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The Extraction of Antioxidant Compounds from *Coriandrum sativum* Seeds by Using Green Solvents

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Abstract: In this study, bioactive compounds from *Coriandrum sativum* seeds were extracted by microwave assisted extraction (MAE) using natural deep eutectic solvents (NADESs). The total antioxidant capacity (TAC) of extracts was determined by using cupric reducing antioxidant capacity (CUPRAC) method. 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) analyses have been employed to measure the free radical scavenging ability of the sample extracts. Five different deep eutectic solvents, using choline chloride in combination with hydrogen bond donors (three polyalcohols and two organic acids) were firstly scanned. Choline chloride and 1,4-butanediol at the molar ratio of 1:4 was the best solvent of choice to extract natural antioxidants to achieve the best level of TAC. The response surface methodology (RSM) was applied to achieve the most advantageous conditions. The optimal process conditions for the maximum TAC value were as follows: 326 watt microwave power, 88 second extraction time, and 10 liquid/solid (L/S) ratio. In this study, we report an efficient, rapid, and green method to extract natural antioxidants from Turkish *Coriandrum sativum* seeds.

Keywords: *Coriandrum sativum* seed, deep eutectic solvent, antioxidant activity, CUPRAC, DPPH, ABTS.

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1. INTRODUCTION

Coriandrum sativum (commonly known as coriander) is one of the oldest and widespread crop species, dating back to around 1550 BC (1). *Coriandrum sativum* is widely distributed in Mediterranean countries (2). The plant has a very distinct flavor and is highly aromatic (3). It is used in the manufacture of detergents, emulsifiers, soaps, and softeners (4). The leaves and seeds are used in many food products, such as liquors, teas, meat, pickles, fish, and bakery (2,3,5). The plant is known for its potential healing properties (3). It has been used as a therapeutic target for treating respiratory disorders, urinary disorders, and digestive ailments such as indigestion, nausea, dyspepsia, and dysentery (2-5). The seeds have been reported to possess pharmaceutical properties such as antidiabetic, antimicrobial, antibacterial, antifungal, analgesic, anti-inflammatory, anticancer, and antiseptic properties (1-3,5-7). The seeds are a potent source of antioxidant compounds like polyphenols, particularly phenolic acids and flavonoids, which are important nutrients in the human diet (8).

Oxygen free radicals in biological cells weaken the immune system and cause several diseases. On the other hand, antioxidants deactivate free radicals before they attack the cell and they eventually leave the body. Lots of studies in epidemiology demonstrated that compounds having antioxidant properties can inhibit the emergence of numerous conditions such as cancer, diabetes, cardiovascular diseases, and Alzheimer's disease (9). Besides, when antioxidants are added to food products, the formation of toxic oxidation products is retarded as well as the shelf life of food is increased (10). A high nutritional quality is provided with the addition of antioxidants to the food products.

Chemical engineers make great efforts to create eco-friendly solvent systems that have low cost and low toxicity. Volatile organic solvents like methanol, hexane, ethanol, chloroform, and acetone have been broadly utilized to extract bioactive components from plants (11). Despite their increased solvation and extraction capability, the toxicity of conventional solvents might pose an environmental and public health threat. Besides, using these solvents leads to

undesirable solvent residues in the extracts. Recently, natural deep eutectic solvents (NADESs) have taken the place of conventional solvents. NADESs were discovered at the beginning of the 21st century as new types of green solvents. NADESs have several benefits such as low cost, biodegradability, easy preparation and pharmaceutically acceptable toxicity (12). NADESs are generally prepared by mixing hydrogen bond donors (HBDs), such as urea, organic acids and polyols with hydrogen bond acceptors (HBAs) (13). The components of NADES interact with each other via hydrogen bonds. One component acts as a hydrogen bond donor, while the other component acts as a hydrogen bond acceptor. NADES has a lower melting point than its individual components. This is owing to the intermolecular hydrogen bonding between the components of NADES (14,15). Choline chloride (ChCl) is a cost effective, biodegradable and non-toxic quaternary ammonium salt. ChCl-based NADESs have been mostly studied for the separation of bioactive materials from plants (16-18).

