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Temat rozprawy doktorskiej w języku angielskim: **"Molecularly imprinted polymers in chemical sensors electrochemically recognizing chosen toxins using a 'gate effect'"**

Temat rozprawy doktorskiej w języku polskim: **„Polimery wdrukowane molekularnie w czujnikach chemicznych elektrochemicznie rozpoznających wybrane substancje toksyczne za pomocą 'efektu bramki'"**

## Streszczenie rozprawy doktorskiej (w języku angielskim)

Developing reliable, fast, simple, and cost-effective analytical procedures for determining toxins is still challenging. Molecularly imprinted polymers (MIPs), a great example of bio-mimicking recognition materials, can meet this challenge.

The present dissertation aimed to devise, fabricate and validate chemical sensors with MIPs as recognition units to selectively determine some toxins encountered in food and dietary supplements using the "gate effect." It describes several crucial issues.

The first part focuses on devising (MIP film)-based chemosensors selective to *N*-nitroso-L-proline (Pro-NO) food contaminant and p-synephrine (SYN) dietary supplement. Initially, Pro-NO and SYN were used as templates. First, the most appropriate functional monomers (FMs) were selected by calculating the stability of the pre-polymerization complexes of templates with selected thiophene-based FMs with the density functional theory (DFT). Then, with the chosen FMs, MIP films were deposited on the surface of conducting transducers by potentiodynamic electropolymerization. Next, the templates were extracted from MIPs. Complete removal of templates from polymers was confirmed by differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), and polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS). The deposited MIPs morphology was determined by surface imaging with atomic force microscopy (AFM). The MIP chemosensors prepared that way were applied for Pro-NO and SYN determination using DPV, EIS, piezoelectric microgravimetry (PM), or surface plasmon resonance (SPR) spectroscopy. Moreover, analytical parameters of the chemosensors, including sensitivity, linear dynamic concentration range, selectivity, and the limit of detection (LOD), were determined.

To better understand the operation principle of MIP-based chemosensors, the second part of the research details an investigation of the so-called "gate effect" mechanism for the electrodes coated with conductive MIP films. Functionalized polythiophene polymer imprinted with SYN

(SYN-MIP) film was used as a model polymer film. Different techniques, including cyclic voltammetry (CV), DPV, EIS, SPR, AFM, and UV-vis spectroscopy, were applied to unravel mechanisms accounting for changes in the electrochemical signal recorded at the electrode coated with the SYN-MIP film due to the binding of SYN analyte.

The above analysis enabled the devising of a self-reporting MIP electrochemical sensor with the covalently immobilized redox probe for label-free determination of the SYN model analyte. For that purpose, a new monomer, a ferrocene derivative (FcM), was synthesized and used for MIP film preparation. Its role was to provide an internal redox probe on the one hand and act as a cross-linking monomer on the other. Applying the system, the same as for the traditional ("gate effect")-operated SYN-MIP film chemosensor, allowed comparing the analytical performance of those two chemical sensors fabricated. Notably, the analytical parameters of the chemosensor with the covalently immobilized redox probe were superior compared to those determined for similar chemosensors lacking a self-reporting system.

The final part of the thesis describes devising and testing self-reporting chemosensors for glyphosate (GLY) herbicide determination. Electroactive molecularly imprinted nanoparticles (MIP NPs) with an internal redox probe were applied as recognition units in these sensors. The MIP NPs were synthesized using a solid-phase synthesis protocol, then characterized, and then covalently immobilized on the surface of electrodes. The electrochemical sensors prepared that way were successfully used for label-free sensing of GLY.