Electrochemical Biosensors for Food Safety Control in Food Processing

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Abstract

Foods from animal and plant origin may represent vehicles of different contaminants (chemical and microbiological) which are responsible for many foodborne diseases. Foods can be contaminated during all stages of the food chain by pathogenic bacteria or chemical compounds originated by environmental pollution or uncorrected use of crop protection products. Food safety is therefore a very important issue in the actual context of the intensive development of the food products. Nutrient monitoring and fast screening of contaminants represent some of the key issues in the agri-food field for assessment of food quality and safety. Conventional methods in food safety analysis are laborious, time-consuming, and require skilled technicians. The demand for the development of simple, fast, accurate, low-cost, and portable analytical instruments is growing and biosensors appear to meet these requirements. A biosensor is an analytical device used to quantify the target of interest in a sample. Generally, it comprises a biorecognition element which is specific toward the target. Molecular recognition events between the recognition element and the target compound elicit a physiochemical or biological signal, which is converted into a measurable quantity by the transducer. The choice of biological element and the optimum transducer depends on the properties of the sample of interest and the type of physical magnitude to be measured. The application of biosensors in food safety analysis sheds new light on the efficient and rapid detection of foodborne toxins,

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allergens, pathogens, toxic chemicals, heavy metals, and other contaminants. In particular, among the variously reported biosensors, electrochemical biosensors have been very popular and widely used due to their simple and well-understood bio-interaction and detection process. Electrochemical biosensors are based on the measurement of the electrical properties of the sample due to the chemical reaction between immobilized biomolecules and the analyte of interest; they use a transducer where electrochemical signals are generated during biochemical reactions and are monitored using suitable potentiometric, amperometric, conductimetric, impedimetric systems of analysis. Therefore, electrochemical biosensors represent a promising tool for food analysis due to the possibility of satisfying specific demands that the classic methods of analysis do not attain: advantages as high selectivity and specificity, which allows the detection of a broad spectrum of analytes in complex samples with minimum sample pretreatment, relatively low cost of construction, the potential for miniaturization, easier automation, and simple and portable equipment construction. Based on the above, this chapter wants to provide general information about biosensors and to highlight the current situation in the literature on electrochemical biosensors for the detection of some microbiological and chemical hazards in food processing.

Keywords

Food safety · Label-free biosensors · Electrochemical impedance spectroscopy

2.1 Introduction

Illnesses resulting from foodborne diseases have become one of the most widespread public health problems in the world today. Internationally, foodborne diseases associated with microbial pathogens, toxins, and chemical contaminants in food present a serious threat to the health of millions of individuals (Redmond and Griffith 2003). Therefore, the assessment of food safety is one key area for the modern food industry. Food from animal and plant origin may represent vehicles of chemical and microbiological contaminants which are responsible for many foodborne diseases. Foods can be contaminated during all stages of the food chain by pathogenic bacteria or chemical compounds originated by environmental pollution or uncorrected use of crop protection products. Food safety is therefore a very important issue in the actual context of the intensive development of food products. The monitoring and fast screening of contaminants represent some of the key issues in the agri-food field for assessment of food quality and safety. Conventional methods in food safety analysis are expensive, laborious, time-consuming, and require skilled technicians (Campuzano et al. 2017). The demand for the development of simple, fast, accurate, low-cost, and portable analytical instruments able to monitor the presence of food hazards is a primary need in the food industry and the biosensors appear to meet these requirements. International Union of Pure and Applied Chemistry (IUPAC) proposed a very stringent definition of a biosensor: "*A biosensor is a self-confident*

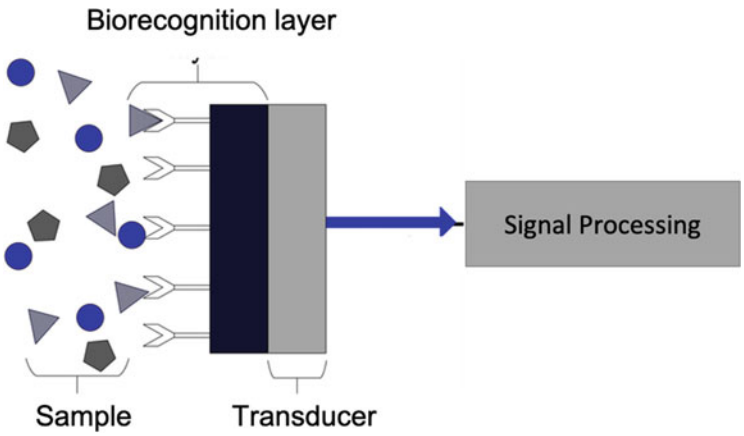

Fig. 2.1 Schematic diagram of a biosensor

integrated device which is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor) which is in direct spatial contact with a transducer element. A biosensor should be clearly distinguished from a bioanalytical system which requires additional steps, such as reagents addition" (Thevenot et al. 2001). Briefly, a biosensor can be defined as an analytical device characterized by a biological recognition element in close or integrated with a detector to identify the presence of one or more specific analytes and their concentrations in a sample (Fig. 2.1). A biosensor aims to provide rapid, real-time, and reliable information about the biochemical composition of its surrounding environment; ideally, it is a device that is capable of responding continuously, reversibly without perturbing the sample (Chandra et al. 2012; Choudhary et al. 2016; Deka et al. 2018; Mahato et al. 2018; Verma et al. 2019).

