



A novel application of carbon dots for colorimetric determination of fenitrothion insecticide based on the microextraction method



A. Larki

Department of Marine Chemistry, Faculty of Marine Science & Marine Science Research Institute, Khorramshahr University of Marine Science and Technology, Khorramshahr, Iran

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ABSTRACT

In this work, the intrinsic colorimetric property of carbon dots (CDs) was utilized for the determination of fenitrothion by applying dispersive liquid-liquid microextraction (DLLME) method. Label free CDs are extracted into carbon tetrachloride via assistance of trioctylmethylammonium chloride (Aliquat 336), which also acts as a disperser agent in this technique. The enriched CDs show an absorption signal at 365 nm, which increases in the presence of fenitrothion. The absorbance increase of CDs in organic phase was used as an analytical signal for the determination of fenitrothion. The synthesized CDs were characterized by UV-visible, fluorescence, Fourier transform infrared (FT-IR) and transmission electron microscopic (TEM). Under the optimized conditions, beer's law was obeyed in the range of 1.0–250.0 ng mL⁻¹ of fenitrothion with the limit of detection for fenitrothion was 0.2 ng mL⁻¹. The relative standard deviation for eight replicate measurements of fenitrothion at concentrations of 25 and 100 ng mL⁻¹ were calculated to be 1.5 and 3.7%, respectively. The proposed method was successfully applied in the determination of fenitrothion in water samples with satisfactory results.

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1. Introduction

Carbon dots (CDs) are the new class of carbon nanomaterials with extraordinary sizes less than 10 nm, which exhibit excitation wavelength-dependent photoluminescence properties based on their displaying size. Significantly, CDs have several advantages, such as excellent optical properties, favorable biocompatibility, water solubility, low toxicity, high chemical stability and simplicity of synthesis [1]. Therefore, CDs have been considered as a promising choice of light-emitting materials for colorimetric systems [2,3]. They have been widely used in bioimaging, improving medical imaging equipment and tiny light-emitting diodes, but have been rarely employed to fabricate chemical sensors [4,5].

Pesticides are widely used in agriculture and household in many countries to prevent and destroy pests. Organophosphorous are one group of pesticides, which are extensively applied as insecticides to increase the agricultural production. One famous member of this family is fenitrothion (FNT), Fig. 1, that is mainly used in agriculture for controlling chewing and sucking insects on rice, cereals, fruits, vegetables, stored grains, and cotton [6,7]. In addition, FNT controls various forest and agricultural pests and is sometimes used to support public health against some diseases such as malaria [8]. The residues of FNT in agriculture can contaminate canal waters as well as the aquatic organism and ultimately endanger human health through food chains. Therefore, it

is necessary to develop analytical methods to survey trace residue amount of FNT in environmental and biological systems for evaluation of the safety and possible risks to human health [9,10].

The most conventional methods for the determination of FNT are based on techniques, such as gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC-MS) [11–13], high-performance liquid chromatography (HPLC) [14,15] electrochemistry methods [16,17] and capillary electrophoresis (CE) [18]. Due to the low concentration of this pesticide and complex matrices, water samples are not directly analyzed using these techniques, so these methods require previous step before the analysis, known as sample preparation. Good sample preparation should be able to increase sensitivity, usually through preconcentration and removal of interfering species [19]. The most popular pretreatment methods are liquid-liquid extraction (LLE) and solid phase extraction (SPE). Although these methods show good extraction and preconcentration efficiency, SPE is time consuming and labor intensive and LLE requires large volumes of poisonous organic solvents [20–22].

Nowadays, various methods based on microextraction have been improved to overcome the disadvantage of the classical solvent extraction that involves the use of large volumes of organic solvents and long extraction times. One of the most common microextraction techniques is dispersive liquid-liquid microextraction (DLLME), which was introduced since 2006 and successfully applied to various analytes in different samples [23–28]. In DLLME method, a mixture of extraction solvent (immiscible solvent) and dispersive solvent (miscible solvent) is injected rapidly into aqueous solution of analyte. Then, a stable cloudy

E-mail addresses: arash_larki@yahoo.com, a.larki@kmsu.ac.ir.

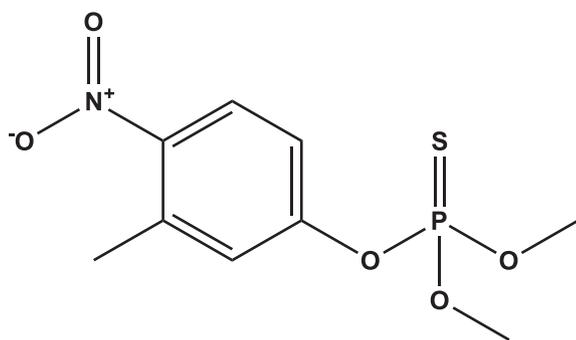


Fig. 1. Chemical structure of fenitrothion.

solution is formed consisting small droplets of the extraction solvent dispersed into the aqueous solution resulting in a large increase in contact area between the two phases. Hence, the analytes are easily transferred into the extraction phase. After centrifugation, the sedimented phase is settled at the bottom of the conical test tube. Some of its remarkable advantages of this technique are simplicity of operation, rapidity, low consumption of solvents and sample, high recovery and high enrichment factor [29–32].

