Journal of Molecular Liquids 257 (2018) 112–120

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Selectivity and sensitivity enhanced green energy waste based indirect-μ-solid phase extraction of carbaryl supported by DFT and molecular docking studies

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ARTICLE INFO

*Article history:*
Received 11 September 2017
Received in revised form 7 February 2018
Accepted 21 February 2018
Available online xxxx

*Keywords:*
4,4′-Bis(4-aminophenoxy)benzophenone
Carbaryl
Spectrophotometry
Formulations
Waters and food grains

ABSTRACT

This work reports on a simple, selective, sensitive, rapid and robust spectrophotometric indirect-μ-solid phase extraction (ID-μ-SPE) of carbaryl with 4,4′-bis(4-aminophenoxy) benzophenone. These methods were performed in a 5 mL disposable syringe with green energy waste as a solid phase extractor in phosphate buffer medium (pH 8.5). The alkaline hydrolysis of carbaryl resulted 1-naphthol, which interacts with the diazotized 4,4′-bis (4-aminophenoxy) benzophenone to produce red colored product ($\lambda_{max}$:450 nm) or interacts with 4,4′-bis(4-aminophenoxy) benzophenone in the presence of an oxidizing agent, Se (IV) to give purple colored product ($\lambda_{max}$:545 nm). The obtained colored products were stable for 45 and 63 h respectively. The resulted colored products obey Beer's law in the range of 0.3–12.0 μg $mL^{-1}$ and 0.3–9.0 μg $mL^{-1}$ for both methods with detection limits ranging from 0.020–0.022 μg $mL^{-1}$. Additionally, the density functional theory calculations and molecular docking studies were performed to explore the stability profiles, intermolecular interactions and related electronic transitions for colored products to complement the experimental results. The developed methods are reliable and reproducible to detect carbaryl residues in its formulations, waters and food grains.

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## 1. Introduction

Carbaryl (1-naphthyl-*N*-methylcarbamate) pesticides are frequently sprayed onto rice cultivating crops due to its efficient action against several pests and to their broad-spectrum of biological activities [1]. It is also used to resist pests on vegetables, cotton, fruits and several different crops including domestic animals and poultries. However, pesticide residue is one of the burning issues for environmental pollution. In recent years farmers spray high dosage of pesticides to increase their yield, which is one of the threats to the environment and human health [2]. According to the European Union and China, the maximum residue limits of several carbamate pesticides in food grains are in the range of 0.02–1 μg $g^{-1}$ [3] and 0.01–0.1 μg $g^{-1}$ [4] respectively. Therefore, it is an urgent need to design a method or material to develop a facile, sensitive and reliable method to determine carbaryl residues in different technical grade and real samples.

The literature survey reports indicate that various analytical instruments such as GC–MS [5], HPLC [6] and LC-MS [7] have been found to determine carbaryl in various environmental, food and biological samples. However, the above mentioned techniques are highly sophisticated and require the specialist to operate the instruments. Recently, few researcher synthesized nanoparticles (NPs) for the determination of carbaryl pesticide residues [8], but suffers from few drawbacks such as usage of harmful chemicals, consumes more time to synthesize NPs and elaborate clean-up procedures (multi-steps) [9]. The crucial step in carbaryl analysis is sample preparation due to its determination in complex solid matrices. Different classical extraction methodologies such as Soxhlet and solvent extraction are adapted from few decades. However, these methods have some disadvantages including, consumption of time for sample preparation and requires more sample quantity for extraction or usage of environmentally harmful chemicals [10]. Song and co-workers have proposed a greener extraction route for the eight carbamate pesticides in rice samples. This method was based on the

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https://doi.org/10.1016/j.molliq.2018.02.099
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microwave assisted water steam extraction on a $C_{18}$ solid phase extraction cartridge with satisfactory results, but the $C_{18}$ SPE cartridge is commercial and highly expensive [11]. Colorimetry and spectrophotometry are versatile, simple and familiar techniques used to determine carbaryl residues in different samples with a wide range of coupling agents [12–18]. Bazrafshan and co-worker have developed a novel molecularly imprinted polymer for the selective microextraction of carbaryl from water samples [19]. Sensitive electrochemical biosensors were developed to detect carbaryl in water samples. These methods were based on the immobilization of acetylcholinesterase on the glassy carbon electrode modified with graphene oxide [20] multiwalled carbon nanotubes/graphene oxide nanorods [21] and Prussian blue (PB)–chitosan (CHIT) hybrid film [22]. A colorimetric sensor was designed for the determination of carbaryl with *p*-amino benzenesulfonic acid functionalized gold nanoparticles using a zeta potential assays [23]. An electrochemical analysis was carried out on the carbaryl analysis in fruit samples using glassy carbon electrode modified with graphene oxide-ionic liquid composite [24]. A high-resolution mass spectrometric technique was developed based on the change of fluorescence spectra of complexes before/after binding with $Eu^{3+}$, diallyl phthalate, and carbaryl. The detection limit of the method was $9.6 \times 10^{-9}$ M [25].

In view of its extensive applications as a pest controlling agent, it is highly recommended to develop a cost-effective, consistent and trustworthy method to assess the quality of insecticide in its formulations and real samples as well. Therefore, we have successfully synthesized a new reagent, 4,4′-bis(4-aminophenoxy) benzophenone for the sensitive spectrophotometric indirect-$\mu$-solid phase extraction (ID-$\mu$-SPE). These methods were based on the interaction of hydrolyzed product (1-naphthol) with a diazotized reagent or with 4,4′-bis(4-aminophenoxy) benzophenone in the presence of the oxidizing agent (Se(IV)). These methods have improved benefits of reproducibility, selectivity and sensitivity than the methods already reported in the literature [12,13,15–17]. The DFT and the transition state modelling studies revealed that the 1-naphthol interacted strongly in the case of oxidative coupling method suggesting the feasibility to form a stable colored product.

