Extraction of antioxidant compounds from the wastes of *Mangifera pajang* fruit: a comparative study using aqueous ethanol and deep eutectic solvent

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Abstract

The extraction of antioxidant compounds from fruits wastes of *Mangifera pajang* using conventional solvent (ethanol) and deep eutectic solvent (DES) was investigated. A statistical optimization study was first performed to maximize the antioxidant activity from ethanol extraction, which led to a maximum antioxidant activity of 11.11 ± 0.06 mg AEAC/g. The optimized parameters were then used in the DES extraction study. Among the several formulations of DESs, the solution where choline chloride mixed with glycerol (CHCL-GLY) resulted in the highest antioxidant activity. Subsequently, the CHCL-GLY formulation was further optimized by adjusting the molar ratio of the glycerol and the water concentration in the solution. The results showed that the CHCL-GLY solution with a molar ratio of 1:2 and addition of 20% water gave the highest antioxidant activity at 11.48 ± 0.09 mg AEAC/g, slightly outperformed the extract obtained by aqueous ethanol, indicating that DESs can be an excellent solvent for extracting antioxidant compounds from plant material which lead to novel industrial applications.

Keywords Antioxidant · Deep eutectic solvent · *Mangifera pajang* · Solvent extraction

1 Introduction

Since a couple of decades ago, there have been concerted efforts in the studies of phytochemicals properties mainly the antioxidant compounds derived from underutilized fruits [1]. In Borneo, there are plenty of underutilized fruits, such as dabai (*Canarium odontophyllum*) and bambangan (*M. pajang*) containing high concentrations of valuable phytochemicals and have been shown in a number of studies [2, 3]. In particular, *M. pajang* or commonly known in local languages as ‘bambangan’, ‘mawang’, ‘embang’, ‘buah pangin’ or ‘membangan’ is fairly abundant underutilized fruit which is only endemic to Borneo Island in the South East Asia [4]. It is known as the largest fruit in *Mangifera* species where its fruit size is three times as large as the commercial mango (*Mangifera indica*). The antioxidant

properties contained in different parts of *M. pajang* were studied by Abu Bakar et al. [5]. Their study indicated that the wastes of the fruit, particularly the kernel and peels contain higher level of total antioxidant concentration compared to its flesh, bringing about a bright prospect to utilize these fruit wastes as natural sources of antioxidant products. Moreover, a recent review paper highlighted the antioxidant properties and economic potential of *M. pajang* [3]. Nevertheless, to date, the potential of the fruit wastes of *M. pajang* have not been exploited for economic purposes.

For an economical utilization of *M. pajang*'s antioxidant, an effective extraction of the phytochemicals involved is crucial before formulating the extract into a desired product. To meet this objective, several potential extraction methods such as the solvent extraction, microwave-assisted

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extraction and ultrasonic-assisted extraction and a few others have been used [6–11]. Amongst, the solvent extraction method has been traditionally used for recovering phytochemicals as it often requires relatively low processing cost and easy to operate [12]. For these, it is widely implemented as separation process in pharmaceutical, food and waste treatment industries [13]. The solvent extraction method typically requires a suitable solvent to separate a desired solute from the solid matrix [14, 15]. In this context, selection of solvent is of paramount important. The common solvents used are hexane, ether, benzene, acetonitrile, methanol, ethanol and chloroform [16]. Nevertheless, these solvent are mostly volatile organic solvents (VOC), which is highly flammable and often exerts negative impacts on environment [17].

In response to the need to obtain high quality phytochemicals that are safe for human consumption, there is a growing need to find an alternative green solvent to extract natural antioxidant compounds from plants. For this purpose, the Deep Eutectic Solvent (DES) has recently attracted considerable attentions for its potential to replace these conventional organic solvents [18, 19]. DES is a mixture consisting of 2 or 3 hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) components. Upon mixing, the HBD and HBA components interact with each other through hydrogen bonding [20]. The most commonly employed HBA is choline chloride while the HBD are amino acids, alcohol, carboxylic acids and sugars [21]. One of the unique features of the DES solution is that it has a lower melting point than that of its individual HBD and HBA components [22]. Note that, the DES have several remarkable advantages such as simple preparation, low costs, good biodegradability, low toxicity and no requirements for subsequent purification steps [18, 23, 24]. Furthermore, the desired physicochemical properties of the DES can be easily adjusted by modifying the compositions of the HBD and HBA components [25]. Because of these attractive properties of the DES, several researchers have studied the applications of DES as extraction media and successfully proved that it is suitable for extracting bioactive compounds from different plants [19, 22, 26–30]. However, to-date, there has been no report on the investigation of the efficiency of DES in extracting antioxidant compounds from the fruit wastes of *M. pajang*. Thus, this study focused on the use of DES and compared its efficiency with the conventional solvent (ethanol) to extract antioxidant compounds from the fruit wastes of *M. pajang*.