In this paper we report the first application of CDs in DLLME for the determination of FNT. Unmodified CDs can be easily extracted into organic phase and exhibit an intense absorption signal at 260 nm. However, in the presence of FNT, the absorbance signal of the enriched phase increases because of the interaction between the FNT and CDs at the colloidal interface of the nanoparticles. The increase in the absorbance of the CDs in organic phase is proportional to the concentration of FNT and this is used as an analytical signal for the determination of this pesticide. To the best of our knowledge this is the first application of DLLME of CDs.

2. Experimental

2.1. Apparatus

Recording the spectra and the absorbance measurements were made by a Jenway UV–vis spectrophotometer model 6320 (England) using quartz cells. The fluorescence spectra were recorded using a Spectrofluorometer (Leng Guang Industrial Co., Ltd. of Shanghai, China), and the excitation and emission bandwidths were both 10 nm. An infrared spectrum was obtained using a Fourier transform infrared spectrometer (Bomem FT-IR spectrophotometer, Canada) to identify the functional groups and chemical bonding of the materials. The TEM images were performed by a Zeiss-EM10C-80 KV transmission electron microscope (Germany). Metrohm 827 pH-meter (Switzerland) was used to measure pH with a combined glass electrode. A model BHG HERMLE centrifuge (Germany) was used for the phase separation.

2.2. Reagents

All chemicals were of analytical grade and double distilled water was used throughout.

A stock solution of fenitrothion ($200 \mu\text{g mL}^{-1}$, Sigma Aldrich, St. Louis, MO, USA) was prepared in ethanol. Working standard solutions were prepared daily by successive dilutions of this stock solution. 1.5% (w/v) solution of trioctylmethylammonium chloride (Merck, Darmstadt, Germany) was prepared by dissolving 0.15 g of trioctylmethylammonium chloride in carbon tetrachloride and diluting to 10 mL in a volumetric flask. pH adjustments were performed with $0.001\text{--}0.1 \text{ mol L}^{-1}$ HCl and NaOH (Merck) solutions.

2.3. C-dots preparation

In a typical preparation process, 3 mL of sodium hydroxide solution (5 M) was added drop wise in 50 mL of filtered sugar cane juice under stirring for 15 min. The mixture was subjected to sonication for 30 min till it becomes reddish brown in color. Afterward this solution was centrifuged for 15 min at 13,000 rpm, so large size and shape particle settled and upper clear solution (C-dots) was separated and stored for subsequent investigation [33].

2.4. DLLME procedure

An aliquot of standard solution of FNT, 1.0 mL of CDs solution (with 1:10 ratio) and 1.0 mL of Britton-Robinson buffer (pH 7.0) were transferred into a 10 mL volumetric flask, diluted to the mark with water and mixed. The resulting solution was transferred to a conical glass test tube and 180 μL of carbon tetrachloride containing trioctylmethylammonium chloride (1.5% (w/v)) was rapidly injected into the solution by a microsyringe and the mixture was shaken for several seconds manually. A cloudy solution which consisted of very fine droplets of CCl_4 dispersed into the aqueous sample was formed. The mixture was then centrifuged at 5000 rpm for 5 min, causing the dispersed fine droplets of the extraction phase to settle down in the bottom of the tube. The upper aqueous phase was eliminated and the enriched yellow CDs ($170 \pm 5 \mu\text{m}$) were removed using a microsyringe, placed into the quartz microcell and its absorbance was measured at 260 nm against the blank. A blank solution was also run under the same procedure without adding any FNT.

2.5. Preparation of samples

The environmental water samples, including the Karun River, Bahmanshir River and Persian Gulf (Khuzestan Province, Iran) were collected filtered using a filter paper (Whatman) and stored in the dark at 4°C . An aliquot of water samples were treated under the recommended DLLME procedure.

3. Results and discussion

3.1. Characterization of CDs

Carbon dots (CDs) were prepared from sugar cane juice by chemical method. CDs in aqueous solution were yellowish and transparent under daylight while showed obvious blue emission under UV light (365 nm) [33]. To investigate the synthesized CDs, the maximum excitation and emission spectra were recorded from 300 nm to 480 nm, and it was observed that with increase in the excitation wavelength caused the emission from CDs shifted to higher wavelengths accompanied with decreased fluorescence intensity. The dependence of excitation and emission is due to difference in the sizes of C-dots rather than presence of emissive traps in C-dots having similar sizes [1]. As can be seen in Fig. 2, (a) the fluorescence spectra of CDs exhibited an obvious peak around 400 nm and (b) UV–Visible spectra of CDs showed an intense peak at 260 nm. These signal intensities of CDs were increased after preconcentration by DLLME procedure and this phenomenon is directly dependent on CDs amount in aqueous solution. Whereas, the UV–Visible spectrophotometer is a simple, cheap and inexpensive instrument and furthermore it is present in all laboratories, the UV–Visible spectra of enriched CDs utilized and recorded in present study.

The morphology and particle size of CDs was investigated in aqueous solution (Fig. 3a) and after preconcentration by recommended DLLME method (Fig. 3b). Transmission electron microscopy (TEM) image of the C-dots shows that they are roughly spherical particles with a diameter of less than 5 nm.

For characterizing the surface groups and structure of synthesis CDs, the FTIR was employed. As shown in Fig. 4, the CDs exhibit peaks at

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