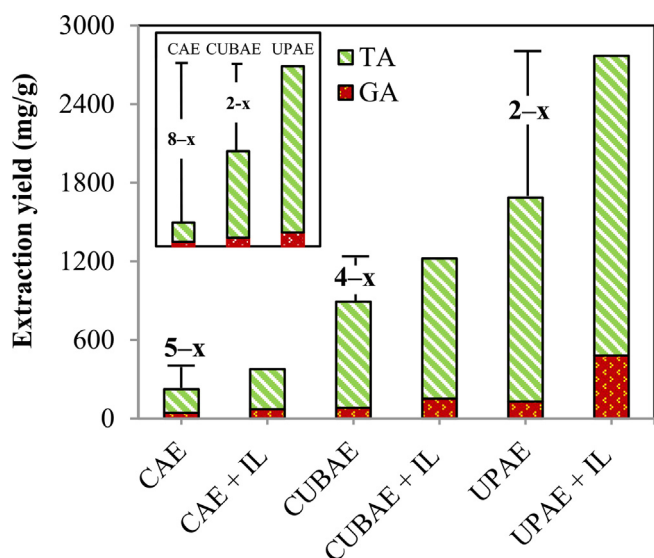

Fig. 3. Performance analysis with and without the presence of ionic liquid and different extraction methods (as inset) from oak galls [temperature 50 °C; solid-to-solvent ratio 1:10; duty cycle 10%; solvent water and [Bmim][BF$_4$]; concentration 0.1 M]

then increases as the ratio increases to 1:20. Smaller values of K_1 and K_2 at ratio 1:10 displayed higher initial reaction rate and maximum yield of phenolic acids compared to other solid-to-solvent ratio. Besides, the experimental values and the calculated values were comparable with high R^2 values for all experiment data set (0.96–0.99) with low RMSD ranging from 2.24 to 5.78 mg/g, demonstrating good fitting of the model towards the extraction process of phenolic acids from oak galls. Thus, it can be established that the Peleg's kinetic model successfully described that extraction capacity controlled the extraction process via UPAE of phenolic acids from oak galls under different conditions [52].

3.5. Characterization of oak galls

3.5.1. Fourier transform infrared (FT-IR) spectrometry analysis

Vibrational spectrum of a compound is considered to be unique characteristic of the molecule, thus, IR spectrometry is used as a fingerprint technique for identification of extract compounds. Therefore, in this study, FTIR spectrometer was used as an analytical method for further clarification to obtain the approximate amount of extraction yield based on its peak intensities.

The broad peak at 3379 cm^{-1} confirmed the presence of O–H group stretching vibration of phenolic compounds while peak 3027 cm^{-1} could be associated to aromatic C–H group [51,53]. Likewise, the C=O carbonyl group and aromatic C=C group at peak 1753 cm^{-1} and 1577 cm^{-1}, respectively, indicates the presence of phenolic acids GA and TA in the extract. It can be observed that the carbonyl peak was intense when the extraction was done via UPAE method instead of CUBAE and CAE as shown in Fig. 6Biii, Bii and Bi, respectively, showing an approximate higher amount of extraction yield [54]. On top of that, the aromatic C=C band at peak 1577 cm^{-1} that appeared upon extraction via UPAE method also demonstrated a much intense peak compared to other methods. As the ionic liquid [Bmim][Tf$_2$N] was used as solvent, peak O=S=O was able to be detected at 1294 cm^{-1} [55]. In addition, ether group of C–O–C at band peak of 1250 cm^{-1} was detected along with the band at 954 cm^{-1} that could be due to aromatic ring vibration of phenolic acids from the extracts. Based from the fingerprint in Fig. 6A–C, UPAE method showed a much intense peaks from various functional groups of phenolic acids compared to other methods. This pattern reflected higher amount of extraction yield in the sample extracts of oak galls extracted via UPAE method, confirmed the efficiency of this method for the process of extraction.

