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New probe for fluorescence detection of *Azinphous ethyl*, *Malathion* and *Heptachlor* pesticides

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ABSTRACT

Luminescence quenching of long lived Eu(III)–Bathophenanthroline (Batho) probe of 1:2 stoichiometric ratio has been studied in acetonitrile in the presence of the pesticides *Azinphous ethyl* (P1), *Malathion* (P2) and *Heptachlor* (P3). The luminescence intensity of Eu(III)–$(Batho)_2$ probe decreases as the concentration of the pesticide increases. Direct methods for the determination of the pesticides under investigation have been developed using the luminescence quenching of Eu(III)–$(Batho)_2$ probe in solution. The detection limits were 0.68, 0.92 and 0.35 μM for P1, P2 and P3, respectively. Stern–Volmer studies at different temperatures indicate that collisional quenching dominates for *Azinphous ethyl*, *Malathion* and *Heptachlor*. The binding constants (K) and thermodynamic parameters (ΔS°, ΔH° and ΔG°) of the interaction of pesticides with the complex were evaluated.

1. Introduction

There are different routes of humans exposure to pesticides appeared in soil, water, air and food such as inhalation, swallowing and skin contact causing acute and chronic health problems for human [1]. Cancer, suppression of the immune system, chronic kidney diseases, endocrine disorders, sterility among males and females, neurological and behavioral disorders were attributed to chronic pesticide poisoning especially among children [2]. The extent of exposure to pesticide determined human health hazards. Misapplication of pesticides cause moderate human health hazards including mild headaches, flu, skin rashes, blurred vision and other neurological disorders while rare, but strict human health hazards include paralysis, blindness and even death [3]. Pesticide pollution into the environment also affects all kinds of lives such as birds, fish, domestic animals, livestock and wildlife [4]. Agricultural tracts consume a huge amount of pesticides, which release into the environment and come into contact with human [5]. The un-prescribed use of pesticides in inappropriate doses is disturbing the soil conditions and destroying the healthy pool of bio-control agents which presence with the vegetation. These agents are friendly for agriculture, which need to be cared and developed by reducing the use of chemicals in agriculture [6].

There is a constant need for the determination of pesticide content in the environment. A list containing species of pesticides, which are considered as a high risk to humans, are monitored by the European Union (EU). Thus, the monitoring of the concentrations of at least those priority species need for rapid, sensitive and versatile methods [7].

The chromatographic techniques, Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC) and Mass Spectrometry (MS) are sensitive and reliable methods to detect the pesticides, but they have some limitations for example: (a) complicated procedure, (b) time consuming treatments, (c) need of highly skills technicians, (d) inability to perform on field [8–14]. Newer techniques have been developed to improve the detection of pesticides, with more sensitive devices as electro analytical techniques, chemical and biosensors, spectroscopic techniques and flow injection analysis (FIA). Sometimes use of one or more method together proved successful in detecting a particular class of pesticide.

A considerable progress has been achieved for the development of fluorescent chemo-sensors for pesticides. These chemosensors have been demonstrated to be time-effective and easier.

The lanthanide cations luminescence offers several advantages with organic fluorescent molecules: sharp, distinctive emission bands allow for easy resolution between multiple lanthanide signals; long emission lifetimes (μs–ms), which make them suitable for detection measurements, and high resistance for bleaching so the experiments could repeat. Batho is one of organic fluorescent molecules used for estimation of trace impurities of heavy metals that reduce the quality of production in pharmacy, food industry, etc. [15,16]. Eu(III) complexes of Batho are used in the fabrication of electroluminescent (EL) devices [17,18].

This work describes the application of fluorescence for investigating the interactions of Eu(III)–$(Batho)_2$ with pesticides *Azinphous ethyl*, *Malathion* and *Heptachlor*, Fig. 1. It also includes the development of

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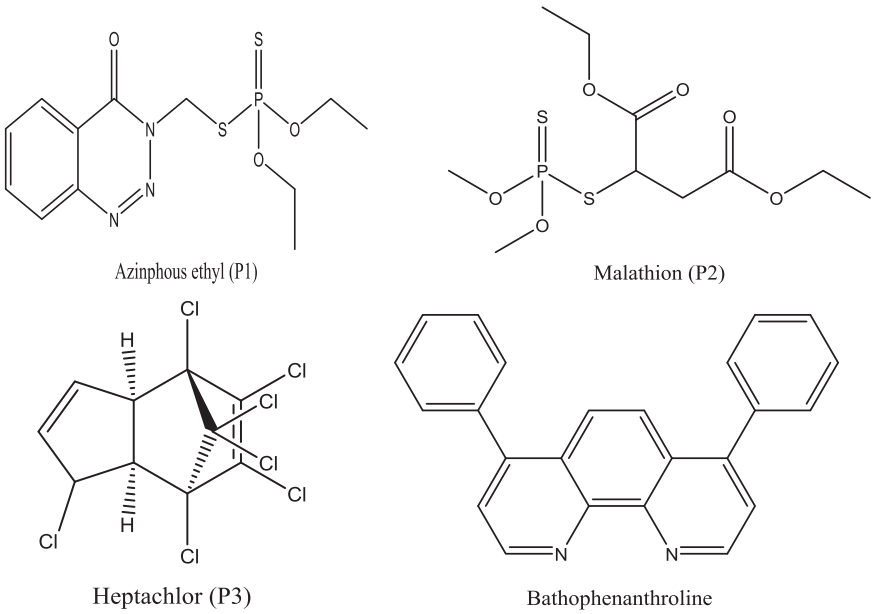

Fig. 1. Structure of pesticide included in the study and structure of bathophenanthroline.

the luminescence methods for detection of the three investigated pesticides.