Extraction is the first step in separating bioactive compounds from plants. The extraction method is important since it affects the efficiency and operational cost. Ultrasound-assistant extraction (UAE), maceration extraction, soxhlet extraction, and microwave-assisted extraction (MAE) are extraction techniques that were extensively used for the recovery of natural products from plant matrices (19,20). Among them, MAE is the fastest technique (21). MAE provides high extraction efficiency and consumes less solvent. Microwave radiation affects the moisture of solid material. The evaporated moisture applies pressure to the cell wall. Eventually, the plant cell wall is broken down, so that target molecules leach out (22).

In this study, natural antioxidants from *Coriandrum sativum* seed were extracted by ChCl-based NADESs. The most important extraction parameters (liquid/solid ratio (L/S), extraction time and microwave power) were optimized by response surface methodology (RSM). Ethanol (EtOH) was used as benchmark solvent to compare the results. The total antioxidant capacity (TAC) of *Coriandrum sativum* peel extracts was ascertained by using cupric reducing antioxidant capacity (CUPRAC) method. The free radical scavenging (FRS) activity was measured by 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) analyses. The results of this research will be the first to examine the antioxidant features of *Coriandrum sativum* seed extracts utilizing NADESs so far, thus being noteworthy in the field of green and sustainable chemistry.

2. MATERIALS AND METHODS

2.1. Plant Material

The Turkish coriander was obtained from a local market (Istanbul, Turkey). The air-dried coriander was ground in a laboratory mill to a screen size of 0.5 mm in order to obtain uniform particle size. The seeds were kept in the freezer until the experiments.

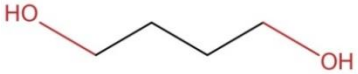
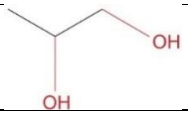
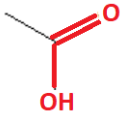
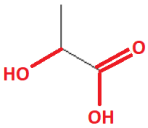
2.2. Chemicals

ChCl, 1,4-butanediol, 1,2-propanediol, ethylene glycol, acetic acid, lactic acid, EtOH, methanol, neocuproine, trolox (TR), ammonium acetate, copper(II) sulfate, DPPH, ABTS, and potassium persulfate were purchased from Sigma Aldrich, USA. Every chemical compound in this study was of analytical grade.

2.3. NADES Preparation

The NADES preparation was carried out by simply mixing two components according to the molar ratios given in Table 1. Water was added to carboxylic acid-based NADESs to decrease the viscosity. First, ChCl and HBDs were weighed on an analytical balance (Mettler Toledo). Next, ChCl and HBDs were mixed at desired molar ratios. The mixture was heated at 333.2 K with stirring until a transparent and homogeneous liquid NADES was formed. The prepared NADESs were stored in the room temperature environment.

Table 1: The composition of ChCl-based NADESs.

HBD	HBD structure	ChCl:HBD molar ratio	Water content (v/v)	Ref
Ethylene glycol		1:4	-	(23)
1,4-butanediol		1:4	-	(21,23)
1,2-propanediol		1:4	-	(23)
Acetic acid		1:2	30%	(22)
Lactic acid		1:2	30%	(16)

2.4. The Extraction Procedure and Instrumentation

The ground *Coriandrum sativum* seeds were put into a 50 mL flask, and NADESs were added into the flask. Except NADESs, ethanol and water were used as the conventional solvents. The flask was placed in the microwave oven (Milestone NEOS-GR). Microwave extractions were performed at different microwave power levels (250 W-350 W), microwave times (60-90 seconds) and liquid-to-solid (L/S) ratios (10-20 mL to 1 g). The experiments were repeated three times. After extractions, the mixtures were left to cool down at room temperature. Finally, the extracts were filtered through a 45 µm nylon filter before UV-Vis analyses. UV-Vis measurements were carried out with a Varian CAY Bio 100 UV-Vis spectrometer (Agilent, USA).

2.5. Statistical Analyses

The variables were systematically investigated with Box-Behnken design (BBD) of RSM. Microwave power (A), time (B), and L/S ratio (C) were the independent variables, and TAC (Y) was the response. TAC values of *Coriandrum sativum* seed extracts were analyzed using a second order polynomial equation (24-26). An analysis of variance (ANOVA) test was applied to analyze results (27).