Fig. 7 summarized important functional groups to provide better understanding on the different peak intensities towards extraction yield. Peaks 3027, 1753, 1577, 1250, 1294 and 954 indicated functional groups aromatic C–H, carbonyl C=O, aromatic C=C, ether C–O–C, O=S=O, and alkene C=C, respectively. It could be clearly observed that all peaks intensities of UPAE method were increased as compared to other methods. This is in agreement with the previous HPLC result showing highest amount of phenolic acids in the plant extract using UPAE method in the presence of ionic liquid. Thus, the observed characteristic fingerprint pattern showing literally high intensity peaks reflected high amount of functional group of GA and TA in plant extract and it was trigger by UPAE and ionic liquid synergistic effect.

3.5.2. Scanning electron microscopy (SEM) analysis

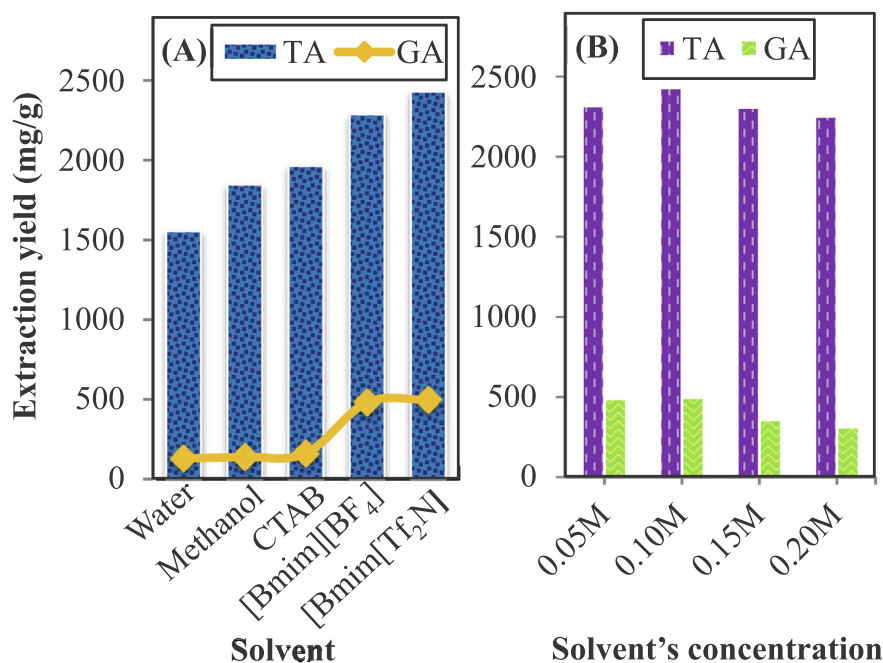The SEM images of outer surface of the sample before and after

Fig. 4. The performance of phenolic acids extraction from oak galls using UPAE method at (A) different solvents [temperature 50 °C; solid-to-solvent ratio 1:10; duty cycle 10%; concentration 0.1 M] and (B) different solvent's concentration [temperature 50 °C; solid-to-solvent ratio 1:10; solvent [Bmim][Tf₂N]; duty cycle 10%]
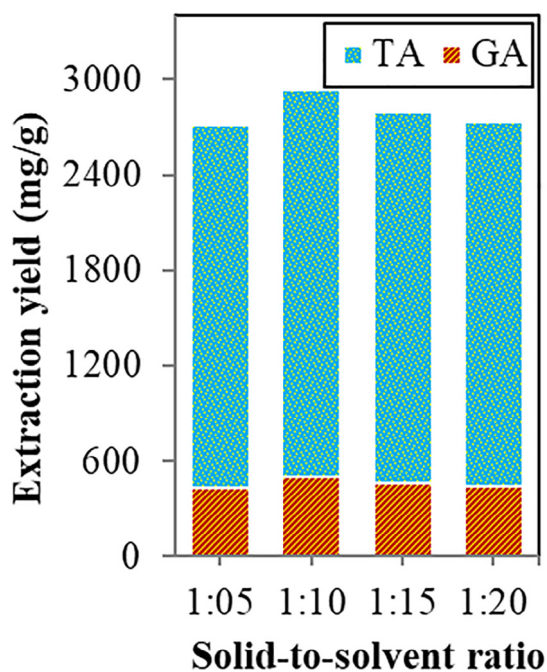

