



Development of sensitive determination method for fungicides from environmental water samples with Titanate nanotube array micro-solid phase extraction prior to high performance liquid chromatography

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HIGHLIGHTS

- ▶ A micro-solid phase extraction was developed utilizing ordered TiO₂ nanotube array.
- ▶ The developed method exhibited good enrichment performance for fungicides.
- ▶ Low LODs indicated that the developed method would be a valuable alternative.

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ABSTRACT

Fungicides have been widely used throughout the world, and the resulted pollution has absorbed great attention in recent years. Present study described an effective measurement technique for fungicides including thiram, metalaxyl, diethofencarb, myclobutanil and tebuconazole in environmental water samples. A micro-solid phase extraction (μ SPE) was developed utilizing ordered TiO₂ nanotube array for determination of target fungicides prior to a high performance liquid chromatography (HPLC). The experimental results indicated that TiO₂ nanotube arrays demonstrated excellent merits on the preconcentration of fungicides, and excellent linear relationship between peak area and the concentration of fungicides was obtained in the range of 0.1–50 $\mu\text{g L}^{-1}$. The detection limits for the targeted fungicides were in the range of 0.016–0.086 $\mu\text{g L}^{-1}$ ($S/N = 3$). Four real environmental water samples were used to validate the applicability of the proposed method, and good spiked recoveries in the range of 73.9–114% were achieved. A comparison of present method with conventional solid phase extraction was made and the results exhibited that proposed method resulted in better recoveries. The results demonstrated that this μ -SPE technique was a viable alternative for the analysis of fungicides in complex samples.

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1. Introduction

Fungicides are widely used for the protection of a variety of crops, fruit, and vegetables due to their properties being stable and resistant to a wide range of pH, temperature and light, which made them easily used (Sukul and Spitteller, 2001). In general, the fungicides are applied directly to the soil or sprayed over crop fields, which make them easily released into the environment. Nowadays, the pollution from them has absorbed much attention, and to decline the use and monitor the residual concentration of them in environment are necessary. Up to now, a variety of chro-

matographic methods have been used for analysis of these compounds (Zhou et al., 2007a,b, 2010; Ji et al., 2009; Viñas et al., 2010; Pizarro et al., 2011; Fontana et al., 2011; Tang et al., 2010; Fries, 2011). In general, before the analysis, a sample enrichment and cleanup step is often used. The enrichment and clean-up procedures include disperse liquid–liquid microextraction (DLLME) (Viñas et al., 2010; Pizarro et al., 2011), solid-phase extraction (SPE) (Zhou et al., 2007a,b, 2010; Fontana et al., 2011), cloud-point extraction (CPE) (Tang et al., 2010), stir bar sorptive extraction (SBSE) (Fries, 2011; Campillo et al., 2010), and solid-phase microextraction (SPME) (Ji et al., 2009), etc. Some of these methods are tedious multi-step procedures which consume large quantities of toxic organic solvents. Solid phase extraction has distinguished from many extraction techniques because of its advantages such

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as lower cost, higher enrichment factor and less consumption of organic solvents. However, the sorbent is the key part which determines whether the enrichment performance is good or not. Hence screening new sorbents for enrichment is a new direction in the environmental analytical chemistry and pollutants monitoring.

Many research groups (Trojanowicz, 2006; Zhou et al., 2006a,b, 2007a,b, 2009; Huang et al., 2010, 2011a,b) have explored the application of several nano-sized SPE sorbents. Nanomaterials can offer several advantages over traditional SPE sorbents such as very large surface areas, which will result in high extraction capacity and high extraction efficiencies. However, the use of nanomaterials has some limitations. When packed column dynamic extraction mode is used, the nano-sized sorbent packed SPE column exhibits high backpressure, which makes it very difficult to adopt high flow rates. When the disperse batch mode is used, the nano-sized sorbent is often difficult to be separated and reused. Because of these disadvantages, it is necessary to develop new nano-sized SPE methods that can be applied to preconcentrate and separate organic compounds from environmental water samples. Recently, a unique μ -Solid-Phase Extraction (μ SPE) has been reported (Basheer et al., 2006, 2007), and this method provided a new approach for method development.

Nowadays, highly ordered TiO₂ nanotube array, as a new nanomaterial of TiO₂ nanotubes, has been an attractive approach for many important engineering applications. These potential applications include photoelectrochemical hydrogen generation, solar cells, hydrogen storage, gas sensing, templates for growth of compound semiconductor nanowires for radiation sensing, substrate for high interfacial bond strength hydroxyl apatite coating in implants, biomedical applications, as catalyst supports and photoelectrocatalytic activity electrode for organic contaminant degradation (Quan et al., 2005; Raja et al., 2006; Zhang et al., 2007). However, to the best of our knowledge, there has been no report using TiO₂ nanotube array on the enrichment and measurement of fungicides. TiO₂ nanotube array offer several advantages over the traditional microsize sorbents such as larger surface area, higher adsorption capacity, easily to prepare large enrichment system, and easily to be recycled. The goal of present study is to develop an effective enrichment and measurement technique with orderly TiO₂ nanotube array fixed on a Ti sheet, which resolved the difficulty of the packed column low flow rate limit and separation and reuse of the disperse batch mode. The developed method is micro-solid phase extraction, in which the Ti sheet with TiO₂ nanotube array is immersed the sample solution and kept a constant height and then the vial is sealed. The sample is stirred at a fixed rate. When the adsorption and desorption reaches an equilibrium the Ti sheet is taken out and eluted, and then the eluent is analyzed on a HPLC.

