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Short communication

Application of bamboo charcoal as solid-phase extraction adsorbent for the determination of atrazine and simazine in environmental water samples by high-performance liquid chromatography-ultraviolet detector

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ABSTRACT

In this article, a new method for the determination of triazine herbicides atrazine and simazine in environment aqueous samples was developed. It was based on solid-phase extraction (SPE) using bamboo charcoal as adsorbent and high-performance liquid chromatography-ultraviolet detector (HPLC-UV) for the enrichment and determination of atrazine and simazine at trace level. Related important factors influencing the extraction efficiency, such as the kind of eluent and its volume, flow rate of the sample, pH of the sample, and volume of the sample, were investigated and optimized in detail. Under the optimal conditions, the experimental results showed that excellent linearity was obtained over the range of 0.5–30 $\mu g\,L^{-1}$ with correlation coefficients 0.9991 and 0.9982, for atrazine and simazine, respectively; and the relative standard deviations of two analytes were 8.3, 8.7%, respectively. The proposed method was successfully applied to the analysis of tap water and well water samples. And satisfactory spiked recoveries were obtained in the range of 75.2–107.1%. The above results indicated that the developed method was an excellent alternative for the routine analysis in environmental field.

1. Introduction

Triazine herbicides, such as atrazine and simazine, provide great benefits for weed control in agricultural domain over past years, however, their residues have attracted great concern worldwide because of widespread use. And they are also in the list of chemical pollutants that need to be more heavily monitored due to their toxicity, persistence, cumulation in the environment and their effects on the environment and health [1,2]. At the same time, according to the European Union Directive, individual pesticide in drinking water must not exceed 0.1 $\mu g\,L^{-1}$ for individual compound and some of its degradation products, and 0.5 $\mu g\,L^{-1}$ for the sum of all compounds [3]. Therefore, it is necessary to develop cheap, simple, rapid and sensitive methods for monitoring their residues in the environment.

The most widely used methods for the determination of triazine herbicides are chromatographic techniques including gas chromatography [4,5] and high-performance liquid chromatography [6], however, generally, without enrichment procedure their instrumental sensitivity and selectivity are insufficient for direct determination of these compounds at trace or ultratrace level in environmental samples. Therefore, a sample enrichment step prior to chromatographic analysis is very necessary. The commonly used sample preparation methods for chromatographic determination include liquid–liquid extraction (LLE), solid-phase extraction (SPE), ultrasonic extraction (USE) and so on. Among the above mentioned sample pretreatment methods, solid-phase extraction is the most common technique for environmental water sample pretreatment because it offers a number of important benefits in comparison with laborious classical LLE, such as reduced solvent usage and exposure, low disposal costs and short extraction times for sample preparation [7]. Recently, cell sorption as a novel and successful mode of SPE has appeared [8–10]. For the SPE procedure, the choice of adsorbent is the most important factor for obtaining higher enrichment efficiency of analytes. And various different types of hydrophobic materials, such as C8, C18, PS-DVB polymer, polytetrafluoroethylene and carbon nanotubes, have been used as adsorbents for the enrichment of triazine herbicides and other environmental pollutants in water samples [2,11–14]. In addition, one problem should be pointed out that some of them are expensive. Therefore, searching cheap and suitable adsorbents for the SPE of target analytes is necessary.

Bamboo charcoal has attracted great attention in recent years because of its special microporous structure and biological

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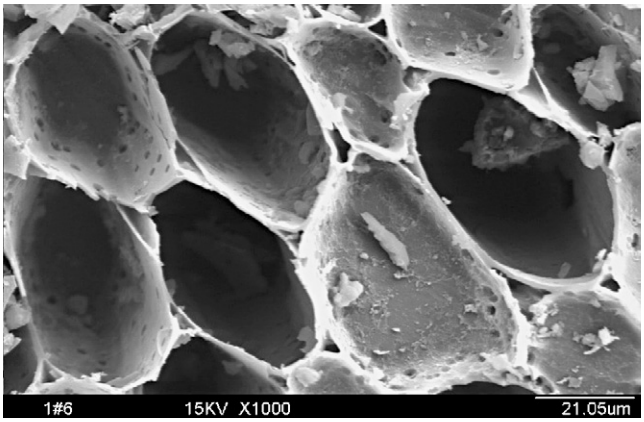

Fig. 1. The picture of bamboo charcoal under Electron Probe X-ray Microanalyzer.

characteristics [15]. Bamboo charcoal burnt at temperatures over 800 degrees centigrade exhibits properties vastly different from the bamboo plant, including a high density and porous structure [16]. Compared with wood charcoal, bamboo charcoal has about 4 times more cavities, 3 times more mineral content and 4 times better absorption rate. In terms of surface area, bamboo charcoal ($300\,m^2\,g^{-1}$) is 10 times greater than wood charcoal ($30\,m^2\,g^{-1}$) [16], and is larger than multiwalled carbon nanotubes (less than $200\,m^2\,g^{-1}$) [17]. Bamboo charcoal is a kind of cheap material (1 US$/500 g), which was much lower than other adsorbents such as PS-DVB polymer, carbon nanotubes and so on. The low price, extremely large surface area and the unique microporous structure make bamboo charcoal a promising adsorbent material for the enrichment of pollutants at trace level or utratrace level in the environment (The picture of bamboo charcoal under Electron Probe X-ray Microanalyzer is given in Fig. 1.) To our knowledge, up to now, no report about solid-phase extraction using bamboo charcoal as adsorbent for the enrichment and determination of triazine herbicides has appeared.

