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Fiber optic profenofos sensor based on surface plasmon resonance technique and molecular imprinting

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ABSTRACT

A successful approach for the fabrication and characterization of an optical fiber sensor for the detection of profenofos based on surface plasmon resonance (SPR) and molecular imprinting is introduced. Molecular imprinting technology is used for the creation of three dimensional binding sites having complementary shape and size of the specific template molecule over a polymer for the recognition of the same. Binding of template molecule with molecularly imprinted polymer (MIP) layer results in the change in the dielectric nature of the sensing surface (polymer) and is identified by SPR technique. Spectral interrogation method is used for the characterization of the sensing probe. The operating profenofos concentration range of the sensor is from 10^{-4} to 10^{-1} μg/L. A red shift of 18.7 nm in resonance wavelength is recorded for this profenofos concentration range. The maximum sensitivity of the sensor is 12.7 nm/log (μg/L) at 10^{-4} μg/L profenofos concentration. Limit of detection (LOD) of the sensor is found to be 2.5×10^{-6} μg/L. Selectivity measurements predict the probe highly selective for the profenofos molecule. Besides high sensitivity due to SPR technique and selectivity due to molecular imprinting, proposed sensor has numerous other advantages like immunity to electromagnetic interference, fast response, low cost and capability of online monitoring and remote sensing of analyte due to the fabrication of the probe on optical fiber.

1. Introduction

Pesticides are the broad range of chemicals which are mainly used to kill or repel the pests on crops. These are widely used on vegetables, ornaments, fruits, grains, etc. and are characterized on the basis of functional groups present in their molecular structure (inorganic, organophosphorus, organochlorine, etc.) and on the basis of their biological activity on target species (herbicides, fungicides, insecticide, etc.) (Hoff and Zoonen, 1999; Hajslovaè et al., 1999). Organophosphorus pesticides (OPPs) are specifically used for controlling the large range of pests on the cotton, vegetables, rice, sugarcane, etc. Further, OPPs are responsible for the inhibition of the activity of nervous system enzyme acetylcholinesterase (AChE) which regulates the acetylcholine. AChE is an enzyme which digests the neurotransmitter acetylcholine by hydrolyzing it. Due to the very high catalytic activity of AChE, it hydrolyzes around 25,000 molecules of acetylcholine (ACh) per second once ACh comes in its domain. The hydrolytic process results in the recycling of the byproduct-choline produced to synthesize ACh again (Quinn, 1987). Thus, OPPs can cause injurious effects to the nervous system of humans even at low concentrations. Due to this, OPPs are also known as neurotoxins (Cremisini et al., 1995; Guerrieri et al., 2002). In addition, these are also eco-toxic to birds, aquatic organisms and bees (Laschi et al., 2007). Profenofos, o-(4-bromo 2-chlorophenyl)-o-ethyl-s-propyl phosphorothioate, is a type of OPP which is extensively used nowadays and therefore a rapid, highly sensitive and selective method is required for its detection. Numerous methods for profenofos detection have been reported in the literature. These methods are mainly based on chromatography, immunology etc. In the case of chromatography various sub-methods like gas chromatography–mass spectroscopy (GC–MS) (Chu et al., 2005; Frenich et al., 2007; Qu et al., 2010), gas chromatography-flame potentiometric detector (GC-FPD) (Li et al., 2007), gas chromatography-nitrogen phosphorus detector (GC-NPD) (Solé et al., 2000), high performance liquid chromatography (HPLC) (Cappielo et al., 2002) and high performance liquid chromatography–mass spectroscopy (HPLC–MS) (Kruve et al., 2008) are in use. However, above methods are quite sensitive and accurate but are time consuming, require expert handling and use expensive instruments. In the immunological methods one of the methods used is enzyme-linked immunosorbent assay (ELISA) (Nunes et al., 1998). Although this shows high sensitivity, selectivity and suitability for the analysis of a large number of samples within a very short time

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interval (Zeng et al., 2007) but the used biological materials are quite expensive. Other methods reported are quartz crystal microbalance (QCM) (Gao et al., 2012) and surface plasmon resonance configuration (Dong et al., 2012). These methods are fast and quite selective but are not useful for online monitoring and remote sensing and are quite expensive. Thus, a highly sensitive, selective, fast, low cost, having capability of online monitoring and remote sensing method for the detection of profenofos is required.