2. Experimental

2.1. Reagents

Thiram, metalaxyl, diethofencarb, myclobutanil and tebuconazole, were purchased from the Institute of Environmental Protection and Monitoring, Department of Agriculture (Beijing, China). A working stock solution (10 mg L⁻¹) of fungicides (Thiram, metalaxyl, diethofencarb, myclobutanil and tebuconazole) was prepared in HPLC grade methanol with the standard solution. All the standard solutions were stored at 4 °C in the refrigerator. The aqueous solutions at a concentration of 10 μ g L⁻¹ were prepared daily by diluting the standard mixture with ultrapure water. HPLC grade methanol and acetonitrile were obtained from Jiangsu Guoda Chemical Reagent Co., Ltd. (Huaian, China). Ultrapure water was prepared in the laboratory using a SZ-93 automatic double pure

distillatory from Shanghai Yarong Biochemical Instrument Factory (Shanghai, China) and all the other solvents were analytical reagents. 1% sodium hydroxide and 1 mol L⁻¹ hydrochloric acid were used for adjusting the pH value of the water samples.

Titanium sheets (99.6% purity) from Beijing Hengli Taiye Co., Ltd. (Beijing, China), Pt electrode was obtained from Shanghai Ruosull Technology Co., Ltd. (Shanghai, China). A 30 V potentiostat was obtained from The Fourth Radio Factory of Shijiazhuang (JWY-30G, Shijiazhuang, China). Preparation and identification of TiO₂ nanotube array were performed as previously reported (Huang et al., 2011a).

2.2. μ -SPE procedure

The TiO₂ nanotube array sheet was directly immersed in the 10 mL solution with a constant depth and then sealed the sample vial. The extraction conditions were as the same of the optimized conditions. The stirring rate of the magnetic stirrer was set at 500 rpm. After the equilibrium between adsorption and desorption basically reached, the TiO₂ nanotube array sheet was taken out and rinsed with ultrapure water in order to remove co-adsorbed matrix substances and then air-dried. TiO₂ nanotube array sheet was directly immersed in a small amount of acetonitrile for complete desorption in an interval of 7 min. After that, the TiO₂ nanotube array sheet was removed, and the acetonitrile was dried with mild stream of nitrogen gas. Then the residue was dissolved in 100 μ L methanol. Finally, 20 μ L of the solution was injected for HPLC analysis.

2.3. SPE procedure

SPE cartridges (Agilent ZORBAXSPE C18 cartridge, 0.2 g, 3 mL polypropylene) were conditioned 5 mL of acetonitrile and 5 mL of water. Extraction of 10 mL solution was carried out under vacuum at a flow rate of 2.6 mL min⁻¹. Subsequently, the cartridge was washed with 3 mL of ultrapure water and dried under a certain negative pressure for 15 min. Analytes were eluted with 2 mL of acetonitrile, and the elutes were evaporated to dryness by a stream of nitrogen gas. The residue was dissolved with 100 μ L of methanol, and 20 μ L of the solution was injected for HPLC analysis.

2.4. HPLC analysis

A high-performance liquid chromatography system, which consisted of two LC-10ATvp pumps and an SPD-10Avp, ultraviolet Detector (Shimadzu, Japan) was used for the separation and analysis. A reversed-phase SunFire™ C18 column (150 mm \times 4.6 mm, particle size 5 μ m, Waters Corporation) was used for separation at ambient temperature and Chromato-Solution Light Chemstation for LC system was employed to acquire and process chromatographic data. The mobile phase was obtained with methanol/water (75/25, v/v), and the flow rate, the injection volume and detection wavelength was 0.5 mL min⁻¹, 20 μ L and 220 nm, respectively.

2.5. Water samples

Four environmental water samples such as river water, lake water, canal water and water from the outlet of wastewater treatment plant were collected for validating the proposed method. River water was collected from Baihe River in Nanyang City, Henan Province, China. Canal water was collected from Gongchanzhuyi Canal in Xinxiang City, Henan Province, China. Lake water was collected from Donghu in Xinxiang City, Henan Province, China. The water sample from the outlet of wastewater treatment plant water sample was collected from Xiaoshangzhuang wastewater treatment plant in Xinxiang City, Henan province, China. All the

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