Sensors and Actuators B 227 (2016) 204–211

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Surface plasmon resonance based optical fiber sensor for atrazine detection using molecular imprinting technique

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ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 9 December 2015
Accepted 12 December 2015
Available online 17 December 2015

Keywords:
Optical fiber
Surface plasmon resonance
Molecular imprinted polymer
Atrazine
Limit of detection

ABSTRACT

We reported a successful effort for fabrication and characterization of surface plasmon resonance based fiber optic sensor to detect atrazine by molecular imprinted technique. The fabrication of sensing probe is done by coating a 40 nm thick silver film over the unclad core of an optical fiber. Further, an over layer of molecular imprinted (MIP) polymer having atrazine as template molecule has been coated over Ag coated region. Spectral interrogation method has been used for characterization of the probe. A red shift of 38 nm in resonance wavelength has been observed for atrazine concentration range of 0 M–10^{-7} M. Sensitivity of the sensor has been found to be 17.34 nm/log M for atrazine concentration of 10^{-12} M. The sensor has lowest detection limit of 1.92×10^{-14} M and quantification limit of 7.61×10^{-14} M. Sensor has been found to be highly selective as well as highly sensitive due to a combined approach of molecular imprinting and surface plasmon resonance. Besides them, sensor has numerous advantages such as low cost, fast response, immune to electromagnetic interface and capability of online monitoring and remote sensing.

1. Introduction:

Atrazine is a white colored solid organic compound having chemical structure as shown in Fig. 1. It is a member of the triazine class, which are basically herbicides used for controlling the broad leaf weeds in crops such as sugarcane, corn, sorghum, pine, grapes, residential lawns, roadway grasses and forestry products [1]. Further, atrazine belongs to the Restricted Use Pesticide (RUP) category, implying that only registered professionals can apply it while its use is prohibited for the general public. It became more popular of the triazines due to its effectiveness against a large spectrum of weeds [2]. Atrazine is generally found in ground water, drinking water and surface water which are highly persistent. The higher level of atrazine in ground water is detected in some region of USA. Atrazine has toxic nature in waste water and is an environmental threat which affects the ecosystem and human health by immune-suppression, reproductive abnormalities, cancer and hormone disruption [3]. According to the World Health Organization (WHO), the maximum contaminant level (MCL) of atrazine in drinking water is 0.2 ppb [4]. This makes the sensing of atrazine important. Numerous methods for atrazine detection have been reported in the literature. Few of them are high performance liquid chromatography (HPLC) [5], gas chromatography-mass spectroscopy (GC-MS) [6], voltametric competitive immunosensor (VMCI) [7], micellar-electro kinetic chromatography (MEKC) [8], thin-layer chromatography [9], multivariate electronic spectroscopy [10], solid phase micro-extraction [11] and surface plasmon resonance (SPR) immunosensor [12]. Some of these methods are highly expensive and take lots of time for experimentation and sample preparation. Few have high detection limit as well as low operating range. Thus, a method with low cost, fast response and having low limit of detection is required.

In recent years, molecular imprinting (MIP) along with SPR technique has been used for the detection of various analytes [13,14]. MIP is a technique used for the creation of specific recognition active sites in an artificial polymer matrix. The binding sites are prepared in such a way that its shape and size are complement to the template molecule. This makes molecular imprinting technique highly selective [15,16]. For the preparation of molecularly imprinted polymer generally functional monomer, cross-linking agent, reaction initiator and template molecules are added in a solvent for polymerization at atmospheric conditions. After polymerization, the template molecules are removed from the polymer which results in the creation of specific active sites in the polymer which have complementary shape and size of template molecule.

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http://dx.doi.org/10.1016/j.snb.2015.12.047
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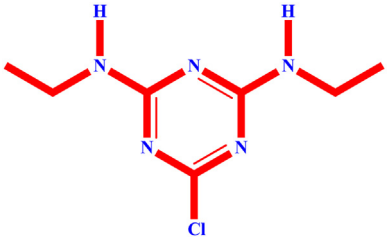

Fig. 1. Chemical structure of atrazine molecule.

When template molecule comes near the active sites, it interacts with these sites by non-covalent interaction which causes the change in dielectric nature of imprinted polymer. This change in dielectric nature was detected by SPR technique.

In the last few years, surface plasmon resonance has become a famous tool for the researchers to detect various types of analytes [17]. Surface plasmon is a quanta of free electron charge density oscillations at a metal-dielectric interface. When p-polarized light is incident on a metal-dielectric interface in Kretschmann configuration at an angle greater than the critical angle, due to matching of wave vectors of evanescent wave (occurs due to total internal reflection) and surface plasmon wave, some fraction of energy of the incident light is transferred to the surface plasmons for its excitation which results in the surface plasmon resonance phenomenon [18]. While using wavelength interrogation method in fiber optic configuration for SPR phenomenon, a sharp dip is obtained in a transmission spectrum at a particular wavelength called resonance wavelength. If there exists a change in dielectric nature of sensing medium, there will be a shift in resonance wavelength due to achievement of resonance condition [19–21]. Numerous studies based on molecular imprinting along with the surface plasmon resonance technique have been reported in the literature [22–24]

In the present study, we report a study for the fabrication and characterization of a fiber optic SPR sensor for atrazine detection using molecular imprinting technique. Fabrication of sensing probe is accomplished by the synthesis of molecular imprinted polymer and its coating over silver (Ag) coated unclad portion of a long optical fiber. The sensing probe is characterized by spectral interrogation method. The sensor working is checked for the atrazine concentration range of 10^{-12} M–10^{-7} M. To achieve the best performance of the sensor, dipping time of polymer coating has been optimized. Effect of pH of atrazine solution on sensor performance has also been checked. Selectivity or the specificity of the sensor has been checked by characterizing the probe using different analytes such as tetracycline, sucrose, urea etc. An approach for the sensitivity enhancement of the sensor by introducing a 10 nm thick Al layer has been used. In addition, the limit of detection and limit of quantification of the sensor have been calculated to check the novelty of the sensor.

