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Nanofluid of zinc oxide nanoparticles in ionic liquid for single drop liquid microextraction of fungicides in environmental waters prior to high performance liquid chromatographic analysis

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ABSTRACT

Using a nanofluid obtained by dispersing ZnO nanoparticles (ZnO NPs) in 1-hexyl-3-methylimidazolium hexafluorophosphate, new single drop microextraction method was developed for simultaneous extraction of three fungicides (chlorothalonil, kresoxim-methyl and famoxadone) in water samples prior to their analysis by high performance liquid chromatography (HPLC-VWD). The parameters affecting the extraction efficiency such as amount of ZnO NPs in the nanofluid, solvent volume, extraction time, stirring rate, pH and ionic strength of the sample solution were optimized. Under the optimized conditions, the limits of detection were in the range of 0.13–0.19 ng/mL, the precision of the method assessed with intra-day and inter-day relative standard deviations were <4.82% and <7.04%, respectively. The proposed method was successfully applied to determine the three fungicides in real water samples including lake water, river water, as well as effluent and influent of wastewater treatment plant, with recoveries in the range of 74.94–96.11% at 5 ng/mL spiking level. Besides to being environmental friendly, the high enrichment factor and the data quality obtained with the proposed method demonstrated its potential for application in multi residue analysis of fungicides in actual water samples.

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1. Introduction

Pesticides are used at various stages in agricultural process to boost the harvesting products. Therefore, contamination of matrices such as soil, water and even the agricultural products with various agrochemicals is a serious threat to human health [1,2]. Owing to properties like high stability and resistant to a wide range of pH, temperature and light, fungicides, one type of pesticides, are widely used for the protection and preservation of a variety of crops, fruits, and vegetables [3]. Fungicides are directly applied to the agricultural soils or sprayed on the field crops [4,5], and hence can easily release away from the application sites by air or rain water and contaminate water bodies. European Union Directive set the maximum allowed concentration of individual and total pesticides to be 0.1 and 0.5 ng/mL, respectively on the quality of water intended for human consumption [6]. Therefore, preconcentration techniques are required to investigate fungicides at trace levels.

There are numerous preconcentration techniques like solid-phase microextraction (SPME) [7–9], dispersive liquid–liquid microextraction (DLLME) [10–12], hollow fiber liquid phase microextraction (HF-LPME) [13], salting-out assisted liquid–liquid extraction [14], ultrasound-assisted emulsification microextraction [15,16], cloud point extraction [17] for the determination of fungicides in water samples. SPME is simple, solvent free and a technique in which efficient extraction is possible. The draw backs of SPME are cost of analysis, analyte carry-over, limited life time due to fiber-fragility and long analysis time. DLLME is the other microextraction technique which is cheap, simple, fast and present high enrichment factor. But difficulty to automation and requirement of environmentally unfriendly extraction solvents are its limitations. HF-LPME is also a simple and inexpensive technique in which high analyte preconcentration and excellent sample cleanup is possible. But, its limitations like long analysis time and memory effect when reusing the hollow fiber could be stated. Even though the use of microextraction techniques decrease environmental impact and the exposure of personnel to solvent vapors [18,19] most of these approaches directly or indirectly consume significant amount of organic solvents which can cause different toxicological problems. Hence, using either relatively green solvents

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or further reducing the amount of these solvents for the intended purpose is still interesting scientific research. Single drop microextraction (SDME) is liquid–liquid microextraction technique in which the amount of extraction solvent is drastically reduced. It is simple, inexpensive, easy to operate, versatile, and has additional qualities like different extraction modes, high enrichment factor and can be fully automated [18]. However, instability and ease of dislodgment of the micro-drop, limited drop volume, and evaporation of the micro-drop due to its volatility and low viscosity are the main problems associated to SDME. To overcome these limitations, investigation of suitable mode of SDME and appropriate solvent (viscous and non-volatile) which can form stable, relatively large drop volume with high extraction quality is required.

Metal oxide nanoparticles (NPs) have attracted considerable attention for their potential application in many technologies [20]. ZnO nanoparticles (ZnO NPs), one of the metal oxide NP, was employed for extraction purpose. Ghaedi et al. [21] used ZnO NPs loaded on activated carbon for efficient extraction of brilliant green dye and for removal of bromophenol red [22] in aqueous solutions. It was also applied as solid-phase adsorbent and as efficient solar photo-catalyst [23]. Wang and his co-authors employed silver NPs decorated ZnO NP sheets as effective surface enhanced Raman scattering substrate and applied for rapid detection of organic pollutants [24]. Besides, preparation and characterization of ZnO nanofluids (ZnO-NFs) and its applications have been reported [25–28].