Biosensors can be classified in agreement with the type of recognition element or the type of signal transduction. As regards the first classification, biosensors are divided into two main groups: catalytic and affinity biosensors. In the first case, the recognition element can be characterized by enzymes, whole cells (bacteria, fungi, cells, yeast), cell organelles, and plant or animal tissue slices. The catalytic sensors have the longest tradition in the field of biosensors: historically, glucose sensing has dominated the biosensor literature and has delivered huge commercial successes to the field. As concerns the affinity biosensors, the biomolecule can be represented by chemoreceptors, antibodies, nucleic acids; they provide selective interactions with a ligand to form a thermodynamically stable complex. The most developed examples of biosensors using complexing receptors are immunosensors, based on the interaction process between an antigen with its specific antibody.

Related to the classification based on transducers, a wide variety of transduction techniques have been developed in biosensing technology; in particular, the most

common are optical, piezoelectric, calorimetric and electrochemical (Thakur and Ragavan 2012).

It is fair to support that most biosensors reported in the literature are based on electrochemical transducers: recent studies have shown that electrochemical-based sensors are the most common and, in particular, electrochemical affinity biosensors are particularly interesting in food analysis (Campuzano et al. 2017; Roariu et al. 2016). This may not be surprising considering that the electrochemical transduction shows, more than others, many advantages including low instrumentation costs, high sensitivity, ease of miniaturization, and relatively simple instrumentation; all these features are highly compatible with portable devices (Malvano et al. 2020).

Furthermore, is worth highlighting that, among electrochemical transducers, the impedimetric ones are optimal for *label-free* detection of bio-interaction, which is based on the direct measurement of phenomena occurring during the biochemical reactions on a transducer surface, concerning a "labeled" detection which relies on the investigation of a specific label (fluorophores, magnetic beads, active enzyme, etc.) (Daniels and Pourmand 2007).

Electrochemical Impedance Spectroscopy is, in fact, a powerful, non-destructive and informative technique, which can be used to study the electrical properties of the sensing device interface and tracing the reaction occurring on it. The application of impedance as a transduction technique, based on the direct monitoring of the interaction between the bioreceptor and its target, enables the production of label-free biosensors for food analysis with significant advantages over labeled ones. By avoiding the laborious and expensive labeling steps, which can cause loss of affinity between the labeled receptor and its target and decrease reproducibility, sensitivity, and selectivity of the biosensor, the use of label-free monitoring reduces biosensor costs and allows analysis in a short time (Rhouati et al. 2016). Thanks to the EIS transduction technique, food biosensor analysis is performed in real-time by studying the change in electrical properties of the electrode surface which depends only on the binding interaction between the analyte and its receptor.

Thus, to respond to the need for food safety control, label-free affinity biosensors can be considered as the most relevant devices for fast measurements of food hazards in food processes, being able to detect a wide range of chemical and microbiological risks through the use of appropriate biomolecules.

In this regard, the last decade has observed phenomenal growth in the field of electrochemical affinity biosensors for analyses of food and beverage, in particular for food safety monitoring.

2.2 Electrochemical Biosensor for Food Safety

This chapter provides an overview of the potential application of electrochemical biosensors for the analysis of chemicals and microorganisms that affect food safety, discussing some examples of the latest advances in this field. A focus on the most commonly responsible for food contaminations, including toxins and mycotoxins,

pesticides, pathogenic bacteria will be presented, pointing out the advantages of electrochemical transduction techniques applied on affinity biosensors.

2.2.1 Mycotoxins

Mycotoxins are a varied group of toxic secondary metabolites produced by molds. They are thermally stable and notoriously toxic, teratogenic, mutagenic, and carcinogenic, which can enter into the human food chain causing severe impact on human health. The risk of mycotoxins are well-recognized worldwide and also the incidence of these compounds is a universal problem: they affect a broad range of agricultural products including cereals, cereal-based foods, dried fruits, wine, milk, coffee beans, cocoa, bakery and meat products, which are the basis of the economies of many developing countries (Evtugyn and Hianik 2019).

The most relevant mycotoxins under a toxicological and legislative point of view are the ochratoxins and aflatoxins; their chemical structures are represented in Fig. 2.2.

In the latest years, there has been a significant effort to improve analytical approaches for the effective determination of mycotoxins: common analytical methods like capillary electrophoresis, and chromatography techniques linked to mass spectrometry (LC-MS, GC-MS), reliable but characterized by sophisticated and expensive instruments and not suitable for real-time and on-site application, try to be replaced with innovative biosensor technologies to obtain reliable, fast, and sensitive measurements with high selectivity and reduced cost.