Fig. 5. The performance of phenolic acids extraction from oak galls using UPAE method at different solid-to-solvent ratio [temperature 50 °C; solvent [Bmim][Tf₂N]; duty cycle 10%; concentration 0.1 M]

Table 2
Values of Peleg's constant K_1 (min g/mg), Peleg's capacity constant K_2 (g/mg), and comparison of experimental and calculated (mg GAE/g) for different solvent [temperature 50 °C; solid-to-solvent ratio 1:10; extraction method UPAE; solvent's concentration 0.1 M; duty cycle 10%]

Solvents	Experimental (mg GAE/g)	K_1	K_2	Calculated (mg GAE/g)	R^2	RMSD (mg/g)
Water	130.76	0.0207	0.0048	135.36	0.98	1.88
Methanol	138.78	0.0073	0.0068	129.66	0.84	1.98
CTAB	161.74	0.0091	0.0058	144.14	0.77	2.82
[Bmim][BF₄]	481.04	0.0191	0.0009	304.18	0.93	10.53
[Bmim][Tf₂N]	497.34	0.0104	0.0004	588.24	0.96	5.78

Table 3
Values of Peleg's constant K_1 (min g/mg), Peleg's capacity constant K_2 (g/mg), and comparison of experimental and calculated (mg GAE/g) for different solvent's concentration [temperature 50 °C; solid-to-solvent ratio 1:10; extraction method UPAE, solvent [Bmim][Tf₂N]; duty cycle 10%].

Solvent's concentration (M)	Experimental (mg GAE/g)	K_1	K_2	Calculated (mg GAE/g)	R^2	RMSD (mg/g)
0.05	489.61	0.0134	0.00005	579.71	0.95	6.60
0.10	497.34	0.0104	0.0004	588.24	0.96	5.78
0.15	357.70	0.0111	0.0016	334.73	0.98	3.42
0.20	311.59	0.0107	0.0021	290.91	0.94	3.50

extraction for oak galls powder at the desired operating condition were captured and compared as illustrated in Fig. 8A–D, respectively. Fig. 8A illustrated the surface of oak galls powder in 500x scale as control. Basically, the oak galls looked alike ball-shaped with numerous protruding blunt horn-like lumps over the external surface. The surface is greyish-brown to brownish-black in colour. Fig. 8B represented the rough rugae-like surfaces governing the whole integument of the sample powder after the extraction process using CAE method. Fig. 8C

and D are the images after extraction using CUBAE and UPAE methods, respectively. It can be clearly seen that the sonication power from the ultrasonic affected the hardness of the sample surface and make oak galls powder looser than before. The sonication waves caused rupture of the plants' cell compared to the non-sonicated one [8]. Previously published studies reported that the ultrasonic process contributes to the water diffusivity increase, and there were disruption and breakdown of cells with elongation of parenchyma calls in sapota [56]. It can be

Table 4

Values of Peleg's constant K_1 (min g/mg), Peleg's capacity constant K_2 (g/mg), and comparison of experimental and calculated (mg GAE/g) for different solid-to-solvent ratio [temperature 50 °C; extraction method UPAE; solvent [Bmim] [Tf$_2$N]; solvent's concentration 0.1 M; duty cycle 10%].