Nanofluids (NFs) are materials comprising of stable suspensions of NPs (<100 nm) in base fluids [29] which can be prepared in different ways [30]. NFs have wide applications in various scientific areas. Suspending small amount of NPs in liquid–liquid system can cause considerable augmentation in mass transfer coefficient, and hence expected to improve the extraction efficiency which is of great interest in recent. A recent review provided the unique liquid–liquid properties, fundamental technologies and NFs application in chemical and bio-analysis methods and devices [31]. Krishnamurthy et al. obtained faster diffusion of a dye droplet in water based NF than in pure water [32]. Fang et al. also observed mass diffusion of rhodamine B to be about 10.71 times in 0.5% Cu NFs than in water alone [33]. The application of NFs to modify the mass transfer coefficient in extraction processes has been reported in recent. Above 121% enhancement in the rate of mass transfer was reported upon adding 0.002% modified Fe₃O₄ and Al₂O₃ NPs to a single drop in liquid–liquid extraction process [34]. The use of NFs to enhance the performance of a pulsed liquid–liquid extraction column was investigated and addition of 0.01–0.1%(v/v) SiO₂ NPs to kerosene increased the mass transfer by a factor of 4–60% [35]. The same research group obtained 60% improvement in mass transfer performance by adding 0.1%(v/v) SiO₂ to kerosene–acetic acid–water chemical system in pulsed liquid–liquid extraction column [36].

Ionic liquids (ILs) are compounds containing exclusively of ions, usually organic cations and organic/inorganic anions [37]. Even though ILs are considered as green alternates to volatile and toxic organic solvents, the issue of their potential biological toxicities has been reported [38–40]. However, due to their astonishing characteristics, ILs have wide application in several aspects of scientific work including as advantageous solvents for sample pretreatment [41]. The application of nanocomposites of different types of NPs and ILs has been reported in recent. Pena-Pereira et al. used nanoconfined IL-rich fibers in headspace SPME of volatile aromatic compounds and obtained high enrichment factors (up to 7400) and low LOD values (0.03–1.27 ng/mL) [42]. Ternary composites of nanocellulose, carbonnanotubes and ILs exhibited excellent extraction efficiency than the corresponding pure ILs in direct immersion SDME of heterocyclic amine [43]. Therefore, combination of ILs and

NPs in the form of IL-NFs may impart certain additional properties to the ILs. In addition, the aforementioned studies are indicators for the possibility of ILs based NFs consumption as extraction solvents for trace analysis of environmental pollutants.

The purpose of this study was to prepare stable 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]) based ZnO-NF for its application in a modified direct immersion single drop microextraction (SDME), namely ZnO-NF-based SDME (ZnO-NF-SDME), for enrichment of fungicides in water samples. The preferences of ZnO-NF for the investigation were initiated from the fact that unlike many metallic NFs, ZnO-NF form stable suspension without additional stabilizers due to the surface charges on ZnO NPs. The stability is crucial for its application in different areas like in extraction procedures. In addition to these, the use of ZnO-NF as a replacements of other organic solvents is relatively non-toxic and it allow the use of large drop volume due to its high viscosity and stability. Furthermore, ZnO-NF-SDME would exhibit higher enrichment factor which would be practically helpful to extract the target analytes at very trace level.

2. Experimental

2.1. Chemicals and reagents

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (AR grade), sodium hydroxide (NaOH) (AR grade) and sodium chloride (NaCl) (GR grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]) were purchased from Aladdin Industrial Corporation (Shanghai, China). Kresoxim-methyl and famoxadone standards (Purity >98%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), while chlorothalonil (Purity, 99.7%) was obtained from AccuStandard, Inc. (New Haven, USA). The physicochemical characteristics of these fungicides are shown in Table 1. HPLC grade acetonitrile and methanol solvents were obtained from Fisher Scientific (New Jersey, USA). Ultrapure water prepared by a Milli-Q Gradient system (Millipore, Bedford, MA, USA) was used throughout the experiments

2.2. Preparation and characterization of ZnO NPs

For the preparation of ZnO NPs, the sol-gel process reported by Gandhi et al. [44] was followed with minor modifications. In detail, 50 mL of 0.4 mol/L Zn(NO₃)₂·6H₂O solution was prepared in water and mixed with 1 mL of [BMIM][BF₄] to obtain colorless and transparent solution up on vigorous stirring. Freshly prepared 30 mL of NaOH (0.8 mol/L) was added in drops under magnetic stirring to obtain precursor Zn(OH)₂ sol and further stirred for another 2 h at room temperature. The obtained Zn(OH)₂ sol was allowed to stand overnight and the supernatant liquid was discarded. The settled precursor was recovered by centrifugation at 10,000 rpm for 15 min followed by washing with water and ethanol several times to remove any aggregates and organic impurities and then vacuum dried at 80 °C. The dried Zn(OH)₂ precursor was grinded and calcined at 300 °C to obtain crystallized ZnO NPs.

The size and morphology of the ZnO NPs were characterized by transmission electron microscopy (TEM; H-7500, Hitachi). X-ray diffraction (XRD) analysis was performed with an X'pert PRO instrument (PANalytical) using Cu-Kα radiation. Effective removal of the NPs from the extractant before HPLC system was confirmed by recording UV–vis spectra with Shimadzu UV-3600 (Kyoto, Japan) in separate experiment.

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