2. Materials and methods

Europium chloride hexahydrate ($EuCl_3 \cdot 6H_2O$) was purchased from Sigma-Aldrich. Pesticides *Azinphous ethyl*, *Malathion* and *Heptachlor* were from Sigma-Aldrich. The structures of the studied pesticides are shown in Fig. 1. Batho was from Merck and all solvents used are of analytical grade quality from Sigma-Aldrich.

Europium stock solution was prepared by dissolving 37.3 mg of $EuCl_3 \cdot 6H_2O$ in 100 ml of ethanol to give a final concentration of 1×10^{-3} mol L^{-1}. For a stock solution of 1×10^{-3} mol L^{-1} of Batho 33.2 mg of solid ligand was dissolved in 100 ml ethanol. Stock solutions of 1×10^{-3} mol L^{-1} of pesticides were prepared by dissolving an appropriate amount in ethanol. The working solution of Eu (III), Batho and pesticides were prepared daily by dilution of the stock solutions in ethanol. Dilution of solutions were carried out by pipetting using a automatic pipette.

3-(2-Benzothiazolyl)-7-diethylamino-coumarin (Coumarin 6) from Sigma was dissolved in ethanol to obtain a solution for quantum yield measurements.

The luminescence spectra and intensities were monitored at the fixed analytical emission wavelength (λ_{em}=614 nm) of the complex in acetonitrile. Luminescence titrations were performed in a 1 cm quartz cuvette by successive addition of pesticides ($0.5–7 \times 10^{-6}$ M) to solutions of 1.0×10^{-6} M $EuCl_3 \cdot 6H_2O$ and 2×10^{-6} MM Batho. The titration data were analyzed according to the modified Stern–Volmer equation to investigate the types of interaction of Eu(III)–complex with the different pesticides. A 1:2 stoichiometry of Eu(III)–$(Batho)_2$ was used in all experiments. The analysis was done by using the decrease of luminescence intensity due to this effect as well as the quenching results from the interaction between the Eu(III)–$(Batho)_2$ probe and pesticides.

3. Experiments

3.1. Instruments

Luminescence measurements were carried out on a JASCO-FP6300 spectrofluorimeter equipped with a 150 W Xenon lamp source and quartz cells of 1 cm path length. The slit widths were 5 nm for both excitation and emission wavelength. All absorption spectra were performed on Shimadzu spectrophotometer equipped with quartz cells.

3.2. Determination of quantum yield

The quantum yield of Eu(III)–$(Batho)_2$ was determined in ethanol at concentration of 5 μM using 3-(2-benzothiazolyl)-7-diethylamino-coumarin (Coumarin 6) in ethanol by the following equation [19]:

$$Q_X = Q_R \frac{(A_R I_X n_X^2)}{(A_X I_R n_R^2)} \quad (1)$$

where Q_R is the quantum yield of the reference (0.78), A_R and A_X are absorbance of the reference (R) and Eu(III)–$(Batho)_2$ (X) at the excitation wavelength. I_R and I_X are the integrated areas under the corrected emission spectra of the reference and Eu(III)–$(Batho)_2$, n_R and n_X are the refractive indexes of the solutions of the reference and Eu(III)–$(Batho)_2$, respectively.

4. Results and discussion

4.1. Interaction of Batho with Eu(III)

The spectrum of Batho in acetonitrile shows a maximum absorption band at 272 nm and around 307 nm due to the $\pi \rightarrow \pi^*$ transition with extinction coefficient of 1.88×10^5 mol^{-1} cm^{-1} L. In addition of Eu(III) to Batho solution the absorbance enhanced, with red shift of about 11 nm indicating the formation of the complex as shown in Fig. 2. The molar absorbance for the Eu(III)–$(Batho)_2$ is about 2.15×10^5 mol^{-1} cm^{-1} L. The complex is stable under the condition of the study, as its absorption in acetonitrile at room temperature was not altered after weeks of monitoring.

In absence of fluorophore the characteristic fluorescence spectra of Eu(III) ions is too weak to be observed. By using Batho, the emission spectra of Eu(III) shows the characteristic band as a result of the intra-molecular energy transfer process between metal and ligand. The excitation maximum of Eu(III)–$(Batho)_2$ is at 290 nm. The luminescence spectrum of the Eu(III)–$(Batho)_2$ probe investigated in acetonitrile shows the characteristic emission bands for Eu(III) ion. The emission band centered at 614 nm ($^5D_0 \rightarrow {}^7F_2$) is