2 Materials and methods

2.1 Chemicals and reagents

Ascorbic acid, 2,2-diphenyl-1-picrylhydrazyl (DPPH) reagent powder, glycerol, ethylene glycol, fructose and absolute ethanol were purchased from Merck (Germany). Aqueous ethanol at different concentrations were prepared by mixing the absolute ethanol with deionized water. Choline chloride was purchased from Sigma-Aldrich (Germany) while glucose was purchased from Fisher Scientific (UK). All chemicals and reagents used were of analytical grade.

2.2 Plant materials and sample preparation

The fresh fruits of *M. pajang* were collected from a retailer in Sarawak, Malaysia. The fruits were cleaned and then the flesh, kernel and peel were separated. The kernels and the peels were dried at 60 °C for 24 h, grounded into fine powders, kept in an air-tight container and stored in a freezer (– 20 °C) until further analysis [5].

2.3 Ethanol extraction of antioxidant compounds from peels and kernels of *M. pajang*

The extraction was conducted according to the method described by Abu Bakar et al. [5] with slight modifications. The sample (0.5 g of peel powder and 0.5 g of kernel powder) were extracted for 2 h with 30 ml of aqueous ethanol at various concentrations (20–100%) and temperature (30–60 °C) on an incubator shaker (SASTEC) which set at a speed ranged from 100 to 300 rpm. Following that, the mixture was centrifuged at 4000 rpm, 25 °C for 20 min and the supernatant was collected and stored for further analysis.

2.4 Optimization of solvent extraction parameters by using response surface methodology (RSM)

2.4.1 Experimental design

Response surface methodology (RSM) was employed to evaluate the effects of 3 independent variables: (A) concentration of ethanol solution, (B) extraction temperature, and (C) extraction shaking speed on the antioxidant activity (Y). The face-centered composite design (CCD) along with quadratic model was used. 20 experimental runs including 8 factorial points, 6 axial points and 6 replicates of center points were performed.

2.4.2 Statistical analysis

The Design Expert 11.0.3 Software (Star-Ease Inc., Minneapolis, USA) was used to perform all the experimental design and the response surface analysis. The experimental data were subjected to statistical analysis and regressions to fit a second order polynomial Eq. (1) representing the effects of independent variables on the given response (dependent) variable:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (1)$$

where Y is the dependent (or response) variable (i.e., antioxidant activity); A, B and C represent the ethanol concentration (%), extraction temperature (°C) and extraction shaking speed (rpm), respectively; β_0 is the intercept coefficients while β_1 , β_2 and β_3 are the linear coefficients; β_{11} , β_{22} and β_{33} represent the quadratic coefficients; β_{12} , β_{13} and β_{23} are the interaction coefficients.

The analysis of variance (ANOVA) was applied to determine the regression coefficients, to investigate the interaction between the dependent and independent variables, and to select the best fit polynomial model for the experimental data. The statistical parameters, including the lack of fit, coefficient of determination, the F-test value, adequate precision and coefficient of variation were analyzed to determine the adequacy of the obtained quadratic response surface (RSM) model. The relationship between the independent variables and the dependent variables was graphically presented via the response surface plots. All the experiments were performed in triplicate.

2.4.3 Validation of the RSM model

The model validation was performed by carried out experiments at optimal extraction conditions. The experimental values and predicted values by the RSM model were compared to determine the validity of the model involved. Values with a confidence level higher than 95% were considered as significant.

2.5 Preparation of deep eutectic solvents (DESs)

The DES were prepared by using the method described by Ozturk et al. [27] and Bajkacz and Adamek [31] with slight modifications. Briefly, the DES components were weighted to meet the required molar ratio presented in Table 1. These components were mixed and heated at 80 °C under constant stirring (200 rpm) until the formation of a homogenous clear liquid. These DES formulations were then used to extract the antioxidant compounds from the fruit wastes of *M. pajang* according to the method described in Sect. 2.3.

