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Ionic liquid-based ultrasound-assisted emulsification microextraction coupled with high performance liquid chromatography for the determination of four fungicides in environmental water samples

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ABSTRACT

A highly efficient and environmentally friendly sample preparation method termed ionic liquid-based ultrasound-assisted emulsification microextraction (IL-USAEME) combined with high performance liquid chromatography has been developed for the determination of four fungicides (azoxystrobin, diethofencarb, pyrimethanil and kresoxim-methyl) in water samples. In this novel approach, ionic liquid (IL) was used as extraction solvent in place of the organic solvent used in conventional USAEME assay, and there is no need for using organic dispersive solvent which is typically required in the common dispersive liquid–liquid microextraction method. Various parameters that affect the extraction efficiency, such as the kind and volume of IL, ultrasound emulsification time, extraction temperature and salt addition were investigated and optimized. Under the optimum extraction condition, the linearities of calibration curves were in the range from 3 to 5000 ng mL^{-1} for target analytes with the correlation coefficient higher than 0.9992. The enrichment factors and the limits of detection were in the range of 88–137 and 0.73–2.2 ng mL^{-1}, depending on the analytes. The environmental water samples were successfully analyzed using the proposed method, and the relative recoveries at fortified levels of 50 and 100 ng mL^{-1} were in the range of 83.9%–116.2%.

1. Introduction

Azoxystrobin, diethofencarb, pyrimethanil and kresoxim-methyl are new fungicides which have a different mode of action compared to traditional fungicides. Azoxystrobin and kresoxim-methyl are strobilurines that act on the respiration process by blocking the transport of electrons within the mitochondria from cytochrome b to cytochrome c_1 by binding a specific site [1]. Diethofencarb is a phenylcarbamate which inhibits phospholipid and fatty acid biosynthesis, and pyrimethanil is an anilinopyrimidine that acts by inhibiting the biosynthesis of methionine by the pathogen [2]. They can be used to protect against gray molds, fungi and other agents that may affect crop yield. However, the residues of these fungicides may enter into the environment through various routes, such as spraying, the discharge of waste water and soil seepage, leading to possible surface and ground water contamination as well as cause public health problems due to their toxicity and persistence. According to the European Union Directive, a maximum allowed concentration of 0.1 μg L^{-1} for individual pesticide and of 0.5 μg L^{-1} for total pesticides in drinking water has been established [3]. The high requirements on water quality have resulted in an increasing need for the reliable, sensitive and rapid analytical technique to monitor the fungicides at trace levels.

Gas chromatography (GC) [4,5] and high performance liquid chromatography (HPLC) [6,7] are the common used techniques for the separation and quantification of fungicides residues in different matrices. Moreover, a previous sample preparation process is required in order to decrease the complexity of the matrix and increase the concentration of target compounds. Application of conventional liquid–liquid extraction (LLE) and solid-phase extraction (SPE) methods was limited with the disadvantages such as time-consuming, labor-intensive and need a large amount of organic solvents [8,9]. Solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) have also been proposed for fungicides extraction. However, the routine application of SPME and SBSE in fungicide monitoring studies still requires solving some practical drawbacks, such as the limited stability of some SPME coatings, cross-contamination risks and the cost of SPME fibers and polydimethylsiloxane coated bars [10,11].

Recent efforts are being placed on the development of miniaturized, efficient and environment-friendly extraction techniques for the analysis of fungicides in complex matrix. Ultrasound-assisted

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emulsification microextraction (USAEME) is an efficient, simple, rapid and cheap extraction technique which was first introduced by Regueiro and coworkers in 2008 [12]. This approach is based on the emulsification of a microvolume of organic extractant in an aqueous sample by ultrasound radiation, and further separation of both liquid phases by centrifugation. In the technique, the application of ultrasonic radiation facilitates the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases. This leads to an increment in the extraction efficiency in a minimum amount of time. USAEME has been widely used for the extraction of organic compounds and metal ions in environmental samples [13–16]. However, organic extraction solvents tend to volatilize under the ultrasonic radiation.

Ionic liquids (ILs) are salts with low melting points that are composed of organic cations and various types of anions, and have been considered as environmental benign solvents [17]. There are aroused increasing interests for their promising role as alternative solvents in organic synthesis, catalysis and electrochemistry [18,19]. ILs have negligible vapor pressure and non-flammability as well as good solubility for inorganic and organic compounds, and have been successfully applied in various areas of analytical chemistry, especially in separation sciences [20–23]. The application of ILs in sample preparation technologies, such as LLE [24], liquid-phase microextraction (LPME) [25,26] and dispersive liquid–liquid microextraction (DLLME) [27,28] has been reported.

In the present study, the application of IL as extraction solvent instead of organic solvent in USAEME was explored, and a novel method of ionic liquid-based ultrasound-assisted emulsification microextraction (IL-USAEME) coupled with HPLC was developed for the determination of four fungicides (azoxystrobin, diethofencarb, pyrimethanil and kresoxim-methyl, the chemical characteristics of these compounds were compiled in Table 1) in environmental water samples. The effects of various experimental parameters, such as the kind and volume of IL, ultrasound emulsification time, extraction temperature and salt addition were investigated and optimized.

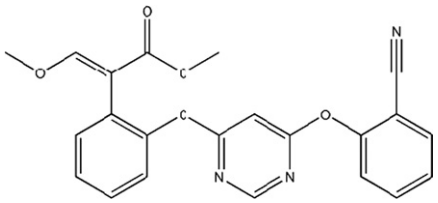
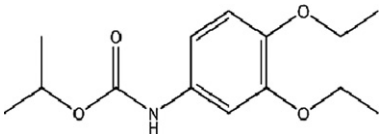
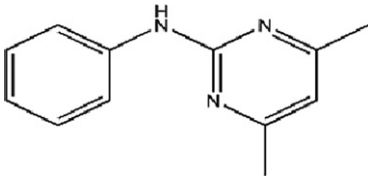
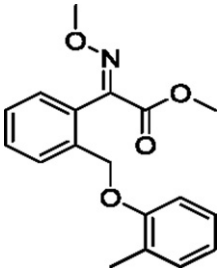
2. Experimental

2.1. Reagents and standards

Azoxystrobin (94%), diethofencarb (98%), pyrimethanil (98%) and kresoxim-methyl (99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The individual stock standard solution were prepared in methanol at a concentration of 100 μg mL^{-1} and stored at 4 °C. The standard working solutions were daily prepared by dilution of stock standard solution with deionized water to the required concentrations.

1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) and 1-octoyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) were purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). The HPLC-grade methanol was obtained from TEDIA Company (Fair lawn, NJ, USA). The water used in the work was purified on a Milli-Q water purification system (Millipore Corporation, Billerica, MA, USA). All chemicals used in this work were of analytical reagent grade or better. All the solvents and water samples were filtered through a 0.45 μm membrane to eliminate particulate matter before analysis.

Table 1
Chemical characteristics of the studied compounds.

Name	Chemical structure	Molecular weight	Molecular formula
Azoxystrobin		403.4	$C_{22}H_{17}N_3O_5$
Diethofencarb		267.3	$C_{14}H_{21}NO_4$
Pyrimethanil		199.3	$C_{12}H_{13}N_3$
Kresoxim-methyl		313.4	$C_{18}H_{19}NO_4$