Fast Dispersive Liquid-Liquid Microextraction Based on Temperature Switching Deep Eutectic Solvent as A Green Extractant

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Research Article

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Abstract

With the development of research, it was found that the dispersive liquid-liquid microextraction (DLLME) was limited by the tedious extraction process and toxic extractant. A thermo-switchable deep eutectic solvent (DES) was applied to the DLLME as a green extractant in this paper. The DES can be dispersed and aggregated by shaking and heating in the water during the extraction process due to the surfactant and thermo-switchable properties, which shortened the extraction time as low as 5 minutes. The feasibility of the developed method was verified using 4 organophosphorus pesticides and 5 pyrethroids as targets in simulated water samples, which showed good precision (RSD%, 0.8-9.7, n=3) and low detection limit (0.16-0.81 $\mu\text{g L}^{-1}$, S/N = 3) under the optimal extraction conditions. This method was used to detect the pesticide content in four natural rivers in Xi'an, and the recoveries of these spiked samples at three concentrations levels were among 81–113%. This is the first time to combine the toxic-free and thermo-switchable properties of DES in DLLME to propose a simple, fast, effective, and green pretreatment method.

Highlights

1. Thermo-switchable deep eutectic solvent was used to simplify the steps of DLLME.
2. A rapid and green extractant was used to detect pesticides in water sample.
3. Without additional equipment to assist in in analyzation.
4. The whole extraction process can be as short as 5 minutes.

1. Introduction

Pesticides, a type of emerging organic pollutants (EOPs), are ubiquitous in the water environment (Fang, et al., 2019). Since China banned organochlorine pesticides, broad-spectrum organophosphorus pesticides and pyrethroid have been widely used due to their high efficacy and easy degradation (Mao, et al., 2020). They are unknown in number, lack extensive ecotoxicological data, and migrate with water bodies, negatively impacting the ecological environment and human health (Bravo, et al., 2020). As far as existing research data is concerned, these pesticides can cause many problems to the human nervous system, immune system, reproductive system and respiratory system even at low concentrations (Albaseer, 2019). Therefore, the detection of pesticide in environmental water is of great significance to public health and ecosystems (A. J. Li, et al., 2020). The commonly used detection methods are gas chromatography and liquid chromatography (Samsidar, et al., 2018). However, because of the low concentration and complex matrix, a pretreatment step is required to enrich and purify them.

Dispersive liquid-liquid microextraction (DLLME) is an efficient and fast liquid-phase microextraction method proposed by Rezaee (Rezaee, et al., 2006) in 2006. The main improvement work is concentrated on innovating the dispersion method (Psillakis, 2019; Saleh, et al., 2009; Zhong, et al., 2019), updating the phase separation method (Guo, et al., 2016; Ngaosi, et al., 2016; Rezaee, et al., 2012; Ye, et al., 2016; Zhong, et al., 2019), and the usage of low-toxic extractants as much as possible. The ionic liquid (Marcinkowska, et al., 2019) which was used to replace the toxic extractant in DLLME (Montalbán, et al., 2018; Wu, et al., 2013) was found to be harmful to environment recently (Montalbán, et al., 2018). Deep eutectic solvents (DES) proposed by Abbott (Abbott, et al., 2004) in 2003, is a new type of designable green solvents consists of two or more non-toxic hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) which are mechanically mixed in a specific ratio at a certain temperature.

Based on the favorable features of eco-friendliness, degradable, simple synthesis, and adjustable properties, applying DES in DLLME to avoid toxic reagents has become popular research (G. Li, et al., 2019). Many hydrophobic DES are

designed to be directly used as extractants to enrich pollutants in water (Ahmadi, et al., 2019; Deng, et al., 2019; Farajzadeh, et al., 2016; Makoś, et al., 2020). Pirsahab et al. (Pirsahab, et al., 2018a) hyphenated liquid-phase microextraction and the freezing of DES in detecting pesticides of environmental water, without any disperser solvent. Jouyban et al. (Jouyban, et al., 2020) used DES as extractant to analyze pesticides in milk, and the extraction process can be facilitated by ultrasound or adding organic solvents as dispersants. However, the above methods together with organic solvents and auxiliary instruments make this hyphenated method becomes cumbersome and compromised seriously the eco-friendly. In this paper, a thermo-switchable and environmental friendly DES reported by Longeras et al. (Longeras, et al., 2020) was used to simplify the DLLME steps.