2.6 Tailoring of DES formulation

The properties of a DES formulation can be altered through adjusting the molar ratio of the components and water content [32]. The DES showing the best extraction efficiency was further studied by modulating the molar ratio of the choline chloride and HBD component (1:2, 1:3 and 1:4). Apart from that, the DES with different addition of water (10–50 wt%) were prepared to study the effect of water content on the DES effectiveness in extracting antioxidant compounds [31].

2.7 Comparison between the optimal conventional ethanol solvent and DES

The extraction efficiencies of both the DES and conventional ethanol were evaluated based on the scavenging activity of the extracts. The scavenging activity of the extracts was estimated by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, which was described by Brand-Williams et al. [33]. An aliquot of 0.1 ml of extract or control (absolute ethanol) was mixed with 3.9 ml of 6×10^{-5} mol/l DPPH in absolute ethanol. The mixture was shaken vigorously and left to stand at room temperature for 30 min in the dark. Next, the mixture was measured using a UV–visible spectrophotometer at wavelength of 517 nm. The free radical scavenging activity was calculated using (2):

Table 1 Different DESs system used in this work

Abbreviation	DES			Molar ratio
	Component 1	Component 2	Component 3	
CHCL-GLY	Choline chloride	Glycerol	–	1:1
CHCL-EG	Choline chloride	Ethylene glycol	–	1:1
CHCL-GLU	Choline chloride	Glucose	Water	1:1:1
CHCL-FRU	Choline chloride	Fructose	Water	1:1:1

Scavenging effect(%)

$$= \left[1 - \left(\frac{\text{Absorbance of sample}}{\text{Absorbance of control}} \right) \right] \times 100 \quad (2)$$

A standard solution of ascorbic acid was prepared according to the method described by Abu Bakar et al. [5]. A standard curve was prepared by plotting the percentage of free radical scavenging effect of ascorbic acid versus its concentration ranging from 0.02 to 0.5 mg/ml. The final result was expressed as mg ascorbic acid equivalent antioxidant capacity in 1 g of sample (mg AEAC/g).

3 Results and discussions

3.1 Solvent extraction of antioxidant compounds from *M. pajang*

The fruit wastes of *M. pajang* were selected as the source of antioxidant compounds as they were reported to possess superior amount of antioxidant compounds [5]. Extraction of the antioxidants is an important step in recovering these valuable compounds. It was noted that the effectiveness of extraction of antioxidant compounds by a given solvent is dependent on several extraction parameters [14, 15]. Therefore, it is essential to determine the optimum extraction parameters to obtain an extract with maximum antioxidant activity. For that, the optimal conditions and effects of independent variables, including the concentration of ethanol solution (A), extraction temperature (B) and extraction shaking speed (C) on the antioxidant activity of extract (Y) were identified through face-centered composite design (CCD).

In the first part of the experimental studies, ethanol was selected as the extraction solvent as it has been considered safe in accordance with the European Food Safety Authority (EFSA) [34]. Previous study showed that a mixture of ethanol and water gives a better extract quality and efficiency [35]. Using this previous study as a reference, mixtures of ethanol–water were prepared with the ethanol concentration ranged from 20 to 100%. In particular, 100% ethanol mixture was used to represent a mono-component solvent system. The extraction temperature is also a critical parameter that should be taken into account as it greatly affects the antioxidant activity of extract. Higher extraction temperature is normally preferred as it results in greater diffusivity of the solutes but it was reported that that lower extraction efficiency was obtained when the extraction temperature exceed 60 °C [36]. In this case, the extraction temperature for the optimization design was set in the range of 30–60 °C. Besides that, it was reported that an increase of shaking speed enhanced the mass

transfer rate and led to a greater extraction performance [37]. Despite the significant contribution of shaking, the effects of shaking speed are often overlooked in many extraction studies. Therefore, the effect of shaking speed on the antioxidant activity was also investigated in this study. The shaking speed used in this study ranged from 100 to 300 rpm, which was based on the study performed by Andrade et al. [38].