Solid-to-solvent ratio	Experimental (mg GAE/g)	K_1	K_2	Calculated (mg GAE/ g)	R^2	RMSD (mg/g)
1:05	432.58	0.0120	0.0009	416.67	0.99	3.26
1:10	497.34	0.0104	0.0004	588.24	0.96	5.78
1:15	457.16	0.0101	0.001	441.99	0.99	2.24
1:20	438.04	0.0105	0.001	432.43	0.99	2.25

proved that the GA may easily be extracted from the severe ruptures on the surface of the samples by sonicated process using UPAE method compared to the CUBAE method due the images attributed from both Fig. 8C and D.

3.6. Proposed mechanism

Based on the HPLC result discussed before, it shows an incredible increased in the extraction efficiency for the sonicated samples as compared to the non-sonicated samples using ionic liquid [Bmim] [Tf$_2$N] as solvent. This verifies the synergistic effect between the ionic liquid and the UPAE method that significantly enhanced the extraction process. This claimed was also highly supported by the previous FT-IR results, indicate the presence of functional groups associated with phenolic acids and ionic liquid [Bmim][Tf$_2$N]. Moreover, the high intensity peaks of UPAE method compared to other methods showing that UPAE was indeed a much efficient method to extract phenolic acids from oak galls.

On top of that, it can be clearly seen from previous microscopic SEM characterization showing a rather looser or rupture powder surface of the oak galls powder under UPAE extraction method as compared to CAE and CUBAE methods. The observations may attributed to a process called cavitation phenomena which may responsible for the enhanced efficiency of UPAE method (Fig. 9) [57]. It can be proposed that the cavitation phenomena originated from the propagation of the mechanical waves formed from the combination of high and low pressure, namely compression and expansion, respectively [58], are the main attributes for the enhanced extraction process. As the UAE induced
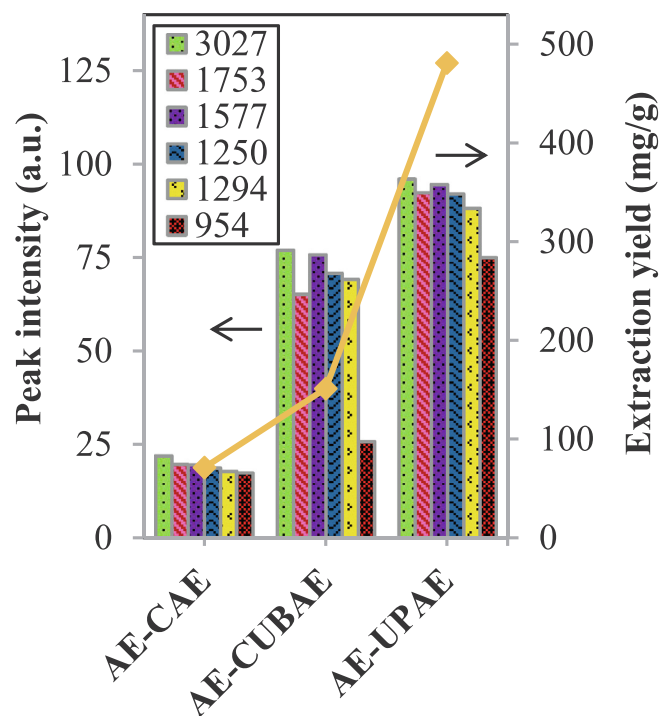

Fig. 7. Peak intensity of different functional groups in oak galls extracted samples after extraction via conventional aqueous extraction (AE-CAE), classical ultrasonic-bath assisted extraction (AE-CUBAE) and ultrasonic-probe assisted extraction (AE-UPAE) methods with extraction yields.

series of both compressions and expansions, the formation of bubbles were formed which then grow and undergo implosive collapse [3]. The acoustic cavitation produced by sonication process provide the chemical, physical and mechanical effects which results to a disruption of cellular wall and gives greater penetration of solvent into the sample materials [40]. This then leads to facilitate the phenolic acids extraction from the oak galls.

