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Electrochemical impedimetric sensor based on molecularly imprinted polymers/sol–gel chemistry for methidathion organophosphorous insecticide recognition

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ABSTRACT

We report here a novel method to detect methidathion organophosphorous insecticides. The sensing platform was architected by the combination of molecularly imprinted polymers and sol–gel technique on inexpensive, portable and disposable screen printed carbon electrodes. Electrochemical impedimetric detection technique was employed to perform the label free detection of the target analyte on the designed MIP/sol–gel integrated platform. The selection of the target specific monomer by electrochemical impedimetric methods was consistent with the results obtained by the computational modelling method. The prepared electrochemical MIP/sol–gel based sensor exhibited a high recognition capability toward methidathion, as well as a broad linear range and a low detection limit under the optimized conditions. Satisfactory results were also obtained for the methidathion determination in waste water samples.

1. Introduction

Organophosphorus (OP) derivatives constitute a major part of the insecticides and pesticides that are very extensively used around the world [1]. These OP derivatives share structural similarities with nerve gases and inhibit the action of enzyme acetylcholinesterase by reacting with the nucleophilic serine in the enzyme's active sites. Acteylcholinesterase enzyme is involved in the transmission of nerve impulses across synapses, and also suppression of acteylcholinesterase activity by OP compounds may result in respiratory malfunctions and death [2–4]. As a result of this acute toxic effect of the OP neurotoxins, environmental monitoring of these compounds in food and water samples is of paramount importance to maintain these compounds below the harmful level for humans and animals. Example of one such OP compound is methidathion that is found in commonly practiced insecticides.

Methidathion, or (MD; S-2,3-dihy-dro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-O,O-dimethyl phosphodithioate) is a non-systemic organophosphorus compound used to control sucking and chewing insects and spiders on many crops, and is commercially available since 1966. Based on its high toxicity, both the European Union and the Codex Alimentarius Commission of the Food and Agriculture Organization (FAO) of the United Nations have established maximum residue limits which are acceptable and not harmful to humans (MRLs) [5–7]. Developing methods for unambiguous detection of methidathion has been a priority for many years, yet one still has to use expensive and nonportable analytical devices for identifying the toxic compound. Chromatographic techniques (GC, HPLC) generally coupled with UV or MS detectors are currently used as reference methods [8–10]. These instrumental methodologies, however, are only suitable for centralized laboratory analysis, and are time consuming and expensive in analytical cost limiting the utility of them to high precision detection and quantification of individual chemicals that are presumed positive from initial screening assessment. New technologies based on biological detection systems have emerged, and can be a good alternative for these classical methods. In the determination of OP compounds, electrochemical biosensors based on the inhibition of acetylcholine esterase (AChE) and immunosensors have been extensively reported in the literature [11,12]. However, despite their high sensitivity, they suffer from major drawbacks including a long and tedious protocol for sample

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preparation, poor selectivity (cholinesterases may inhibit also many other compounds in case of enzymatic assays), and are limited to single use [13]. Therefore, scientists have focused on the development of new methods for selective, sensitive and stable detection of organophosphate pesticides. One of the most efficient approaches is the use of molecularly imprinted polymers (MIP) modified electrodes that promises to produce highly stable and target specific recognition elements for sensors [14–18]. MIPs have widely been used as sensitive components in chemical/biological sensors for many compounds due to their associated advantages such as low cost, simplicity, mechanical/chemical stability, reliability and a wide choice of templates and functional polymers [19–21]. Although MIP based sensing approaches have expanded the field of sensor applications, the shortcomings such as low sensitivity still exist. Sol–gel is a promising way to improve the performance of the MIP based sensor surfaces. Sol–gel inorganic framework formation around the MIP template can favourably enhance the permeability and porous structure, and may have the potential to overcome the limitations of MIP based sensors to some extent. Therefore, the combination of MIP methodology and sol–gel technique could be an ideal approach to construct electrochemical sensing devices.

