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1. Introduction

Natural deep eutectic solvents (NADES) are a modern class of solvents, which have an ionic character and consist of a mixture of organic compounds with a melting point significantly lower than that of the individual components (and separately present at ambient temperature in the solid state).¹⁻⁵ A large number of ionic solvents have been used for several years as extractants of metals⁶⁻¹⁰ and chemical compounds (*e.g.* flavonoids, proteins, polysaccharides, and phenols)^{11,12} from various kinds of samples: food,¹³⁻¹⁶ plant,¹⁷⁻¹⁹ sewage,²⁰ and water samples.^{21,22} Although, the application of stable NADES (based on natural compounds, particularly primary metabolites, such as organic acids, amino acids, and sugars) is in accordance with the principles of green chemistry, it is still a novum in a field of analytical chemistry.



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The purpose of this work was the optimization of selected metal extraction efficiency from barley grass (*Hordeum vulgare* L.). Firstly, the extraction of metal complexes from a plant, with a system in which natural deep eutectic solvents (NADES) play the role of an extractant, was referenced. The prediction, employing computational research – the COSMO-RS (COnductor like Screening MOdel for Real Solvents) model, was carried out. Secondly, after the selection of nine different types of natural deep eutectic solvents, the extraction procedure was elaborated taking into account the total concentration of four metals: manganese, copper, zinc, and molybdenum in powdered barley grass samples. During the optimization of the extraction process, three parameters were checked: time, temperature and water quantity in the NADES composition. Due to the changes in the viscosity and density of NADES, the mentioned factors crucially influence the efficiency of analytes transferring to the extractant. In order to determine the total amount of extracted metals, inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) was employed. The accuracy of the established methodology was tested using a certified reference material (CRM). The obtained results confirmed the adequacy of NADES utilization for effective extraction of metals from plants and can be treated as a premise for the future application of these extractants in speciation analysis of metals.

In general, the solvents with eutectic properties consist of (1)two or more hydrogen bond acceptors (HBA), whose role is played by tertiary or quaternary ammonium salts and (2) a hydrogen bond donor (HBD) - a group of organic acids, sugars, and amino acids mixed in a specific molar ratio.^{23,24} The mentioned components, binding together through hydrogen bonds, form a mixture characterized by eutectic properties, such as a large dropping point and being in a liquid state below 150 °C.²⁵ Changing the composition of these solvents allows preparing a large number of eutectic mixtures that will have different physicochemical properties such as freezing point, viscosity, conductivity, and pH.26,27 One of the most common compounds used to form NADES is choline chloride (ChCl).12,28,29 It is a cheap, biodegradable, and non-toxic quaternary ammonium salt that can be extracted from biomass, or easily synthesized. In combination with hydrogen bond donors such as urea, carboxylic acids (for example oxalic, citric, succinic, and amino acids), or renewable polyphenols (e.g. glycerol and carbohydrates), ChCl is capable of forming NADES rapidly.

This research is a continuation of our previous work³⁰ and is focused on searching for the most effective NADES, for throughput extraction of metals from plant samples. This work is focused on the optimization of the extraction efficiency of manganese, copper, zinc, and molybdenum from powdered



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barley grass (*Hordeum vulgare* L.) using NADES accompanied by the ICP-MS/MS determination of the mentioned metals. The accuracy of the proposed method was verified by the analysis of a CRM. Additionally, a computational tool called COSMO-RS was for the first time used to simulate and predict an optimized extraction solvent combination.

To the best of our knowledge, there are currently no reports on the optimization and validation of a method for extracting metals from plants using NADES. The proposed research presents new possibilities of preparing samples for future speciation analysis of elements crucial for human body functioning and problematic from the point of view of their speciation analysis.

2. Materials and methods

2.1 Chemicals and materials

The dried ground barley grass was purchase from Intenson (Poland) and stored at 4 °C until analysis. The CRM ERM-CD281 Rye grass was delivered by Institute for Reference Materials and Measurements (IRMM), Belgium. ChCl, glycerol, betaine, ethylene glycol, malic acid, citric acid, fructose, glucose, β alanine, methanol, hydrochloric acid, hydrogen peroxide, all of the analytical reagent grade, were purchased from Sigma Aldrich (USA). Nitric acid, of purity for trace element analysis, was obtained from Fluka (Switzerland). High purity water (18 M Ω cm⁻¹) was produced by using a Milli-Q Elix 3 Water Purification System Millipore (France). The calibration curves were obtained using a solution of Environmental Spike Mix $(1000 \text{ mg L}^{-1} \text{ of Fe}, \text{ K}, \text{ Ca}, \text{ Na}, \text{ and Mg and } 100 \text{ mg L}^{-1} \text{ of Ag}, \text{ Al},$ As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, and U; matrix 5% HNO₃) purchased from Agilent Technologies (USA).