Previous studies argued that the ultrasound extraction is a combined of different mechanisms between erosion, sheer stress and fragmentation. Erosion discussed on the accessibility of the extraction medium by the implosion of cavitation bubbles on the surface of the plant matrix,
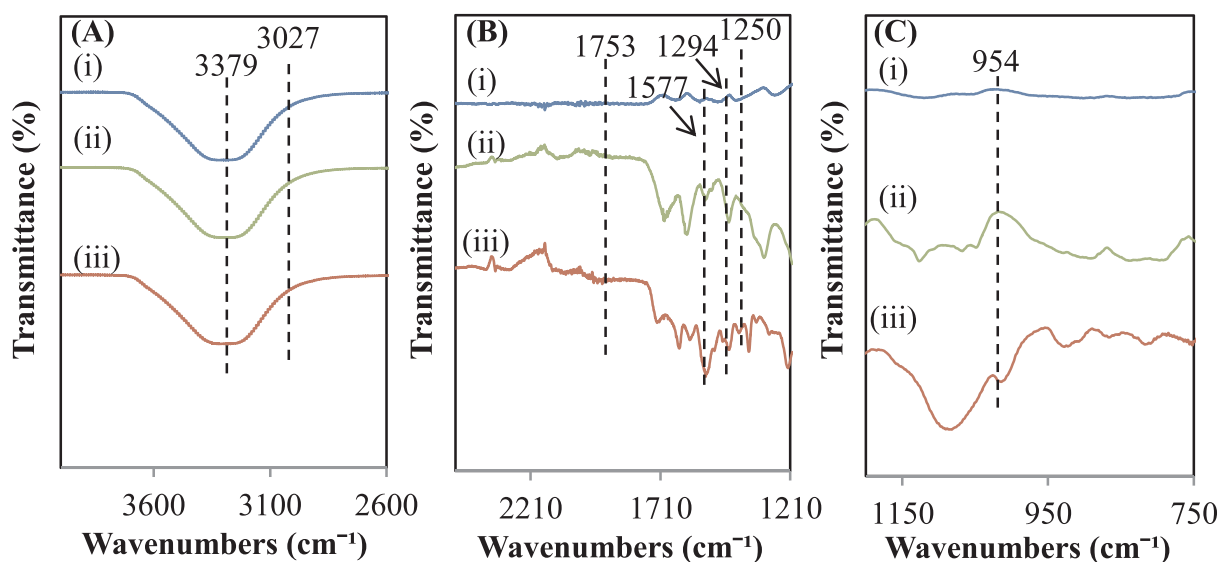