2.6. TAC Analyses

TAC of *Coriandrum sativum* seed extract was analyzed by CUPRAC method (27-29). CUPRAC method is based on the reduction of cupric neocuproine complex (Cu(II)- Nc) to yellow-orange colored cuprous chelate (Cu(I)-Nc) in the presence of antioxidants. First, x mL extract was added to the test tube, including 3 mL of reagent mixture (1 mL of 10 mM $CuCl_2$, 1 mL of 7.5 mM Nc and 1 mL of 1 M NH_4Ac buffer). Then, (1.1-x) mL H_20 was added to the mixture, which made up to a final volume of 4.1 mL. The mixture tube was capped. After 30 min, the absorbance was read at 450 nm (A_{450}) against a reagent black. The absorbance is linearly correlated with the antioxidant capacity (30). TAC is expressed as TR equivalent (mmol TR/g-dried sample (DS)) as given in Eq. 1 below (27-29,31):

$$\text{TAC (mmol TR/g - DS)} = \frac{A_s}{\varepsilon_{TE}} \frac{V_m}{V_s} D_f \frac{V_\varepsilon}{m} \quad (1)$$

where A_s refers to the recorded absorbance value, V_s indicates the sample volume, V_e is the extract volume, V_m signifies the total volume, ε_{TE} refers to the molar absorptivity coefficient in TR equivalent, D_f is the dilution factor (when needed), and m refers to the mass of the DS.

2.7. Determination of DPPH Free Radical Scavenging Activity

DPPH free radical scavenging assay is one of the most popular antioxidant assays, which was reported by Sánchez Moreno et al (32). DPPH free radical scavenging activity of sample extract was ascertained based on its ability to react with stable DPPH free radical. Antioxidants in sample extract reduce the stable purple-colored radical DPPH into the yellow-colored DPPH-H by donating hydrogen atoms to the DPPH free radical, thereby neutralizing its toxic effect (33). DPPH method is as follows: First, x mL sample extract was added into a test tube, including (2-x) mL methanol and 2 mL 0.2 nM DPPH. The tube was stoppered and left to stand for 30 min in the dark. After 30 min, the absorbance was read at 515 nm against MeOH. All the assays were replicated three times. Findings were given in mean ± standard deviation. Corrected absorbance values (Δ_A) were utilized to determine DPPH free radical scavenging activity by using the following equation (29,31):

$$\Delta_A = A_{DPPH} - (A_E - A_0) \quad (2)$$

where A_{DPPH} is the absorbance of DPPH reagent without the sample, A_E is the absorbance of the extract, and A_0 is the absorbance of the extract without DPPH reagent.

DPPH free radical scavenging activity is expressed as mmol TR/g-DS based on the TR standard calibration curve. The DPPH free radical scavenging activity was derived from the following equation (29):

$$\text{DPPH free radical scavenging activity (mmol TR/g-DS)} = \frac{\Delta_A}{\varepsilon_{TE}} \frac{V_m}{V_s} D_f \frac{V_E}{m} \quad (3)$$

2.8. Determination of ABTS Free Radical Scavenging Activity

The $ABTS^+$ free radical has been widely used as a tool to determine the free radical scavenging activity of antioxidants. ABTS assay is based on the reduction of chromogenic reagent $ABTS^+$ in the presence of antioxidants. Chromogenic $ABTS^+$ solution is prepared by the following procedure. $ABTS^+$ (50 nM) is diluted with distilled water to a final concentration of 7.0 nM. $K_2S_2O_8$ is added to the solution, the final concentration of $K_2S_2O_8$ is 2.45 nM in the solution. The obtained $ABTS^+$ solution is left for 12-16 hours at ambient temperature. The application of ABTS assay is as follows: x mL sample extract is mixed with (4-x) mL methanol and 1 mL $ABTS^+$ solution (1:10 diluted with methanol). The absorbance is read at 734 nm against ethanol after $ABTS^+$ addition. The corrected absorbance value, Δ_A, is calculated by the equation below

$$\Delta_A = A_{ABTS} - (A_E - A_0) \quad (4)$$

where A_{ABTS} refers to the absorbance of $ABTS^+$ reagent without the sample, A_E is the absorbance of the extract, and A_0 is the absorbance of the extract without $ABTS^+$ reagent.

