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Graphene based solid phase extraction combined with ultra high performance liquid chromatography–tandem mass spectrometry for carbamate pesticides analysis in environmental water samples

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ABSTRACT

In this paper, graphene, a new sorbent material, was synthesized and used for solid-phase extraction (SPE) of the six carbamate pesticides (pirimicarb, baygon, carbaryl, isoprocarb, baycarb and diethofencarb) in environmental water samples. The target analytes can be extracted on the graphene-packed SPE cartridge, and then eluted with acetone. The eluate was collected and dried by high purity nitrogen gas at room temperature. 1 mL of 20% (v/v) acetonitrile aqueous solution was used to redissolve the residue. The final sample solution was analyzed by ultra performance liquid chromatography-tandem quadrupole mass spectrometry (UPLC–MS/MS) system. Under optimum conditions, good linearity was obtained for the carbamates with correlation coefficient in the range of 0.9992–0.9998. The limits of detection ($S/N = 3$) for the six carbamate pesticides were in the range of 0.5–6.9 ng L^{-1}. Relative standard deviations (RSD) for five replicate determinations were below 5.54%. RSD values for cartridge-to-cartridge precision ($n = 7$) were in the range of 1.27–8.13%. After proper regeneration, the graphene-packed SPE cartridge could be re-used over 100 times for standard solution without significant loss of performance. The enrichment factors for the target analytes were in the range of 34.2–51.7. The established method has been successfully applied to the determination of carbamate pesticide residues in environmental water samples such as river water, well water and lake water.

1. Introduction

As less-toxic alternatives to organophosphorus and organochlorine classes, carbamates, composed of the ester of carbamic acid with various substituents, are widely used in agricultural production as pesticides [1,2]. Although carbamates can disintegrate to some extent, they have been found frequently remaining in fruit, vegetables and crops as a result of excessive use [3]. Carbamate pesticides may also enter into the environmental water systems through various paths, including spraying, soil seepage, storage and the discharge of waste water, leading to possible contamination of the environmental water [4,5]. As inhibitors of acetylcholinesterase, carbamate pesticides could affect nerve impulse transmission, inducing dramatic toxicological effects in human beings. Moreover, carbamates and their metabolites are suspected to be carcinogens and mutagens [6]. So carbamate pesticides are included on the priority list issued by the United States Environmental Protection Agency (EPA) [7].

Therefore, the monitoring of the carbamate residue levels in various environmental water systems is of special concern to human health and environmental safety. The European Union Directive on drinking water quality (98/83/EC) established a maximum allowed concentration of 0.1 μg L^{-1} for each individual pesticide and 0.5 μg L^{-1} for total pesticides [8]. In this sense, reliable, sensitive and rapid analytical methods are urgently needed for the determination of carbamate pesticides at trace levels.

Different techniques have been employed for the determination of carbamate pesticides in water and the most commonly preferred methods are liquid chromatography (LC) [9–11] and gas chromatography (GC) [12] coupled to a large number of detectors. As the thermolability of carbamate pesticides may lead to difficulty in direct GC analysis, carbamate pesticides are usually derivatized on-line [13] or off-line [14] for GC analysis. In this case, some authors do not recommend the use of GC for the analysis of carbamate pesticides and consider LC to be the most convenient technique [15]. As the carbamate pesticides are usually found

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at trace concentration levels, it is necessary to carry out preconcentration and/or cleanup steps prior to instrumental analysis. Various sample preparation techniques have been employed for the extraction of carbamates from water sample, such as liquid–liquid extraction (LLE) [16], solid phase extraction (SPE) [17], solid-phase microextraction (SPME) [18], hollow fiber liquid-phase microextraction (HF-LPME) [10], single-drop microextraction (SDME) [19] and dispersive liquid–liquid microextraction (DLLME) [20]. SPE as a technique well known for its large enrichment capacity is presently the most extended method for the preconcentration of carbamate pesticide residues from water samples. In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain good recovery and high enrichment factor [21,22]. Octadecyl-bonded silica [23], polymeric sorbent [24], and mixed-mode sorbent [25] have already been used for the SPE of carbamate pesticides from water samples.

In recent years, various carbon-based materials have been adopted as SPE adsorbents because of their specific properties and high stability. Graphene, a new class of carbon nanomaterial, has sparked much interest because of its remarkable mechanical, thermal and electronic properties since it was discovered by Geim in 2004 [26,27]. With a two dimensional honeycomb lattice composed of carbon atoms, graphene possesses an ultra-high specific surface area (theoretical value 2630 $m^2 g^{-1}$) [28], and both sides of the planar sheets are available for molecule adsorption [29,30]. Besides, as graphene is an electron-rich, hydrophobic nanomaterial with large specific area and π–π electrostatic stacking property [31,32], it has been served as an extraordinarily wonderful adsorbent or extraction material [33]. Nowadays, graphene and graphene-based materials have been used as adsorbents for the extraction and preconcentration of chlorophenols [34], glutathione [35], sulfonamide antibiotics [36], phthalate acid esters [37], organophosphate pesticides [38], heavy metals [39], polycyclic aromatic hydrocarbons [40], macrolides [41] and malachite green [42]. Amine modified graphene has been used to remove fatty acids and other interfering substances for the analysis of pesticides in oil crops [43].