In this work, we report a novel, fast, inexpensive, MIP based analyte-sensor to detect methidathion in waste water samples. The sensing platform was architected by the combination of a molecularly imprinted technique and sol–gel method on an inexpensive, portable and disposable screen printed carbon electrode surface. Electrochemical impedimetric detection technique was employed to perform the label free detection of the target analyte on the designed MIP/sol–gel integrated platform. The prepared electrochemical MIP/sol–gel based sensor exhibited a high recognition capability toward methidathion, as well as a broad linear range and a low detection limit under optimized conditions. Satisfactory results were also obtained for the methidathion determination in waste water samples. To the best of our knowledge, this is the first report on the integration of MIP/sol–gel matrix to design an impedimetric detection system for the detection of methidathion. The use of a sol–gel matrix is expected to improve immobilization efficiency of MIP on the electrode surface, which in turn will enhance the stability and selectivity of the designed sensor. We expect that our designed MIP based sensor has the potential to open new horizon towards the label free detection of other OP compounds, and could be easily extended to other target analytes.

2. Experimental

2.1. Chemicals

Chemicals including organophosphorus pesticides (methidathion, malathion, fenthion, parathion and chlorfenvinphos) and functional monomers: methacrylic acid (MAA); 2-(trifluoromethyl)acryl acid (TFMAA); itaconic acid (IA); acrylamide; N, N-diethylamino ethyl methacrylate (DEAEM); N, N-methylene bis acrylamide (MBAA); cross-linker ethylene glycol dimethacrylate (EGDMA); initiator 1,1-azobisisobutyronitrile (AIBN); solvents (dimethylformamide DMF, methanol) and acetic acid, tetramethoxysilane (TMOS); poly(ethylene glycol) 600 (PEG); potassium ferrocyanide ($K_4Fe(CN)_6$); potassium ferricyanide ($K_3Fe(CN)_6$),were all purchased from Sigma-Aldrich (France).

2.2. Molecular modelling and computational design

The molecular modelling was performed using a work station from Research Machines running the CentOS 5 GNU/Linux operating system, configured with a 3.2 GHz core 2 duo processor, 4 GB memory and running the SYBYL 7.3 software suite (Tripos Inc., St. Louis, Missouri, USA). A virtual library of 20 functional monomers was designed and screened against of molecular models of methidathion, using the LEAPFROG algorithm [22]. All structures were minimized and Gasteiger–Huckel charges were applied. The binding energies values of electrostatic, hydrophobic, Van der Waals forces, and dipole–dipole interactions were obtained. Monomers which gave the highest binding score were selected for the polymer preparation [23].

2.3. Apparatus

All electrochemical measurements were carried out on an AUTOLAB PGSTAT100 potentiostat/galvanostat equipped with a frequency response analyzer system (Eco Chimie, Netherlands) controlled by two Autolab softwares, frequency response analyzer (4.9) for impedance and general purpose electrochemical system (4.9) for voltammetry. Screen printed carbon electrodes (SPCEs) were fabricated using a DEK 248 screen-printing system as reported for 2-electrode systems [24]. The SPCE consists of a conventional three electrode configuration with graphite modified by MIP or NIP particles/sol–gel as the working (4-mm diameter disk) and counter electrode (16 mm × 1.5 mm curved line), and Ag/AgCl (16 mm × 1.5 mm straight line) as the pseudo-reference electrode. All measurements were performed in a solution of 1.0 mM ferri/ferrocyanide couple $[Fe(CN)_6]^{4-/3-}$ in PBS, pH 7.3, as a back-ground electrolyte, with the frequency range of 1000 Hz to 1 Hz and at the potential of 0.6 V.

2.4. Preparation of bulky imprinted polymer particles

A set of polymers was synthesized based on the results of the computational modelling. Several monomers (MBAA, IA, MAA, DEAEM, acrylamide and TFMAA) which showed the highest binding energy towards the template were selected. The molar ratio of the template, functional monomer and cross-linker was 1:4:20, respectively. The polymer was synthesized by mixing 1 mM methidathion (template molecule), 20 mM EGDMA (cross-linker), 40 mg of AIBN (initiator) and 4 mM of a suitable monomer in 5 mL of DMF. The mixture was degassed with N_2 for 10 min, sealed in a glass bottle and thermally polymerized in an oil bath at 80 °C for 12 h. After synthesis, the polymer monolith was ground and wet sieved with methanol to obtain particles with a diameter of 45–100 m. Particles were collected, washed intensively using Soxhlet extraction with methanol/acetic acid solution (90/10, v/v) and oven-dried and packed (50 mg) into glass SPE cartridges. Corresponding blank or non-imprinted polymers (NIPs) were prepared using the same protocol in the absence of the template.

