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Research on Molecular Imprinting Technology and MIP-Based Sensors in Food Safety Detection

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Abstract. With the increasing awareness of healthcare, research on food safety has become a focus of researchers. Pesticide residues, veterinary drug residues, heavy metals, and food additives in the food caught the attention of researchers. Therefore, achieving accurate and rapid detection of target objects in food is of great significance for maintaining physical health of human beings. Detecting these target objects based on sensors is an effective way for people to ensure food safety. However, the detection matrix is relatively complex and the concentration of the target substance is extremely low, which bring difficulties for the detection. Therefore, new functional materials with specific identification are selected for sensor modification. Molecular imprinting technique (MIT) has a unique advantage including high selectivity and good stability. This technology can be used to prepare molecularly imprinted polymers (MIPs) which exhibit specific identification. Therefore, using MIP-based sensors for detecting target substances in food can improve detection accuracy. This work focuses on the discussion of MIT and MIP-based sensors. Meanwhile, this work summarizes the application of MIP-based sensors in food safety.

Keywords: Molecular Imprinting Technology; Sensor; Molecularly Imprinted Polymers; Detection; Preparation.

1. Introduction

Food security is an important issue which is related to social stability and public health. With the improvement of living standards, higher requirements are put forward for food security. Problems including pesticide residues, veterinary drug residues, heavy metals, food additives in the food have thrust into the public eye. Their security has become a global concern. Although the traditional food detection methods are accurate, they often have problems such as complicated operation, expensive equipment and long test time. Therefore, the exploration of fast, sensitive and economical detection technology has become an important subject in scientific research and practical application. As a emerging area of materials science, molecular imprinting technique (MIT) provides some new ideas and solutions.

MIT displays unique advantages including high selectivity, good stability and repeatability. This feature makes MIT a great potential on food security detection. This technology can be used to prepare molecularly imprinted polymers (MIPs) which exhibit specific identification. MIP-based sensor is considered to be a good way to achieve accurate and high-speed detection [1-3].

This work summarizes the progress and application of MIT in food security sensor field. The types of molecular imprinting technique are discussed. In addition, the applications of MIP-based sensor in food safety are also outlined. By analyzing the existing research results, this paper aims to provide inspirations for researchers and promote the further development of MIT in the field of food safety detection.

2. MIPs

MIPs have the characteristic of specific recognition, which is of great significance for their applications. Therefore, understanding the working principle of MIPs for achieving specific recognition is crucial. Meanwhile, different preparation methods can also affect the recognition efficiency of MIPs for target substances.

2.1. Working Principle

Molecular imprinting material is a kind of polymer material which with special bonding ability to the template material [4, 5]. The earliest research on molecular imprinting technology originated in immunology, where antibodies have the ability to specifically recognize corresponding antigens. Professors Wulff and Sarhan proposed the concept of imprinting. With the development of research, molecular imprinting materials are now gaining widespread attention. The ability of specific binding is derived from specific functional groups, physical adsorption, covalent bonding, ligand receptor interactions, hydrophilic/lipophilic interactions, and molecular biorecognition. After polymerization, polymeric films with imprinted cavities can be obtained, which match the size and shape of the template molecules. In addition, the as-prepared polymers are highly selective and can serve as specific binding sites for the template molecules.

2.2. Covalent Method

Molecular imprinting material have three main components which are template molecule, functional monomer and crosslinking agent. Template molecule usually works as a target of detection. It can be protein, biomolecule, simple molecule and organic molecule. Template molecules have one or more specific recognition sites on the template molecule which make functional monomer can specific interaction with it. The functional monomer specific interacts with template molecule, by using crosslinking agent to aggregate function monomer. The above process can produce a polymer which with a three-dimensional network structure formed by cross-linking between functional monomers. Afterwards, chemical or physic process is used to remove template molecule. It leaves behind a MIP with a special cavity.

2.3. Non-Covalent Method

Compare to covalent method, the template molecule does not need to be joined in the non-covalent method. So, it is also been called pre-assembly method. It displays the advantage of easy fabrication. It has a wide selection of functional monomers and eluents. This synthesis method also has certain limitations. Its synthesis efficiency is relatively low. The internal cavities in the as-prepared MIPs may be not enough to capture the target molecules.

3. MIP-Based Sensors

MIPs have the characteristic of specific recognition. MIPs can be used in sensors to improve detection accuracy.

3.1. MIP-Based Electrochemical Sensor

Molecular imprinting technique can be combined with electrochemical techniques to prepare MIP-based electrochemical sensor. In electrochemical sensors, MIPs are usually fixed on the electrode as the working electrode. When target molecule binds with molecular imprinting polymer, the electrochemical characteristics of the electrode changes. By measuring the changes in current, potential, or conductivity, the target analyte can be detected. Its design is simple, sensitive, responsive, cost-effective, portable, easy to miniaturize and automate, making it suitable for clinical diagnosis, environmental monitoring, and food analysis. In 2005, a combined molecular imprinting and thick film electrochemical sensor for cholesterol detection had been developed by Chou and Liu. The gold working electrode was modified by MIPs. By self-assembly, a molecularly imprinted membrane is formed on the surface of the electrode. Through this method, efficient detection of cholesterol has been achieved [1].

