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Review

Electrochemical strategies for detection of diazinon

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Abstract

Diazinon (DZN) was first registered as an insecticide in the U.S. However, it was categorized in the limited group of pesticides due to its high toxicity for birds, aquatic animals, and humans. Like other organophosphorus pesticides, this compound exhibits inhibitory effects on the acetylcholinesterase enzyme. The inhibition of the enzyme leads to the accumulation of acetylcholine and causes the death of insects. DZN is considered a toxic compound for humans due to its high adsorption via skin and inhalation, which leads to the emergence of different symptoms of toxicity. When DZN is used for plants, the compound residues in crops enter the food chain bringing about different health problems. Moreover, the compound is easily washed by surface water and enters the groundwater. Its entrance into aquatic envi-ronments can negatively affect a wide range of non-targeted organisms. Thus, researchers seek to find fast and precise methods for the analysis of DZN. The electrochemical method for recognizing the compound in real samples is preferable to other analytical methods. Because this method can be used without spending time preparing the sample, it is simple, fast, and cost-effective. Since such determinations may be made by using electrochemical sensors and biosensors, numerous researchers have developed such sensors for DZN detection, and different sensitive materials were used in order to improve the selectivity, sensitivity, and detection limit. The present study aims to present the main progress and performance characteristics of electrochemical sensors and biosensors used to detect DZN, as it is reported in a number of relevant scientific papers published mainly in the last decade.

Keywords
Pesticide; electrochemistry; modified electrodes

Introduction

Pesticides are used worldwide to protect agricultural crops and avoid plant damage caused by pests. Organophosphates are the most extensive and diverse class of pesticides [1]. The organo-phosphorus pesticides (OPPs) and organic ester derivatives of phosphorus are widely used as insecticides in agriculture [2,3]. Diazinon (DZN) with the scientific name O,O-diethyl-O-(2- isopropyl-4-methyl-6-pyrimidinyl)-O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl)-phosphorothioate is

widely used as an insecticide in agriculture. DZN is ranked as the most common organophosphorus pesticide globally after malathion [4-6]. Although DZN is a thiophosphoric ester, it shares a common mechanism of toxicity with other organophosphorus insecticides like chlorpyrifos, malathion and parathion [7]. DZN inhibits acetylcholinesterase (AChE) and prevents acetylcholine (ACh) hydrolysis in cholinergic synapses and neuromuscular junctions. Therefore, it leads to abnormal accumulation of ACh in the nervous system [8]. Since that pesticide is chemically stable, its improper application can result in environmental contamination [9] and ultimately threaten human health [10,11]. The compound belongs to the contact insecticide group and kills the insects by altering typical neurotransmitters in their nervous system [7]. U.S. Environmental Protection Agency (EPA) canceled all residential uses of DZN in 2004. Nowadays, it is only allowed to be used in agricultural environments [12]. DZN is relatively stable and mobile and cannot be absorbed by soil [13,14]. Microbial degradation in the soil is the most important process for DZN removal from the environment [7]. Conducted studies demonstrated that half-lives of DZN in soil were 21 to 103 days depending on the type of soil [15]. A compound called diazoxon is formed by DZN hydrolysis and is rapidly hydrolyzed to oxypyrimidine, which is more mobile in the environment than the original compound [7]. In addition, DZN can be decomposed by the photolysis process. In this case, the half-life of this compound on the soil surface is estimated to be between 17.3 to 37.4 hours [14]. DZN and its metabolites can be contaminated the groundwater considering their stability and mobility [13]. In the atmosphere, DZN is transformed into diazoxon, which is a more powerful AChE inhibitor compared to DZN, with a half-life of 4 hours [16]. Low levels of DZN applied outdoors can be carried indoors through airflow, dust, soil, and pets exposed to the compound [17].

The main problem of DZN application is that it can be absorbed by plant roots in soil [18]. The compound can degrade in leafy vegetables, forage crops, and grass with half-lives ranging from 2 to 14 days. However, low temperature and high oil content cause the half-life of DZN to increase in plants [18]. Pyrimidinol, as well as hydroxypyrimidinol, are the compounds resulting from DZN hydrolysis in plants. Since diazoxon can also be found in plants, the measured pyrimidinol may be a product of diazoxon hydrolysis rather than DZN hydrolysis [19]. DZN poses relatively high toxicity to vertebrates. Once entering the body, DZN is decomposed to diazoxon by oxidation which is more toxic than DZN and mainly inhibits acetylcholinesterase (AChE) [20]. The oxidation of DZN to diazoxon is carried out by the liver microsomal enzyme and requires O_2 and NADPH. DZN can also be decomposed through oxidation in the liver. Both reactions are likely to be catalyzed nonspecifically by the same mixed-function oxidase. Hydrolases further decompose DZN in the microsomal and other intracellular functions inside the liver. Mammals metabolize diazoxon with an estimated half-life of 2 to 6 weeks. Insects lack the hydrolysis step, and hence, the toxic substance is rapidly accumulated in their bodies.

The toxic compound can enter the body through skin contact, feeding, and inhalation [21]. The signs and symptoms of toxicity by DZN are similar to other toxins inhibiting AChE. Depending on the exposure period, different symptoms emerge, including colic, diarrhea or vomiting, vertigo, headaches, miosis, bradycardia, sudden drop in blood pressure, convulsion, and apnea after several minutes to hours of exposure [22,23]. Since DZN is lipid-soluble, it has the potential to be stored in fat tissues so that it can heighten delayed toxicity. It is important to detect and control organophosphorus chemicals regarding their toxicity and adverse effects on human life.

So far, various in vitro methods have been proposed to detect those compounds, such as high-performance liquid chromatography (HPLC) [24,25], liquid chromatography coupled with mass spectroscopy (LC-MS) [26], gas chromatography-mass spectrometry (GC-MS) [27], capillary gas

chromatography [28], electrochemical analysis [29-32], and colorimetric method [33]. However, the above methods suffer from several inherent flaws. For example, despite their high precision, instrumental analysis methods are usually time-consuming and expensive. Some methods require complicated isolation processes, careful washing steps, and reagent addition. The colorimetric assays are not sensitive enough to detect pesticide traces [34].

However, electrochemical analysis has many advantages, including simplicity, repeatability, good stability, high sensitivity, and no need to sample preparation steps compared to other detection techniques mentioned above [35-49]. A drawback of this method is that it suffers from weak selectivity, which is resolved by modifying the electrode surface to improve the sensitivity and selectivity of electrochemical sensors and avoid surface fouling [50-63]. Chemical modification of electrodes is a quite useful technique for detecting organophosphorus toxins [64]. Such technologies are appropriate alternatives to increase the electron transfer rate in electrochemical sensors [65-70].