Among mycotoxins, Ochratoxin A (OTA) is one of the most abundant in a wide range of agricultural commodities, ranging from cereals grains to dried fruits to wine and coffee, in a few micrograms per kilogram amounts. In the European Union, the

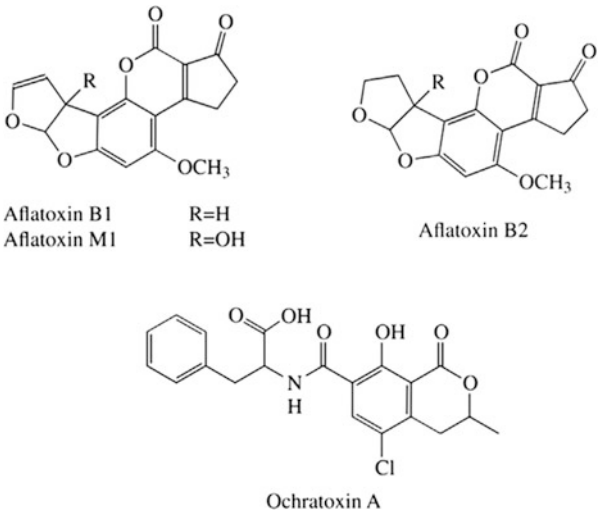

Fig. 2.2 Chemical structures of the main aflatoxins and ochratoxins

maximum limits established for OTA in different food products are fixed in Commission Regulation (EC) N° 1881/2006 and ranged from 10 μg/kg for instant coffee and dried fruits to 0.5 μg/kg for dietary foods intended specifically for infants.

Different electrochemical immunosensors have been reported in the literature for the detection of OTA amount in food matrices at least equal to the acceptable limits of OTA allowed by regulation.

Badea et al. (2016) immobilized monoclonal antibody on screen-printed gold electrodes through bovine serum albumin used as "anchor" for the covalent immobilization of the anti-OTA antibodies: all the steps of the immunosensor construction and also the immunochemical reaction between surface-bound antibody and OTA were analyzed using cyclic voltammetry and electrochemical impedance spectroscopy. The specific interaction between antibody and OTA induces an increase in electron transfer resistance at the interface sensor/solution that is correlated with the concentration of OTA in the sample: the detection of OTA was achieved by EIS in the linear range 2.5–100 ng/mL. The developed immunosensor was also used to detect OTA amounts in licorice extracts samples.

Malvano et al. (2016a) proposed two different antibody immobilization techniques on gold electrodes: oriented and not oriented. The comparison between the two monoclonal anti-OTA immobilization procedures underlined the advantages of oriented one, which showed a more ordered and homogeneous antibody layer that guarantees a higher number of molecules effectively exposed to antigen interaction. The linear range (0.05–25 μg/kg), the very low detection limit (0.05 μg/kg), and high sensitivity (26.45 kΩ mL/ng) showed the potential of the immunosensor as a highly capable analytical device for fast measurement of OTA traces. Tests with cocoa beans were also performed by the authors to study the feasibility of applying the immunosensor for the detection of OTA in food samples.

To exploit the advantages of cheap electrodes, characterized by low-cost fabrication and mass production, Malvano et al. (2016b) proposed a capacitive OTA immunosensor on screen-printed carbon electrode modified with electrodeposited gold nanoparticles. Using the electrochemical impedance spectroscopy it was observed that the capacitance was the best parameter that described the reproducible change in electrical properties of the electrode surface at different OTA concentrations, and it was used to investigate the analytical performances of the developed immunosensor. Under optimized conditions of monoclonal antibody amount, the immunosensor showed a wide linear range between 0.3 and 20 ng/mL with a limit of detection of 0.34 ng/mL, making it suitable for the analytical determination of OTA in food matrices.

Despite the high selectivity guaranteed by the use of antibodies, the main drawback for the development of immunosensors is due to the high cost of specific monoclonal antibodies used for the biorecognition process. Nucleic acid aptamers, obtained by the in vitro selection process SELEX, represent an alternative approach of receptors for affinity biosensors production. The use of aptamers as biomolecular recognition is justified by their low-cost synthesis, high reproducibility, and higher stability due to their nucleic-acid chemical nature. Additionally, they can be easily

combined with different chemical labels/groups that provide flexibility for adaptation to different platforms (Miranda-Castro et al. 2016).

In addition to the choice of aptamers as alternative biorecognition molecules, nanostructured platforms based on conductive materials, including conducting polymers, gold nanoparticles (AuNPs), quantum dots (QDs), magnetic beads and carbon nanomaterials, represented, in the latest years, an interesting approach for electrochemical signal enhancement, to improve sensitivity and the stability of biomolecules activity (Campuzano et al. 2017).

To improve the electrical conductivity of the non-homogeneous electrode surfaces, Rivas et al. (2015) developed an impedimetric biosensor using a 3-′-aminated aptamer selective to OTA recognition. The immobilization of the aptamer was carried out, on screen-printed carbon electrodes modified with an electropolymerized film of polythionine and iridium oxide nanoparticles (IrO2 NPs). The aptasensor showed the lowest limits of detection reported so far label-free impedimetric detection of OTA, equal to 5.65 ng/kg.