2. Experimental

2.1. Reagents

Plastic clad silica (PCS) optical fiber with core diameter of 600 μm and numerical aperture of 0.37 was procured from Fiberguide Industries. Atrazine and 2-hydroxyethyl methacrylate (HEMA) were purchased from TCI Co. Ltd, Japan. Phenol and aluminum wire were purchased from Sigma Aldrich Co. Ltd., India. Ethylene glycol dimethacrylate (EGDMA), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$) were purchased from Merck India. N,N′- azobisisobutyronitrile (AIBN) was purchased from Otto Kemi. NaCl, tetracycline and melamine were purchased from CDH Bioscience Pvt. Ltd., while urea and glucose were purchased from Merck Specialties Pvt. Ltd. Silver wire (99.9% pure) was purchased from local vendor. All the chemicals were used without any purification.

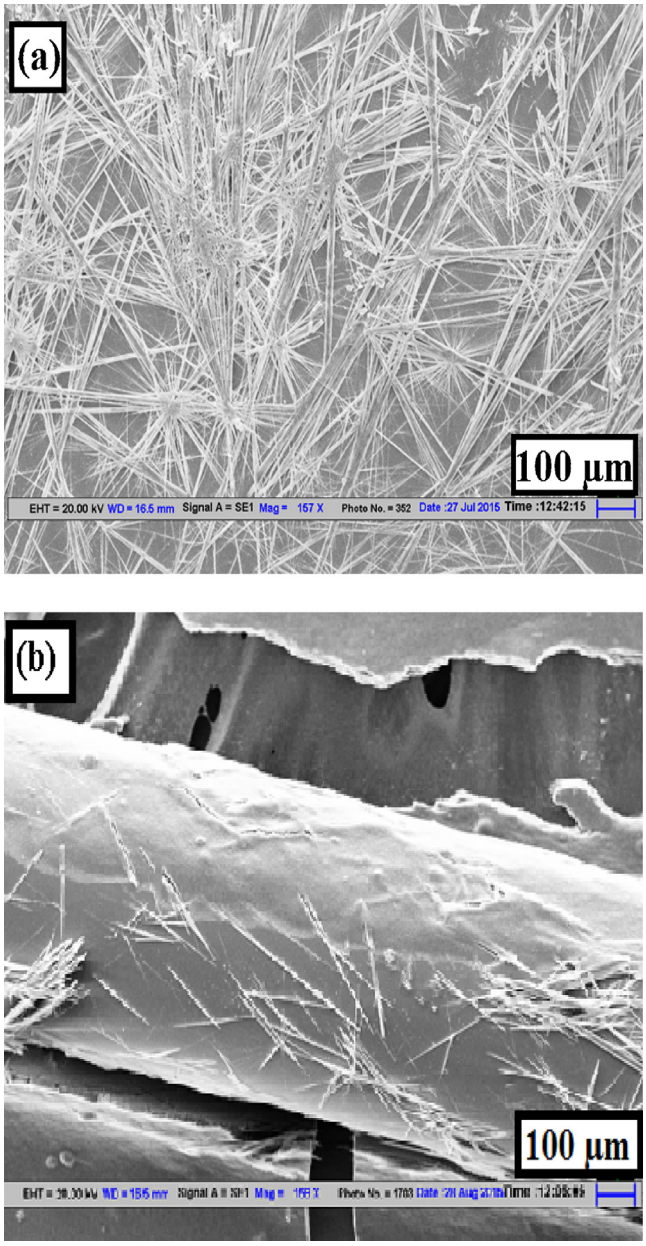

Fig. 2. (a) SEM image of polymer having atrazine as a template molecule, phenol and HEMA as a functional monomer coated on a (a) glass substrate and (b) fiber optic probe. The images are at the scale of 100 μm.

2.2. Synthesis of MIP

For the synthesis of the molecularly imprinted polymer, firstly a phosphate buffer solution of 0.1 M, pH 7 was prepared by mixing 3.4118 g of $Na_2HPO_4{\cdot}2H_2O$ and 2.7301 g of $NaH_2PO_4{\cdot}2H_2O$ in 350 ml distilled water using a homogenizer. In the second step of polymer synthesis, atrazine and phenol (used as monomer) were mixed with molar ratio of 2:1 in the 1000 μl prepared phosphate buffer. The solution was mixed for 3 h under laboratory conditions to form a phenol-atrazine complex [25]. Prepared complex was further mixed with 25 mg of AIBN, 6250 μl of HEMA and 2500 μl of EGDMA under nitrogen gas flow for 30 min to obtain