Nanotechnology has been considered a technology of general use, being common in almost all technological sectors. This is due to the fact that the interactions between different materials when they are at the nanoscale (10^{-9} m), are able to generate new properties where unique phenomena may occur, different from those observed at the macroscopic scale, thus giving rise to the possibility of new applications for these materials [71-90]. Various materials such as carbon-based nanomaterials, metal oxides, metals complex, polymers, and biological compounds can be used to modify electrode surfaces [91-107].

This work aims to explain the current developments in electrochemical sensors and biosensors for monitoring DZN.

Development of electrochemical DZN sensors

Electrochemical sensors are the most rapidly growing group of chemical sensors among presently available systems for practical applications. The most common electrochemical system used for laboratory study is made up of a reference electrode, counter electrode, and a working electrode (sensing electrode) immersed in an electrolyte which measures the potential and current generated from oxidative or reductive reactions. The working principle behind electrochemical sensors involves the generation of electrical signals from the analyte of interest, which is affected by the concentration of the analyte [108-112].

DZN is an electrochemically-active molecule, but its direct determination is difficult because of the weak response of DZN in conventional electrochemical sensors. Different types of electrode modifications for electrochemical methods have been developed for the determination of DZN because they possess high sensitivity, short analysis time, good handling convenience and low cost.

This section introduced examples of developed electrochemical DZN sensors. Then, Table 1 tabulates information about the electrochemical sensor, electrochemical method, limit of detection (LOD), and linear range, which have been reported by various works.

In 2003, a simple and easy electrochemical method was used by Erdogdu for the determination of DZN. In this method, the surface of the glassy carbon electrode was coated with Nafion-perfluorinated ion-exchange powder (NCGCE), and square-wave voltammetry (SWV) was used for the quantitative estimation. The author demonstrated that the peak current slightly changed in the potential range from 0 to 0.35 V because DZN could not be reduced in this potential range. However, a sudden increase was observed in the peak current at 0.40 V. The effect of SW response was studied in the mentioned conditions because the peak current for DZN obtained in SWV depended on

different parameters such as SW amplitude, SW frequency, and step height. Hence, modulation amplitude, 25 mV; modulation frequency, 14 Hz; modulation step, 4 mV s^{-1} were considered optimal conditions for DZN detection. The results of the Erdogdu study showed that combining the SWV and electrode surface modification with Nafion film worked excellently for DZN detection. Thus, the proposed voltammetric procedure for DZN detection could be useful in many different applications. In this method, the minimum LOD for diazinon was reported to be 75 nM. The results of 20 successive measurements showed a coefficient of variation of 1.9 % for NCGC electrodes. Therefore, the modified electrode possessed a good reproducibility surface [113].

Arvand *et al.* [114].used the differential pulse voltammetric (DPV) methods to investigate the electrochemical behavior of DZN at carbon paste electrode modified with tris(ethylenediamine) cobalt(II) iodide (Co-CPME). Cobalt complex showed an anodic peak at 620 mV (*vs.* Ag/AgCl, in KNO$_3$ 0.1 M as supporting electrolyte) at Co-CPME. In the presence of DZN, anodic peak intensity increased with increasing concentration of DZN that confirming the electrocatalytic activity of cobalt complex for oxidation of DZN (EC' mechanism). Under optimized conditions, a linear calibration curve for diazinon was obtained in the range from 0.05 to 27.0 μg/L with a detection limit 0.015 nM (3*Sb/m*). Applications of the modified electrode to the determination of DZN in different water samples were also tested. The results showed a very good precision (RSD < 0.04 %) and a very stable voltammetric response towards DZN [114].

In a study by Motaharian *et al.* an electrochemical sensor based on molecularly imprinted polymer (MIP) nanoparticles for selective and sensitive determination of DZN pesticides was developed. The nanoparticles of DZN imprinted polymer were synthesized by suspension polymerization and then used to modify carbon paste electrode composition to prepare the sensor. Cyclic voltammetry (CV) and SWV methods were applied for electrochemical measurements. The obtained results showed that the carbon paste electrode modified by MIP nanoparticles (nano-MIP-CPE) has a much higher adsorption ability for DZN than the CPE-based non-imprinted polymer nanoparticles (nano-NIP-CPE). Under optimized extraction and analysis conditions, the proposed sensor exhibited excellent sensitivity (95.08 μA L μmol^{-1}) for DZN with two linear ranges of 2.5 to 100 nmol L^{-1} (R^2 = 0.9971) and 0.1 to 2.0 μmol L^{-1} (R^2 = 0.9832) and also a detection limit of 0.79 nmol L^{-1}. The sensor was successfully applied for the determination of DZN in well water and apple fruit samples with recovery values in the range of 92.53–100.86 % [115].

Ghodsi and Rafati described a voltammetric sensor for DZN pesticide determination based on DZN reduction on glassy carbon electrode surface modified with multi-walled carbon nanotubes covered by TiO$_2$ nanoparticles (MWCNTs/TiO$_2$NPs/GCE). Voltammetric investigations were carried out by CV, linear sweep voltammetry (LSV), DPV and SWV. MWCNTs/TiO$_2$NPs nanocomposite was characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) techniques. The MWCNTs/TiO$_2$NPs nanocomposite showed suitable synergic electrocatalytic properties in DZN reduction, which resulted in the completely sensitive determination of DZN in the laboratory and real samples, including city piped water and agricultural well water. Linear range, LOD and LOQ obtained by MWCNTs/TiO$_2$NPs/GCE sensor were 11.0 to 8360.0 nM, 3.0 nM and 10.0 nM successively. Also, the sensor was successfully examined for DZN determination in real water samples, including agricultural well water and city piped water and obtained results showed acceptable recovery amounts [116].

Khadem *et al.* introduced the composition of carbon paste electrodes modified with MIP and MWCNTs as the easy-to-use electrochemical sensor (MWCNTs-MIP/CPE) for selective and sensitive determination of DZN pesticide in environmental and biological samples. The MWCNTs enhance the

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sensor responses due to increasing of the electrode surface area, as well as improving the electron transfer between the electrode and the supporting electrolyte. The presence of MIPs can greatly increase the selectivity of the electrode. Instrumental parameters affecting the square wave voltammetric response were adjusted to obtain the highest current intensity. The obtained linear range was 0.5 nM to 1.0 μM. The detection limit of the sensor was 0.13 nM and the relative standard deviation for analysis of the target molecule by the proposed sensor was 2.87 % [117].

Akyuz and Koca constructed a mimic enzymeless electrochemical sensor (M-Eless-ES) based on the terminal alkynyl substituted manganese phthalocyanine (MnPc-TA) and 4-azido polyaniline (N$_3$-PANI) hybrid and tested as a sensitive and selective pesticide sensor. During the construction of ITO/MnPc-TA/N$_3$-PANI electrode, MnPc-TA was firstly deposited on indium tin oxide coated glass substrate (ITO) with Langmuir Blodgett (LB) technique. Then 4-azidoaniline (N$_3$-ANI) was bonded to the terminal alkynyl substituents of MnPc-TA (ITO/MnPc-TA/N$_3$-ANI) with click chemistry (CC), and finally, ANI groups of the solid MnPcTA/N$_3$-ANI hybrid film was electropolymerized on ITO surface to form ITO/MnPc-TA/N$_3$-PANI electrode. The structure of the modified electrode was characterized by SWV, XRD, FT-IR and SEM analyses. The result of the analyses indicated successful construction of ITO/MnPc-TA/N$_3$-PANI electrode. ITO/MnPcTA/N$_3$-PANI electrode was tested as a potential sensor for various pesticides and the results showed that it was used as a sensitive sensor for the DZN with LOD of 0.062 μmol dm^{-3} and a wide linear range [118].