Mejri-Omrani et al. (2016) covered the surface of a gold electrode with a conductive polypyrrole layer and used fourth-generation polyamide amine dendrimers for the covalent immobilization of an aptamer for OTA detection formed by 36 nucleotides with the sequence NH2-(CH2)6-–5′GATCGGGTGTGGGTGGCGTAAAGGGAGCATCGGACA-3′.

The aptasensor showed a range of up to 5 μg/L and a detection limit of 2 ng/L of OTA, and no matrix effects were observed during the analysis of OTA in red wine.

In more recent years, metallic nanomaterials advantage was exploited for the development of electrochemical label-free aptasensors. Gold nanoparticles combined with carboxylic porous carbon represented an excellent carrier for both the immobilization of DNA-aptamers and the amplification of the impedimetric signal (Wei and Zhang 2017). Under optimized conditions, the change in the charge transfer resistance of the electrode showed a log-linear relationship to OTA concentration in the range 10^{-8}–0.1 ng/mL, with the limit of detection equal to 10^{-8} ng/mL. Recovery studies were performed in soybean samples by spiking 10^{-6} ng/mL and recoveries ranged from 95% to 108%.

A more complex structure based on bimetallic (Cu–Co) Prussian Blue analogs (PBAs) coupled to gold nanoparticles was used to develop an impedimetric aptasensor (Gu et al. 2019). The chemical composition and crystal structure of the bimetallic matrix guaranteed excellent electrochemical conductivity and strong aptamer binding interaction, achieving a very low limit of detection equal to 5.2 fg/mL.

In addition to Ochratoxins, Aflatoxins are a group of mycotoxins characterized by a great carcinogenic power. Coupling the advantages and the effectiveness of monoclonal antibodies with different strategies for signal enhancement, a lot of electrochemical label-free immunosensors were proposed in literature characterized by satisfactory performances.

Li et al. (2017) constructed a label-free impedimetric immunosensor based on gold three-dimensional nanotube ensembles: AFB1 monoclonal antibodies were immobilized on the surface using a staphylococcus protein A layer, obtaining a

limit of detection equal to 1 pg/mL. In another example, Costa's group reported an impedimetric immunosensor based on carbon nanotubes and an Au electrode for monitoring AFB1 (Costa et al. 2017): in this immunosensor, the carbon nanotubes exhibited an exceptional surface/volume ratio and excellent electrical properties.

Bhardwaj et al. (2019) showed an immunosensor in which anti-AFB1 was immobilized on the surface of an ITO glass electrode coated with graphene QDs and AuNPs: the electrocatalytic activity of the AuNPs improved the electronic properties of the composite GQDs-AuNPs, reaching a linear range from 0.1 to 3.0 ng/mL. Yagati's group reported an impedimetric immunosensor that selectively detects AFB1 at the lowest level by utilizing polyaniline nanofibers (PANI) coated with gold (Au) nanoparticles composite-based indium tin oxide (ITO) disk electrodes. The Au-PANI acted as an effective sensing platform having high surface area, electrochemical conductivity, and biocompatibility which enabled greater loading deposits of capture antibodies. As a result, the presence of AFB1 has screened in a linear range 0.1–100 ng/mL with a detection limit of 0.05 ng/mL (Yagati et al. 2018).

A platform of Poly(3,4-ethylenedioxythiophene) (PEDOT) and graphene oxide (GO) composite decorated with spherical gold nanoparticles (AuNPs) has been used for the immobilization of anti-aflatoxin B1 covalently immobilized using EDC/NHS coupling. The proposed amperometric immunosensor exhibits a very high sensitivity within two linear range of 0.5–20 ng/mL and 20–60 ng/mL, respectively (Sharma et al. 2018).

A ferrocene-modified gold electrode was proposed by Malvano et al. (2019) as a platform for the immobilization of monoclonal anti-AFB1. In this work, the authors developed a label-free immunosensor, using the impedimetric technique, characterized by linearity in the range 0.01–10 ng/mL and a limit of detection of 0.01 ng/mL.

In more recent years, different electrochemical aptasensors with optimum performances were developed in alternatives to immunosensors. A very novel magnetically assembled aptasensing device has been designed for label-free determination of AFB1 by employing a disposable screen-printed carbon electrode covered with a polydimethylsiloxane (PDMS) film (Wang et al. 2018a, b). The bio-probes were firstly prepared by immobilization of the thiolated aptamers on the Fe_3O_4Au magnetic beads, which were rapidly assembled on the working electrode of SPCE, by using a magnet placed at the opposite side. The developed method allowed the construction of an impedimetric aptasensor with a wide linear range between 20 pg/mL and 50 ng/mL with a low detection limit of 15 pg/mL, opportunely used in peanuts samples.

