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Use of magnetic effervescent tablet-assisted ionic liquid dispersive liquid–liquid microextraction to extract fungicides from environmental waters with the aid of experimental design methodology

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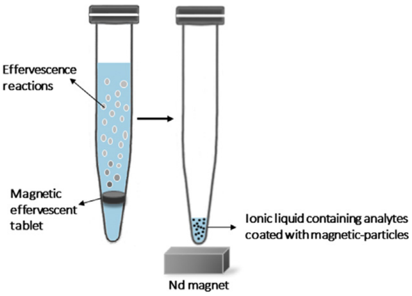
HIGHLIGHTS

- A novel magnetic effervescent tablet was prepared for the detection of fungicides.
- Extractions were screened by PB design and optimized through CCD design.
- Analytes could be rapidly and efficiently extracted upon field inspection.
- The extractant could be separated without centrifugation.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel effervescence-assisted microextraction technique was proposed for the detection of four fungicides. This method combines ionic liquid-based dispersive liquid–liquid microextraction with the magnetic retrieval of the extractant. A magnetic effervescent tablet composed of Fe_3O_4 magnetic nanoparticles, sodium carbonate, sodium dihydrogen phosphate and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonimide) was used for extractant dispersion and retrieval. The main factors affecting the extraction efficiency were screened by a Plackett–Burman design and optimized by a central composite design. Under the optimum conditions, good linearity was obtained for all analytes in pure water model and real water samples. Just for the pure water, the recoveries were between 84.6% and 112.8%, the limits of detection were between 0.02 and 0.10 μg L^{-1} and the intra-day precision and inter-day precision both are lower than 4.9%. This optimized method was successfully applied in the analysis of four fungicides (azoxystrobin, triazolone, cyprodinil, trifloxystrobin) in environmental water

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Abbreviations: AALLME, air-assisted liquid–liquid microextraction; ANOVA, analysis of variance; CCD, central composite design; DLLME, liquid–liquid microextraction; EALLME, effervescence-assisted microextraction; EFs, enrichment factors; [HMIM]NTF_2, 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonimide); [HMIM]Cl, 1-hexyl-3-methylimidazolium chloride; [HMIM]PF_6, 1-hexyl-3-methylimidazolium hexafluorophosphate; IL-DLLME, ionic liquid-based dispersive liquid–liquid microextraction; ILs, ionic liquids; LC, liquid chromatography; LLE, liquid–liquid extraction; LODs, limits of detection; LPME, liquid-phase microextraction; MNPs, magnetic nanoparticles; MSPE, micro-SPE; MSPD, matrix solid-phase dispersion; [OMIM][NTF_2], 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonimide); [OMIM]Cl, 1-octyl-3-methylimidazolium chloride; [OMIM]PF_6, 1-octyl-3-methylimidazolium hexafluorophosphate; PB design, Plackett–Burman design; RSD, relative standard deviation; SBSE, stir bar sorptive extraction; SPE, solid phase extraction; SPME, solid-phase microextraction; S/N, signal to noise; UV, ultra violet.

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samples and the recoveries ranged between 70.7% and 105%. The procedure promising to be a time-saving, environmentally friendly, and efficient field sampling technique.

1. Introduction

Concern about the relationship between health and the use of agrochemicals has increased in recent years. Fungicides, one of the most relevant groups of pesticides, are extensively used to control fungal infections in crops, cereals, fruits and vegetables [1]. The fungicides azoxystrobin, triazolone, cyprodinil and trifloxystrobin are frequently used to protect different cropping systems from fungal pathogens such as the diseases of powdery mildew, downy mildew, *erysiphe graminis*, and anthracnose [2–4]. As a result of their widespread use, fungicide residues are known to enter the environment by storage, spraying, spills and runoff, as well as factory wastewater discharge [5]. Moreover, fungicides may contaminate surface and groundwater and cause potential risks to human health due to their suspected toxicity, endocrine disruptive effects, and carcinogenic and developmental/reproductive toxic effects at low level [6,7]. The European Union has set maximum permitted concentrations of individual and total pesticides in water intended for human consumption as 0.1 and 0.5 ng/mL, respectively [8]. Hence, the monitoring of trace levels of pesticides in water has recently attracted considerable attention, and the development of simple, green, highly sensitive, and easily performed analytical methods for determining fungicides is of great importance.