Accordingly, Zahirifar *et al.* employed a carbon paste electrode modified with multi-walled carbon nanotubes (MWCNT/CPE) to detect DZN in solutions and real samples (fruit juices). The obtained results showed that CNTs increased the sensor response due to their large surface area, improved electrocatalytic activity, and enhanced electron-transfer rate between electrode and electrolyte. The MWCNT/CPE electrode could recognize DZN in fruit samples with a desirable LOD with little interference of other compounds. Because the thickness of CNT can affect the electrode response, Zahirifar et al. recorded the amount of CNT used to make an optimized CNT/CPE electrode and its effect on the peak current of DZN. The results showed that the peak current rose as the quantity of CNT increased. The maximum peak current level was observed when the amount of CNT increased up to 10 %. However, any amount higher than 10 % negatively affected the sensor response in DZN detection. The researchers introduced the sensor as a proper candidate for the recognition of DZN in foodstuffs regarding its ability to detect DZN in the concentration range of 0.1 to 10 nM by the designed electrode. The limit of detection for DZN in this sensor was determined by the DPV technique, and it was found to be 0.45 nM [119].

Tadayon and Jahromi constructed a sensitive and selective electrochemical sensor based on bimetallic gold and palladium nanoparticles coated on a mixture of reduced graphene oxide and multiwall carbon nanotube nanocomposite modified glassy carbon electrode (Au–Pd/rGO––MWCNTs/GCE)for determination of an organophosphorus insecticide, DZN. The effect of various parameters includes pH of the solution, scan rate, accumulation time and potential, and instrumental parameter was optimized. Under optimized conditions, the proposed sensor showed that the stripping oxidation peak current of DZN was linearly proportional to its concentrations in an appropriate range of 0.009 to 11.3 μM with a LOD and LOQ of 0.002 and 0.009 μM, respectively. Finally, the Au–Pd/rGO–MWCNTs/GCE was successfully used for measurement of DZN in water, apple and cucumber samples recoveries ranging from 96 to 105 % [120].

Ghiasi *et al.* employed the composition of graphene quantum dots (GQDs), chitosan (CS), and nickel molybdate nanocomposites (NiMoO$_4$, NMO) for the modification of activated glassy carbon electrode (NMO/GQDs/CS/GCE$_{ox}$) as an electrochemical sensor for DZN determination (Figure 1).

The NMO/GQDs/CS/GCE$_{ox}$ for precise and swift analysis of DZN in cucumber and tomato as real samples has been effectively used as a sensitive voltammetric sensor. Under optimized conditions, the constructed sensor illustrated a linear range between 0.1 to 330.0 µM and a LOD of 30.0 nM using differential pulse voltammetry methods [121].
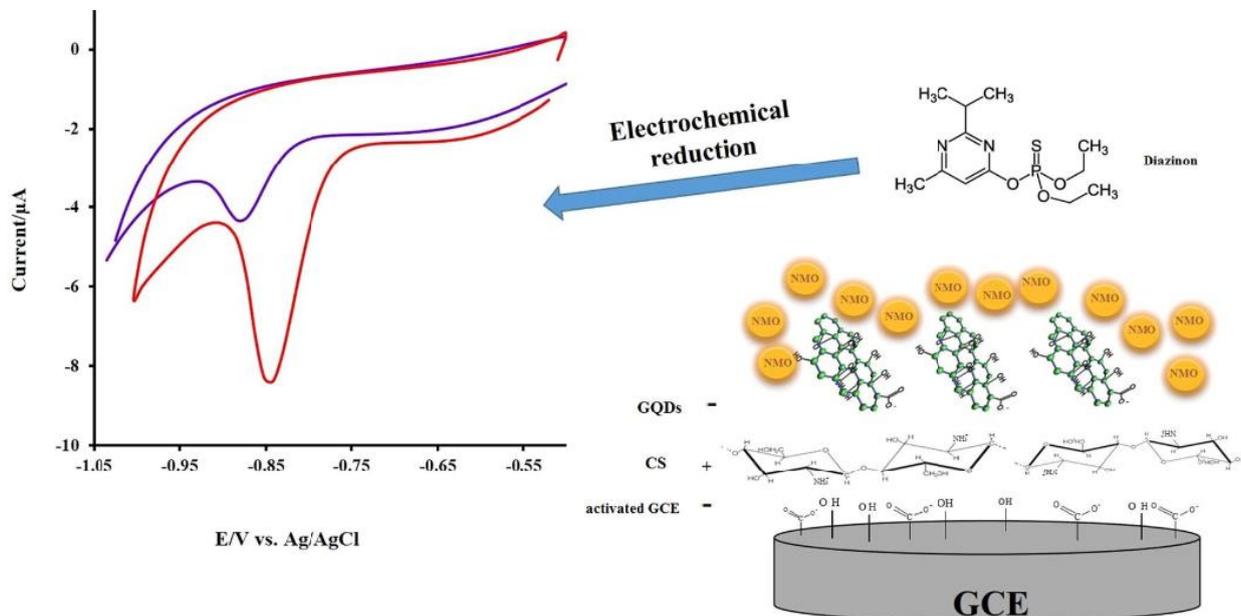

Figure 1. *Electrochemical sensor based on modified glassy carbon electrode with graphene quantum dots, chitosan and nickel molybdate nanocomposites for the determination of diazinon [121]*