Aptamer against AFM1 was immobilized on a glassy carbon electrode covered with polymeric neutral red (NR) dye obtained by electropolymerization. In the presence of AFM1, the cathodic peak current related to the NR conversion decreases and an increase of the charge transfer resistance measured by electrochemical impedance spectroscopy was observed. In optimal conditions, this makes it possible to determine AFM1 from 5 to 120 ng/L in standard solutions with a limit of detection of 0.5 ng/L. The aptasensor was validated on the spiked samples of cow and sheep

Table 2.1 Electrochemical affinity biosensors for mycotoxins detection

Analyte	Interface	Transduction technique	Range	LOD	Reference
Patulin	AuE/ZnONRs/AuNPs/Apt	DPV	0.5–50 ng/mL	0.27 pg/mL	He and Dong (2018)
Zearalenone	SPCE/BSA/MAb	DPV	0.25–256 ng/mL	0.25 ng/mL	Yugender Goud et al. (2017)
Zearalenone	AuE/p-PtNTs/AuNPs/thionin labeled GO	AMP	0.5 pg/mL–0.5 μg/mL	0.17 pg/mL	He and Yan (2019)
Fumonisin F1	GCE/AuNPs/Apt	EIS	0.1–100 nM	2 pM	Chen et al. (2015)
Zearalenone	GCE/Au-Pt NPs/MAb	DPV	0.005–50 ng/mL	0.5 pg/mL	Liu et al. (2017)
Zearalenone	GCE/chitosan/conjugate of zearalenone with BSA	DPV	10 pg/mL–1000 ng/mL	4.7 pg/mL	Xu et al. (2017a, b)
Zearalenone	SPCE/Fe_2O_3/HRP	DPV	1.88–45 ng/mL	0.57 ng/mL,	Regiart et al. (2018)
DON	GCE/AuNPs/4nitrophenylazo	EIS	6–30 ng/mL	0.3 ng/mL	Sunday et al. (2015)
DON	SPCE/AuNPs/Polypyrrole/Ab	DPV	0.05–1 ppm	8.6 ppb	Lu et al. (2016)
Fumonisin B1	SPCE/AuNPs/Polypyrrole/Ab	DPV	0.2–4.5 ppm	4.2 ppb	Lu et al. (2016)
Fumonisin B1	GCE/chitosan/DON-BSA	DPV	0.01–1000 ng/mL	5 pg/mL	Qing et al. (2016)
T-2 Toxin	GCE/chitosan/DON-BSA	DPV	0.01–100 μg/mL	0.13 μg/mL,	Wang et al. (2018a, b)

AuE:gold electrode; SPCE: screen-printed carbon electrode; ZnONRs: ZnO nanorods; Apt: aptamer; BSA: bovine serum albumin; MAb: monoclonal antibody; p-PtNTs: porous platinum nanotubes; AuNPs: Gold nanoparticles; GCE: glassy carbon electrode; Au-Pt NPs: gold-platinum nanoparticles; HRP: Horseradish peroxidase

milk, reaching a reliable detection of the 40–160 ng/kg of mycotoxin (Smolko et al. 2018).

Ochratoxins and Aflatoxins are the most common mycotoxins present in the food sample, but there are other substances, less common but not with less harmful effects on human health. The following table (Table 2.1) summarizes some recent example of electrochemical affinity biosensors developed for the detection of different toxins and mycotoxins.

2.2.2 Pathogenic Bacteria

Foodborne illnesses caused by pathogenic bacteria represent an important threat to the health of people. Pathogens are infectious agents that cause disease; they include microorganisms such as fungi, bacteria, and molecular scale infectious agents including viruses and prions. Among these, *Escherichia coli* O157:H7, *Salmonella*, *Listeria monocytogenes*, *Campylobacter*, *Helicobacter*, *Staphylococcus aureus*, and *Bacillus cereus* are the most common and are responsible for approximately 90% of all foodborne diseases (Dye 2014).

Conventional methods for pathogenic bacterial identification involve various culturing techniques and different biochemical tests which are very time-consuming, requiring 2–4 days. Analysis time and sensitivity are the most important limitations related to the usefulness of bacterial testing. An extremely selective detection methodology was also required because low numbers of pathogenic bacteria are often present in a complex biological sample along with many other nonpathogenic bacteria. Tedious and time-consuming detection methods have prompted several groups in recent years to develop other techniques to reduce the detection time like Polymerase Chain Reaction (PCR) and Enzyme-Linked Immunosorbent Assay (ELISA). However, both techniques have limitations that exclude their extensive implementation. These limitations include accurate primer designing, the requirement of specific labeled secondary antibodies, and their failure to distinguish spore viability (Cesewski and Johnson 2020).

Recently, numerous electrochemical biosensors have been developed using impedimetric, potentiometric, and voltammetric techniques for the detection of several bacteria and parasites: a lot of novel approaches of working modification were carried out to develop very sensitive electrochemical biosensors.

E. coli are bacteria that naturally occur in the intestinal tracts of humans and warm-blooded animals to help the body synthesize vitamins. One pathogenic strain, *E. coli* O157:H7, produces toxins that damage the lining of the intestine, causes anemia, stomach cramps and bloody diarrhea, and serious complications called hemolytic uremic syndrome (HUS) and thrombotic thrombocytopenic purpura (TTP). Several electrochemical biosensors have been developed for the detection of this pathogenic bacteria in food products (Doyle 1991).

