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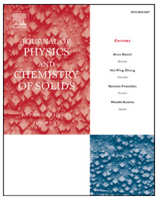

Designing of fluorescent and magnetic imprinted polymer for rapid, selective and sensitive detection of imidacloprid via activators regenerated by the electron transfer-atom transfer radical polymerization (ARGET-ATRP) technique

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ABSTRACT

In this work, we report on a dual-behavior electrochemical/optical sensor for sensitive determination of Imidacloprid by fluorescent dye (fluorescein, FL) and imprinted polymer modified europium doped superparamagnetic iron oxide nanoparticles (FL@SPIONs@MIP). The imidacloprid (IMD)-imprinted polymer was directly synthesized on the Eu-SPIONs surface via Activators regenerated by the electron transfer-atom transfer radical polymerization (ARGET-ATRP) technique. Preparation, characterization and application of the prepared FL@SPIONs@MIP were systematically investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), fluorescence spectroscopy and electrochemical techniques. The electrochemical experiments exhibited a remarkable selectivity of the prepared sensor towards IMD. Determination of IMD by the square wave stripping voltammetry method represented a wide linear range of 0.059–0.791 $\mu g\,L^{-1}$ with a detection limit of 0.0125 $\mu g\,L^{-1}$. In addition, the fluorescence method shows a linear range of 0.039–0.942 $\mu g\,L^{-1}$ and LOD of 0.0108 $\mu g\,L^{-1}$. The fluorescence property of prepared FL@SPIONs@MIP was used for rapid, on-spot but selective detection of IMD in real samples. The proposed electrode displayed excellent repeatability and long-term stability and was successfully applied for quantitative and trace level determination of IMD in several real samples.

1. Introduction

Imidacloprid (IMD), the first member of the neonicotinamide family has crossed a milestone in insecticide research, having been launched in 1991 [1]. IMD is the most popular insecticide in agriculture for the control of sucking insects such as leaf and plant hoppers, whiteflies, etc. [2]. Owing to their wide and growing application, high stability (more than 30 days in soil having pH 5–7) and good water solubility, a sharp rise of IMD was observed in food and soil samples [1]. As a consequence, serious environmental pollution and health related issues have been reported recently. The tolerance limit of IMD is also defined by the European Union (EU), which lies in the range of 0.01–3 $mg\,kg^{-1}$ for many fruits and vegetables, higher than this quantity can create toxic effects to living organisms [3].

Initially, for IMD detection, standard analytical methods such as high performance liquid chromatography (HPLC), gas chromatography (GC) and liquid chromatography (LC) combined mass spectrometry (MS) are commonly used. Obana et al. reported the development of multiresidue analysis of nitenpyram, IMD, and acetamiprid in foods with a HPLC-UV diode-array detection system [4]. Subhani et al. have developed a combination of ion chromatography with online post-column photoactivation and fluorescence detection for simultaneous determination of IMD and carbendazim in natural waters [5]. Despite the precision, these methods suffer from some disadvantages such as high cost, long analysis times and a requirement for sample pretreatment (like derivatization, extraction and purification), which is not suitable for real-time detection of IMD. Currently, a variety of methods such as enzyme-linked immunosorbent assay [6], surface plasmon resonance biosensors [3], colorimetric [7], nanoplasmonic biochips with a smartphone [8] and electrochemical sensors [9,10] are also reported for trace level detection

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of IMD. The proposed methods are very good in terms of sensitivity, however, they still lack the selectivity feature. Therefore, to protect human beings from health risks, a basic, rapid, economic, selective and handy analysis or food monitoring systems is required, which could be able to detect the trace level of IMD, prior to their consumption.

Regarding the requirements of selectivity elements of the chemical sensor, biological receptors such as antibodies are very attractive in terms of specificity and sensitivity. However, they are usually characterized by high price, low stability, intolerance to extreme pH, temperature and organic solvents [11,12]. Synthetic organic receptors are alternatives to these biological counterparts, in which molecularly imprinted polymers (MIPs) possess significant potential as robust and effective receptor matrices with commercial availability and numerous applications [13]. Contrary to the biological receptors, MIPs possess high stability, low cost, freedom to design, comparable selectivity and therefore are a potential candidate as a recognition element for sensor fabrications [14]. However, before taking place in the commercial or portable sensing system, MIP-based sensors still need to overcome some of their major drawbacks. The most important one is the distance of imprinted cavities from the sensor surface, which results in incomplete template extraction or rebinding and results in poor signal quality [15]. In order to avoid this problem and enhance the signal, researchers have focused on a combination of nanomaterials with MIPs. The small size of nanomaterials provides a large surface area to the imprinted material with more recognition sites on the surface [16].

Using the advantages of MIPs as a recognition element and nanotechnology, recently, Zhang et al. have developed a combination of graphene and a molecularly imprinted polymer (MIP) based electrochemical sensor for sensitive and selective determination of IMD residue [17]. The proposed sensor not only possesses good selectivity and sensitivity, but also extraordinary good reproducibility, which is always the difficulty in the electrochemical determination field. Similarly, Dai et al. have proposed dual-template MIP based electrochemical sensor for selective recognition and detection of electroactive IMD and non-electroactive bensulfuron-methyl molecules [18].