ABTS free radical scavenging activity is determined with the following equation (29):

$$\text{ABTS free radical scavenging activity (mmol TR/g-DS)} = \frac{\Delta_A}{\varepsilon_{TE}} \frac{V_m}{V_s} D_f \frac{V_E}{m} \quad (5)$$

ABTS free radical scavenging activity is expressed as mmol TR/g-DS based on the TR standard calibration curve.

3. RESULTS AND DISCUSSION

3.1. DES Selection

Five different types of NADES were synthesized to determine the most potent NADES. NADES combinations were prepared based on the published data (34). Molar ratios are written in Table 1. ChCl salt was chosen as HBA. Several polyols and organic acids were selected as HBD, which are considered to be renewable, nontoxic, and biodegradable (35). To evaluate the extraction capability of NADES, pure ethanol and water were used as the benchmark solvents.

ChCl:alcohol ratio (1:4) was used according to the literature data. Mahmood et al. studied the antioxidant activity of *Chlorella vulgaris* plant extracts. In that study, polyols were tested as HBDs. Among different ChCl to HBD ratios (1:1, 1:2, 1:3, 1:4), the 1:4 ratio was determined as the most ideal ratio for all the NADES combinations (35). ChCl:alcohol ratio of 1:1 is not suitable to use due to the high viscosity and high surface tension of ChCl (36). Therefore, a ChCl-to-alcohol ratio of 1:4 is chosen to keep the interactions going well (37).

NADES extraction capacity is mainly affected by the following factors: H-bonding interactions, polarity, viscosity, and pH (21,38). High viscosity is one of the most important disadvantages of NADES because high viscosity leads to the mass transfer resistance of molecules entering the liquid surface. Carboxylic acid-based NADESs possess high viscosity. The addition of water in carboxylic acid-based NADESs would reduce the viscosity (39). Cui et al. emphasized that 30 % water content (v/v) in NADESs decreases the viscosity. However, an excessive amount of water breaks the hydrogen bond network in the eutectic solution, thereby reducing the hydrogen bonding interactions between NADES and polyphenolics (40,41).

From all different type of NADESs, ChCl:1,4-butanediol (1:4) provided the best TAC value. Apparently, ChCl:1,4-butanediol has the most favorable electrostatic and hydrogen-bond interactions with the target molecule (35). Besides, alcohol-based NADESs showed better TAC values than carboxylic acid-based NADESs. The high performance of alcohol-based NADESs is associated with multiple hydrogen bonding networks, which interact with target molecules and establish strong connections (42). Ethanol extract showed relatively low antioxidant activity, which may be due to the non-synergistic effects with the target molecules (43). Similarly, flavonoid extraction from *Flos Sophoroa imaturus* plant has been conducted by Wang et al. and the team reported that ChCl:1,4-butanediol (1:4) is the best solvent among all ChCl-based NADESs (including glycerol, glycol, 1,3-butanediol, citric acid, lactic acid, glucose and sucrose as the HBDs) (44).

The positions of –OH groups in HBD is also a significant factor affecting the extraction capability of the solvent. For example, 1,2-propanediol and 1,4-butanediol have the same number of –OH groups (see Table 1). However, -OH groups of 1,2-propanediol are at vicinal position, which is unfavorable for 1,2-propanediol. Here, 1,2-propanediol produces steric hindrance, which results in the reduced possibility of interactions with the target molecules. On the other hand, 1,4-butanediol has –OH groups at terminal position, which overcome the intermolecular forces, and thereby mass transfer limitations (45). Moreover, 1,4-butanediol has a longer alkyl chain than ethylene glycol and 1,2-propanediol. 1,4-butanediol here seemed to be less affected by intermolecular repulsions due to the alkyl chain length (35). To sum up, HBD structure is an important factor for solute-solvent interactions and should be considered in the solvent selection (17).