An electrochemical immunosensor for rapid detection of *E. coli* O157:H7 have been proposed by Xu et al. (2017a, b): the immunosensor was prepared by layer-by-layer assembly involving the formation of 11-amino-1-undecanethiol self-assembled monolayer onto a gold electrode and the immobilization of AuNPs followed by the incorporation of Chitosan-MWCNTs–SiO_2/thionine nanocomposites and AuNPs multilayer films. Finally, anti-E.coli O157:H7 antibodies were covalently bound and electrochemical impedance spectroscopy was used to obtain a calibration curve for heat-killed *E. coli* O157:H7, by measuring the increase in the charge transfer resistance as the antigen concentration increased. The working range was 4.12×10^2–4.12×10^5 CFU/mL.

Gold microelectrodes modified with maleic anhydride/(hycroxyethyl)-methacrylate polymer film were used to immobilize anti-*E.coli* and to develop a

capacitive label-free immunosensor able to detect *E.Coli* cells at least equal to 70 CFU/mL (Idil et al. 2017). Graphene electrodes were modified with chitosan/polypyrrole/carbon nanotubes/gold nanoparticles layer (Guner et al. 2017) and CuO/cysteine (Pandey et al. 2017) for the immobilization of monoclonal antibodies to detect *E. Coli* O157:H7 at least equal to 30 CFU/mL and 3.8 CFU/mL, respectively.

Malvano et al. proposed two different impedimetric immunosensors for the sensitive detection of *E. coli* O157:H7: in the first one, monoclonal antibodies were immobilized on a strontium titanate perovskite layer ($SrTiO_3$) synthesized on a platinum electrode. Under optimized conditions, the capacitive immunosensor showed a detection range from 10^1 to 10^7 CFU/mL and an LOD of 10 CFU/mL (Malvano et al. 2018a). A lower limit of detection (3 CFU/mL) was found afterward exploiting the high conductive properties of ferrocene-modified gold electrodes use as a platform for the antibodies immobilization. The immunosensor was used to analyze milk and meat samples obtaining a good agreement with the results of ELISA analysis (Malvano et al. 2018b).

More recently, Jafari et al. (2019) used a TEOS/MTMS sol-gel on gold microelectrodes to immobilize monoclonal antibodies for *E. Coli* O157:H7 detection. Through electrochemical impedance spectroscopy transduction technique, the immunosensor was able to detect the microorganism with a limit of detection equal to 1 CFU/mL. The same limit of detection was reached by Wilson et al. (2019) using an Ag-interdigitated microelectrode array through the immobilization of a peptide as a biorecognition element.

As regards other pathogenic bacteria responsible for foodborne diseases, Sheikhzadeh et al. (2016) reported the combination of poly[pyrrole-co-3-carboxyl-pyrrole] copolymer and aptamer for the development of a label-free electrochemical biosensor suitable for the detection of *S. Typhimurium.* Impedimetric measurements were facilitated by the effect of the aptamer/target interaction on the intrinsic conjugation of the copolymer and subsequently on its electrical properties. The aptasensor detected *S. Typhimurium* in the concentration range 10^2–10^8 CFU/mL with high selectivity and with a limit of quantification of 100 CFU/mL and a limit of detection of 3 CFU/mL. The suitability of the aptasensor for real sample detection was demonstrated via recovery studies performed in spiked apple juice samples.

A label-free impedimetric aptamer-based biosensor for S. *typhimurium* was also fabricated by grafting a diazonium-supporting layer onto SPCEs followed by the immobilization of an aminated-aptamer. This strategy allowed obtaining a dense aptamer layer, which resulted in high sensitivity with a limit of detection of 8 CFU/mL (Bagheryan et al. 2016). Also, a novel outer membrane antigen (OmpD) was used for the first time as a surface biomarker for detecting *S. typhimurium*. Anti-OmpD antibody was used as detector probe in an impedimetric immunosensor using graphene-graphene oxide-modified SPCEs. The developed method was able to selectively detect *S. typhimurium* in spiked water and juice samples with a sensitivity up to 10 CFU/mL (Mutreja et al. 2016).

Izadi et al. (2016) proposed an electrochemical DNA-based biosensor for *Bacillus cereus* in milk and infant formula. They explored AuNPs to prepare a modified pencil graphite electrode that could detect Bacillus cereus as low as 100 CFU/mL.

Gold-interdigitated electrode arrays were realized for the detection of *L. monocytogenes*, using polyclonal antibodies: the devices were able to detect until 160 CFU/mL (Chen et al. 2016) and 39 CFU/mL of bacteria (Wang et al. 2017a, b), using different antibodies immobilization techniques.

Other electrochemical biosensing platforms have also been reported for the determination of *S.aureus*. CNT-coated Au-tungsten microwire electrodes (Yamada et al. 2016) and PEI/CNT composite on Au microwire electrode (Lee and Jun 2016) were used as a platform for the immobilization of polyclonal antibodies. Both the biosensors were able to show the same LOD of 100 CFU/mL. Higher performance in the detection limit was reached by Primiceri et al. (2016) who proposed a biochip based on an interdigitated microelectrode array able to quantitatively detect two of the most common food-associated pathogens, *Listeria monocytogenes* and *Staphylococcus aureus*, with a detection limit as low as 5.00 CFU/mL for *L. monocytogenes* and 1.26 CFU/mL for *S. aureus.*

2.2.3 Pesticides

According to the US Environmental Protection Agency (EPA), pesticides are defined as any substance or mixture of substances intended for repelling, destroying, or controlling any pest. Due to their high insecticidal activity, they are widely used in agriculture to protect crops and seeds by destroying insects, bacteria, and rodents and other weed animals (World Health Organization 2016).