2.2 Preparation of NADES

The procedure of NADES synthesis was based on the heating method,⁵ for which about 10 mL of solvent can be produced. The adapted protocol also allows preparing NADES with a known amount of water. The two-component mixture containing a calculated amount of water was transferred into a capped bottle and placed on a magnetic stirrer in a water bath below 50 °C, with agitation till a clear liquid was formed (about 30–90 min).

2.3 Instrumentation

An Agilent 8900 ICP Triple Quadrupole Mass Spectrometer (Tokyo, Japan), as an element-specific detector for the quantification of metal content in barley grass, was used. The spectrometer interference was equipped with Pt cones. The position of the torch and the nebulizer gas flow were adjusted daily, with emphasis place on the decrease of the level of CeO^+ (below 0.2%), to minimize the risk of occurrence of polyatomic interference caused by oxides. The RF power was 1550 W, nebulizer gas flow – 1.03 L min⁻¹, and collision gas flow (helium in ICP-MS/MS) – 5.0 mL min⁻¹. The total concentrations of the selected metals were calculated by monitoring the mass/charge

ratios: 55 (⁵⁵Mn), 63 (⁶³Cu), 66 (⁶⁶Zn) and 95 (⁹⁵Mo), determined in the on-mass mode after the production in plasma of singly positively charged ions. The most probable sources of monitored isotopes in the sample were the compounds of Mn^{2+} , Cu^{2+} , Zn^{2+} and Mo^{4+} , respectively. The working conditions were optimized daily using a 1 µg L⁻¹ solution of Li, Y, and Tl in 2% (v/v) HNO₃.

A Bandelin Sonorex Model 1210 ultrasonic bath (Germany), MPW Model 350R centrifuge (MPW Warsaw, Poland), and water bath with thermostatically controlled temperature (Mammert, Germany), during extraction procedures, were used. Microwave digestion Speedwave® four Berghof (Germany) for samples' mineralization and during the extraction procedure was used.

2.4 Sample preparation

2.4.1 Mineralization of samples toward metal determination in barley grass. To determine the total amount of elements, the barley grass powder (0.2 g dry mass) was digested by microwave-assisted mineralization with a mixture of 5 mL of HNO₃ and 3 mL of H_2O_2 . The digests, to a final volume of 25 mL with Milli-Q water, were diluted. Further dilutions for ICP-MS/ MS analysis were prepared using 2% (v/v) nitric acid solution and 10 ng mL⁻¹ of yttrium (⁸⁹Y) as an internal standard.

2.4.2 Extraction procedure. The various conditions of the process were checked (temperature and time of extraction and the water content in solvent) to optimize the yield of extraction using the chosen NADES. The selection of solvents for metal species extraction was based on the results obtained in the frame of our previous studies.³⁰

Ground samples (0.05 g of dry barley grass powder) were extracted by vortexing at 30 °C for 30 minutes with 2 mL of each solvent. The obtained solutions were centrifuged for 20 min at 10 000 rpm at 21 °C. Part of the solutions (1 mL) was digested by microwave-assisted mineralization with a mixture of 5 mL of HNO₃ and 3 mL of H₂O₂ (the procedure is described in Paragraph 2.4.1). The yield of extraction was calculated as:

 $Extraction_{efficiency} =$

 $\frac{\text{amount of metal in solution after extraction}}{\text{total amount of metal in barley grass}} \times 100\%$

3. Results and discussion

3.1 Simulation by the COSMO-RS method

The first part of the work was to predict the procedure of metal complex extraction from plant-based samples on a reference system in which the NADES is the extractant. For computational research, zinc was taken into account as its complexes were previously extracted from barley grass.³⁰ Solvents consisting of 45 hydrogen bond acceptors and 22 hydrogen bond donors were selected. For various cation–anion combinations, in total almost 1000 NADES, a prediction of extraction efficiency in the proposed problem was performed. The calculations were made at three ratios of HBD : HBA 0.5, 1.0, and 2.0, and a temperature of 25 °C for zinc complexes with glycine and quercetin (one for

amino acids and one for flavonoid complexes – the combinations of zinc and ligands most commonly found in plants³¹).