3.2 Optimization of the extraction parameters via RSM

3.2.1 Experimental design and statistical analysis

The antioxidant activities of extracts under different extraction conditions are tabulated in Table 2. The experimental values were relatively close to the predicted values, indicating a satisfactory model. The experimental data were used in regression analysis to compute the model (i.e. polynomial equation) coefficients. Table 3 shows the regression coefficients and the equation obtained is as follow:

$$Y = 11.28 - 0.3804A + 0.2026B - 0.3237C + 0.1635AB + 0.1592AC - 0.5781BC - 1.11A^2 - 0.3886B^2 - 1.31C^2 \quad (3)$$

The analysis of variance (ANOVA) suggested that the experimental data could be represented using the quadratic polynomial model. The ANOVA showed that the experimental data gave high coefficient of determination (R^2) of 0.9714, indicating a high level of correlation between the model and experimental data [39]. Since R^2 is close to unit, this demonstrated that the effect of independent variables, which include ethanol concentration (A), extraction temperature (B) and the extraction shaking speed (C) on the antioxidant activity can be well-described by the model. Additionally, a large F-value (37.74) and small p value (< 0.0001) was obtained, implying the model is statistically significant (Table 4). Additionally, the lack of fit p value was calculated as 0.0995, showing that the adequacy of model to precisely estimate the variation. The coefficient of variation (CV %) was 3.28% for the response which indicates satisfactory reproducibility of the model. The model also displays adequate precision value (17.279), implying an adequate signal of model.

3.2.2 Effects of independent variables on the antioxidant activity

The antioxidant activity of bioactive compounds is a measure of ability of these compounds to scavenge the free radicals and inhibit the chain reaction of oxidation process [40]. It was reported that the radical scavenging ability of

Table 2 Experimental design for extraction, experimental and predicted values of response

STD	Factor 1: ethanol concentration (%)	Factor 2: extraction temperature (°C)	Factor 3: agitation speed (rpm)	Response: antioxidant activity (mg AEAC/g)	
				Actual value	Predicted value
1	20	30	100	8.93	8.72
2	100	30	100	7.36	7.32
3	20	60	100	9.87	9.96
4	100	60	100	9.40	9.20
5	20	30	300	8.67	8.91
6	100	30	300	8.18	8.14
7	20	60	300	7.74	7.83
8	100	60	300	7.46	7.72
9	20	45	200	10.77	10.55
10	100	45	200	9.76	9.79
11	60	30	200	10.64	10.69
12	60	60	200	11.33	11.09
13	60	45	100	9.93	10.30
14	60	45	300	10.21	9.65
15	60	45	200	11.48	11.28
16	60	45	200	11.26	11.28
17	60	45	200	10.91	11.28
18	60	45	200	11.04	11.28
19	60	45	200	11.41	11.28
20	60	45	200	11.19	11.28

Table 3 Regression coefficient values for antioxidant activity

Regression coefficient	Antioxidant activity (Y)
Intercept (β_0)	11.28
A—ethanol concentration (β_1)	− 0.3804
B—extraction temperature (β_2)	+ 0.2026
C—agitation speed (β_3)	− 0.3237
AB (β_{12})	+ 0.1635
AC (β_{13})	+ 0.1592
BC (β_{23})	− 0.5781
A ² (β_{11})	− 1.11
B ² (β_{22})	− 0.3886
C ² (β_{33})	− 1.31
R ²	0.9714

Table 4 ANOVA of regression coefficient of the fitted quadratic equation from all the independent variables

Parameter	Antioxidant activity (Y)	
	F-value	p value
Model	37.74	< 0.0001
A—ethanol concentration	13.75	0.0041
B—extraction temperature	3.90	0.0765
C—agitation speed	9.95	0.0102
AB	2.03	0.1845
AC	1.93	0.1953
BC	25.41	0.0005
A ²	32.09	0.0002
B ²	3.95	0.0750
C ²	44.62	< 0.0001

the antioxidant compounds are due to the delocalization on the aromatic ring of the phenolic compounds [41]. In other word, evaluating the free radical scavenging capacity is a promising way to indicate the presence of phenolic compounds. For that, DPPH scavenging activity was used in this study to evaluate the antioxidant activity of the extracts. The ANOVA revealed substantial influence of independent variables on the antioxidant activity. Specifically, an independent variable with large F-value and small p value less than 0.05 can have significant impact on the

response variable. In this study, the F-value and p value obtained from ANOVA are tabulated in Table 4. Based on Table 4, the model demonstrated that the first-order linear and quadratic effect of ethanol concentration (A and A²) at the level of $p < 0.05$, manifesting the ethanol concentration greatly influence the antioxidant activity of extracts. The three-dimensional response surface plot evaluating the effects of independent variables is shown in Fig. 1. Based on Fig. 1a and b, it was observed that the concentration of ethanol greatly influenced the antioxidant activity, where

