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Optical sensing of 3-phenoxybenzoic acid as a pyrethroid pesticides exposure marker by surface imprinting polymer capped on manganese-doped zinc sulfide quantum dots

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ABSTRACT

The present communication deals with the synthesis of luminescent Mn-doped ZnS quantum dots (QDs) anchored to surface imprinted polymer for the optical sensing of 3-phenoxy benzoic acid (3-PBA) in urine samples. The combination of sensing and surface functionalization not only improves the selectivity of the method, but also increases the optosensing ability of the material for non-phosphorescent substances. The developed material was utilized for the selective and sensitive detection of 3-PBA in urine samples. The proposed method shows good linearity with a regression coefficient (R^2) of 0.98. The limit of detection was found to be 0.117 μM. The method has an acceptable precision and accuracy which are found to be less than 8% and 80–90% respectively at three different concentrations. The quenching constant of quantum dot-molecular imprinted polymer was found to be 3.4 times higher to that of the quantum dot-non imprinted polymer (QD-NIP) as calculated by Stern–Volmer equation. The sensing method developed has shown immense utility to detect 3-PBA in complex biological samples like urine.

1. Introduction

In recent years, molecularly imprinting polymers (MIPs) have shown promising applications in analytical chemistry, and this synthesized MIPs will have selective binding sites for the template of interest. The selectivity mainly depends on the size and shape of the cavity and its rebinding interaction ability [1,2]. This MIPs have several advantages like simple to prepare, higher stability and affinity for the analyte recognition and cost-effective. Due to these advantages, MIPs have found applications for bioseparations, diagnostic assays, sensors and biocatalysts [3].

Optical sensing is found to be a straightforward method for the detection of analytes of interests, and it has attracted wide attention from the researchers. Quantum dots (QDs) as optical sensors have increased use for sensing applications because of their size-dependent optical properties, large surface to volume ratios and quantum size effects [4–8]. Advantages of QDs include high photo stability and photoluminescence efficiency, sharp emission profile and size-dependent emission wavelengths due to which they adopted for sensing of various compounds in different matrices [9,10]. Since sensing technology is entirely based on specificity, so modification of the luminescent QDs at its surface is very important for its applications in the analysis. Cadmium based quantum dots fabricated with silica have been used for optosensing of pyrethroids [11]. Surface modification of QDs by using a molecular imprinting technique paved a good approach for development of optical sensors. The MIP fabricated QD (QD-MIP) will provide the selectivity to the material due to presence of binding sites on the polymer matrix, which helps in the separation of analytes. The combination of selectivity of MIP with fluorescent properties of QDs provides newer applications for the detection of the non phosphorescent analyte as it will possess specific recognition ability and variable intensity to the analytes of interest [12,13]. Thus the surface modification of QDs of imprinted polymer leads to change in phosphorescence intensity when the target analyte is recognized by the material [14]. Among the luminescent materials, Mn and Cu doped ZnS are the widely used material in several fields such as photoluminescence materials, in color television, radar and electroluminescence materials [15–19]. There are reports available, which utilizes the advantages of phosphorescence of QD-MIP. Yan and co-workers developed a method to optosense the pentachlorophenol in water by utilizing the concept of

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phosphorescence quenching using Mn doped ZnS quantum dots, while Lin et al. applied this for the chemiluminescence detection of 4-nitrophenol in tap water [8]. Mn doped ZnS QDs fabricated with MIP was also used for the trinitrotoluene sensor through the fluorescence quenching as demonstrated by Gao et al [20]. To the best of our knowledge, no application has been reported for the detection of 3-phenoxybenzoic acid (3-PBA) in urine samples.

3-PBA is a non-specific and frequently detected metabolite of pyrethroids such as cypermethrin, deltamethrin, permethrin, cyhalothrin etc. and used as a general marker for the exposure to these pyrethroids. Besides its antiestrogenic activity, it is also considered as endocrine disruptor chemical [21–23]. The ill effects of pyrethroids and 3-PBA are massive ingestion include agitation, hypersensitivity, tremor, salivation, choreoathetosis and seizures [24–26]. There is strong evidence of its role in determining the exposure of pyrethroids in occupational workers [27]. Thus, it is necessary to detect and analyze 3-PBA so that the implications of pyrethroids on human health can be known. This will provoke its low usage, which, subsequently minimize the ill-effects.

3-PBA has been detected by an ELISA (Enzyme-linked immunosorbent assay) method [28] but it involves a tedious sample preparation. Several other methods have been reported in the analysis of pyrethroid metabolites. These include high-performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry (LC–MS) [29,30], gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) [31–34] and immunoassay based methods [35,36]. Although, these methods have an advantage to quantify 3-PBA in several matrices, but they are not compatible for on-field sensing and monitoring applications. In the present communication, an attempt has been made to form molecular recognition sites on the surface of Mn doped ZnS using the molecularly imprinted technique, which is capable of selective extraction of 3-PBA from complex biological matrices. The developed method is found to be simple, rapid and selective for the 3-PBA detection in urine samples.