2.5. Preparation of the MIP/sol–gel modified electrodes

In order to prepare screen printed carbon electrodes, modified with different MIP and NIP particles/sol–gel, the following procedure was adopted: sol–gel solution was prepared by mixing 150 mL of the precursor tetramethoxysilane (TMOS) with 413 mL of distilled water, 400 mL of HCl 1 mM, and 37 mL of PEG 600. This mixture was sonicated for 15 min and stored for one night at 4 C°. The particles of MIP and NIP were mixed with the sol–gel solution, and 2 μL of the obtained solution was quickly deposited on the surface of the working electrode, and allowed to dry for 3 h at room temperature.

3. Results and discussion

3.1. Modelling of the best monomer

Formation of a complex between the template molecule and functional monomers is the first step in the preparation of MIPs. The monomer that can interact with the template most intensively will give the complex with the highest stability. The present work was focused on the selection of monomers with strong affinity for the target molecule methidathion, the polymers synthesis using these monomers, and subsequently their testing in rebinding experiments. Our previous work has successfully demonstrated the usefulness of computational approaches for elucidating and modelling the interaction strengths of MIPs in solid phase extraction methods [8,25]. Preliminary, the results obtained by modelling experiments were compared with those of a rebinding experiment using impedance detection (Table 1). To perform impedimetric measurements, the MIPs synthesized using different monomers were immobilized on the screen printed electrode surface, and the obtained sensor was incubated for 20 min with the solution of methidathion in PBS (200 μg L^{-1}). Electrochemical impedance spectroscopy (EIS) was recorded in 10 mL of PBS (pH 7.4) containing 1.0 mM ferri/ferrocyanide couple $[Fe(CN)_6]^{4-/3-}$ as the redox active reagent. In order to calculate charge transfer resistance (R_{ct}), the impedance values were fitted to an electrical circuit (Supplementary Fig. 1) which was designed based on the features of the obtained impedance spectrum. The values of electron transfer resistance ($\Delta R = R_{ct2} - R_{ct1}$, where R_{ct1} and R_{ct2} are resistances obtained in the absence and presence of methidathion, respectively) was determined.

From Table 1, it is evident that the experimental results were in good correlation with the computer approximations. MBAA-based MIP sensor demonstrated the largest electron transfer resistance ΔR (22.15 kΩ), which is consistent with highest binding energy between MBAA and the methidathion molecule. MIP sensor made by IA demonstrated also the highest electron transfer resistance ΔR (22.08 kΩ), which was in agreement with computational modelling (-26.49 kcal mol^{-1}). Whereas other monomers including DEAEM, TFMAA, MAA, and acrylamide with lowest binding energies gives the lowest electron transfer resistance. Thus, the experimental results confirmed the reliability of the computational method used in our studies and clearly indicated that MBAA is the most suitable monomer to produce the methidathion imprinted polymer sensor. This monomer was therefore used for further experiments.

3.2. Specific character of MIP-sensor

In order to characterize the specificity of the MIP sensor toward its template molecule, methidathion, the nonimprinted polymer (NIP) was synthesized in the same conditions as that described for the MIP polymer but without the template molecule. The NIP was immobilized on the screen printed carbon electrode surface, and used as a control experiment under similar experimental conditions as for the MIP sensor. Fig. 1 displays the impedance spectra obtained for the imprinted and nonimprinted sensors under similar experimental conditions. The results show that the MIP sensor recognizes easily its template molecule because we noted an increase in the impedance of the imprinted sensor when it was dipped into 200 μg/L methidathion solution for 20 min (Fig. 1b). In contrast, the same impedance value response was observed when NIP sensor was incubated with 200 μg/L methidathion solution for 20 min. These results proved clearly the presence of a specific cavity for methidathion within the MIP sensor which makes the recognition and thus uptake of this template molecule very easy in the incubation solution.

Table 1
Correlation between interaction energy (kcal mol^{-1}) of the molecular complexes between methidathion and functional monomers, and the charge transfer resistance of the MIP-sensor prepared with corresponding monomers.