Polarity is also an important factor affecting the efficiency. Polyphenolic compounds are highly polar compounds. According to the "like dissolves like" principle, solvents with high polarity are better for polyphenolic extractions (33). Although water molecules are highly polar and have a relatively low TAC value (46).

3.2. TAC Optimization

The extraction parameters, including time, microwave power, and L/S ratio, were optimized by using BBD. The levels of variables and their actual values were given in Table 2. The outcomes were fitted to a quadratic polynomial equation by using multiple regression analysis given below as Eq. 6.

$$TAC = 0.036 + (7.125E\text{-}003)A + 0.016B - (8.875E\text{-}003)C - (9.000E\text{-}003)AC \quad (6)$$

The ANOVA test was performed to discover the interactions between the variables and the optimum process conditions (see Table 3). The model F value of 14.20 and p value less than 0.05 imply that the model is important (47). The terms having p values less than 0.05 are considered important. In these circumtances A, B, C, and AC are important model terms (40). The small coefficient of variation (C.V. % =18.42) value also proved the remarkable reliability of the model. The adequate precision is 12.304, pointing out that the model could be used to navigate the design space (36,43,48).

Table 2: The levels of variables and their actual values.

Run	Power (A) Watt	Time (B) Second	L/S ratio (C) -	TAC (Y) mmol TR/g-DS
1	250.00	75.00	20.00	0.036
2	300.00	90.00	20.00	0.031
3	300.00	75.00	15.00	0.034
4	250.00	75.00	10.00	0.027
5	300.00	60.00	10.00	0.034
6	350.00	75.00	10.00	0.062
7	300.00	75.00	15.00	0.034
8	250.00	60.00	15.00	0.014
9	250.00	90.00	15.00	0.042
10	300.00	90.00	10.00	0.064
11	350.00	60.00	15.00	0.012
12	300.00	60.00	20.00	0.014
13	300.00	75.00	15.00	0.034
14	350.00	75.00	20.00	0.035
15	300.00	75.00	15.00	0.034

Table 3: The results of ANOVA test.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	3.697E-003	6	6.162E-004	14.20	0.0002
A-power	4.061E-004	1	4.061E-004	9.36	0.0121
B-time	2.113E-003	1	2.113E-003	48.70	< 0.0001
C-Liquid/Solid	6.301E-004	1	6.301E-004	14.53	0.0034
AB	1.822E-004	1	1.822E-004	4.20	0.0675
AC	3.240E-004	1	3.240E-004	7.47	0.0211
BC	4.225E-005	1	4.225E-005	0.97	0.3470
Residual	4.338E-004	10	4.338E-005		
Lack of Fit	4.338E-004	6	7.230E-005		
Pure Error	0.000	4	0.000		
Cor Total	4.131E-003	16			
Statistical parameters					
Std. Dev.	6.586E-003				
Mean	0.036				
C.V. %	18.42				
PRESS	2.166E-003				
R-Squared	0.8950				
Adj R-Squared	0.8320				
Pred R-Squared	0.4756				
Adeq Precision	12.304				

3-D response surface curves were plotted to visualize the relationship between the factors and the response (40,43). As seen from Figs. 1a and 1b, increasing microwave power enhanced the response. Apparently, increasing temperature reduced the surface tension and viscosity of the solvent, so that solvent could effectively penetrate into the cell matrix (35,39,41,48).

As seen from 1b, at different microwave powers, the TAC value was increased as the microwave time increased. In the optimization study, microwave time was kept under 90 seconds because bioactive compounds decomposed after 90 seconds due to the prolonged irradiation (33). Keeping irradiation times short reduces energy consumption at the same time (33,43).

As understood from Fig. 1c, the TAC value increased as L/S ratio decreased at different microwave time levels. It is clear that an adequate solvent amount enhances the contact area between the cell matrix and the solvent, which increases the mass transfer rate (36). On the other hand, increasing the solvent amount more than it is supposed to be shall break the interactions between the solvent and the focused compounds, thereby decreasing the efficiency (33,49,50).