Topsoy *et al.* described a new simple, sensitive, and easy method to manufacture voltammetric sensor based on MWCNT-screen-printed electrode modification with poly(ε-caprolactone)/chitosan (PCL/CHS) electrospun nanofibers (PCL/CHS nanofiber/MWCNT-SPE). The images of unmodified and modified electrodes in DZN detection are shown in Figure 2.
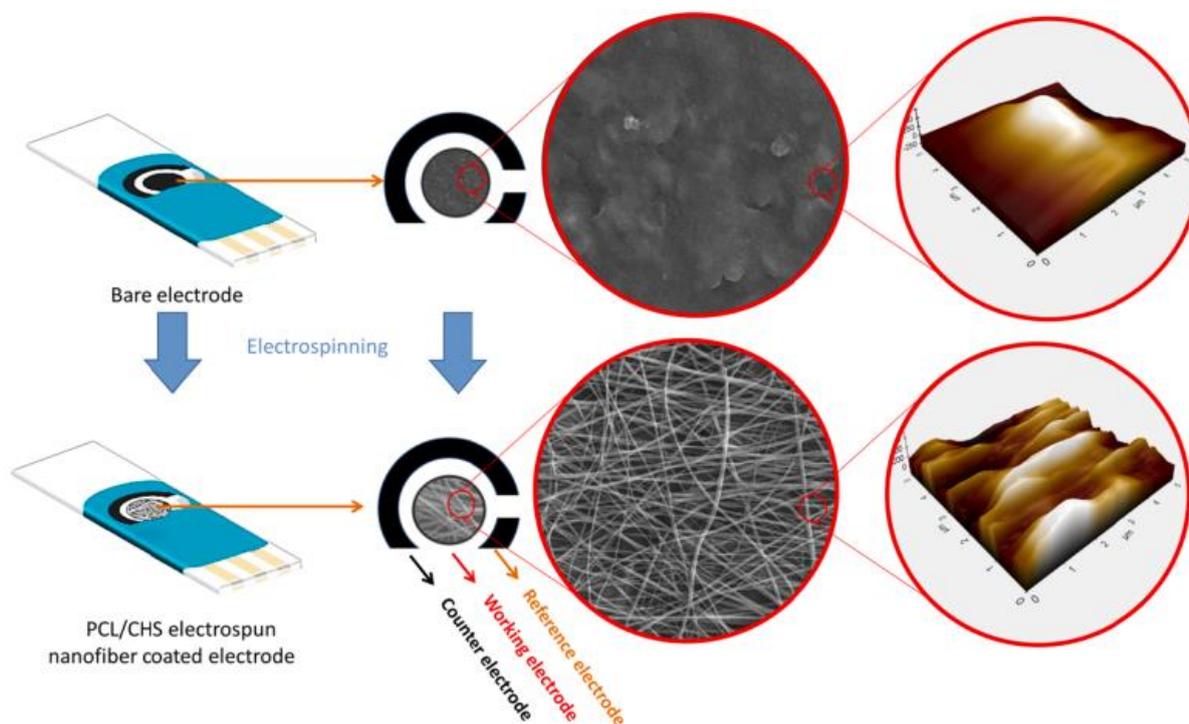

Figure 2. *The schematic diagram of bare MWCNT-SPE and PCL/CHS nanofiber-modified MWCNT-SPE [122]*

The effects of different parameters such as coating thickness, analyte concentration, pH value of the buffer solution, and scan rate on the electrochemical behavior of unmodified and modified screen-printed carbon electrodes were investigated via CV, DPV, and electrochemical impedance spectroscopy (EIS) techniques. The spinning time, pH value and scan rates were optimized at 6 min, 5.25, and 50 mV s^{-1}, respecttively. The prepared PCL/CHS nanofiber/MWCNT-SPE displayed good electrochemical performances with a wide detection range of 3.0–100.0 nM in 0.1 M acetate buffer solution (pH 5.25), and a detection limit of 2.888 nM, respectively. Meanwhile, the sensor was successfully applied for the determination of DZN in the tomato juice sample with recovery values in the range of 93.27–108.30 % [122].

Porto *et al.* presented, for the first time, a fast and highly sensitive electrochemical method for the determination of three organophosphorus compounds (OPs), DZN, malathion (MLT), and chlorpyrifos (CLPF), using a modified pyrolytic graphite electrode (PGE) coupled to batch injection analysis system with multiple pulse amperometric detection (BIA–MPA). The PGE was modified by a nanocomposite based on functionalized carbon nanotubes and silver nanoparticles (CNTf-AgNP/PGE). The OPs samples were directly analyzed on the modified working electrode surface by BIA-MPA system in Britton-Robinson (BR) buffer 0.15 mol L^{-1} at pH 6.0. The MPA detection of DZN, MLT and CLPF was performed using two potential pulses, which were sequentially applied on modified PGE at − 1.3 V (100 ms) and +0.8 V (100 ms) for selective determination of these three OPs and working electrode cleaning, respectively. Under optimized conditions, the sensor presented a linear range of 0.1–20.0 µM for DZN. The LOD and LOQ of 0.35 and 1.18 µM for DZN were obtained. Also, CNTf-AgNP/PGE sensor exhibited high sensitivity of 0.068 mA µM for DZN detection. Furthermore, the BIA-MPA system provided an analytical frequency of 71 determinations per hour for the direct determination of these OPs in water and food samples. The modified PGE coupled to BIA-MPA system showed high stability of electrochemical response for OPs detection with a relative standard deviation (RSD) of 1.60 % (*n* = 20). The addition-recovery studies of the proposed method were carried out in tap water, orange juice, and apple fruit real samples, which showed suitable recovery values between 77 and 124 % [123].

Table 1. *Features of various electrochemical sensors for the analysis of DZN.*

Electrochemical sensor	Electrochemical method	LOD, nM	Linear range	Ref.
NCGCE	SWV	75.0	0-5.0 µM	[113]
Co-CPME	DPV	0.015	0.05-27.0 µg / L	[114]
nano-MIP-CPE	SWV	0.79	2.5-2000.0 nM	[115]
MWCNTs/TiO$_2$NPs/GCE	CV, SWV	3.0	11.0-8360.0 nM	[116]
MWCNTs-MIP/CPE	SWV	0.13	0.5-1000.0 nM	[117]
ITO/MnPcTA/N3-PANI electrode	SWV	62	-	[118]
MWCNT/CPE	DPV	0.45	0.1-10.0 nM	[119]
Au–Pd/rGO–MWCNTs/GCE	SWASV	2.0	0.009-11.3 µM	[120]
NMO/GQDs/CS/GCE$_{ox}$	DPV	30.0	0.1-330.0 µM	[121]
PCL/CHS nanofiber/MWCNT-SPE	DPV	2.888	3.0-100.0 nM	[122]
CNTf-AgNP/PGE	BIA-MPA	354.0	0.1-20.0 µM	[123]

Development of electrochemical DZN biosensors

Biosensor-related research has experienced explosive growth over the last two decades. A biosensor is generally defined as an analytical device that converts a biological response into a quantifiable and processable signal [124]. In most biosensors developed so far, electrochemical detection has been used in one way or another, i.e., amperometric, voltammetric, and impedimetric

detection. The basic principle for electrochemical biosensors is that chemical reactions between the immobilized biomolecule and target analyte produce or consume electrons which cause some change in the measurable electrical properties of the solution, such as electric current, conductance, and potential [125-128].