Functional monomer	Binding energy (kcal mol^{-1})	ΔR (kΩ)
N, N-Methylene Bis Acrylamide, MBAA	−29.36	22.15
Itaconic Acid, IA	126.49	22.08
Acrylamide	−25.75	15.2
N, N-Diethylamino Ethyl Methacrylate, DEAEM	−24.55	14.7
2-(Trifluoromethyl)-acryl acid (TFMAA)	−15.35	10.6
Methacrylic acid (MAA)	−14.78	15.1

3.3. Effect of incubation time

Incubation time of the MIP sensor in the target molecule solution is one of the main parameters affecting rebinding of the template molecule. In order to determine the effect of the

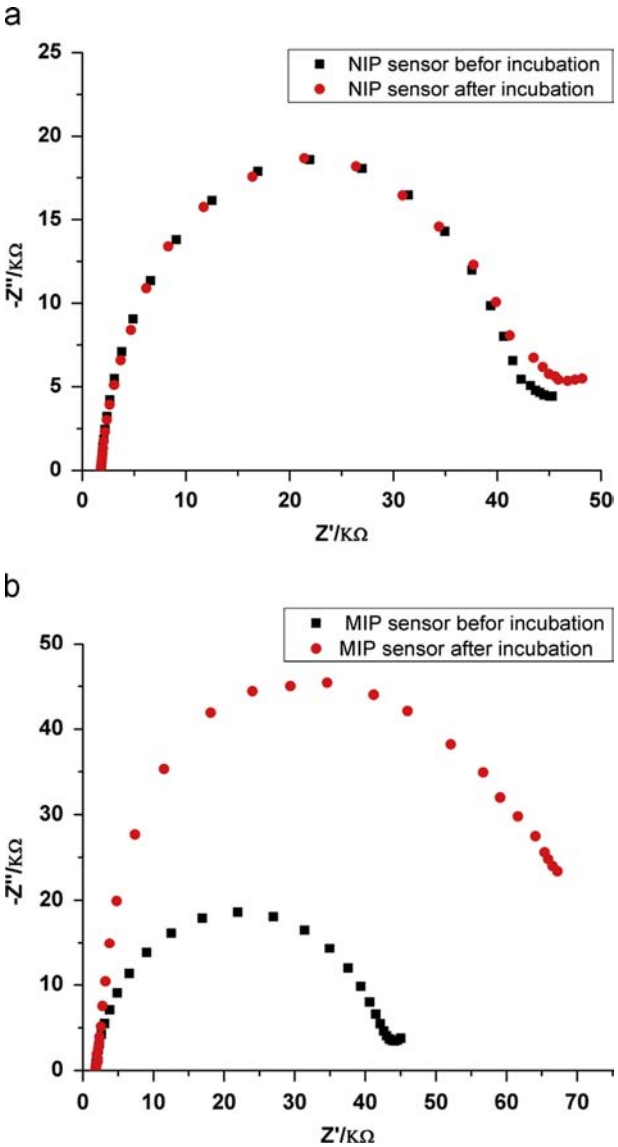

Fig. 1. Nyquist plots of 1 mM $[Fe(CN)_6]^{4-/3-}$ for (a) NIP and (b) MIP modified electrodes before and after incubation in 200 μg/L methidathion solution for 20 min.

incubation time on the impedimetric detection of methidathion, the MIP sensor was incubated with PBS solution containing 200 μg L^{-1} methidathion for different periods of time, and Nyquist plots of the MIP senor was recorded for each respective period. The relationship between the electron transfer resistance and the incubation time was studied in the range of 0–30 min. Fig. 2 shows that the increased incubation time resulted in subsequent increase in the electron transfer resistance. This can be correlated to the fact that the amount of methidathion rebound on the recognition sites of the MIP sensor increased with the increase of the incubation time. This resistance remained almost constant when the incubation time was above 20 min, implying that the adsorption equilibrium was reached under these experimental conditions (Fig. 2). Thus an incubation time of 20 min was selected for further experiments.