2. Experimental

2.1. Chemicals and reagents

All the reagents used in the study were of analytical grade unless otherwise stated. Zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$), manganese (II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) (97% purity), tetraethyl orthosilicate ($\geqslant$99%) (TEOS), 3-Aminopropyl triethoxy silane ($\geqslant$98%) (APTES), 3-mercaptopropyl triethoxy silane (MPTS) and 3-phenoxybenzoic acid (3-PBA) were procured from Sigma Aldrich (St. Louis, MO, USA). All the solvents used were procured from Merck (Darmstadt, Germany) and Sd. Fine Pvt. Limited (Mumbai, India). Sodium sulfide ($Na_2S{\cdot}xH_2O$) purchased from Sd. Fine Pvt. Limited (Mumbai, India). Phosphate buffer saline (PBS) of 30 mM was prepared as a stock solution by addition of 30 mM of Na_2HPO_4 and 30 mM of NaH_2PO_4. The pH of the buffer solution was maintained by 30 mM H_3PO_4 and 0.1 M NaOH solutions. Fresh aqueous solutions in milli Q water of standards and samples were prepared during experiments.

2.2. Synthesis of MPTS capped Mn doped ZnS quantum dots

The MPTS capped Mn doped ZnS quantum dots were synthesized by following the earlier reported method with slight modification [10]. Briefly, to a three necked flask, $ZnSO_4$ (10 mmol), $MnCl_2$ (1 mmol), and 50 mL of water was added and the mixture was stirred under nitrogen at room temperature for 10 min. To this, 10 mL of aqueous solution containing Na_2S (10 mmol) was added drop wise and kept the mixture under stirring for 30 min. To this, MPTS (0.5 mmol) dissolved in 10 mL of ethanol was added, and the reaction was kept for 20 h on stirring at room temperature. To ensure the purity and crystalline, the synthesized material was thoroughly washed with ethanol and water to remove unreacted parts. The material was kept in the oven at 90 °C for drying, which leads to highly crystalline QD.

2.3. Synthesis of MIP capped Mn doped ZnS QDs

To a 50 mL flask, 10 mL alcoholic solution of 3-PBA (100 mg, template) and 250 μL of APTES (functional monomer) was added and stirred for 30 min. To the resultant mixture, 1 mL of TEOS (cross-linker) was added, and the mixture was kept stirring for 5 min. Then MPTS capped Mn doped ZnS QDs (400 mg) and 2 mL of 6% aqueous ammonia solution was added and stirred for 16 h. The non-imprinted polymer (NIP) was synthesized simultaneously without adding template. The resulting MIP and NIP were obtained after centrifugation and washed with ethanol followed by water and oven dried before use. The template was removed from QD-MIP (Quantum Dot-Molecularly Imprinted Polymer) through washing with methanol: acetic acid (9:1, *v*/*v*) several times. Finally, the particles were dried for further use.

2.4. Instrumentation

The size of the nanocrystal was observed using transmission electron microscopy (TEM, Tecnai-G2-SPIRIT FEI, Netherland). A drop of aqueous solution of QDs was placed on the copper grid to obtain images after sonication and coated with formvar. Absorbance, excitation and band gap energy were derived using a spectrophotometer, (SPECORD 210 PLUS, Analytik Jena, Germany). Fluorescence spectra of the QDs were obtained at an excitation and emission spectral wavelength of 330 and 590 nm, respectively (LS 55 photoluminescence spectrometer, Perkin Elmer, UK). The interactions of the functional group characterization of MPTS capped Mn:ZnS QDs and MIP modified QDs were performed using Fourier transformed infrared spectroscopy (FTIR) (Nicolet 6700, Thermo scientific, USA). The crystal lattice of the synthesized QD was obtained by using X-ray diffraction (XRD) using Cu target source (SEIFERT, Germany) at ACMS Lab, IIT Kanpur.

2.5. Photoluminescence study

Different concentrations of 3-PBA (0.15–60 μM) were prepared from stock solution. An aliquot of 2.5 mL of each concentration of 3-PBA and 2 mL of PBS buffer (pH 8) was mixed with 2.5 mL of Mn: ZnS QD-MIP solution (20 mg L^{-1}) and then the system was stabilised at rest for few minutes for interacting the analyte with QD-MIP. The complete dispersion was collected, and from this 3 mL volume of the mixture was transferred to a cuvette for the photoluminescence study. The same procedure was followed for the QD-NIP (Quantum Dot-Molecularly non-Imprinted polymer) interaction with the template (3-PBA) at the specified concentrations. The urine samples used in the study were spiked at given concentrations and were diluted 50 times with water prior to the analysis. The phosphorescence quenching was measured at an excitation wavelength of 330 nm by keeping the slit width of 15 nm and an emission filter at 515 nm.

2.6. Selectivity study

The selectivity of the synthesized QD-MIP was performed by taking 2, 5-dihydroxy benzoic acid (2,5-DHBA) at the concentrations of 0.15–60 μM using the same procedure described above. All other parameters of the analysis were same.