Electrochemical biosensors, as a subclass of biological sensors, consist of a biological sensing element and an electrochemical transducer. The recognition element (enzymes, antibodies, DNA/RNA, proteins or other biomolecules) reacts selectively with the target analyte, and as a result, an electrical signal is produced and then transmitted via the transducer to the signal processor [129-132]. A bioreceptor allows the binding between the specific analyte of interest with the sensing surface for measurement with minimum intervention from other components in a complex mixture. So, parallel development in the immobilization of bioreceptors through robust attachment methods like electro-deposition and nanoparticle-bound entities at the working electrode interface is a significant step in the improved application of biosensors in various analytes analysis. The selection of robust and suitable immobilization methodology and precise selection of the bioreceptor molecule plays a great part in the better specificity, selectivity, and affinity for their target analytes in electrochemical biosensing.

This section introduced examples of developed electrochemical DZN biosensors. Then, Table 2 tabulates information about electrochemical biosensor, electrochemical methods, limit of detection (LOD), and linear range, which have been reported by various works.

Somerset *et al.* constructed a biosensor for organophosphate and carbamate detection with a gold electrode coated with a mercaptobenzothiazole (MBT) self-assembled monolayer (SAM) and a polyaniline derivative poly(o-methoxyaniline, POMA) or poly(2,5-dimethoxyaniline, PDMA) polymer film in the presence of polystyrene sulfonic acid (PSSA), on which AchE was immobilized (Au/MBT/POMA-PSSA/AChE or Au/MBT/PDMA-PSSA/AChE biosensors). The pesticide biosensors were applied in the aqueous phase detection of DZN and carbofuran pesticides using Osteryoung SWV and DPV at low frequencies. Between 85 and 94 % inhibition of the Au/MBT/PDMA-PSSA/AChE and Au/MBT/POMA-PSSA/AChE biosensors, respectively, by 1.19 ppb of these neurotoxins attests to their potency. Both Au/MBT/PDMA-PSSA/AChE and Au/MBT/POMAPSSA/AChE biosensors exhibited low detection limits, which were calculated using the inhibition methodology. The Au/MBT/POMA-PSSA/AChE biosensor exhibited lower detection limits of 0.07 ppb for DZN and 0.06 ppb for carbofuran than the Au/MBT/PDMA-PSSA/AChE sensor system that had detection limits values of 0.14 ppb for DZN and 0.11 ppb for carbofuran. The average sensitivity of the pesticide biosensor systems is 4.2 µA/ppb [133].

In 2007, Albuquerque and Ferreira used acetyl cellulose–graphite composite film modified with Cobalt phthalocyanine (CoPc) to modify the electrode surface (CoPc-CGCE). First, graphite powder was mixed homogeneously with CoPc. Then, acetyl cellulose was applied to the mixture. After homogenization, the final composite was applied to polycarbonate support. Tyrosinase and bovine serum albumin (BSA) were then immobilized on the modified electrode's surface (Tyr-BSA-CoPc-CGCE) by adding glutaraldehyde. The authors used the biosensor to measure organophosphorus and carbamates concentration. First, the immobilized tyrosinase enzyme activity was evaluated by measuring the quantity of catechol consumed or o-quinone formed in the reaction (Figure 3). They monitored the increased concentration of o-quinone produced or the reduced concentration of the consumed catechol at a potential of -0.20 and +0.60 V, respectively. After stabilizing the background current, all amperometric measurements were carried out with the biosensor at a constant potential of -0.20 V versus Ag/AgCl as the counter and reference electrode. To detect pesticides using a biosensor containing tyrosinase, they measured the enzyme activity in two steps using a solution

containing catechol. In the first step, the biosensor was submerged in a solution containing catechol. The enzyme on the surface of the electrode converted the catechol to o-quinone, and then o-quinone produced was measured at −0.20 V after 2 minutes. In the second step, the biosensor was submerged in the catechol solution after adding a given amount of pesticide, and the biosensor activity was evaluated after 2 minutes. The results show that methyl parathion and carbofuran can lead to a competitive inhibition process of the enzyme, while diazinon and carbaryl act as mixed inhibitors. Linear relationships were found for methyl parathion (6.0–100.0 ppb), DZN (19.0 to 50.0 ppb), carbofuran (5.0–90.0 ppb) and carbaryl (10.0–50.0 ppb). Analysis of natural river water samples spiked with 30 ppb of each pesticide showed recoveries between 92.50 and 98.50 % and relative standard deviations of 2 % [134].
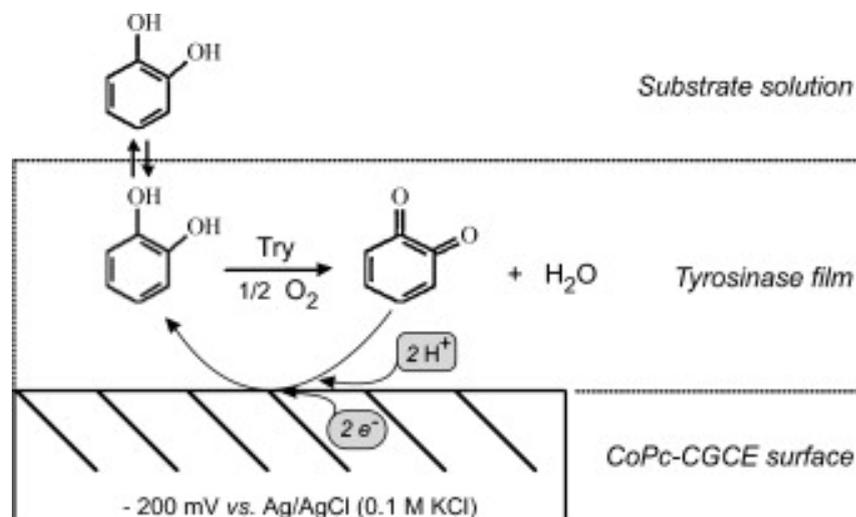

Figure 3. *Principle of the enzymatic and electrochemical coupled reactions for the detection of catechol as substrate [134]*

Somerset *et al.* modified a gold disc electrode with a mercaptobenzothiazole selfassembled monolayer prior to polyaniline electropolymerization, followed by AChE immobilization and polyvinyl acetate coating in creating a thick film electrode (Au/MBT/PANI/AChE/PVAc) for sensitive organophosphorous pesticide detection. The dual role of polyaniline shows electrocatalytic activity towards thiocholine and serves as an immobilization matrix for the AChE as an enzyme, and that of polyvinyl acetate as a binder in this thick film electrode is demonstrated. Relatively low detection limits were obtained for the Au/MBT/PANI/AChE/PVAc pesticide bioelectrodes using the inhibition methodology and an incubation time of 20 min. The values for the detection limits were 0.147 ppb for DZN and 0.172 ppb for fenthion in acetone-saline phosphate buffer solution [135].

Zehani *et al.* developed two novel impedimetric biosensors for highly sensitive and rapid quantitative detection of DZN in an aqueous medium using two types of lipase, from Candida Rugosa (microbial source) (CRL) and porcine pancreas (animal source) (PPL) immobilized on the functionalized gold electrode (CRL immobilized gold electrode, PPL immobilized gold electrode). Lipase is characterized to specifically catalyze the hydrolysis of ester functions leading to the transformation of DZN into diethyl phosphorothioic acid (DETP) and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP). The developed biosensors both presented a wide range of linearity up to 50 µM with a detection limit of 10 nM for CRL immobilized gold electrode biosensors and 0.1 µM for PPL immobilized gold electrode biosensor. A comparative study was carried out between the two biosensors and the results showed higher efficiency of CRL immobilized gold electrode biosensor.