Molecular imprinting is a recently developed technique used to fabricate the tailor made recognition sites for a specific template molecule. This is carried out by freezing the template molecule into a polymer. Template molecule, functional monomer, initiator and cross linker are mixed into a solvent and left into appropriate environmental condition for polymerization. The template molecule is removed from the polymer after polymerization which causes the creation of three dimensional specific binding sites for the template molecule. Thus, the shape and size of binding sites on polymer are complementary to template molecule. This makes the molecular imprinting highly specific for template molecule (Haupt and Mosbach, 2000; Cheong et al., 2013). Molecularly imprinted polymers (MIP) are advantageous due to their easy synthesis steps, low cost and capability to be stable in harsh environment. When template molecule comes into the domain of binding sites, it recognizes the template molecule and binds due to covalent/non-covalent interactions. This causes the change in the dielectric property of the polymer (Verma and Gupta, 2013). SPR technique has the potential to detect the change in dielectric properties of any material over a gold/silver coated substrate. Due to its fast response, high sensitivity and label free detection of analytes SPR technique has been widely used for the development of various kinds of biosensors (Homola, 2003; Gupta and Verma, 2009). The technique can also be used to monitor the interaction between large molecules such as proteins, antigens, antibodies and also for the detection of the small molecules due to its high sensitivity. Numerous studies have been reported in the literature with the combination of surface plasmon resonance and molecular imprinting together for bio-sensing applications (Li et al., 2002; Shrivastav et al., 2015a). High sensitivity due to SPR technique and high specificity due to molecular imprinting make this combination quite advantageous.

In the present study, we report a surface plasmon resonance and molecular imprinting based fiber optic biosensor for the detection of profenofos. Sensing probe is fabricated by coating a thin film of silver layer over unclad core of a multimode fiber followed by the coating of MIP film having profenofos as template molecule. As discussed above, when profenofos molecule comes into vicinity of the polymer, it binds with the binding site and changes the refractive index of the polymer. This is recognized using surface plasmon resonance by observing the shift in resonance wavelength in spectral interrogation method. Control experiments have been performed for the verification of the role of molecular imprinting. To get the best performance of the sensor, the concentration of profenofos for the synthesis of MIP has been optimized. In addition, the performance of the sensor is checked for profenofos solutions of different pH values. To check the selectivity of the sensor, experiments are performed with different analytes of OPPs group and some other analytes. Limit of detection of the present sensor has been compared with the previously reported studies in the literature to check the novelty of the sensor.

2. Experimental

2.1. Reagents

Plastic clad silica (PCS) optical fiber having 600 μm core diameter and numerical aperture 0.4 was purchased from Fiberguide Industries. Profenofos, parathion, omethoate and trimethylopropane trimethacrylate (TRIM) were purchased from Sigma Aldrich Pvt. Ltd. Methacrylic acid (MAA) and tetracycline hydrochloride (TC) were purchased from CDH Bioscience Pvt. Ltd. Dimethyl sulfoxide (DMSO), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$), urea and glucose were procured from Merck India. Silver wire (99.99% pure) was purchased from a local vendor. Profenofos, MAA, TRIM and DMSO were used as template molecule, functional monomer, cross-linker and solvent, respectively, for the synthesis of MIP. Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$) were purchased for the preparation of phosphate buffer solutions. Parathion, omethoate, glucose, urea and tetracycline were used for the selectivity test of the probe. No further purification of chemicals was carried out for the experiments.

2.2. Apparatus

For the coating of Ag thin films over the core of the fiber HINDHIVAC coating unit (model: 12A4D) was used. Abbe refractometer having resolution of 0.001 was used to measure the refractive index of various solutions. To characterize optical fiber probes, a tungsten halogen lamp (model: AvaLight-HAL) was used. A spectrometer (model: Avaspec-3648) was used for recording the transmittance spectra. Both were purchased from AVANTES.

2.3. Fabrication of probe

The probes were fabricated in three steps. In the first step, a 40 nm thick Ag layer was coated over the unclad portion of the fiber. In the second step, the Ag coated probes were further coated with non-imprinted polymer (NIP/polymer with template molecule profenofos). The third step involves the removal of template molecule from the NIP. The removal of template molecule from NIP causes the imprinted sites onto the polymer. For the first step, the plastic cladding from 1 cm length of the 17 cm long PCS fiber was removed from the middle portion using a sharp blade. The unclad portion of the fiber was then washed three times by acetone and ethanol successively. It was further cleaned by ion bombardment process in vacuum at the chamber pressure 5×10^{-2} mbar. The cleaned core was then coated with a 40 nm thick Ag film using thermal evaporation method. The uniform layer of silver was achieved by using an automatic gear system fixed in thermal evaporation coating unit which rotates the fiber with uniform speed. A quartz crystal thickness monitor, calibrated using ellipsometry, is installed in the system chamber to monitor the thickness of the coating. The monitor holds an accuracy of 0.1 nm. To ensure the uniform coating/thickness of the film, the rate of coating was controlled at 0.04 nm/s. This completes the first step of the probe fabrication. In the second step the synthesis of the polymer with template molecule was performed and was coated over the Ag film. For the synthesis of the polymer, a pre-polymerization solution was prepared. To prepare pre-polymerization solution 0.065 mM profenofos, 0.670 mM MAA and 0.431 mM TRIM in 10 ml DMSO were mixed in ultrasonic bath for 10 min. The solution was kept under nitrogen gas environment for 15 min. The solution was immediately left for pre-polymerization. To polymerize the pre-polymerization solution, the thermal polymerization method was used. The fiber was dipped into the pre-polymerization solution and was kept vertical in the solution by holding it using a clamp and stand arrangement in the oven. After completing 16 h in the oven, the fiber was then extracted very slowly from the polymerized solution and kept overnight to