In this paper, the performance of graphene-packed SPE cartridge for the extraction of carbamate pesticides from water samples prior to UPLC–MS/MS analysis was first demonstrated. The six targeted carbamate pesticides are pirimicarb, baygon, carbaryl, isoprocarb, baycarb and diethofencarb, their chemical structures are shown in Fig. 1. These compounds have benzyl, naphthyl or pyrimidyl in their structures, so they can exhibit strong π-stacking interaction with the large delocalized π-electron system of graphene, to be selectively adsorbed on graphene. The parameters influencing the extraction efficiency were investigated, including the type and volume of eluent solvent, the pH and volume of sample solution. For the efficient separation and quantification of the six carbamates, the UPLC and MS/MS conditions were optimized. The established method was validated and cartridge-to-cartridge precision was evaluated. The performance of graphene-packed SPE cartridge was compared with conventional sorbents such as C_{18} and graphitized carbon black. Finally, the proposed method was applied to the determination of the six carbamate pesticide residues in river water, lake water and well water samples.

2. Experimental

2.1. Chemicals and materials

Pirimicarb (99.2%), diethofencarb (99.5%), baygon (99.5%), isoprocarb (99.2%), carbaryl (99.5%) and baycarb (99.5%) were purchased from Dikma technologies Co., Ltd. (Beijing, China). The standard stock solutions of carbamates were prepared in dark brown flask with methanol as solvent and stored in the dark at −18 °C. The standard working solution was freshly prepared by diluting the stock solution with water. Graphite powder (99%) and hydrazine hydrate (50%) were purchased from J&K technology Co., Ltd. (Beijing, China). $KMnO_4$, P_2O_5, $K_2S_2O_8$, H_2O_2 (30%) and concentrated H_2SO_4 (95–98%) were of analytical grade and were purchased from Huaxin Chemicals Co., Ltd. (Baoding, China). Acetontrile, formic acid and methanol were of HPLC grade and were purchased from MREDA technologies Co., Ltd. (Beijing, China). Experimental water was doubly distilled de-ioned water.

The empty SPE cartridges (3 mL) and SPE frits were purchased from Dikma technologies Co., Ltd. (Beijing, China). AGT Cleanert ODS C_{18} cartridges were purchased from Agela Techonologies INC. (Delaware, USA). VARIAN Bond Elut PRS cartridges were purchased from Varian Co. (USA). Envi-carb graphitized carbon black cartridges were purchased from Supelco Co. (USA).

2.2. Instrumentation

Chromatographic separation was performed on an ACQUITY™ Ultra Performance Liquid Chromatography system (Waters, Milford, MA, USA), consisting of a binary solvent delivery system and an autosampler. MS/MS detection was performed on a Xevo® TQ tandem quadrupole mass spectrometer (Waters, USA) equipped with an electrospray ionization (ESI) source. Data were acquired and processed with MassLynx V4.1 software.

JEM-100SX Transmission Electron Microscope (TEM) (Jeol Ltd, Japan), JEM-7500F Scanning Electron Microscope (SEM) (Jeol Ltd, Japan) and TU-1901 UV–vis spectrometer (Persee, China) were used to characterize the lab-produced graphene. The SPE experiments were performed on an HSE series solid-phase extraction device with a vacuum pump (Tianjin HengAo technology development Co., Ltd., Tianjin, China). MTN-2800D pressure blowing concentrator was purchased from Auto Science Co., Ltd. (Tianjin, China).

2.3. Chromatographic conditions

The chromatographic separation was performed on an ACQUITY UPLC® BEH C_{18} column (2.1 × 100 mm i.d., 1.7 μm, Waters, made in Ireland) preceded by a BEH C_{18} VanGuard™ pre-column (2.1 × 5 mm i.d., 1.7 μm, Waters, made in Ireland). The mobile phase consisted of (A) 0.1% formic acid solution and (B) acetonitrile. The eluting conditions were as follows: 0–4 min, linear gradient from 30% to 40% B; 4–6 min, linear gradient from 40% to 45% B; 6–6.5 min, linear gradient from 45% to 90% B; 6.5–6.6 min, the composition of B dropped from 90% to 30%; 6.6–8.0 min, the composition of B was kept at 30%. The flow rate was 0.4 mL min^{-1}. The strong wash volume was 200 μL (90% acetonitrile, 0.1‰ formic acid) and the weak wash volume was 600 μL (10% acetonitrile, 0.1‰ formic acid). The column temperature and autosampler temperature were maintained at 40 °C and 15 °C, respectively. The injection volume was 10 μL.

2.4. Mass spectrometric conditions

Mass spectrometry was performed on a Waters Xevo® TQ tandem quadrupole mass spectrometer equipped with electrospray ionization (ESI) source. The conditions of ESI source were as follows: Source temperature 150 °C; Desolvation gas temperature, 550 °C; Desolvation gas (N_2) flow rate, 850 L h^{-1}; Cone gas (N_2) flow rate, 50 L h^{-1}; Capillary voltage, 4.00 kV; Collision gas (Ar) flow rate, 0.15 mL min^{-1}. All the six compounds were analyzed in positive ESI mode and multiple-reaction monitoring (MRM) mode was selected for quantification.