Moreover, it presented good accuracy and reproducibility and had very good storage and multiple-use stability for 25 days when stored at 4 °C [136].

Arvand and Dehsaraei constructed a chemically modified glassy carbon electrode by graphene oxide (GO), functionalized double-strand DNA (ds-DNA) and gold nanorods (GNRs). Interaction between oxygenated groups of GO and GNRs with amine-thiol groups of ds-DNA was used to construct a sandwich-modified electrode named GNRs/ds-DNA/GO/GCE. Then, they examined the response of the GNRs/ds-DNA/GO/GCE to the sensing of DZN. To find the effects of modifiers on DZN detection, CV and electrochemical impedance spectroscopy were used in each modification step. The pH and scan rate were optimized at 6.0 and 0.1 V s^{-1}, respectively. The dynamic range of GNRs/ds-DNA/GO/GCE in DZN determination was studied by amperometry with the linear concentration range of 1.9 to 56 μM and a detection limit of 0.19 μM. Finally, the application of modified electrode was evaluated on two polluted river water samples with 98.5 to 101 % recovery [137].

Pajooheshpour *et al.* employed an enzyme-less electrochemical biosensor based on a glassy carbon electrode modified with bovine serum albumin (BSA) templated Au-Pt bimetallic nanoclusters and graphene nanoribbons (GNRs) (Au-Pt@BSAGNRs/GCE) for the determination of DZN. The synthesized novel sensing layer not only demonstrated attractive structural features but was known to possess excellent electrochemical characteristics, which enabled the development of a reliable, sensitive, robust and selective electrochemical sensor for DZN. The electrochemical properties of the biosensor were investigated by CV, square wave anodic stripping voltammetry (SWASV) and electrochemical impedance spectroscopy. The results showed that Au-Pt@BSAGNRs/GCE significantly catalyzes the oxidation and reduction of DZN during electrochemical detection. The linear ranges of DZN were between 0.01 to 10.0 and 10.0 to 170.0 μM, with a detection limit of 0.002 μM. The results indicate the excellent capability of the method for the detection of DZN in real samples in comparison with the standard method [138].

Hassani *et al.* developed a novel label-free electrochemical thiolated aptasensor immobilized on gold nanoparticle-modified screen-printed gold electrodes (aptamer/ Au NP/ SPGEs) in order to detect minimum levels of DZN in biological samples with high sensitivity and fast performance, as illustrated in Figure 4.
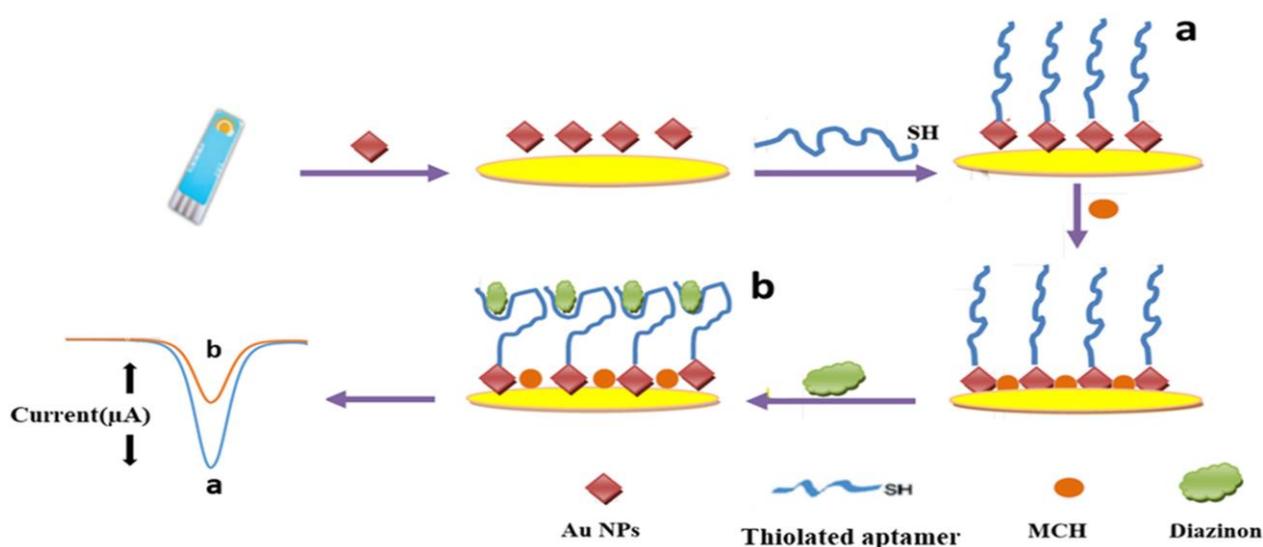

Figure 4. *Schematic construction of the designed aptasensor for detection of diazinon [139]*

Electrochemical impedance spectroscopy and CV were used to characterize the electrochemical properties of the novel aptasensor. Electrochemical detection was carried out through DPV in

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$[Fe(CN)_6]^{3-/4-}$ solution. Fluctuation of the current was examined in the DZN concentration range of 0.1 to 1000.0 nM. According to the results, the designed aptasensor has exhibited the minimum limit of detection for DZN (0.0169 nM) [139].

Zare *et al.* developed an electrochemical biosensor for the detection of DZN. For this purpose, they modified the surface of a glassy carbon electrode with MWCNTs and poly-l-lysine to immobilize a double-strain DNA (ds-DNA) on the surface of the electrode (DNA/PLL/MWCNTs/GCE). The interaction of DZN with ds-DNA was transduced via electrochemical impedance and UV–Vis spectroscopy in the first step. The results revealed an interaction between DZN and ds-DNA. L-lysine as a polycation and small-sized MWCNTs provides a surface with positive charges and a high surface area for the immobilization of ds-DNA. This interaction leads to reduced interfacial charge-transfer resistance (R_{ct}). The difference in the R_{ct} before and after the interaction is considered a suitable signal for DZN detection. The proposed biosensor has a low detection limit (0.3 nM), a wide linear dynamic range (0.001–100.0 μM), and high selectivity for the determination of DZN. Finally, the performance of the biosensor for detecting DZN is verified in real samples such as river water, agricultural wastewater, lettuce juice, and tomato juice [140].

