



The simultaneous determination of isoproturon and carbendazim pesticides by single drop analysis using a graphene-based electrochemical sensor



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ABSTRACT

The simultaneous determination of two pesticides, namely isoproturon and carbendazim, by single drop analysis using a graphene-based electrochemical sensor with square wave stripping voltammetry was developed. A 60 μ L aliquot of the test sample was applied onto the sensor and analyzed, where clear electro-oxidation peaks from the isoproturon and carbendazim were detected. After the assay conditions were optimized by univariate analysis of the amount of graphene, type and concentration of supporting electrolyte, applied sample volume, accumulation potential and time, square wave frequency, step potential and amplitude, then the analytical characteristics were then evaluated. The oxidation peak currents varied linearly for concentrations over 0.02–10.0 mg/L ($R^2 = 0.9991$) for isoproturon and 0.50–10.0 mg/L for carbendazim ($R^2 = 0.9990$). The detection limits ($3S_b/S$) were 0.02 and 0.11 mg/L for isoproturon and carbendazim, respectively. The proposed method could be applied to determine the isoproturon and carbendazim concentrations in water, soil and vegetable samples, where the recoveries of the spiked samples were acceptable (81.4–107%) and the results were statistically similar to those obtained from the standard HPLC–UV method. Therefore, the proposed method showed a great promise as an inexpensive and simple sensor, with additionally a shorter analysis time.

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1. Introduction

Pesticides are a group of chemicals that are specifically developed and produced for use in the control of agricultural and public health pests. However, their extensive use in agriculture, which can lead to an accumulation of pesticide residues that can impose a serious risk to human health and the environment worldwide. Thailand is an agricultural country where pesticides are increasingly used for the protection of a large variety of crops, such as rice, fruits, and vegetables. Consequentially, pesticide residues may be widely distributed and so enter the food chain, as well as gain access into the aqueous environment through runoff and leaching from the soil into the ground and surface waters. Therefore, the development of simple, portable, sensitive, selective, and green analysis methods for the rapid and precise detection of pesticide residues in environmental samples has become increasingly important for homeland security and health protection.

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Traditional methods of analysis, such as ultraviolet spectroscopy [1,2], capillary electrophoresis [3,4], spectrophotometry [5], gas chromatography [6,7], and liquid chromatography [8,9], have been widely used for the determination of pesticides. Routinely, high performance liquid chromatography (HPLC) [10–12] is the main analytical technique for the determination of pesticides. However, this method has a number of disadvantages, including the requirement for complicated non-portable instruments, skilled operating technicians, long analysis times, complicated sample pretreatments and the use of toxic organic solvents, all of which limit the application primarily to laboratory settings and prevent its use for rapid analysis under field conditions. Quantitative detection of some pesticides using electrochemical biosensors [13–16] that are based on specific enzyme activities have emerged in the past few years as the most promising alternatives to detect pesticides. However, these methods suffer from a relatively poor stability and reproducibility, and require extensive pre-treatment steps with long analysis times. Together with their high cost these drawbacks make them unsuitable for routine or high throughput analyses. To overcome this problem, a non-enzymatic sensor based upon

stripping voltammetric analysis of pesticides appears to be an alternative approach [17–21].

Two interesting pesticides to determine in environmental samples are isoproturon and carbendazim compounds due to their effects on humans, animals and plants. Isoproturon, one of the most commercially significant agricultural herbicides, mainly enters the environment during its application to the soil before plants emerge and also to soils around growing crops. This herbicide has been classified as very toxic to aquatic organisms and is mobile in the soil [22]. Carbendazim is a benzimidazole based fungicide that has extensive applications in agriculture to protect crop plants from pathogenic fungi and to help eradicate or reduce pathogenic fungi population levels locally, and so has an important role in plant disease control. Moreover, isoproturon and carbendazim are hazardous substances controlled by the Department of Agriculture, Ministry of Agricultural and Cooperatives, Thailand. A stripping voltammetric-based method for the determination of isoproturon and carbendazim has been reported using various electrodes; a wall-jet glassy carbon electrode (GCE) in the flow stream [17], clay-modified GCE in the presence and in the absence of cetyltrimethylammonium bromide (CTAB) surfactant [23,24], a polypyrrole modified GCE [25], and multiwalled carbon nanotube (MWCNT) modified GCE [26,27]. Other research has presented carbendazim quantification by voltammetry using various modified electrodes, such as MWCNT/polymeric methyl red modified-GCE [28], and cyclodextrin/graphene hybrid nanosheet modified GCE [29]. However, these methods have only been applied for the determination of individual compounds rather than for their simultaneous analysis. The use of the above GCEs or modified GCEs is relatively expensive, they are difficult to machine and require laborious electrode pre-treatment/polishing steps, are time-consuming and require several steps of electrode modification. A boron-doped diamond (BDD) electrode has also been proposed for the determination of carbendazim and fenamiphos in natural waters by square-wave voltammetry [30]. Nevertheless, a BDD electrode is rather expensive. Furthermore, the aforementioned stripping voltammetric determination of isoproturon and carbendazim was performed in a conventional electrochemical cell that requires a large sample and reagent volume.