The results from the model examination for 22 HBD and 45 HBA compounds revealed that lower $\log K$ was obtained for hydrogen bond donors like choline compounds (chloride, tet-rafluoroborate, and nitrate), glycine, nicotinic acid, and lidocaine for amino acids and flavonoids. For flavonoids, lower $\log K$ was obtained for beta-alanine, glycine, histidine, and citric acid. Higher $\log K$ was observed for choline fluoride and zinc chloride.

The results from the model examination for 45 HBA compounds indicated lower $\log K$ for amino acid extraction – triethylene glycol, glycine, and proline, and for flavonoids – citric acid, oxalic acid, tricarballylic acid, gallic acid, L-(+)-tartaric acid, triethylene glycol, glycine, and proline.

Comparing the results of the extraction efficiency with the model properties of the equilibrium constant $(\log K)$ indicates that the lower the log *K* for extractants the higher their extraction efficiency. The results suggest that theoretically, the equilibrium prevailing in the solution, the possibility of action and a group of solvent extraction can be determined. The ability to extract metal compounds, but not the group of compounds responsible for their binding, can be confirmed through experimental tests (Table 1).

The presented method is based on the conductor like a screening model for real solvents (COSMO-RS), whose only input datum is the chemical structure of the compounds forming the system. Thus, it is a purely predictive model without the need to refer to experimental research. COSMO-RS combines an electrostatic theory of locally interacting molecular surfaces (which are determined by QM calculations) with a statistical thermodynamics methodology, details can be found elsewhere.^{32,33}

The calculations presented in this work were carried out using the commercial implementation of COSMO-RS, namely, COSMO*therm* software (version C3.0 of 17.05.2018) purchased from COSMOlogic GmbH & Co. KG (Leverkusen, Germany) with the use of the integrated programming environment in MAT-LAB (MathWorks, Inc., version 2017a).

3.2 Optimization of extraction conditions

Many factors can affect the extraction efficiency, among which the most important are the concentration of the solvent, extraction time, solid–liquid ratio, and extraction temperature. These parameters change the viscosity and density of NADES, which directly disturbs the efficiency of the transfer of analytes from samples to the extractant. A single-factor test was performed for one factor that varied at different levels while other factors were fixed.

3.2.1 Effect of water addition. The addition of water to NADES may lead to weakening of the hydrogen bonding interaction between the components of the solvents.³⁴ For this reason, the amount of water needed to be optimized in the first place. The percent of water in NADES advantageously reduces

Table 1 COSMO-RS predicted NADES/water partition coefficient of aqueous solutions of Zn compounds

				log K					
	Glycerol	Glucose	Citric-acid	Glycerol	Glucose	Citric-acid	Glycerol	Glucose	Citric-acid
Zn-Rutin (1 : 2)			Zn-Rutin (1 : 1)			Zn-Rutin (1 : 0.5)			
ChCl	10.13	5.73	3.59	13.22	9.24	7.44	16.32	13.06	11.97
Betaine	9.67	4.62	1.83	13.73	9.24	6.73	17.31	14.10	12.53
β-alanine	5.59	2.24	0.82	7.08	4.16	2.49	8.28	6.07	4.71
Zn-Quercetin(1:2)			Zn-Quercetin(1:1)		Zn-Quercetin (1:0.5)				
ChCl	9.69	6.57	4.30	11.08	8.68	7.24	12.40	10.59	9.76
Betaine	11.79	8.14	5.33	14.20	11.33	9.37	16.20	14.28	13.11
β-alanine	8.86	6.02	3.92	9.67	7.49	5.84	10.22	8.74	7.61
Zn-Glycine (1 : 2)			Zn-Glycine (1:1)			Zn-Glycine (1 : 0.5)			
ChCl	-1.57	-2.01	-1.46	-0.92	-1.52	-1.32	-0.22	-0.82	-0.70
Betaine	-1.09	-1.84	-1.88	-0.17	-1.07	-1.48	0.70	-0.03	-0.37
β-alanine	-1.47	-1.81	-1.54	-1.08	-1.46	-1.51	-0.75	-1.11	-1.24
Extraction efficiency for Zn (%)									
ChCl				53.1	64.5	89.5			
Betaine				54.1	65.0	85.0			
β-alanine				54.0	72.7	91.0			