Khosropour *et al.* [141] synthesized the vanadium disulfide quantum dots (VS$_2$QDs) by a facile hydrothermal method and doped them on the graphene nanoplatelets/carboxylated multiwalled carbon nanotubes (GNP/CMWCNTs) as a new group of the nanocomposite. They incubated the VS$_2$QDs-GNP/CMWCNTs nanocomposite on a glassy carbon electrode with the DZN binding aptamer (DZBA) through electrostatic interaction (GCE/VS$_2$QDsGNP/CMWCNTs/DZBA). The GCE/VS$_2$QDs-GNP/CMWCNTs/DZBA was used for the low detection of DZN by monitoring the oxidation of $[Fe(CN)_6]^{3-/4-}$ as the redox probe. The characterizations of the modified electrode were performed by several electrochemical methods, including CV, DPV, and EIS. The DZBA selectively adsorbs DZN on the modified electrode, leading to a decrease and increase in the current of DPV and charge transfer resistance (R_{ct}), respectively, as analytical signals. The developed electrochemical aptasensor at the optimal conditions has a low LOD equal to 1.1×10^{-5} and 2.0×10^{-6} nM with wide dynamic ranges of 5.0×10^{-5}-10 nM and 10^{-5}-10 nM for DPV and EIS calibration curves, respectively. Moreover, the analytical approach was further utilized for DZN determination in human serum, Zayandehrood river water, soil, apple, and lettuce samples and the GCE/VS$_2$QDs-GNP/CMWCNTs/DZBA/BSA aptasensing strategy exhibited a recovery rate from 97.0 to 107.0 % [141].

Table 2. *Features of various electrochemical biosensors for the analysis of DZN*

Electrochemical sensor	Electrochemical method	LOD	Linear range	Ref.
Au/MBT/PDMA-PSSA/AChE	SWV	0.14 ppb	-	[133]
Au/MBT/POMAPSSA/AChE	DPV	0.07 ppb		
Tyr-BSA-CoPc-CGCE	Amperometric	-	19.0–50.0 ppb	[134]
Au/MBT/PANI/AChE/PVAc	Amperometric	0.147 ppb	-	[135]
CRL immobilized gold electrode	Impedimetric	10.0 nM	0.01-50.0 μM	[136]
PPL immobilized gold electrode		0.1 μM	0.1-50.0 μM	
GNRs/ds-DNA/GO/GCE	Amperometric	190.0 nM	1.9 - 56.0 μM	[137]
Au-Pt@BSAGNRs/GCE	SWASV	0.002 μM	0.01-170.0 μM	[138]
aptamer/ Au NP/ SPGEs	DPV	0.0169 nM	0.1-1000.0 nM	[139]
DNA/PLL/MWCNTs/GCE	Impedimetric	0.3 nM	0.001-100.0 μM	[140]
GCE/VS$_2$QDs-GNP/CMWCNTs/DZBA/BSA	Impedimetric	2.0×10^{-1} nM	10^{-5}-10.0 nM	[141]
	DPV	1.1×10^{-14} M	5.0×10^{-5}-10.0 nM	

Conclusion

Diazinon is a pesticide belonging to the organophosphorus pesticides class, which is widely used in agriculture to control pests in soil, vegetables, and fruits. Residues of pesticides can enter the food chain and cause many problems. DZN is considered one of the most important contaminants, and its amount in the environment, waters, and crops should be managed due to its toxicity and long half-life. Thus, we need analytical methods to be able to detect the amount of that compound quickly. The electrochemical technique has many advantages for environmental research compared to other analytical techniques; for example, it does not require sample preparation steps and is fast, simple, cost-effective, and non-destructive. The limit of detection obtained by this technique possesses good sensitivity to the target molecules and environmental applications. In addition to sensitivity, the technique's specificity in recognizing the target molecule is critical. The challenging problems associated with promoting specificity and selectivity make the researchers seek new substances to modify electrodes and develop new electrochemical sensors. Thus, different modifying methods have been used to recognize DZN, which are different in terms of the type of the working electrode, the applied technique, and the method of modifying the surface. From the above discussion, it is evident that nanomaterials, such as CNTs, graphene, metal nanoparticles,*etc.*, are promising materials for fabricating electrochemical sensors by signal amplification, thereby improving the sensitivity of the assay. Nanotechnology is one of the likely areas to show encouraging prospects for developing sensors for the detection of DZN by overcoming the shortcomings of currently-available analytical procedures. Although each method can detect DZN, it seems that the techniques based on biological components such as DNA and enzymes have the lowest LOD for recognition of DZN compared to other techniques. However, biological receptors allow for specific recognition of the target molecules and are widely used in the detection, bioassays, and chemical sensors.

Apart from these advantages, the real challenges for the future are those of good electrode materials, miniaturization and of measurements in as close to real-time as possible.

Another trend for future research on electrochemical sensors is to develop them for in vivo analysis and continuous testing as well as for in vitro testing. Sensor arrays for detecting multi-analyte will be required and the densities of arrays for more complete and rapid information need to increase. Microfluidic sensor systems, capable of expanding sizes of arrays while reducing sample volume, as well as non-invasive biosensors, will revolutionize sensor techniques and technology.

References

[1] R. Osterauer, H. Kohler, *Aquatic Toxicol*ogy **86** (2008) 485-494. https://doi.org/10.1016/j.aquatox.2007.12.013

[2] G. K. Sidhu, S. Singh, V. Kumar, D. S. Dhanjal, S. Datta, J. Singh, *Critical Reviews in Environmental Science and Technology* **49** (2019) 1135-1187. https://doi.org/10.1080/10643389.2019.1565554

[3] Q. Long, H. Li, Y. Zhang, S. Yao, *Biosensors & Bioelectronics* **68** (2015) 168-174. https://doi.org/10.1016/j.bios.2014.12.046

[4] A. Salehzadeh, R. Abbasalipourkabir, B. Shisheian, A. Rafaat, A. Nikkhah, T. Rezaii, *Drug and Chemical Toxicology* **42** (2019) 280-285. https://doi.org/10.1080/01480545.2018.1449852

[5] D. G. Karpouzas, K. B. *Advances in Microbial Physiology* **51** (2006) 185-122. https://doi.org/10.1016/S0065-2911(06)51003-3

A. L. Nejad

J. Electrochem. Sci. Eng. **12(6)** (2022) 1041-1059

[6] *National pesticide information center*, Diazinon, Technical Fact Sheet. http://npic.orst.edu/factsheets/archive/diazinontech.html (accessed September 17, 2022)

[7] *Environmental Risk Assessment for Diazinon*, Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Office of Pesticide Programs, U.S. Government Printing Office: Washington DC, USA, 2000.