Fig. 1 **a** Effect of interaction between ethanol concentration and extraction temperature on antioxidant activity (AB); **b** effect of interaction between ethanol concentration and extraction agitation speed on antioxidant activity (AC); **c** effect of interaction between extraction temperature and extraction agitation speed on antioxidant activity (BC)

the antioxidant activity increased when the concentration of ethanol decreased from 100 to 60% and when the concentration of ethanol increased from 20 to 60%. This behavior may be attributed to the affinity and interaction between the polar solvent and antioxidant compounds in

the plant matrix. Generally, polar antioxidant compounds in the plant matrix are easier to be isolated by using highly polar solvent due to favorable thermodynamics for the formation of solvent–solute forces. On the contrary, a non-polar solvent can only dissolve the non-polar compounds leading to unfavorable thermodynamics [16]. In this context, it can be said that the polarity of antioxidants is similar to the polarity of ~60% ethanol–water mixture. This finding confirms that antioxidant compounds in the fruit wastes of *M. pajang* has high polarity and this is reasonable since approximately 90% of the major antioxidant compounds content in the fruit wastes of *M. pajang* are phenolic acids, which is hydrophilic in nature [3, 42, 43]. The addition of water (polarity index of 9.0) to the ethanol solvent (polarity index of 5.2) might create a high-polar medium that allows the solvent system extract antioxidant compounds of *M. pajang* from both ends of the polarity range [16, 44]. A similar relationship of ethanol concentration and the antioxidant activity was observed in the previous study performed by Liyana-Pathirana and Shahidi [45], where ethanol at a concentration around 50% yielded higher amount of phenolic compounds from wheat than other solvent composition. Additionally, Gullón et al. [34] found that the optimum concentration of ethanol for the extraction of antioxidant compounds from *Eucalyptus globulus* is 56%, which is in accordance to our findings. Their studies confirm that extraction with binary solvent or aqueous ethanol mixture contributes to higher antioxidant capacities.

Interestingly, the combined effects of the ethanol concentration with both the extraction temperature (AB) and extraction shaking speed (AC) were insignificant in our study ($p > 0.05$). Based on this finding, it can be deduced that there is no significant correlation between AB and AC. As depicted in Fig. 1a, changes in ethanol concentration and temperature revealed that maximum antioxidant activity was obtained when the ethanol concentration was around 60% and the temperature was around 50 °C. It is worth to highlight that at ethanol concentration of around 60%, an increase in temperature did not show any profound effect and this suggests that the antioxidant activity might relies on its individual effect and their interactive effect is not significant. For the interaction between ethanol concentration and shaking speed (AC), Fig. 1b shows that both parameters presented a linear relationship, where elevating both parameters up to a certain level lead to decomposition of antioxidant compounds. This suggests that the interactive effect of AC on the antioxidant activities is less significant. Therefore, it can be presumed that the antioxidant activity solely relied on linear effect of each parameter.

Aside from the effects of ethanol concentration, the antioxidant activity of extracts also depended on the

interactive effect of extraction temperature and shaking speed (BC), with p value of 0.0005 and the first-order linear and quadratic effect of extraction shaking speed (C and C^2) at the level of $p < 0.05$. Figure 1c visualizes the interaction between the extraction temperature and shaking speed (BC). As shown in Fig. 1c, it was found that the antioxidant activity of extracts increased with temperature and shaking speed. Beyond these values, the antioxidant activity gradually declined. This phenomenon may be related to the mass transfer behaviors, which depends on the interactions of solubility, internal diffusion and bulk transport of the antioxidant compounds. It is known that in the extraction process, the solutes (antioxidant compounds) must first diffuse to reach the surface of solid matrix that is affected by convection before being transferred to the bulk solvent. In other words, the transportation of solutes to the bulk of solvent solution is limited by the convective mass transfer [46]. From Fig. 1c, it was observed that the antioxidant activity of extracts increased with the increased temperature and shaking speed. This is reasonable as the elevated temperature facilitates the breakdown of cellular constituents of plant cells which increases the solubility of solutes (antioxidant compounds) and diffusion rate of solutes to the bulk solvent [47]. In respect to the elevated extraction temperature, accelerating shaking speed can create more turbulence which enhances the mass transfer coefficient and improves the convective mass transfer. The further increment of mass transfer then allows rapid diffusion and solubilization which produce extracts with high antioxidant activity [37].