Fungicide determination is routinely performed by LC with UV [1,9,10] or mass spectrometric detection [11,12]. Before instrumental analysis, samples are prepared via a variety of protocols. LLE and SPE are conventional sample preparation techniques. However, these sample preparation methods require large quantities of organic solvents are tedious and time-consuming [13,14]. Therefore, several miniaturized, effective and environmentally friendly sample preparation techniques, including SPME [15], MSPD [16], MSPE [17], SBSE [18], and LPME [19], have been introduced for the preparation of pesticide samples for analysis. LPME, one of the most widely used sample preparation techniques, combines sampling, extraction, separation and concentration.

Based on the methodology of LPME, DLLME is one typical sample preparation technique. The DLLME process is generally established in a ternary solvent system, which contains disperser solvent, extraction solvent and an aqueous sample containing the target analytes [20]. When the mixture solution of extraction and disperser solvent is injected into samples, a cloudy solution quickly forms due to the cosolvency of the disperser solvent with the other two solvents; an extraction equilibrium is established nearly instantaneously between the extraction solvent and the aqueous solution thanks to the extensive surface contact [21].

ILs are considered “green” solvents because of their tunable physicochemical properties, high chemical and thermal stability, and negligible vapor pressure at room temperature [22]. ILs are beginning to be exploited as alternative solvents in many extraction systems [23–25]. Because of the greater viscosity and surface tension of ILs, larger and more stable microdroplets are formed using ILs than microdroplets formed with traditional organic solvents. These merits are highly desirable for DLLME. In IL-DLLME, an IL works as the extraction solvent to extract the target analyte from the sample with satisfactory recoveries and high enrichment factors [26,27].

In IL-DLLME, solvent dispersion is usually assisted by organic solvents or by applying additional energy such as vortexing [28,29], shaking [30], heating [31], or ultrasound [32]. In recent years, several novel disperser-solvent-free techniques, such as AALLME and EALLME, have been developed. Compared to EALLME, AALLME is cumbersome because it requires multiple sequences of suction and ejection. EALLME, which operates on the basis of effervescent reaction, was first introduced by Lasarte-Aragones et al. in 2014 [33]. The extraction solvent was dispersed into water through the carbon dioxide produced by an added glacial acetic acid solution and the sodium carbonate contained in the samples. Although this method is both highly sensitive and repeatable, it is not convenient for outdoor inspection due to the preparation required for the extraction solution and sample liquid.

Collection of the extraction solvent is usually accomplished by centrifugation, which may increase the time required for the whole extraction procedure. Shi et al. proposed using magnetic nanoparticles to gather the extraction solvent (1-octanol) in the classic DLLME. Another approach for the magnetic retrieval of an ionic liquid in IL-DLLME was introduced by Zhang et al. in 2012 [34]. Following the conventional IL-DLLME step, a magnetic sorbent is dispersed into the sample by vortexing; this sorbent then adsorbs the ILs through hydrophobic forces. Finally, the combination of ILs and sorbent is recovered using an external magnet. However, the solvent dispersion and recovery steps cannot be completed synchronously.

In this paper, we pose a novel analytical technique denoted magnetic effervescent tablet-assisted ionic liquid dispersive liquid–liquid microextraction (META-IL-DLLME). Due to the successful combination of effervescence dispersion and magnetic recovery, this method will reduce some limitations of the classic IL-DLLME. The extraction solvent is retrieved through iron oxide nanoparticles, and this step is accompanied by a dispersion that is chemically assisted by an effervescent reaction. As a result, the dispersion and collection of the green extractant can be completed almost simultaneously. After a series experimental design, including single-factor experiments, a PB design and a CCD, the proposed method was applied to the extraction of fungicides from real environmental water samples. Under the current conditions, this method requires a certain temperature to aid the disintegration of the effervescent tablet, and we will perform further studies with the aim of developing easier sample preparation techniques.

2. Experimental

2.1. Reagents and materials

All pesticide standards (azoxystrobin, triazolone, cyprodinil and trifloxystrobin) were obtained from the Agricultural Environmental Protection Institution (Tianjin, China) with purities ranging from 97% to 98%. HPLC-grade acetonitrile and methanol were purchased from Dikma (Beijing, China), and deionized water was purified using a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Analytical-grade sodium ethanol and acetone were purchased from Beijing Chemical Factory (Beijing, China). Analytical-grade sodium carbonate, citric acid and sodium dihydrogen phosphate dihydrate were acquired from Sinopharm Chemical Reagent Company (Beijing, China). [HMIM]Cl, [HMIM]PF_6, [OMIM]Cl and