Fig. 6. FT-IR spectra of oak galls powder after extraction via different methods namely (i) CAE, (ii) CUBAE and (iii) UPAE.
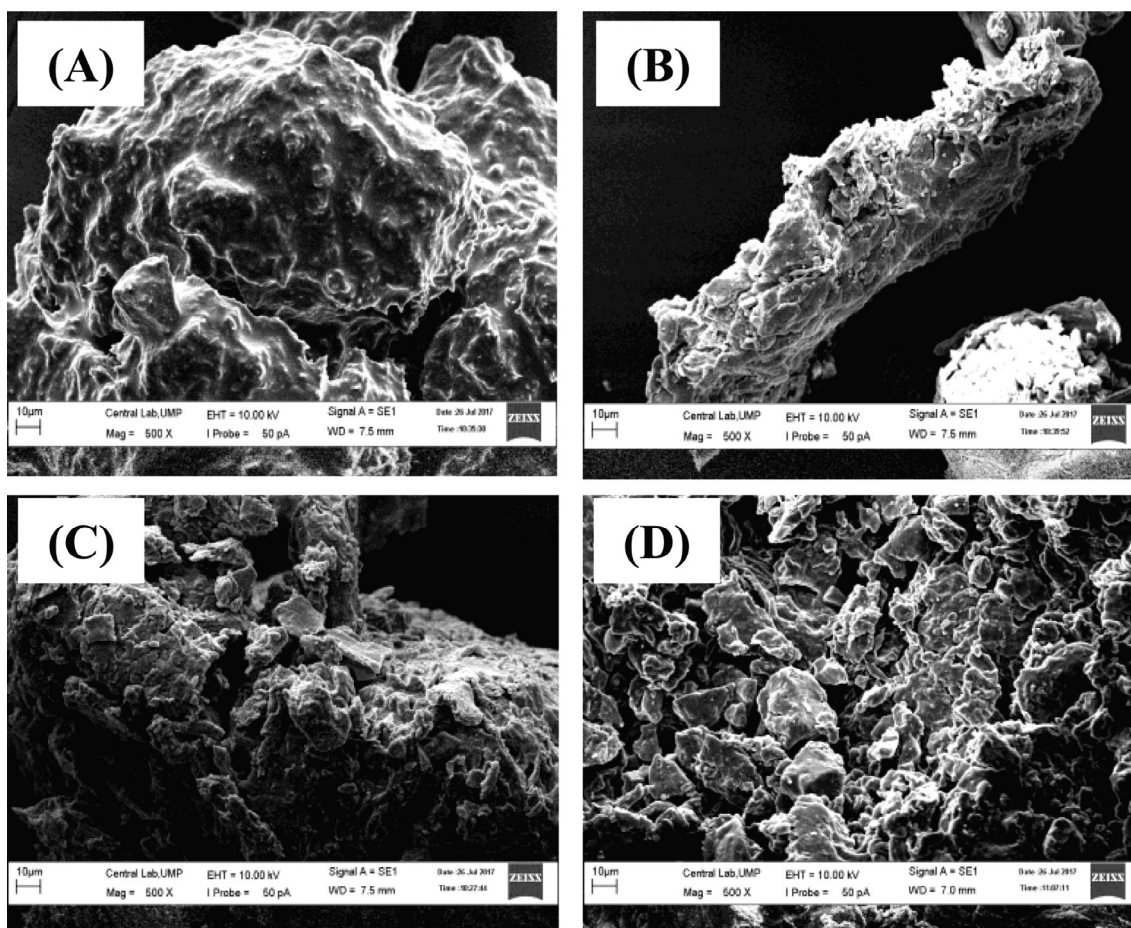
Fig. 8. SEM Microscopic observation (magnitude 500x) of oak galls surface (A) control, (B) after CAE (C) after CUBAE and (D) after UPAE [temperature 50 ˚C; solvent [Bmim][Tf$_2$N], solvent's concentration 0.1 M, sample-to-solvent ratio 1:10; duty cycle 10%]