However, the presence of pesticide residue in food, water, and soil has become a very critical problem in environmental chemistry.

Pesticides are classified in several ways, according to their toxicity (dangerous, highly dangerous, moderately dangerous, and slightly dangerous) and their lifetime (permanent, persistent, moderately persistent, and not persistent). Often, they are classified according to the use as insecticides, miticides, herbicides, nematicides, fungicides, molluscicides, and rodenticides. Referring to the chemical structure, the commonly reported main classes are organochlorines, organophosphates, carbamates, and pyrethroids. In addition to these common classes of pesticides, there are other chemical classes employed as herbicides, hormonal, amides, nitro compounds, benzimidazoles, bipyridyl compounds, ethylene dibromide, sulfur-containing compounds, copper, or mercury, among others. (Garcia et al. 2012).

The monitoring and the fast quantification of pesticides and their residues have become extremely important to ensure compliance with legal limits. The analysis of these compounds is an important issue due to their potential bioaccumulation, high toxicity, and their long-term damage risk, also for the use at low concentration. Food safety assurance requires fast and easy analytical tools to work alongside confirmatory methods such as chromatography coupled to mass spectrometry that require very expensive equipment, long analysis times, high reagent sample volumes, and

qualified personnel (Kumar et al. 2015). Due to these limits, alternative methodologies for pesticide detection have been recommended in the last few years: the most relevant ones are those based on electrochemical methods. Table 2.2 summarizes the strategies and features of the electrochemical immunosensors developed for the quantification of different kinds of pesticides in food products.

The most used approach for the electrochemical label-free biosensors based on non-competitive pesticides detection was Electrochemical Impedance Spectroscopy but also voltammetry technologies were adopted.

In 2017, a very innovative enzyme inhibition-based biosensor, immobilizing AChE enzyme on cysteamine-modified electrode, was proposed to sensitively detect carbamate and organophosphate compounds with an extremely fast response. The working principle of the biosensor is based on the high-affinity interaction between the investigated pesticides (Carbaryl, Paraquat, Kresomix–Methyl, Dichlorvos, Chlorpyrifos–Methyl Pestanal, Phosmet) and the active site of the enzyme. The capability of CBs and OPs compound to form a very stable complex with the enzyme causes an impedimetric change, allowing to go up very fast to the presence of the toxic compounds in food matrices. The proposed biosensor showed linearity between 5 and 170 ppb for carbamates and 2.5–170 ppb for organophosphate compounds (Malvano et al. 2017).

As highlighted above, also for pesticide detection nucleic acid aptamers have represented an alternative approach in the biosensor field. Novel aptasensors based on the impedimetric and voltammetric transduction techniques were developed in the last years; strategies and features are summarized in Table 2.3.

Detection limits at the picomolar level are reported for a lot of the developed assays and the proposed sensors show that the combination of novel transduction materials and strategies with improved recognition elements can push toward lower and lower achievable detection limits.

2.3 Future Perspectives

Ensuring food safety is the main interest both for the food industry and for consumers. The guarantee of food safety requires fast and specific controls for all contaminants, chemicals, and bacteria, which are harmful to human health.

Despite common analytical techniques that are time-consuming, require highly trained personnel, are expensive and require steps of sample pretreatment, increasing the time of analysis, among food and beverage industries exists a growing demand in biosensing technologies as simple, rapid, cheap, low-cost, and portable analytical devices for the monitoring of chemical and microbiological contaminants (toxins, mycotoxins, pathogenic bacteria, pesticides, and allergens) that endanger the food safety. In particular, the electrochemical biosensors systems have been demonstrated to have advantages like portability, shortened analysis time, ease of operation, novice-friendly, and direct analysis with no sample preparation procedures. Thus, the electrochemical sensing arrays have been acknowledged as reliable tools for