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their viscosity, which facilitates the transfer of the analyte during extraction. The water content in NADES from 0 to 30% was not tested due to the obtained then a high extractants' viscosity, which can disrupt the mixing with the sample and fraction collection. Therefore, addition of a range of water contents, from 40 to 80%, was investigated.

The results revealed that using a NADES consisting of β alanine and citric acid, the extraction efficiency, for all examined metals, significantly increased when the water content rose from 40% to 50% (see Fig. 1g). This effect is, with high possibility, dependent on the decrease of NADES viscosity in this range, which might have facilitated the transfer of analytes from the sample to the extraction solvent. For a higher water percent in the solvent, the extraction efficiency of manganese, copper, zinc, and molybdenum remained almost at the same level. As an optimal value for the formation of this kind of NADES, a water content of 80% was taken for further studies.

Taking into account the effectivity of extraction in the case of ChCl-citric acid NADES it was observed the increase of this parameter when the content of water in the solvent increased from 40 to 50% (Fig. 1a). On the other side, the extraction efficiency was strongly reduced when the water content increased more. The probable explanation can be the loss of the existing hydrogen bonds, which as a consequence can disrupt the NADES structure. A 50% water content in the solvent was chosen for the subsequent investigations.



Fig. 1 The influence of the amount of water added to the mixture on the extraction efficiency of metals from barley grass: (a) ChCl : citric acid (1 : 1), (b) ChCl : glucose (2 : 1), (c) ChCl : glycerol (1 : 2), (d) betaine : citric acid (1 : 1), (e) betaine : glucose (2 : 1), (f) betaine : glycerol (2 : 1), and (g) β -alanine : citric acid (monitored isotopes: ⁶³Cu – blue line, ⁶⁶Zn – green line, ⁵⁵Mn – dark blue line, and ⁹⁵Mo – orange line), T = 40 °C, and t = 30 min.

In the next step, ChCl with glucose (2 : 1) and glycerol (1 : 2) aqueous mixtures was probed as an extractant of metals. The extraction yield enhanced with the increased addition of water (from 40% to 80%, see Fig. 1b and c). Such an effect can be combined, once more, with the reduction of NADES viscosity. Therefore, as an optimal value of water content (for the two types of mixtures), 80% was selected. Similar observations, as mentioned in the previous paragraph, can be made when instead of ChCl, betaine (as a HBA) was applied (Fig. 1d–f). Based on the obtained results as the best extractant solvents containing betaine and citric acid or glucose or glycerol, 80 or 60 or 60 percent of water in the mixture were chosen as optimal, respectively.

3.2.2 Effect of extraction time. The extraction time is the next significant parameter which should be taken into consideration during the optimization of extraction efficiency. In the present work, a range of extraction time from 10 min to 50 min was examined. The influence of extraction time on the concentration of metals in seven different extractants is shown in Fig. S1 in the ESI.[†]

From the presented results it can be concluded that, in general, the increase of extraction time up to 30 min intensifies the metal's extraction efficiency. No meaningful differences in values were noted, after that time of the process. Additionally, it was followed that occasionally the extraction efficiency for selected metals decreased after 40 min of the test (see Fig. S1[†]).



Fig. 2 Influence of extraction temperature on the extraction efficiency of metals from barley grass: (a) ChCl : citric acid (1 : 1), (b) ChCl : glucose (2 : 1), (c) ChCl : glycerol (1 : 2), (d) betaine : citric acid (1 : 1), (e) betaine : glucose (2 : 1), (f) betaine : glycerol (2 : 1), and (g) β -alanine : citric acid (monitored isotopes: ⁶³Cu – blue line, ⁶⁶Zn – green line, ⁵⁵Mn – dark blue line, and ⁹⁵Mo – orange line), under optimal extraction conditions (see Sections 3.2.1 and 3.2.2).