brings to the extraction enhancement [59]. Next is the fragmentation which explained the situation where collision happened between particles and ultrasonic waves, that eventually cause a reduction in the particle size, hence increased the surface area of the sample solid material resulting in higher mass transfer and escalated the extraction rate also yield [40]. On the other hand, the mechanism called sheer stress happened during irradiation of a solid-liquid mixture by the ultrasound. Sheer forces were generated within the liquid and at the
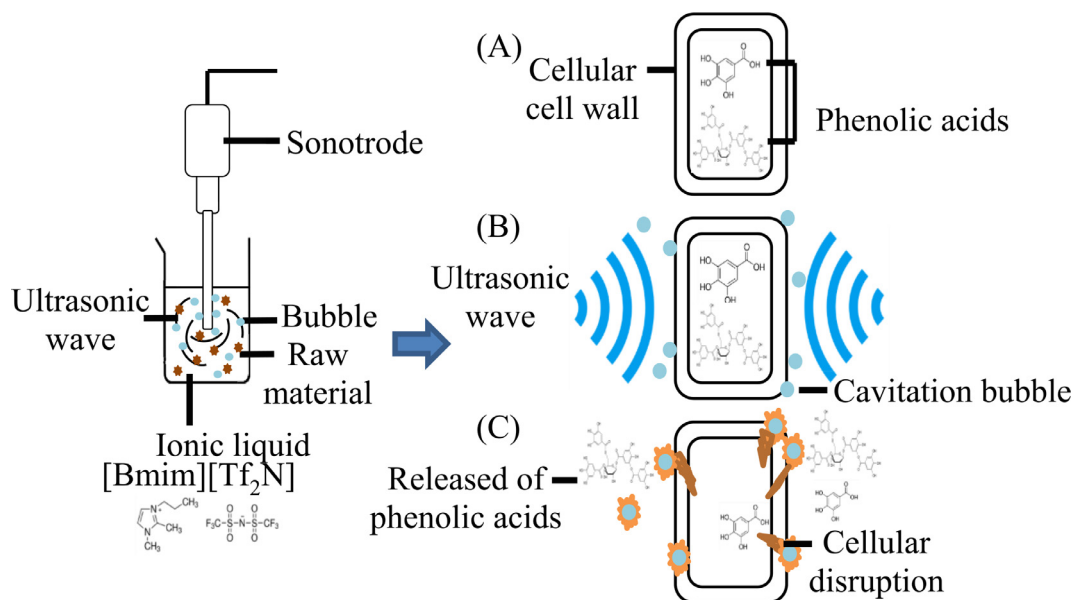

Fig. 9. Proposed mechanism for effect of ultrasonic wave on the surface of oak galls powder (A) oak galls cell, (B) Breakdown of cell wall by ultrasonic wave and (C) Cellular disruption and the release of phenolic acids.

vicinity of solid materials. It was the result from evolution, which comes from oscillation and collapse of the cavitation bubbles within the extraction medium [40]. Thus, the cavitation effect from the UPAE and the majestic characteristic of the ionic liquid [Bmim][Tf$_2$N] indeed synergistically performed in improving the extraction yield of phenolic acids from the oak galls.

The tremendous advantages of sonication method over conventional method can remarkably contribute to the enhancement in industrialisation or up scaling process. In this study, higher yield obtained using UPAE are of major interest from an industrial point of view, since this technology is a promising alternative to the existing process with minimum alteration. This study has discovers the application in aqueous extraction where organic solvents can be replaced with a green solvent-ionic liquid, with reduction in solvent usage, and shortening the extraction time. Besides, the ultrasound process also has been recognised for potential industrial application in the phyto-pharmaceutical extraction industry for a wide range of herbal extracts, as well as in edible oil industry to improve process efficiency and reduce extraction time [60,61]. The application of ultrasonic process to improve extraction efficiency in industrial scale would represent worthwhile economic gains. On top of that, the commercially viable and scalable of ultrasonic equipment engineering has high potential to be considered as the industrial-scale ultrasonic aided extraction system.

4. Conclusions

This research was carried out to determine the performance of UPAE method in extraction of phenolic acids from oak galls using an excellent solvent, ionic liquid [Bmim][Tf$_2$N]. The UPAE method significantly yielded a much higher extraction yield with the presence of ionic liquid compared with the absence of ionic liquid. The maximum amount of phenolic acids extracted was 497.34 mg/g and 2430.48 mg/g for GA and TA, respectively. The process was at its highest peak at temperature 50 °C with sonication intensity 8.66 W/cm^2 and 10% duty cycle, diluted in solvent [Bmim][Tf$_2$N] at concentration 0.10 M with sample-to-solvent ratio 1:10 for 8 h. Additionally, Peleg's model was successfully predicted the extraction process of phenolic acids from oak galls, indicating that both UPAE method and ionic liquid [Bmim][Tf$_2$N] enhanced the extraction capacity. It is believed that further investigation in this area may contribute to understanding the potential of UPAE with ionic liquid as alternative green solvent in extracting the phenolic acids which can contribute in many sectors such as nutritional, pharmaceutical and also cosmeceutical fields.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2019.104876.

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