Table 2.2 Electrochemical immunosensors for pesticides detection in food

Analyte	Interface	Transduction technique	Range [M]	LOD [M]	Reference
Carbofuran	gelatin/Ab/GA/L-Cys/Au electrode	EIS	4.52×10^{-10}–4.52×10^{-6}	4.52×10^{-10}	Liu et al. (2015)
Chlorpyrifos	Ab/protein A/AuNPs/PDDA/gold IDAMs	EIS	1.43×10^{-9}–1.43×10^{-6}	1.43×10^{-9}	Jia et al. (2015)
Chlorpyrifos	BSA/Ab/protein A/gold IDAMs	EIS	2.85×10^{-9}–2.85×10^{-4}	3.99×10^{-11}	Cao et al. (2015)
2,4-D	Ab/AuNPs-PANABAMWCNTs/SPE	EIS	4.52×10^{-9}–4.52×10^{-7}	1.36×10^{-9}	Fusco et al. (2017)
Parathion	Ab/fG/SPE	EIS	3.43×10^{-13}–3.43×10^{-9}	1.79×10^{-13}	Mehta et al. (2016)
Atrazina	BSA/Ab/AuNPs/Au	DPV	$2.32*10^{-10}$–2.32×10^{-9}	7.42×10^{-11}	Liu et al. (2014a, b)
Chlorpyrifos	BSA/Ab/GS-MB/AuNPs/GCE	CV	2.85×10^{-9}–1.43×10^{-6}	1.60×10^{-10}	Qiao et al. (2014)
Atrazine	ATR-BSA/PAMAM/AET/Au/GCE	CV	4.64×10^{-11}–4.64×10^{-6}	5.56×10^{-9}	Giannetto et al. (2014)
Chlorpyrifos	BSA/Antigen/Co3O4/PANI/ITO	CV	0–2.85×10^{-5}	2.85×10^{-8}	Wang et al. (2017a, b)
Paraquat	GEC	SWV	1.20×10^{-8}–2.63×10^{-7}	3.11×10^{-11}	Liu et al. (2014a, b)

GA: glutaraldehyde; L-cys: L-cysteine; PDDA: poly (diallydimethylammonium chloride); IDAMs: interdigitated array microelectrodes; BSA: bovine serum albumin; PANABA: polymer poly-(aniline-co-3-aminobenzoic acid); MWCNTs: multi-walled carbon nanotubes; SPE: screen-printed electrode; fG: graphene sheets functionalized; GS-MB: graphene sheets-methylen blue; GS-PEI: graphene sheets-ethyleneimine polymer; ATR: atrazine; PAMAM: poliamidoaminic dendrimers; AET: 2-aminoethanethiol; ITO: indium tin oxide; SWNTs; GEC: graphite composite electrode

Table 2.3 Electrochemical aptasensors for pesticides detection in food

Analyte	Interface	Transduction technique	Range [M]	LOD [M]	Reference
Carbendazim	MCH/aptamer/Au electrode	EIS	5.23×10^{-11}–5.23×10^{-8}	4.29×10^{-11}	Eissa and Zourob (2017)
Acetamiprid and atrazine	MCH/aptamer/GOPTS/PtNPs microwires modified Au IDEs	EIS	1.00×10^{-11}–1.00×10^{-7} (acetamiprid) 1.00×10^{-10}–1.00×10^{-6} (atrazine)	1.00×10^{-12} (acetamiprid) 1.00×10^{-11} (atrazine)	Madianos et al. (2018)
Acetamiprid	MCH/aptamer/Ag-NG/GCE	EIS	1.00×10^{-13}–5.00×10^{-9}	3.30×10^{-14}	Jiang et al. (2015)
Acetamiprid	MCH/aptamer (oligo 1)/AuNPs/PANI/GSPEs	DPV	2.50×10^{-7}–2.00×10^{-6}	8.60×10^{-8}	Rapini et al. (2016)
Malathion	Aptamer/SA/CHIT-IO/FTO	DPV	3.03×10^{-12}–3.03×10^{-8}	3.03×10^{-12}	Prabhakar et al. (2016)
Chlorpyrifos	Aptamer/AMP/CuONFs-SWCNTs/Nafion/GCE	DPV	2.85×10^{-10}–4.28×10^{-7}	2.00×10^{-10}	Xu et al. (2018)
Chlorpyrifos	BSA/aptamer/Fc/MWCNTs/OMC/GCE	CV	2.85×10^{-9}–2.85×10^{-4}	9.41×10^{-10}	Jiao et al. (2016)
Chlorpyrifos	BSA/aptamer/GO/Fe_3O_4/CB-CS/GCE	CV	2.85×10^{-10}–2.85×10^{-4}	9.41×10^{-11}	Jiao et al. (2017)

MCH: 6-Mercap-1-hexanol; GOPTS: (3-glycidyloxypropyl)trimethoxysilane; PtNPs: platinum nanoparticles; IDEs: interdigitated electrodes; GSPEs: graphite screen-printed electrodes; SA: streptavidin; CHIT-IO: chitosan-iron oxide nanocomposite; FTO: fluorine tin oxide; AMP: amino-modified capture probe; CuONFs: copper oxide nanoflowers; SWCNTs: single-walled carbon nanotubes; Fc: ferrocene; OMC: mesoporous carbon; GO: graphene oxide; CB: carbon black

automated on-site analysis of mycotoxins in food processing and manufacturing industries.

Moreover, research results achieved in recent years confirm that nanomaterial usage had been rapidly growing in the development of electrochemical biosensors. Analytical performances of the biosensors.

systems increased enormously with the incorporation of nanomaterials: low detection limits up to sub/picomolar and sub/femtomolar levels and wide linear analytical ranges were achieved with nanomaterials and nanocomposites of synergetic combinations.

Therefore, the development of new materials and the application of nanostructures to biosensor systems could lead to the development of highly sophisticated analytical systems.

The speed of analysis and the low cost of the transduction instrumentation makes the electrochemical biosensors the most promising devices, for routine applications by common users, ensuring high analytical performance in terms of sensitivity and low detection limits.

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