To our best knowledge, this paper applies a thermo-switchable DES to the DLLME for the first time to analysis nine pesticides, which can simplify the dispersion and collection steps of the DLLME simultaneously. During the extraction process, a homogeneous system was formed in ten seconds, and the extractant can aggregate within 1 minute by heating and adding sodium chloride. Nine organophosphorus pesticides and pyrethroids in water samples were successfully analyzed by HPLC with UV detector.

2. Experimental

2.1 Chemicals and reagents

Oleic acid (OA, 99% purity) was purchased from Energy Chemical, and lidocaine (LD, 99% purity) was purchased from Macklin. Organophosphorus pesticide standards and pyrethroid standards ($1000 \mu\text{g mL}^{-1}$) were purchased from BeNa Culture Collection (China), and the Chemical structural formula can be seen in the supplementary material. Methanol (HPLC grade) was purchased from Welch Materials, Inc. (China). Sodium chloride was purchased from Tianzheng Chemical Reagent Company (China). Water samples of the four rivers were sampled from Bahe, Weihe, Luhe and Fuhe in Xi'an, and they were sealed and stored at 4°C and protected from light. Preparation and characterization of DES, and real sample preparation process can be seen in the supplementary material.

2.2 Instrumentation

Chromatographic separation was completed using SHIMADZU HPLC (HPLC-20A) comprising: SIL-20A autosampler and SPD-20A UV detector; Bruker Fourier transforms IR spectrometer (Tensor27); Bruker Superconducting Nuclear Magnetic Resonance Spectrometer (ADVANCE III, 400MHZ).

2.3 Extraction procedure

Figure 1 shows the extraction process of this method. 100 μL of DES was added as an extractant to a colorimetric tube containing 25 mL of the water sample, and then shake to form a homogeneous system. A certain quality of sodium chloride solid (NaCl) is added to the system, and then the separation in two phases appear rapidly after shaking for tens of seconds and standing in a 40°C water bath. As the temperature of the system rises and the polarity changes, the proportion of OA in the DES becomes higher, and the extractant floated on the surface of the water sample, which is consistent with the report of Longeras et al. (Longeras, et al., 2020). Collect the extractant and dissolve it in 200 μL methanol, which was injected into HPLC system for analysis. Besides, Conditions of HPLC are described in supplementary materials.

3. Results And Discussion

3.1 Optimization of extraction conditions

In this study, thermo-switchable DES was selected as the extractant in DLLME. Several important parameters of extraction process were investigated with 20 µg L⁻¹ spiked to seek high extraction efficiency, all experiments were repeated three times (n = 3) in parallel.

3.1.1 Extracting solvent

DES with different OA: LD molar ratios (1:1, 2:1 and 3:1) were synthesized, and the ratio of OA and LD is 2:1 was selected as the optimal ratio for DLLME, which remaining solution after collection is close to clear indicates that as much extractant as possible has been collected. Moreover, as the volume of the extractant decreases, the peak area of the targets gradually increases (Fig. 2-a), which indicates the volume is sufficient to enrich the targets in the water sample, hence 100 µL is selected as the optimal extractant volume.

3.1.2 Addition of inorganic salt

Under the influence of inorganic salts, the phase transition of DES occurred due to the Hofmeister effect (Hyde, et al., 2017). Appropriate amount of salt can improve extraction efficiency by increasing the polarity of water phase and reducing the solubility of the targets in the water phase. However, the excess inorganic salts will increase the viscosity of the solution, resulting in the decrease the diffusion coefficient and further reduce the extraction efficiency. It was found that an aqueous two-phase system formed in addition of sodium sulfate in DES, while the sodium carbonate causing DES fail to aggregate, so NaCl was selected as the optimal salt among several common inorganic salts. The correlation between chromatographic peak area and the quality of NaCl shows in Fig. 2-b, and the concentration of 2.00 mol L⁻¹ was selected as the optimal quality.