3.4. Selectivity

In order to demonstrate the selective character of the MIP sensor systems, the latter were incubated with different types of organophosphorates pesticides (malathion, fenthion, parathion and chlorfenvinphos) having molecular structure similar to the methidathion, at the concentration of 200 μg L^{-1}. The sensor was washed with distilled water after each incubation step. Fig. 3 displays the impedance spectra of the imprinted sensor (electron transfer resistance, ΔR) at indicated incubation medium. The result shows

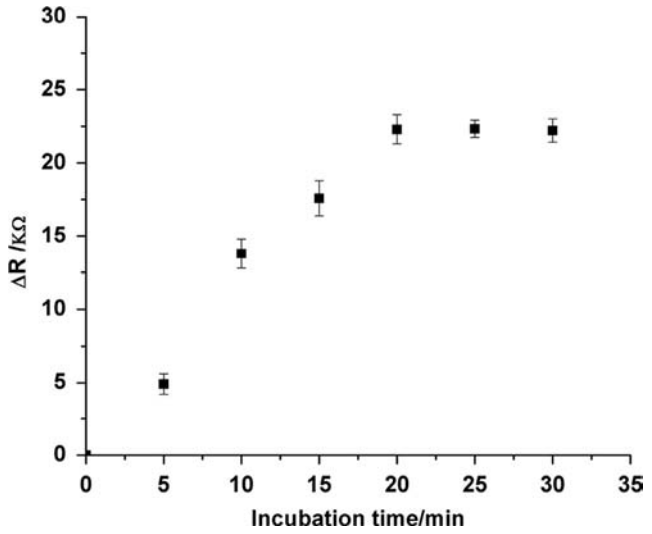

Fig. 2. Dependence of impedance spectra of an imprinted sensor on incubation time in the presence of 200 μg L^{-1} methidathion.

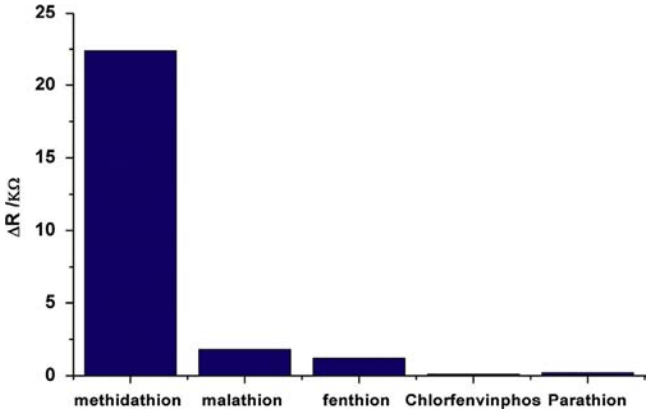

Fig. 3. Impedance responses of the imprinted sensor after incubation in various solutions with different organophosphate pesticides 200 μg L^{-1}.

that the developed impedimetric MIP sensor does not respond to other organophosphate pesticides, therefore indicating that this sensor is highly selective for the detection of methidathion. Indeed, the binding character of the produced MIP is driven by specific interactions between functional groups from methidathion and the artificial receptor sites (i.e. hydrogen bonds).

3.5. Analytical performance of the designed MIP sensor towards detection of methidathion

In order to demonstrate the applicability, the designed sensor was incubated with different concentrations of methidathion (40–200 μg/L) for 20 min. The plates were removed from the solutions, washed with distilled water and finally characterized by impedance spectroscopy. For electrochemical measurements, the modified sensor served as working electrode and electrochemical impedance (EI) spectra was recorded in a solution of 1.0 mM ferri/ferrocyanide couple $[Fe(CN)_6]^{4-/3-}$ in PBS, pH 7.3 and illustrated in Fig. 4a. The results show that the impedance values increased with increasing methidathion concentrations. This can be attributed to the rebinding of methidathion into the recognition sites of MIP sensor, preventing the electron transfer of redox probes onto the electrode surface. A linear relationship between the methidathion concentration and impedance value was obtained by covering the concentration in the range from 40 to 200 μg/L (Fig.4b). The linear regression equation was ΔR (kΩ)= 0.1088 C (μg/L)+0.54, with a correlation coefficient of 0.9927. The limit of detection (LOD) is calculated to be 5.14 μg/L based on the equation LOD=$3S_b$/m, where S_b is the standard deviation of the blank response and m is the slope of the calibration plot (0.1088 kΩ L μg^{-1}). Although the maximum residue limit tolerated for methidathion in water is 20 μg/L according to the European Food Safety Authority (EFSA), however, the contaminated water samples have much more with methidathion than the detection limit recommended by the water protection authorities. The lower detection limit suggests that the developed sensor in this study can be relevant and efficient for the determination of methidathion in contaminated water samples.