The optimum conditions for the highest TAC value (TAC: 0.070 mmol TR/g - DS) were determined as follows: 326.10 Watt microwave power, 88.40 second extraction time, and 10.03 L/S ratio. For practical convenience, the verification experiment was performed under the conditions of 326 Watt microwave power, 88 second microwave time, and 10 L/S ratio. The verification experiment confirmed the accuracy of the predicted model with less than 0.02 % error (39).

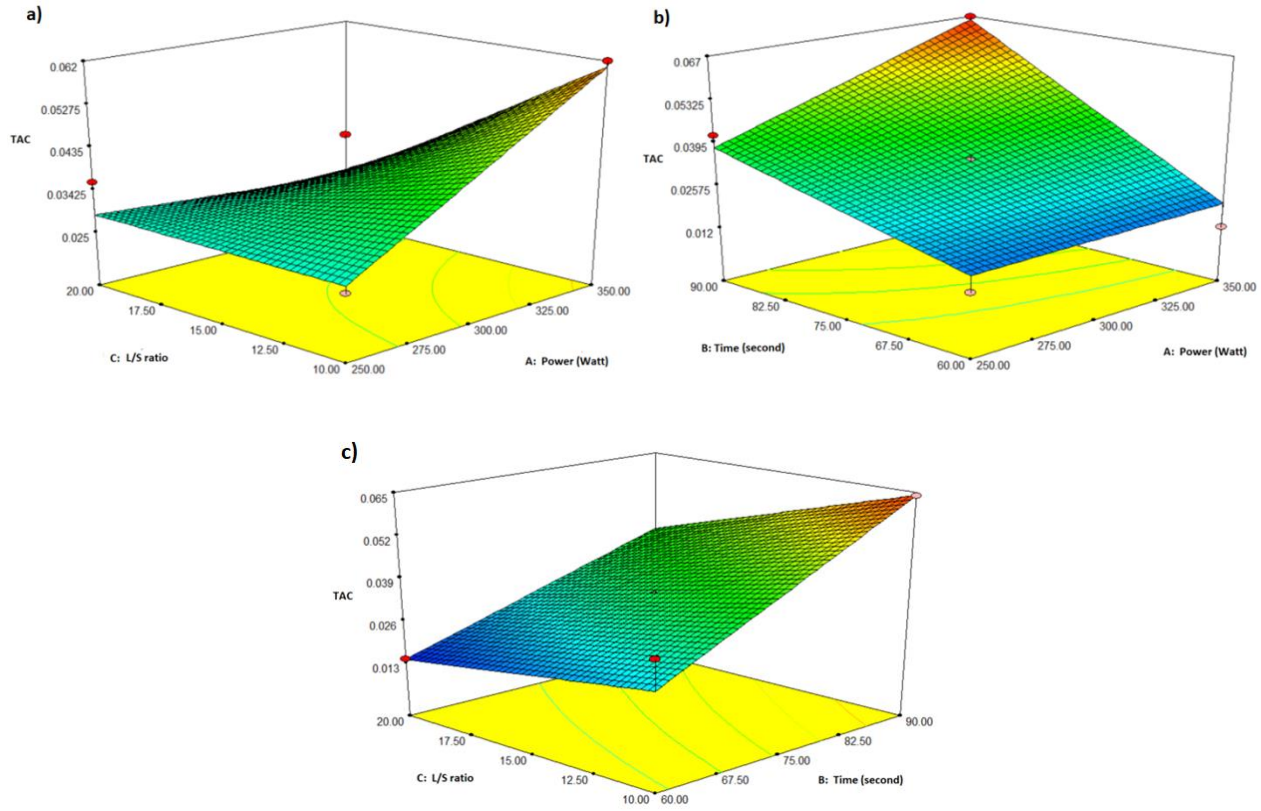


Figure 1: The plots of a) L/S ratio versus power, b) time versus power, c) L/S ratio versus time.

