OPTICAL SENSOR FOR THE DETECTION OF GLYPHOSATE USING SURFACE PLASMON RESONANCE AND MOLECULAR IMPRINTING TECHNIQUE

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Abstract

An optical sensor based on surface plasmon resonance (SPR) and molecularly imprinted polymer (MIP) for glyphosate detection was developed. The sensor was prepared via synthesis of MIPs on a gold electrode in the presence of glyphosate as the template molecule and chitosan as the functional monomer by either bulk or surface imprinting. MIP was deposited on the gold surface using the spin coating technique. The sensor preparation conditions, *i.e.* the thickness of thin film, the method of template removal, pH on the sorption capacity of the MIP SPR sensor and the effect of salt concentration on the rebinding of glyphosate, were optimized. For these conditions, the sensor has a good linear response *vs.* glyphosate concentration. The optical detection selectivity was investigated towards the binding of glyphosate metabolites revealing selectivity towards glyphosate. Furthermore, the sensor shows a potential for further large-scale applications with good repeatability and stability during cyclic detections.

- MOTIVATION and RESULTS

Glyphosate has been introduced to the consumer market as a broad-spectrum herbicide in 1974. It has quickly become the most regularly used herbicide applied in agricultural, industrial, and domestic settings due to its property as enzyme inhibitor in microorganisms,

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plants, and fungi[1]. But glyphosate is still matter fraught with controversy about its hazard potential. The WHO International Agency for Research on Cancer classified glyphosate as "probably carcinogenic to humans"[2]. The European Framework Directive on water set a glyphosate standard of 0.1 μg/L in drinking water, while the maximum level is 700 μg/L in USA[3]. In Vietnam, decision has been taken to ban it on April 10th, 2019[4]. Liquid or gas chromatography coupled to mass spectrometry is common method for glyphosate analysis due to its high sensitivity and selectivity. However, these methods are time-consuming, high instrument operating costs, and require special equipment[5]. Consequently, the trend is to develop fast, simple, low-cost and selective sensors for glyphosate detection and monitoring in natural and drinking water.

Many SPR sensors have been studied and applied to environment, food and drug analyses[6]. Introduction of the MIP technique has become a motivation for the development of MIP SPR sensors owing to their high selectivity, sensitivity, simplicity and reliability[7]. MIPs are obtained by polymerisation of template, monomers and cross-linker in the presence of a solvent. Templates are then removed from the polymeric matrix, which is capable of specific rebinding of the analyte via size, shape and functional groups[5]. Chitosan is a cheap, nontoxic, biodegradable, and biocompatible cationic polysaccharide obtained from the chitin shells of crustaceans[8]. Chitosan is used for many applications such as MIP for sensors, tissue engineering, separation film, water treatment[9].

In this work, the glyphosate MIP-SPR sensor is prepared through polymerisation of chitosan as a monomer in the presence of the glyphosate and epichlohydrin as template molecule and cross-linker, respectively.
Results: MIP and NIP (non-imprinted polymer) receptors made by bulk or surface imprinting technique were first compared for two-glyphosate concentrations (Fig. 1). MIP has a better selectivity and sensitivity than NIP. Moreover, surface imprinting preparation exhibits a better selectivity and sensitivity than the bulk imprinting one. Therefore, we decided to study and to test the effect of pH and NaCl concentration on the glyphosate behaviour for the surface imprinting method only. Furthermore, the extraction optimization of MIP receptor at different pHs was investigated for removing glyphosate efficiently from MIP layer. We observed a decrease in the receptor response for increasing NaCl concentration, the MIP signal being higher than the NIP one (Fig. 2). This could be due to either the change in the ionic strength and the double layer thickness or the competition between the target molecule, glyphosate, and the counter-ions, Na+ and Cl–. The MIP-SPR sensor was also tested with respect to its sorption capacity *vs.* pH for different glyphosate concentrations, and its selectivity *vs.* glyphosate metabolites.

Keywords: optical sensor, glyphosate, surface plasmon resonance, molecularly imprinted polymer