The goal of this study is to exploit the adsorptive potential of bamboo charcoal as solid-phase extraction adsorbent for the enrichment of atrazine and simazine at trace level. Related important factors influencing the extraction efficiency, such as the kind of eluent and its volume, flow rate of the sample, pH of the sample, and volume of the sample, were investigated and optimized in detail. At the same time, the proposed enrichment procedure was used for the determination of atrazine and simazine at trace level in environmental water samples.

2. Experimental

2.1. Reagents and materials

HPLC-grade methanol and acetonitrile were purchased from Tedia company Inc. (Fairfield, OH, USA). Acetone was chromatographic grade, and purchased from Fuchen chemical reagent factory (Tianjin, China). Atrazine were purchased from Dr. Ehrenstorfer (Augsburg, Germany) (purity 99.5%). Standard stock solution of atrazine was prepared by dissolving appropriate amount into methanol. Simazine standard with a concentration of $100\,mg\,L^{-1}$ was purchased from Institute of Environmental Protection and Monitoring, Department of Agriculture (Beijing, China). These solutions were further diluted into $10.0\,mg\,L^{-1}$ with methanol and stored at 4 °C. Fresh working solutions were prepared daily by appropriate dilution of the stock solution with purified water.

Bamboo Charcoal (Quzhou Minxin charcoal company, Zhejiang, China) as an indoor air fresher was purchased from a local market. The picture of bamboo charcoal under Electron Probe X-ray Microanalyzer is given in Fig. 1. Before use to develop SPE method, it was triturated and sieved through a 80 mesh sieve and dried at 80 °C for 2 h. Through the observation of JCXA-733 Electron Probe X-ray Microanalyzer, bamboo charcoals with an average length of 3–15 μm was obtained. Bamboo charcoal includes 81.21% carbon element, 2.52% hydrogen element, and 16.27% other components.

2.2. Apparatus

The high-performance liquid chromatography-ultraviolet detector (HPLC-UV) equipment used was an Agilent 1100 HPLC system including a ultraviolet detection, a quaternary pump, a column thermostat and an automatic sample injector with a 100 μL loop. A personal computer equipped with an Agilent ChemStation program for HPLC was used to process chromatographic data. A reversed-phase VP-ODS C18 column (250 mm × 4.6 mm i.d., particle size 5 μm) (Shimadzu, Japan) was used for analysis of two triazine herbicides at 25 °C. The mobile phase was obtained with acetonitrile/water (70/30, v/v), and the flow rate, the injection volume and detection wavelength was $0.5\,mL\,min^{-1}$, 100 μL and 223 nm, respectively.

Preparation of bamboo charcoal packed cartridge was performed by modifying an Agilent AccuBond SPE ENV PS DVB cartridge (1000 mg, 6 mL, polypropylene), which was obtained from Agilent Technologies, USA. After the PS-DVB packing was removed, 1.0 g bamboo charcoal, which had been pretreated, was packed in the SPE cartridge. The polypropylene upper frit was reset at the upper end of the cartridge to hold the bamboo charcoal packing in place. Then the outlet tip of the cartridge was connected to a SHB-III vacuum pump (Great wall scientific and trade Co. Ltd., Zhengzhou, Henan), and the inlet end of cartridge was connected to PTFE suction tube whose other end was inserted into sample solution. In order to reduce the interferences of organic contaminants, the entire SPE assembly needed to be washed with 50 mL methanol and enough purified water before the first use.

2.3. Solid-phase extraction

The cartridge packed with bamboo charcoal was pretreated by washing with 2 mL acetonitrile and 10 mL purified water prior to each SPE procedure. Then 100 mL purified water sample spiked with two compounds was passed through the pre-conditioned cartridge at the optimum flow rate. After the sample solution had passed through, the cartridge was washed with 10 mL purified water to remove co-adsorbed matrix materials from the cartridge. Then the bamboo charcoal column was dried by negative pressure for 10 min. Subsequently the analytes retained on the SPE cartridge were eluted with 10 mL acetonitrile. In order to simplify the SPE procedure, further concentration of extract was not performed. Finally, the extract was then analyzed by HPLC-UV with an injection of 100 μL.

2.4. Water samples

In this experiment, two real world environmental water samples, tap water and well water, were used for evaluating the feasibility of the developed method. Tap water was collected from our lab. Well water sample was collected from Baotuquan of Jinan, Shandong Province. Before the environmental water samples were used, they were filtered through 0.45 μm micropore membranes and stored in brown glass bottoms at 4 °C, respectively.