 Table 2
 Optimized conditions for the NADES-exploited extraction of metals from barley grass

Components			Water	Temperature of	Time of
HBA	HBD	Molar ratio	content [%]	extraction [°C]	extraction [min]
ChCl	Citric acid	1:1	50	40	30
ChCl	Glucose	2:1	80	50	40
ChCl	Glycerol	1:2	80	60	30
β-	Citric	1:1	80	30	40
alanine	acid				
Betaine	Citric acid	1:1	60	40	40
Betaine	Glucose	2:1	60	50	50
Betaine	Glycerol	1:2	60	40	30

However, exceptionally for the experiment in which citric acidbetaine NADES was applied, the extraction efficiency increased when the time of the process was over the range of 40 min. Taking into account that after this length of time, approximately 100% metal extraction efficiency was achieved, a 40 min extraction period was finally selected, as optimal, in the case of utilization of the mentioned NADES.

3.2.3 Effect of temperature on the efficiency of metal extraction. An elevated temperature, in general, facilitates the transfer of the corresponding metal compounds from the sample to the extraction solvent, which causes the improvement of the extraction efficiency. Moreover, it also reduces the viscosity of the extractant and makes the mixing of the solvent with the sample easier. Therefore, the extraction was carried out at temperatures from 20 to 60 °C. The process carried out above 60 °C was not probed, due to the risk of disrupting the structure of NADES guaranteeing the inaccessibility of eutectic properties.

The extraction efficiency of metals, from the sample to β alanine–citric acid solvents, was significantly increased with temperature increasing from 20 to 40 °C and after that decreased (see Fig. 2g). The reason can be related to the decrease of extractant viscosity below 40 °C or degradation of the solvent's structure, in the higher temperatures. As an optimal extraction temperature for this NADES, 30 °C was chosen and employed for further investigations.

For the next group of NADES, containing ChCl, the optimal temperature at which the highest extraction yield was noted was different for each of the analyzed elements (compare Fig. 2a-c). As optimal, a temperature of 40 °C was chosen, in the case of ChCl-citric acid NADES, due to the satisfactory extraction efficiency from the point of view of the total examined analytes. In the case where the extractant was ChCl with glucose, the extraction efficiency increased for all analyzed elements with the temperature raised from 20 to 50 °C. At 60 °C, the extraction efficiency of manganese, zinc, and molybdenum remained at the same level, while the copper extraction efficiency slightly decreased. Therefore, in this case, 50 °C as the optimal extraction temperature was chosen. A different pattern, when the extractant was ChCl with glycerol, was observed - two maxima of yield for 30 and 60 °C have been noticed. The latter one was chosen as the optimal because the extraction yields obtained then were the highest for all analyzed elements.

Afterwards, the extraction temperature was optimized using extractants in which betaine played the role of a HBA. When citric acid was assigned as the HBD and the experimental temperature changed from 20 to 40 °C, the extraction efficiency of manganese, copper, zinc, and molybdenum increased (Fig. 2d-f). Then, with a further increase of the experimental temperature, the efficiency decreased, so 40 °C was taken as the optimal temperature. The same value was selected in case of the betaine-glycerol NADES, while for the betaine-glucose system the best results were obtained at 50 °C. The temperatures above 50 °C tended to stabilize the extraction yield, which is not in agreement with observations noted for the extraction of manganese using choline chloride and citric acid and the ICP-OES technique.35 In that case, the best results were obtained at 95 °C, which is not a suitable temperature to carry out the speciation analysis experiments but is, on the other hand, our main future goal.

The optimized conditions of the extraction of the selected metals from barley grass, with the application of seven different NADES, are summarized in Table 2.



Fig. 3 Comparison of the NADES extraction efficiency of manganese (blue), copper (orange), zinc (grey), and molybdenum (yellow).

According to the presented protocol, the listed conditions should guarantee the highest efficiency of manganese, copper, zinc, and molybdenum extraction from barley grass powder (Fig. 3).

3.3 Method validation

To verify the correctitude of the extraction parameter selection, the same four metals from the CRM (Rye grass), were extracted. The total content of manganese, copper, zinc, and molybdenum was determined, which allowed establishing the extraction efficiency of the mentioned metals from the CRM (Table 3).