3.2. MIP-Based Fluorescence Sensor

By using fluorescent materials such as quantum dots, graphene quantum dots, gold nanoparticles, and metal-organic framework materials, MIPs with fluorescence properties can be synthesized and used in conjunction with traditional fluorescence sensors. Using molecular imprinted membranes to immobilize target molecules, this sensor can have a lower detection limit and a wider detection range. Furthermore, these sensors can be applied to microfluidic chip platforms to improve analytical efficiency and reduce costs. Wang et al. developed a fluorescent sensor that can specifically and selectively target 2,4-dichlorophenoxyacetic acid (2,4-D) using molecularly imprinted materials [2].

3.3. MIP-Based Capacitive Sensor

MIT has a great compatibility to various types of sensors. The working principle of capacitive sensors typically involves binding MIPs with target molecules such as drugs, and organic pollutants to form a composite material. When the target molecule binds to molecularly imprinted polymer, the result of the binding will affect the capacitance value of the electrode. Therefore, by measuring the changes in the capacitance, it is possible to quantitatively analyze the target molecule. A capacitive sensor, which is used for detecting paracetamol, is reported by using MIPs to modify the sensors. It has high sensitivity, good regeneration performance, and excellent selectivity.

4. Application

4.1. Food Safety

Nowadays, there is widespread concern about food safety, and a lot of researches have been conducted on detection in food safety realm. The specific binding ability and high sensitivity of molecular imprinting materials, as well as their reliability, have given them an unprecedented advantage in this field. Compared to the large number of interfering molecules in food that exist in rapid test strips, molecular imprinting materials have a stronger specificity. Compared to large spectrometers that have slow detection speeds and high requirements for samples, the high sensitivity of MIPs perfectly solves this problem.

4.2. Detection of Pesticide Residues in Plants

With the continuous advancement of chemical technology, there is a growing number of researches focused on agricultural applications which inevitably lead to the misuse of pesticides [5]. Because of its high specificity and affinity, MIPs can enrich and separate the target pesticide molecules from the complex plant sample matrix. MIPs can also be used in combination with modern analytical techniques such as gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). These technologies have high sensitivity and selectivity. Meanwhile, it can effectively separate and quantify the target molecule bound to the molecularly imprinted material, thereby achieving accurate detection of pesticide residues in plants. Compared with traditional sample pretreatment methods, the use of molecular imprinting materials can simplify the sample pretreatment process. In addition, it can reduce the introduction of interfering substances in sample handling, thereby improving the accuracy and efficiency of analysis.

The advantage of molecular imprinting materials is that they have a wide range of applications. Molecular imprinting technology can be used to detect traditional organophosphorus pesticide residues. It can also be expanded to the detection of new pesticides and herbicides. Chlorpyrifos and diazinon are common plant pesticides which are frequently tested. Musavi et al. used molecular imprinting membranes to create sensors for targeted detection [3].

4.3. Detection of Veterinary Drug in Ingredients

MIP-based sensors can achieve specific recognition of target substances. Molecular imprinting materials show unique advantages. By combining with molecular imprinting polymer, the detection of these sensors shows high sensitivity and precision. A current-type sensor can be constructed by coating molecular imprinting material on the electrode, which can be used to screen hormone veterinary drugs such as nandrolone. It is reported that molecularly imprinted materials are used to selectively detect testosterone in liquid phase by using a sound wave sensor with artificially imitated recognition elements [4].

5. Limitations

Although MIPs-based sensors have effectively improved detection accuracy, this technology still has limitations [6]. It is still lack of sufficient researches on molecular imprinting materials. A large numbers of molecular imprinting materials are still at the laboratory stage. Including most of the sensors and detection applications mentioned above have not been utilized in commercial and daily life. Moreover, molecular imprinting polymers have strong specificity, which makes them difficult to be effectively utilized outside of laboratories. Besides, the template molecules used in molecular imprinting membrane technology must have certain characteristics that can be specifically selected by functional monomers in order to be used in this technology. Simple molecules are not suitable for molecular imprinting materials.

6. Conclusion

In this work, the preparation of MIPs is discussed. Meanwhile, MIPs-based sensors have been proven to achieve accurate and rapid detection of target objects. Molecular imprinting materials have the characteristic of high selectivity. As for traditional detection methods, it is easily influenced by interfering factors, resulting in inaccurate or even incorrect detection results.

Molecular imprinting materials have the advantage of reusable. But current methods involve the same elution steps, which could prevent them from fully realizing their reusable feature in the home use area. Although molecular imprinting materials have made significant progress in the laboratory, they still have a lot of room for improvement in the future. In the future, utilizing magnetic nanoparticles to achieve rapid and efficient separation of MIPs will become a promising research direction. In addition, improving the preparation method will help increase the binding rate between MIPs and target molecules. In conclusion, in-depth researches on MIT and MIPs in the future will promote the development food safety.

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