However, it was realized that the antioxidant activity of extracts started to decrease when the temperature and shaking speed beyond certain values. This was likely due to the thermal degradation of antioxidant compounds at high temperature. This suggests that further increment of temperature likely cause thermal degradation of antioxidant compounds [48]. Similar finding was reported by Sarkar and Ghosh [49], where the further increase of extraction temperature reduced the antioxidant activity of extract. With regard of the shaking speed, it can be said that optimum shaking speed is sufficient to overcome the mass transfer limitations [50]. Further increase of shaking speed beyond the optimal value is found to affect the extraction process. This is possible as high shaking speed may create a shear force that cause damage to the antioxidant structures and this consequently reduce the antioxidant activity [51]. This finding is in good agreement with previous study conducted by Andrade et al. [52]. In their study, extracts with higher antioxidant activity were obtained at an extraction shaking speed of 150 rpm which is relatively close to our finding.

3.2.3 Optimization of independent variables and verification of the results

The numerical optimization was performed by using the desirability function method to determine the optimum conditions that give an extract with maximum antioxidant activity. The optimized conditions for this study were 54% ethanol concentration, 51 °C extraction temperature and 178 rpm of shaking speed. The predicted response value at optimized conditions was 11.38 mg AEAC/g (DPPH free radical scavenging effect of 91.57%). The suitability and adequacy of model was verified by conducting experiment at optimum conditions obtained from the model. Under these optimum conditions, the average experimental value was 11.11 ± 0.06 mg AEAC/g (DPPH free radical scavenging effect of 91.09%). The experimental value closely agreed with the predicted value, i.e., with error margin 2.37%, % (within the 95% confidence interval of the fitted model), proving that the model is well fitted for the extraction of antioxidant compounds from *M. pajang* under the optimal extraction conditions.

3.3 Screening of DESs

From the perspective of sustainable development, it is important to use green solvent for the extraction of antioxidant compounds from the natural plants in order to reduce negative impact on the environment, e.g., reduces energy consumption and wastes. DES is a green solvent and it was found that it exhibits the ability to increase interaction with phenolic compounds, which further increase the extraction efficiency [21]. In this study, 4 different choline-chloride-based DES formulations prepared at molar ratio of 1:1 were prepared and their extraction efficiencies for antioxidant compounds were evaluated. The selection of DES components is important as the components of DES determine its physicochemical properties, which can greatly affect the extraction efficiency. In the present study, choline chloride was chosen as the HBA component due to its low cost and non-toxicity [25]. The choline chloride when combined with polyols (glycerol and ethylene glycol) and sugar (glucose and fructose) forms a safe deep eutectic solvent [53]. The formation of DESs were confirmed by the appearance of the DES as described by literature; both choline chloride-glycerol (CHCL-GLY) and choline chloride-ethylene glycol (CHCL-EG) solutions formed transparent and uniform liquid. On the other hand, choline chloride-glucose (CHCL-GLU) formed faintly yellow non-viscous liquid and choline chloride-fructose (CHCL-FRU) formed a faintly yellow viscous liquid [54].

These solvents were used to extract the antioxidant from fruit wastes of *M. pajang* using the optimum extraction conditions described in previous section. The efficiency of DES as solvent is shown in Fig. 2a. Among all the tested solvents, CHCL-GLY showed the best extraction efficiency by obtaining antioxidant activity at 7.40 ± 0.05 mg AEAC/g, followed by CHCL-EG at 6.96 ± 0.07 mg AEAC/g, CHCL-GLU at 6.45 ± 0.07 mg AEAC/g and CHCL-FRU at 5.59 ± 0.05 mg AEAC/g.

Interestingly, the extracts obtained by CHCL-GLY and CHCL-EG solutions displayed comparable antioxidant activities. It is worth noting that, a higher extractability of CHCL-GLY can be attributed to the presence of an additional -OH group presents in glycerol. The additional -OH group can induce higher polarity which further facilitates the extraction process [27]. In general, polar antioxidant compounds from a plant source are easier to be isolated by using polar solvent because it is thermodynamically favorable due to the increasing formation of the solvent-solute forces [16]. Given that the polarity of CHCL-GLY is higher, therefore, more polar antioxidant compounds from the fruit wastes of *M. pajang* can be extracted. The CHCL-GLY showed the best extraction efficiency among the DES and therefore it was chosen in further experiments.

3.4 Tailoring of DES formulation

The physicochemical properties of DES can be easily adjusted by tailoring the DES components [25]. In this regard, the effects of molar ratio and water content in CHCL-GLY DES were studied to obtain the best formulation of CHCL-GLY capable of extracting the antioxidant compounds from fruit wastes of *M. pajang*.