Based on the obtained results, it can be concluded that the experimentally obtained metal contents in the CRM are of the same order of magnitude as listed by the manufacturer, and mainly within the given values of errors (except zinc). Namely, the average experimental value calculated for this metal was higher than allowed. The possible explanation can be the contamination of the glassware or chemical reagents used. In the case of barley grass, the producer, unfortunately, did not indicate the contents of the analyzed metals on the packaging. The authors confronted the obtained experimental values with those described by other authors in earlier studies.^{36,37} Unluckily, the comparison of values did not afford the accordant conclusions because the content of the metals in plants depends strongly on the place of their cultivation.

The validation of the method of elemental analysis, following the international guidelines described under the ISO/ IEC 17025:2005 protocol, was carried out. The parameters, such as linearity, precision, accuracy, limits of detection (LODs), and limits of quantification (LOQs), were assessed.

The precision of the method was evaluated by analyzing ten independent experimental preparations for each metal – test samples made against the internal standard and the %RSD of metals calculated. The accuracy of the obtained data was high and repeatable (%RSD) and was in the range from 0.52 to 2.36%.

The purpose of carrying out the linearity test is reflecting the capacity of the entire analytical system to display a linear response and proportionality of the signal intensity to the relevant concentration range of the analyte. Curves were linear in the range 0.5–100.0 μ g L⁻¹, with r^2 above 0.999. The linear regression data for the calibration plot suggest a good linear relationship between the intensity of the metal signal and its

Table 3 The average total content of the elements in barley grass, the CRM, and CRM metal contents provided by the manufacturer (n = 3, \pm SE)

	Total content of the element $[\mu g g^{-1}]$						
Element	CRM	CRM exp.	Barley grass				
Mn	82.00 ± 4.00	84.73 ± 0.19	39.36 ± 0.35				
Cu	10.20 ± 0.50	10.56 ± 0.22	5.94 ± 0.20				
Zn	30.50 ± 1.10	34.93 ± 0.57	39.86 ± 0.37				
Мо	2.22 ± 0.12	$\textbf{2.18} \pm \textbf{0.06}$	1.59 ± 0.02				

concentration over a wide range. The correlation coefficient was indicative of high significance.

The LOD, based on the values of standard deviations (SD) from 10 measurements of a blank, was calculated to be 0.5–1.2 μ g kg⁻¹, while the LOQ (3.3 LOD) was estimated to be 1.7–4.0 μ g kg⁻¹.

Additionally, NADES can be used as sustainable solvents due to their low cost of starting materials (urea, ChCl, sugars, and organic acids), which can often be obtained in high purity and characterized by high efficiency in the analysis of food.

4. Conclusions

The optimization of an effective technique of extraction of metals and metal species from barley grass was established for selected NADES extractants. Namely, the extraction duration, temperature and content of water in NADES were optimized. The highest extraction efficiency is characteristic for extractants, in which the addition of water is at least 50%. Therefore, it can be stated that with NADES viscosity decreasing, the extraction efficiency increases. The optimal temperature and duration of extraction depend on the type of eutectic solvent utilized in the process.

Manganese, copper, zinc, and molybdenum were extracted from a CRM, under optimized conditions, and analyzed by ICP-MS/MS in helium mode, to check the correctness of the proposed extraction and detection parameters. The obtained extraction efficiencies for the metals analyzed from the CRM allows concluding that the proposed extraction parameters were correctly optimized. Moreover, the suitability of ICP-MS/MS developed as a method for high-throughput analysis of the total contents of analytes under concern in the CRM was also confirmed.

To sum up, the NADES can be successfully employed as the effective extractants of metals from plant samples (here barley grass). However, the extraction parameters should be selected for each element individually. It is worth mentioning that depending on the molecular weight of the metal complexes, that need to be extracted, an appropriate NADES composition should be applied. Natural solvents with eutectic properties show promise as better candidates, for carrying out effective extraction processes, than organic solvents. Firstly, the application of NADES results in obtaining higher extraction efficiencies. Secondly, they are non-toxic and safe for the environment.

Author contributions

L. R. conceived the presented idea. N. O. and M. M. carried out the experiments. L. R. encouraged N. O. to investigate and supervised the findings of this work. K. P. performed the COSMO-RS experiments. L. R. wrote and M. M. edited the text of manuscript.

Conflicts of interest

The authors declare that they have no conflict of interest.

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