3.1.3 Water bath conditions

Figure 2-c and Fig. 2-d shows the relationship between the chromatographic peak area and the water bath conditions (water bath time and temperature). The polarity of the extractant is close to the polarity of the targets with the best conditions, which can reach the best extraction efficiency. The phase transition behavior is due to the change of oleate into more hydrophobic OA in DES with increasing temperature (Janke, et al., 2014). The results show that the 40 °C can be the optimal water bath temperature, and 5 min was considered as the optimal water bath heating time may be explained by that the pesticides are not stable in hot water.

3.2 Analytical performance

To validate the method of thermo-switchable DES applied in the DLLME, the water samples were spiked with the pesticides with 3 concentrations, and all the experiments were performed in triplicate. Some factors have been used to investigated the performance of this method, and the results are shown in Table 1.

3.2.1 EF and ER%

EF is calculated by Equation 1, and ER% is calculated by Equation 2.

$$EF = \frac{Ca, final}{Cs, initial}$$

1

$$ER^{0/0} = \frac{na}{ns} \times 100 = \frac{ca \times va}{cs \times vs} \times 100 = EF \times \frac{va}{vs} \times 100$$

2

Where $C_{a, \text{final}}$ is the concentration of the targets in the receptor phase, and $C_{s, \text{initial}}$ is the initial concentration of the targets in the water sample. Where n_a represents the mass of the targets in the initial sample, n_s represents the amount of the targets in the extractant after extraction, and V_s and V_a represent the volume of the sample and the extractant, respectively.

The EF of this method to detect 9 pesticides was ranged from 57.3-78.2 and recovery was ranged from 66.7-85.2% shows in table 1, which was performed with $20 \mu\text{g L}^{-1}$ of pesticides. It is hypothesized that the higher extraction rate of Phoxim and Profenofos are due to their strong hydrogen bond with DES, and the higher extraction rate of Fenpropathrin and Fenvalerate are due to the stronger hydrophobic interaction between them and DES. This DES also features long carbon chains with strong hydrophobicity and a complex hydrogen bonding network, which allows for good extraction ability of certain polar substances and non-polar substances that can form hydrogen bonds.

3.2.2. Linearity, LODs and LOQs

The linearity was assessed through matrix-matched calibration curves for the 9 pesticides at 7 concentration levels, and this method was linear over the range of $2\text{-}200 \mu\text{g L}^{-1}$ or $5\text{-}200 \mu\text{g L}^{-1}$. The calibration curves of all analytes demonstrate good linearity, with correlation coefficients ranging from 0.9942 to 0.9995. The LOD and LOQ were in the range of $0.16\text{-}0.81 \mu\text{g L}^{-1}$ and the LOQ is $0.52\text{-}2.70 \mu\text{g L}^{-1}$, which were calculated using a signal-to-noise ratio of 3:1 (S/N = 3) and 10:1 (S/N = 10), respectively.

3.2.4. Precision

The precision was evaluated in terms of inter-day and intra-day precision through relative standard deviations (RSDs), all the experiments were repeated three times in parallel. As shown in table 1, the blank sample with spiked concentration $20 \mu\text{g L}^{-1}$ of 9 pesticides were found to has the RSDs ranged from 5.4-9.7% in inter-day (n=3) experiment and 0.8-9.1% in intra-day (n=9).

Table 1

Analytical performance

Pesticides	Line range ($\mu\text{g L}^{-1}$)	R^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	EF	ER%	Intra-RSD (% n=3)	Inter-RSD (% n=9)
Phoxim	5-200	0.9975	0.57	1.89	73.3	85.2	3.8	5.4
Profenofos	5-200	0.9963	0.43	1.45	61.9	72.0	5.0	9.7
Triazophos	2-200	0.9993	0.49	1.65	58.4	67.9	4.5	5.8
Chlorpyrifos	2-200	0.9974	0.49	1.66	57.3	66.7	2.1	7.1
Bifenthrin	5-200	0.9946	0.81	2.70	59.3	69.0	0.8	8.1
Beta cypermethrin	2-200	0.9942	0.36	1.13	59.5	69.2	1.1	8.0
Etofenprox	2-200	0.9951	0.30	1.02	57.7	67.1	2.5	8.4
Fenpropathrin	2-200	0.9995	0.23	0.77	63.6	73.1	9.1	7.9
Fenvalerate	2-200	0.9959	0.16	0.52	78.2	90.9	5.7	8.3

3.3 Real sample analysis of river water

Four natural rivers in Xi'an were selected to detect and estimate the recovery of spiked river to verify the possibility of this method in practical application. The HPLC chromatograms of the blank Weihe River and three spiked rivers are shown in Fig. 2-e. The recovery results of spiked rivers are shown in the supplementary material, indicating that no pesticides were detected in the four water samples. The recovery of all targets in the four spiked river water samples were among 81-113, and the RSD% ranged from 1.7–11.8%. Above results demonstrated the potential application of the method for the determination of pesticide content in environmental water.