3.4.1 Effect of the molar ratio of DES components on the antioxidant activity of extracts

The viscosity of the DES is high and this can reduce the solute diffusion from the plant material to the bulk liquid. A few studies showed that the viscosity of the DES can be reduced by altering the molar ratio of the DES components [19, 55]. Therefore, different molar ratio of CHCL-GLY (1:1 to 1:2, 1:3 and 1:4) were prepared with 30 wt% of water. The molar amount of choline chloride was kept constant in this study; whereas the molar ratio of CHCL-GLY was controlled up to 1:4 as beyond this molar ratio, the DES is not stable and formation of liquid is not possible. This may due to the excessively high number of hydroxyl groups, where the amount of salt available is not adequate to form hydrogen bonding with the available hydroxyl groups, which in turn causes the mixture to become heterogeneous and remains in a semisolid phase [53].

Figure 2b shows the antioxidant activities of extracts under the influence of different molar ratios of CHCL-GLY components. It was found that the antioxidant activity obtained was 10.95 ± 0.03 mg AEAC/g, 9.30 ± 0.12 mg AEAC/g and 8.57 ± 0.14 mg AEAC/g, when the molar ratio was set at 1:1 to 1:2, 1:3 and 1:4, respectively. Remarkably, a total increment of 48% in antioxidant activity was obtained when the molar ratio of CHCL-GLY was altered from 1:1 to 1:2. The increment may due to the increase of molar amount of polyol in CHCL-GLY mixture. The increase of molar amount of polyol in the CHCL-GLY mixture reduced the viscosity and surface tension of the mixture, hence enhancing the mass transfer rate and dissolution of bioactive compounds [32]. Nevertheless, the antioxidant activity of extracts showed downward trend as the molar ratio increased further to 1:3 and 1:4. This trend can be explained by the excessive amount of polyol (glycerol) in the mixture, where a large number of hydroxyl group in the mixture hinder the interaction between the chloride ions and the bioactive compounds [56]. Overall, the experimental results indicated that the CHCL-GLY formulation at molar ratio 1:2 led to an extract with the highest antioxidant activity. This finding is found to be in agreement with the work conducted by Ozturk et al. [27], where the total phenolic content of orange peels were at maximum when the molar ratio of choline chloride and glycerol was at 1:2. Aside from that, Ozturk et al. [27] also observed a decreased trend of the total phenolic content when the molar ratio of DES changed from 1:2 to 1:3 and 1:4. Hence, the CHCL-GLY at molar ratio 1:2 was used in the subsequent experimental study.

3.4.2 Effect of water content in DES on the antioxidant activity of extracts

Apart from modulating the molar ratio of DES components, the addition of water can also reduce the DES viscosity [32]. CHCL-GLY at molar ratio of 1:2 shown in earlier section show great ability to produce highest antioxidant activity of the *M. pajang* extracts. Thus, the concentration of water in CHCL-GLY (molar ratio 1:2) was varied from 10 wt% and to 50 wt%; 30 wt% is the base case. Other experimental parameters were kept at the optimum operating conditions stated in the earlier section.

Figure 2c shows that the CHCL-GLY at molar ratio 1:2 and with addition of 20 wt% water displayed best extraction efficiency, with antioxidant activity measured at 11.48 ± 0.09 mg AEAC/g. Furthermore, it was observed that when the water content in DES increased from 10 to 20% wt%, the antioxidant activity of extract increased by 4.18%. Clearly, the addition of water improves the extraction efficiency. The is possible as the addition of water could reduce the viscosity and consequently, enhances

Fig. 2 **a** Total antioxidant activity of *M. pajang*'s fruit wastes at optimum operating conditions using choline chloride-based DES as solvent, where, *CHCL-GLY* choline chloride-glycerol, *CHCL-EG* choline chloride-ethylene glycol, *CHCL-GLU* choline chloride-glucose, *CHCL-FRU* choline chloride-fructose; **b** total antioxidant activity of *M. pajang*'s fruit wastes at optimum operating conditions using *CHCL-GLY* at different molar ratio (1:1, 1:2, 1:3 and 1:4); **c** total antioxidant activity of *M. pajang*'s fruit wastes at optimum operating conditions using *CHCL-GLY* at 1:2 with different water content (10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%)

the rate of mass transfer and dissolutions of antioxidant compounds [19]. Another possible explanation could be credited to an increased polarity of DES by adding water, which facilitates the extraction of antioxidant compounds of the plant from both ends of the polarity range [44]. A point to note that, upon further increment of water content to 30, 40 and 50 wt%, the extraction efficiency showed downward trend. The antioxidant activity

obtained using *CHCL-GLY* at 1:2 with 30, 40 and 50 wt% were 10.95 ± 0.03 mg AEAC/g, 9.66 ± 0.11 mg AEAC/g and 7.76 ± 0.12 mg AEAC/g, respectively. This downward trend is reasonable as high dilution of water may reduce the hydrogen bond and led to disappearance of the DES structure and its unique property. Consequently, the solubility of antioxidant extracts in the DES solution decreases and this lead to lower extraction efficiency [22].