3.6. Reproducibility, repeatability and stability of the sensor

One of the most important factors in developing a practical MIP sensor is the regeneration and reproducibility of the sensitive

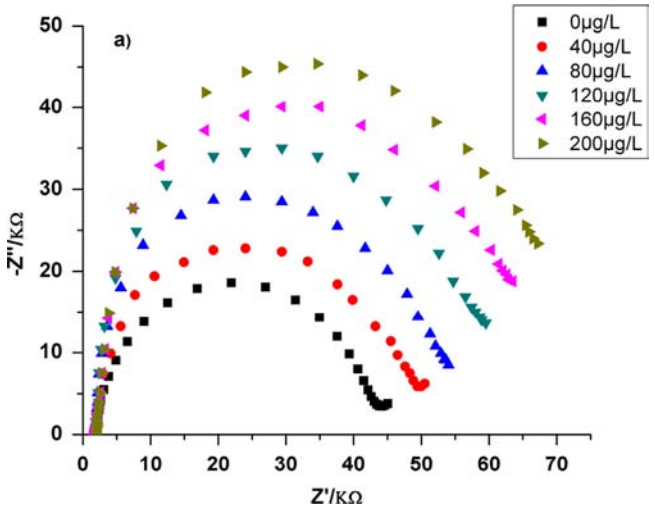

Fig. 4. (a) Impedance spectra of MIP sensor after 20 min incubation in solutions with different concentrations of methidthion. All measurements were performed in a solution of 1.0 mM ferri/ferrocyanide couple $[Fe(CN)_6]^{4-/3-}$ in PBS, pH 7.3.

Table 2
Recovery rates obtained after analysis of methidathion from tap water using an MIP impedimetric sensor.

Spiked concentration ($\mu g\ L^{-1}$)	Recovery (%)	RSD (%)
20	99	2.5
40	98	3.68
80	100.1	3.9
100	100.3	2.3

cavities. In order to test the reproducibility of the proposed technique, three MIP impedimetric sensors were constructed under identical experimental conditions. For 200 μg/L of methidathion, relative impedance change was obtained by using each of the MIP impedimetric sensors. The standard deviation of the response obtained did not exceed 6%. In order to test the regeneration potential of the imprinted sensor, the renewal of the MIP surface was easily achieved via extraction of the template molecule methidathion using acidified methanol solution. The experiments were performed with 5 replicates in methidathion solution using the same MIP impedimetric sensors, and it was observed that the electrochemical impedance spectroscopy response of the methidathion did not change for five successive uses. In order to obtain data on the stability of this sensor, the MIP sensor was stored in the fridge at 4 °C for three weeks, and the impedance values decreased only by 3% after this much period of time, which indicates the good sensor stability over extended period of time.

3.7. Application to waste water

The reliability of the impedimetric sensor was evaluated, by using this later to analysis of methidathion in tap water doped with different concentrations of pesticide. Results are summarized in Table 2. The concentration of methidathion was calculated by the standard addition method. The recovery was between 98% and 103% and the calculated RSD was less than 4%, suggesting that impedimetric determination of methidathion using an MIP sensor was effective and sensitive. Moreover, the obtained results demonstrated that the proposed method can be successfully used in the determination of methidathion in other real samples.

4. Conclusion

In the current study, a novel MIP/sol–gel impedimetric sensor has been successfully designed for the detection of methidathion organophosphorus insecticide. The sensor was based on the immobilization of a low amount of the MIP bulk polymer by encapsulation in a sol–gel matrix on a screen printed electrode surface. The selection of highly specific and selective monomer for target analyte by impedimetric method was in good agreement with the results obtained by computational modelling experiments. In the proof of concept experiments, the sensor was applied to measure the target analyte in real tap water samples. The developed MIP sensor exhibited excellent analytical performances in term of sensitivity and selectivity. Regeneration, reproducibility and stability were also reliable with the newly designed electrochemical sensor. In addition, the fabrication procedure was very simple, and the sensor design could be easily extended as a promising alternative tool for other pesticides detection.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.07.012.

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