3.3. Comparisons of TAC measurements with DPPH and ABTS Free Radicals Scavenging Assays

DPPH and ABTS free radical scavenging activities of the seed extract were determined at the optimum extraction conditions and compared with EtOH extract. Antioxidant capacity findings are written in Table 4 and shown in the graph Fig. 2. As seen, TAC values were higher than DPPH and ABTS free radical scavenging values, which can be explained by the fact that lipophilic antioxidants were not able to donate a hydrogen atom or an electron to stabilize DPPH and ABTS free radicals by converting them to the non-radical species (30). The TAC value and radical scavenging activity values of ethanol extract were less than those obtained by ChCl:1,4-butanediol extract. Obviously, ChCl:1,4-butanediol extract is a better free radical scavenger than ethanol extract in the ranges of studied MAE conditions (30). This might be owing to strong hydrogen bonding interactions between the NADES and the extract (14). More specifically, the interactions between –OH group of phenolic compounds and the anion of choline chloride salt might be the main motivation behind DES-based separation (29,42).

Table 4: TAC, ABTS and DPPH values of *Coriandrum sativum* seed extracts.

Solvent	Extraction conditions	TAC mmol TR/g-DS	DPPH mmol TR/g-DS	ABTS mmol TR/g-DS
DES	MAE (326 W, 88 second, 10 L/S)	0.070	0.013	0.045
EtOH	MAE (326 W, 88 second, 10 L/S)	0.024	0.009	0.006

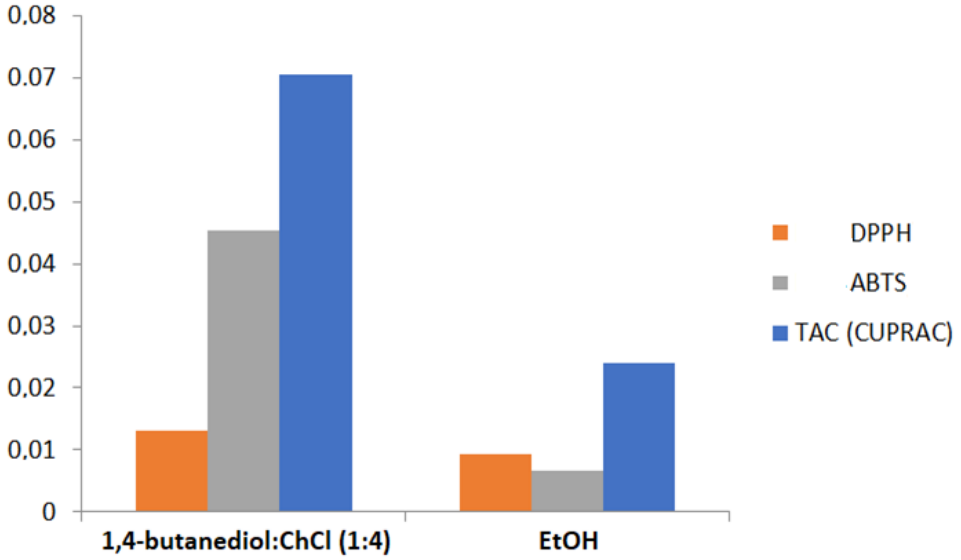


Figure 2: Graphical representation of antioxidant assay results.

4. CONCLUSION

In this study, ChCl:1,4-butanediol (1:4) was selected as the most efficacious solvent system to extract antioxidant compounds from *Coriandrum sativum* seed using MAE. Under the optimum conditions of 326 Watt microwave power, 88 second extraction time and 10 L/S ratio, TAC value was obtained as 0.070 mmol TR/g – DS. ChCl:1,4-butanediol (1:4) has yielded better results than conventional solvent ethanol at the optimum conditions in terms of CUPRAC, ABTS and DPPH assays. In the present work, we show a rapid, green, efficient and cost-effective method for the extraction of natural antioxidants from Turkish *Coriandrum sativum* seeds. This study is significant as being the first time to introduce the extraction of natural antioxidants from Turkish *Coriandrum sativum* seeds by using the green solvents of 21st century called NADESs.

Declarations

Ethical approval
There are no ethical approvals required for the research.

Consent to Publish
Consent to publish was obtained from all participants.

Consent to Participate
All participants were consented to participate in this study.

Funding
The authors have not received any financial support and have no conflict of interest to report in the preparation of this manuscript.

Competing Interest
The authors declare no competing interests, financial or otherwise.

Availability of data and materials
All data and materials are available in this manuscript.

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