3.5 Comparison to other methods

Table 2 listed some performance parameters of other pretreatment methods using DES and compares them with this method. The main advantage of this method is to shorten the DLLME time by using a green DES as extractive solvent. For other methods in the table, they need additional equipment to assist in the dispersion, which is more time-consuming. In particular, the organic solvents used in method(2), (3) and (4) with intrinsic drawbacks of toxicity, non-biodegradability and high cost. The LOD and EF of this method was comparable with others in general, and the extraction procedure of the proposed method was completed without any additional equipment to disperse and collect the extractant. Furthermore, in comparison to other reported sample pretreatment methods the proposed method has a greener extractant. The results proved the tremendous potential of this thermo-switchable DES for detecting pesticides at trace levels in the water environment with the simpler mode of dispersing and collecting extractant with shorter extraction time (5 mins).

Table 2
comparison to other reported methods

Extraction method	Targets	Toxic reagent	Dispersion/collection method	Extraction time (min)	LOD	Ref
DLLME-based on solidification of DES (1)	Benzoylurea insecticides	No	Centrifuge, nitrogen-blow and freeze	15	0.09-0.16 $\mu\text{g L}^{-1}$	(Pirsaheb, et al., 2018)
Ferrofluid-SPME (2)	Organophosphorus pesticides, fenitrothion, diazinon and chlorpyrifos	Methanol	Vortex assisted/Magnetic	36	0.30-0.15 $\mu\text{g L}^{-1}$	(Bazmandegan-Shamili, et al., 2018)
Ultrasound-assisted-IL-DLLME (3)	Organophosphorus pesticides	Acetonitrile	Ultrasound and Centrifuge	>15	0.1 $\mu\text{g kg}^{-1}$	(Liu, et al., 2020)
UAE-DES-MSPE (4)	7 kinds of pesticides	Acetonitrile	Ultrasound/Vortex assisted	>11	0.02-0.05 $\mu\text{g mL}^{-1}$	(Zhao, et al., 2020)
Temperature switching DES- DLLME (5)	Organophosphorus pesticides and pyrethroids	No	Shaking/Heating	5	0.16-0.81 $\mu\text{g L}^{-1}$	This work

4. Conclusions

In this study, a simplified DLLME method with green and thermo-switchable DES for preconcentration was combined. Different kinds of organophosphorus pesticides and pyrethroids in river were analyzed and detected. The established method with good linearity, reproducibility, LOD and LOQ proved DES is suitable to replace traditional toxic extractants in DLLME, and this new method can solve traditional methods problems in detecting pesticides. Above all, the developed method is a fast, facile, environmentally friendly and cheap method for the pretreatment and analysis of pesticides in water.

Declarations

Declaration of Competing Interest

The authors report no declarations of interest.

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Credit Author Statement

Qian Liu: Experiment, Data curation; Zhiqiang Li: Method development; Liulin Wei: Modification and Editing; Xiaomei Chen: Original draft preparation; Yidong Xu: Technical support; Jingchan Zhao: Supervision

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Figures

Figure 1

Schematic diagram of the extraction process. DES was added as an extractant, and phase transition behavior occurred after NaCl was added and water bath was heated. Finally, recover and dissolve the DES with methanol after phase transition and detected by HPLC.

Figure 2

Optimization of extraction process(a) The influence of the amount of DES on recovery, and 100 µL was selected as the optimal volume; (b) The influence of the amount of NaCl, and the concentration of 2.00 mol L⁻¹ is selected as the optimal quality; (c) The influence of water bath heating temperature, and 40 °C can be the optimal water bath temperature; (d) The influence of water bath heating time, and 5 min was considered as the optimal water bath heating time; (e)HPLC Chromatograms of water sample and spiked water sample, indicating that no targets were detected in the river water.

Supplementary Files

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