3.5 Comparison between the optimal conventional ethanol solvent and DES

Based on the results presented above, it can be concluded that the CHCL-GLY at molar ratio 1:2 and the addition 20 wt% water produced extracts with highest antioxidant activity (11.48 ± 0.09 mg AEAC/g, DPPH free radical scavenging effect of 91.74%), slightly outperforms the aqueous ethanol (11.11 ± 0.06 mg AEAC/g, DPPH free radical scavenging effect of 91.09%). Noted that the extraction results using the DES only shows small improvement over the ethanol, which is reasonable, considering the concentration of ethanol was optimized in this study to obtain best extraction efficiency. Also, the antioxidants contain in the fruit wastes of *M. pajang* are polar in nature [3]. Since both the ethanol and CHCL-GLY are also highly polar, it is reasonable that effective extraction ability can be achieved and the magnitude of increment is small. Even so, this finding still highlights the potential of DES in solubilizing the hydrophilic antioxidant compounds.

The present findings are in agreement with some previous reports. Bubalo et al. [57] showed that the DES composed of choline chloride and oxalic acid with 25% of water enhanced the extraction of phenolic compounds from grape skin compared to water and aqueous methanol extractions. Besides that, Ozturk et al. [27] also proved that both the choline chloride-based DES when paired with polyol (glycerol and ethylene glycol) outperformed the aqueous ethanol in extracting the bioactive compounds from the orange peels, where the total phenolic content obtained by using choline chloride-ethylene glycol DES, choline chloride-glycerol DES and ethanol are 3.61 mg GAE/g, 3.33 mg GAE/g and 2.62 mg GAE/g, respectively. These results confirmed the potential of DES as a good alternative to the conventional solvent for the extraction of antioxidant compounds from plant source.

Aside from better extraction efficiency, DES is of low cost. Cruz et al. [58] clearly highlighted most typical DES such as CHCL-GLY are comparable in cost to other organic solvents, this shall eliminate much of the concern with their use. Moreover, DES used in this study were prepared, simply by mixing two or three components under heat treatment and no further purification steps are implemented [23]. In contrary, it is known that volatile-by products tend to lodge more in ethanol and distillation process is necessary for purification purpose. In this context, it can be said that the preparation of DES is simple and require lower cost since the distillation process for ethanol is a repetition of vaporization and condensation which require higher cost [59].

Another positive feature of DES is their thermal stability. For the thermal stability, [60] has showed that the DES composed of choline chloride and glycerol at molar ratio of 1:2 decomposed at 175.5 °C (derived from thermal-gravimetric analysis), which manifesting the high stability of CHCL-GLY DES over wide range of temperature. Also, DES is unique for their recyclability. In this context, [61] successfully proved the recyclability of DES in six-run test, while keeping similar extraction efficiency. This is also one of the good properties that stand out in distinguishing the DES from conventional organic solvent.

4 Conclusion

In the present study, the extraction efficiencies using conventional ethanol solvent DES were compared on the basis of extracting the antioxidant compounds from fruit wastes of *M. pajang*. An extract with maximum antioxidant activity (11.11 ± 0.06 mg AEAC/g) was obtained by using the conventional aqueous ethanol. Meanwhile, by using CHCL-GLY DES at molar ratio of 1:2 with addition of 20 wt% water, an extract with the highest antioxidant activity (11.48 ± 0.09 mg AEAC/g) was obtained, which outperformed the aqueous ethanol under the optimal extraction conditions. This significant finding implies that the extraction of antioxidant compounds by using DES is feasible. Further studies such as purification and evaluation of the quality of antioxidant compounds from DES is of great interest and ought to be studied. Furthermore, evaluation of the extraction efficiency using recycle-DES can also be considered. A point to note that, it is possible that the DES experience structural change during recycle-extraction process, thus, it is of great interest to analyze if the structural changes affect the extraction performance.

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Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest with materials discussed in this manuscript.

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