In the era of nanotechnology and nanomaterials, the field of sensor designing has been developed and upgraded in many aspects. Now, sensors were miniaturized and modernized by the incorporation of imprinted polymer nanomaterials as a part of recognition or transducer elements. To explore some new dimensions of nanomaterials and MIP combinations, in this work, an IMD-imprinted dual mode sensor has been developed for the trace level detection of IMD in various real samples. For the fabrication of imprinted IMD-sensors, a fluorescent superparamagnetic iron oxide nanoparticles (SPIONs) based temperature responsive magnetic molecularly imprinted polymer is designed. To analyze the trace level concentration of IMD with high selectivity, the synthesized SPIONs have been modified with fluorescent dye (fluorescein, FL) and atom transfer radical polymerization (ATRP) initiator in a step-by-step manner i.e. FL@SPIONs@initiator. The modified SPIONs along with two functional monomers i.e. vinyl derivative of cysteine and *N*-isopropyl acrylamide (NIPAm), cross-linker and template (i.e. IMD) was polymerized via activators regenerated by an electron transfer-ATRP method (ARGET-ATRP), results in designing fluorescent and magnetic imprinted polymer nanoparticles (FL@SPIONs@MIP). Afterwards, the dual-sensing behavior of FL@SPIONs@MIP as an electrochemical sensor and as bulk material for on-site detection of IMD through fluorescence measurement was explored. The FL@SPIONs@MIP was successfully employed for the detection of IMD in aqueous as well as real samples viz. fruit juice, vegetable extracts, soil and water, without any cross-reactivity study.

2. Experimental section

2.1. Reagents and apparatus

3-Aminopropyl triethoxysilane (APTS), N,N′-bisacrylamide, Europium nitrate pentahydrate [$Eu(NO_3)_3 \cdot 5H_2O$], ethyl-2-bromo isobutyrate, L-cysteine, acrylic acid, *N*- hydroxysuccinamide (NHS), 1-ethyl-3-(3-dimethyl amino-propyl) carbodimide (EDC), and *N*-isopropyl acrylamide (NIPAM) were purchased from TCI Chemicals (India) and Spectrochem Pvt. Ltd. (Mumbai, India). Some other chemicals and reagents i.e. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), copper chloride ($CuCl_2$), bipyridyl, IMD, ascorbic acid (AA), sodium hydroxide (NaOH), nitric acid, tetrahydrofuran (THF), toluene, methanol, diethylether, dimethylsulphoxide (DMSO), ethyl acetate and absolute ethanol (99%) were purchased from Spectrochem Pvt. Ltd. (Mumbai, India) and Alfa Aesar (India).

The electrochemical analysis viz., cyclic voltammetry (CV) and Square wave stripping voltammetry (SWSV) were performed on a CH instrument (USA, model number 660C) using a three-electrode cell assembly, consisting of Ag/AgCl (3.0 M KCl), a platinum wire and an MIP modified-PGE as reference, counter and working electrodes, respectively. Morphological images of bare and modified electrodes were recorded using a field emission scanning electron microscope (FE-SEM), Zeiss Supra-55. For the binding study, IR analysis was carried on a Varian Fourier transform infrared [FT-IR (USA)] spectrophotometer. The fluorescence spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrophotometer. UV characterization was done by a UV–visible spectrophotometer (Shimadzu, UV-1800). All the experiments were done at room temperature i.e. 25±°C, under ambient conditions. The powder X-ray diffraction (XRD) study of nanomaterials was done by a Bruker D8 X-ray diffractometer. The theoretical section related to the experiments was discussed in the supporting information (Sections S1 to S5).

2.2. Preparation of cysteine monomer

An acryloyl derivative of cysteine was used as a functional monomer (Cys-monomer) for the synthesis of an IMD-imprinted polymer. For the synthesis of cysteine derivative, 1.0 mM of cysteine dissolved in 50.0 mL NaOH (0.1 M) was taken in a round-bottom flask and kept in an ice bath. To the solution, 1.0 mL of acryloyl chloride was added in a dropwise manner and the mixture was stirred for 1 h at 40 °C. A solid product was obtained, which was filtered, dried and stored in a vacuum oven.

2.3. Synthesis of europium-doped superparamagnetic iron oxide nanoparticles

Europium doped-SPIONs were synthesized by the co-precipitation of Fe (II) and Fe (III) in the presence of NaOH [19]. In a round-bottom flask, 0.02 mol $FeCl_3 \cdot 6H_2O$, 0.01 mol $FeSO_4 \cdot 7H_2O$, $Eu(NO_3)_3$ (20 mL, 10 ppm) and 7.5 mL of NaOH were added and the mixture was placed for magnetic stirring at 60 °C for 30 min in the N_2 atmosphere. The obtained black precipitate was filtered and washed with ethyl acetate, dried in a vacuum oven and stored in a desiccator.

2.4. Synthesis of silane modified fluorescein dye (Silane@FL)

For the synthesis of silane@FL, 3.0 mM of 3-Aminopropyl triethoxy silane was added in 5.0 mL toluene. Separately, a FL dye solution was prepared by dissolving 0.015 mM FL in 4.0 mL methanol along with 0.15 mM NHS, 10.0 mM EDC and 1.5 mL of distilled water. The FL dye solution was added to the silane solution and 1.0 mL trimethylamine was added to maintain the pH of 9.0. The whole mixture was kept under stirring for 4 h at 37 °C. The resulting product was dried and stored in vacuum desiccator.

2.5. Synthesis of 2-bromo-2-methyl-N-3-(triethoxy silyl) propanamide: ATRP-initiator

For the synthesis, 0.1 mL of 2-bromoisobutryl bromide dissolved in 10.0 mL toluene was injected to the solution of 3-Aminopropyl triethoxy silane (0.18 mL in 10.0 mL toluene). After that, 0.1 mL of triethylamine