## 2. Experimental section

### 2.1.1. Instrumentation

A UV–vis spectrophotometer, model U 3400 equipped with 10 mm stopped quartz cells and pH meter, model Li-129 (supplied by Elico Pvt. Ltd., Hyderabad, India) was employed in this study. A HITACHI, S3000H Scanning Electron Microscopy (SEM) was used to characterize the surface morphology of green energy waste.

### 2.1.2. Chemicals and reagents

In the present study, analytical grade chemicals, reagents, and double-distilled water were used. 5% and 10% wettable carbaryl pesticide formulations (technical grade) samples were obtained from Bayer India Ltd., India. 4,4′-dichlorodiphenyl sulfone, 4-aminophenol, anhydrous potassium carbonate, sodium hydroxide, methanol, sodium nitrite, sodium selenite, acetone, and chloroform were purchased from SD fine Chemicals, India. 3.0% sodium hydroxide, 0.3% sodium nitrate, 0.1% sodium selenite solutions were prepared freshly and stored in the refrigerator at 4 °C. 5 mL of disposal syringe (acts as an ID-$\mu$-SPE device) was purchased from DORA group of companies Ltd., India.

A 1.0 mg $mL^{-1}$ technical grade carbaryl stock (95.5%) solution was prepared by weighing 104.69 g of carbaryl in 10 mL of methanol and diluted to 100 mL in a volumetric flask. Then after, 10 mL of this solution was subsequently diluted to 100 mL methanol to prepare working solution. The stock solution of carbaryl was refrigerated at 4 °C. 3.0% 4,4′-bis (4-aminophenoxy) benzophenone (BAPB), 3.0% sodium hydroxide and 0.3% sodium nitrate solutions were prepared by weighing the appropriate amounts and dissolved in double-distilled water. Phosphate buffer (pH 8.5) was prepared by adding required quantity of concentrated sulphuric acid to monopotassium dihydrogen phosphate in 500 mL volumetric flask.

### 2.1.3. Step-wise preparation of 4,4′-bis(4-aminophenoxy) benzophenone (BAPB)

The synthesis of 4,4′-bis(4-aminophenoxy) benzophenone (BAPB) involves the following steps [26]:

Step 1: To the dry and clean three-neck round bottom flask fitted with dropping funnel and Dean-Stark trap.

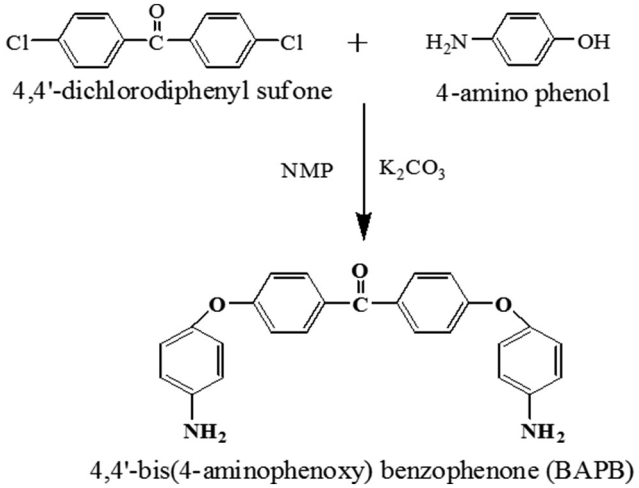
Step 2: Then after, 4.50 g of 4,4′-dichlorodiphenyl sulfone, 2.15 g of 4-aminophenol and 4.0 g of anhydrous potassium carbonate and 10 mL of 1-methyl-2-pyrrolidone were added to the flask under the flow of nitrogen gas.

Step 3: Later, the mixture was stirred vigorously at 1000 rpm and heated at 140 °C. 10 mL of toluene was taken into dropping funnel and added dropwise for 3 h. The solvents (water and toluene) were evaporated and trapped into the Dean-Stark trap. Further, the reaction temperature was increased to 180 °C and allowed to react for 18 h to complete the reaction.

Step 4: The reaction mixture was cooled to ambient temperature. Then 50 mL of acetone was used to wash the reaction mixture. The dark brown colored solid product was filtered and further subjected to washing with 30 mL of acetone. The obtained product was re-dissolved in double-distilled water and acidified with concentrated hydrochloric acid as illustrated in Scheme 1. Finally, the obtained solid product was filtered and washed successively with double-distilled water and methanol. The yellow colored solid product (yield: 72%) was dried at 130 °C for 2 h and stored in a desiccator.

### 2.1.4. Procurement and composition of green energy waste

In this study, green energy waste was used as a solid phase extraction substrate. The green energy waste resulted from esterification process of Jatropha seeds. This untreated waste is lethal due to the methanol concentration. So, dumping of such residues is the biggest challenge for the scientists due to their impact on the environment. Nowadays there is a demand for clean energy, and therefore bioenergy sector is expanding. The reuse of the wastes for different research aspects may possibly lead to the improvement of some cost-effective technologies. The green energy waste was mainly procured from Green Energy Development Centre, Feng Chia University, Taichung, Taiwan (ROC). It was washed, soaked in double-distilled water for overnight and washed 3–4 times to reduce the methanol concentration. Finally, the waste was oven dried at 105 °C to remove the total moisture and then ground into powder. The physical features of green energy waste are given in Table 1 as suggested in previously reported literature [27].




**Scheme 1.** Synthesis of 4,4′-bis(4-aminophenoxy) benzophenone (BAPB).

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