In recent years, screen-printed three-electrode sensors challenge the use of conventional electrodes. This is due to their low cost, disposability, portability, ease of fabrication and modification with various materials, flexibility in design as well as commercial availability. The screen-printed sensors can be used for the rapid and sensitive analysis of many target analytes. They can be considered as a disposable electrochemical cell onto which the sample droplet is placed and then adheres to the sensor by its surface tension. Thus, no wall is required to be built to keep back the solution and prevent outpouring. Therefore, they are highly suitable for working with microvolumes and decentralized assays [31]. The coupling of disposable screen-printed sensors with stripping voltammetric techniques is more favorable than conventional stripping analysis because the procedures are greatly simplified [32].

Graphene is a single layer of sp^2 -hybridized carbon atoms packed into a honeycomb two-dimensional sheet. One of the promising applications of graphene is in electrochemical sensing because of its high electrical conductivity and large surface area that can effectively promote the electron transfer between the target molecule and the electrode. Therefore, graphene was selected as an electrode modifier. Encouragingly, the combination of the graphene-based screen-printed sensor and square wave stripping voltammetry may open up new opportunities for a fast, simple, and low-cost electrochemical method for the simultaneous determination of isoproturon and carbendazim, in environmental water or soil samples, and in harvested food.

In this work, a rapid, simple and low-cost method for the simultaneous quantification of isoproturon and carbendazim by square wave stripping voltammetry using disposable graphene-based screen-printed sensors was developed for the first time. There is no requirement to use a conventional cell because the low-cost graphene-based sensor was used as an electrochemical cell with three integrated electrodes. Only a single 60 μ L drop of the sample solution is required to be dispensed onto the surface of the sensor for each stripping voltammetric measurement. The fabrication of the graphene-based sensor, optimization of the experimental conditions, analytical performance of the method, and its application to real samples are presented in the following sections.

2. Experimental

2.1. Chemicals and reagents

Standard solutions of isoproturon and carbendazim were prepared fresh each day by appropriate dilution of the stock standard solutions of isoproturon (HPLC grade, 99.9%, Sigma–Aldrich, Germany) and carbendazim (HPLC grade, 99.2%, Sigma–Aldrich, Germany) with ethanol (Emsure[®], Merck, Germany). A 1 M perchloric acid (HClO_4) solution, which served as a supporting electrolyte, was prepared by dilution of concentrated HClO_4 (analytical grade, 70–72%, 1.68 g/mL, Merck, Germany) with Milli-Q water (resistivity $\geq 18.2 \text{ M}\Omega/\text{cm}$), obtained from a Milli-Q Ultrapure Water Purification System (Millipore, USA).

The electrochemical sensors were in-house screen-printed (Section 2.3) using carbon ink (Electrodag PF-407C, Acheson, USA), silver ink (silver/silver chloride paste 70/30, Gwent, UK), graphite (<20 μm , Sigma–Aldrich, Switzerland), and graphene (SkySpring Nanomaterials, USA). Diethylene glycol monobutyl ether (Fluka, UK) and 2-butoxyethyl acetate (Sigma–Aldrich, Germany) were used as solvents for the modified carbon ink.

2.2. Apparatus

Voltammetric measurements were performed with a PalmSens potentiostat (Palm Instruments BV, The Netherlands) controlled by the PSTrace program and a personal computer. The graphene-based electrochemical sensor was comprised of a three-electrode configuration with the graphene-modified carbon electrode as the working electrode, a carbon counter electrode and a silver/silver chloride reference electrode. The electrochemical experiments were housed in a Faraday cage to prevent electrical noise. The scanning electron microscopic (SEM) images of the surface of the working electrodes were taken using a scanning electron microscope (JSM-5410LV, JEOL, Japan).

2.3. Fabrication of the graphene-based electrochemical sensor

The graphene-based electrochemical sensor with the three integrated electrodes (Fig. 1) was fabricated in three printing steps. Firstly, the silver ink was printed through the mesh onto the PVC substrates to form the reference electrode and connector, and then dried at 55 $^\circ\text{C}$ for 1 h. Secondly, the homogenized mixture of 1.0 g carbon ink, 0.2 g graphite powder and 20 drops of 1:1 (v/v) diethylene glycol monobutyl ether: 2-butoxyethyl acetate was printed onto the counter electrode position and dried at 55 $^\circ\text{C}$ for 1 h. Thirdly, 10.7 mg graphene was dispersed into 25 mL ethanol to form a homogenous dispersion under ultrasonication for 2 h, dried in an oven at 100 $^\circ\text{C}$ for 1 h, ground, and then mixed with 1.0 g carbon ink, 0.2 g graphite powder and 20 drops of the of above 1:1 (v/v) diethylene glycol monobutyl ether: 2-butoxyethyl acetate

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