[8] C. Timchalk, *Organophosphate Insecticide Pharmacokinetics. Handbook of Pesticide Toxicology*, R. Krieger, Ed., *Academic Press: San Diego*, **2** (2010) 1409-1433. https://doi.org/10.1016/B978-0-12-374367-1.00066-5

[9] Y. Yi, G. Zhu, C. Liu, Y. Huang, Y. Zhang, H. Li, J. Zhao, S. Yao, *Analytical Chemistry* **85** (2013) 11464-11470. https://doi.org/10.1021/ac403257p

[10] S. Mostafalou, M. Abdollahi, *Toxicology* **409** (2018) 44-52. https://doi.org/10.1016/j.tox.2018.07.014

[11] P. Wang, H. Li, M. M. Hassan, Z. Guo, Z.-Z. Zhang, Q. Chen, *Journal of Agricultural and Food Chemistry* **67** (2019) 4071-4079. https://doi.org/10.1021/acs.jafc.8b07201

[12] Environmental Protection Agency, *I.R.E.D Facts, Diazinon*, Pesticides and Toxic Substances, U.S. Office of Pesticide Programs 2004. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=10004G10.TXT (accessed September 17, 2022)

[13] EPA, *Reregistration Eligibility Decision (RED) for Diazinon, Pesticides and Toxic Substances*, U.S. Government Printing Office, Washington DC, USA, 2006. https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/red_PC-057801_31-Jul-06.pdf

[14] P. E. Howard, *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Lewis Publishers, Inc., Chelsea MI, USA, 1991 209. ISBN 9780873713283

[15] A. G. Hornsby, R. D. Wauchope, A. E. Herner, *Pesticide Properties in the Environment*, Springer-Verlag, New York, USA, 1996, 83. ISBN 978-0-387-94353-4

[16] *ToxGuide for Diazinon*; U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, 2006. https://www.atsdr.cdc.gov/toxguides/toxguide-86.pdf

[17] M. K. Morgan, D. M. Stout, P. A. Jones, D. B. Barr, *Environmental Research* **107** (2008) 336-342. https://doi.org/10.1016/j.envres.2008.03.004

[18] M. A. Kamrin, *Pesticide Profiles: Toxicity, Environmental Impacts, and Fate*, Lewis Publishers, Boca Raton FL, USA, 1997, 157. https://doi.org/10.2134/jeq1998.00472425002700040038x

[19] T. R. Roberts, D. H. Hutson, *Metabolic Pathways of Agrochemicals - Part 2: Insecticides and Fungicides*, The Royal Society of Chemistry: Cambridge, UK, 1999, 258. https://doi.org/10.1039/9781847551375-00937

[20] A. Kretschmann, R. Ashauer, K. Hitzfeld, P. Spaak, J. Hollender, B. I. Escher, *Environmental Science & Technology* **45** (2011) 4980-4987. https://doi.org/10.1021/es1042386

[21] D. C. Villeneuve, R. F. Willes, J. B. Lacroix, W. E. J. Phillips, *Toxicology and Applied Pharmacology* **21** (1972) 201-205. https://doi.org/10.1016/0041-008X(72)90010-5

[22] J. R. Reigart, J. R. Roberts, *Organophosphate Insecticides. Recognition and Management of Pesticide Poisonings, 5th ed.*, U.S Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Office of Pesticide Programs, U.S. Government Printing Office, Washington DC, USA, 1999, 34-47.

[23] S. L. Wagner, *Diagnosis and Treatment of Organophosphate and Carbamate Intoxication*, in *Human Health Effects of Pesticides*; M. C. Keifer, Ed., Hanley and Belfus, Philadelphia, USA **12** (1997) 239-249.

[24] M. Behbahani, A. Veisi, F. Omidi, M.Y. Badi, A. Noghrehabadi, A. Esrafili, H. R. Sobhi, *New Journal of Chemistry* **42** (2018) 4289-4296. https://doi.org/10.1039/C7NJ03788K

[25] A. Concha-Meyer, S. Grandon, G. Sepulveda, R. Diaz, J. Antonio Yuri, C. Torres, *Food Chemistry* **295** (2019) 64-71. https://doi.org/10.1016/j.foodchem.2019.05.046

[26] V. K. Gupta, A. K. Singh, L. K. Kumawat, S*ensors and Actuators B* **195** (2014b) 98-108. https://doi.org/10.1016/j.snb.2013.12.092

[27] J. Li, X. Teng, W. Wang, Z. Zhang, C. Fan, *Journal of Separation Science* **42** (2019) 1990-2002. https://doi.org/10.1002/jssc.201800975

[28] P. Vinas, N. Campillo, I. Lopez-Garcia, N. Aguinaga, M. Hernandez-Cordoba, *Journal of Chromatography A* **978** (2002) 249-256. https://doi.org/10.1016/S0021-9673(02)01443-7

[29] D. Guziejewski, S. Skrzypek, W. Ciesielski, *Environmental Monitoring and Assessment* **184** (2012) 6575-6582. https://doi.org/10.1007/s10661-011-2442-7

[30] B. Ondes, M. Soysal, *Journal of the Electrochemical Society* **166** (2019) B395-B401. https://doi.org/10.1149/2.0631906jes

[31] V. K. Gupta, L. P. Singh, R. Singh, N. Upadhyay, S. P. Kaur, B. Sethi, *Journal of Molecular Liquids* **174** (2012) 11-16. https://doi.org/10.1016/j.molliq.2012.07.016

[32] E. Ceballos-Alcantarilla, C. Agullo, A. Abad-Somovilla, J.V.M. A. Abad-Fuentes, *Food Chemistry* **288** (2019) 117-126. https://doi.org/10.1016/j.foodchem.2019.03.007

[33] D. Ferri, P. Gavina, A. M. Costero, M. Parra, J.-L. Vivancos, R. Martinez-Manez, *Sensors and Actuators B-Chemical* **202** (2014) 727-731. https://doi.org/10.1016/j.snb.2014.06.011

[34] Y. Rong, H. Li, Q. Ouyang, S. Ali, Q. Chen, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **239** (2020) 118500. https://doi.org/10.1016/j.saa.2020.118500

[35] M. Tefera, S. Admassie, M. Tessema, S. Mehretie, *Analytical and Bioanalytical Chemistry Research* **2** (2015) 139-150. https://dx.doi.org/10.22036/abcr.2015.11928

[36] H. Mahmoudi-Moghaddam, S. Tajik, H. Beitollahi, *Food Chemistry* **286** (2019) 191-196. https://doi.org/10.1016/j.foodchem.2019.01.143

[37] H. Karimi-Maleh, A. Khataee, F. Karimi, M. Baghayeri, L. Fu, J. Rouhi, R. Boukherroub, *Chemosphere* **291** (2022) 132928. https://doi.org/10.1016/j.chemosphere.2021.132928

[38] N. Rajabi, M. Masrournia, M. Abedi, *Chemical Methodologies* **4** (2020) 660-670. https://doi.org/10.22034/chemm.2020.109975

[39] J.A. Buledi, N. Mahar, A. Mallah, A.R. Solangi, I.M. Palabiyik, N. Qambrani, F. Karimi, Y. Vasseghian, H. Karimi-Maleh, *Food and Chemical Toxicology* **161** (2022) 112843. https://doi.org/10.1016/j.fct.2022.112843

[40] H. Mahmoudi-Moghaddam, S. Tajik, H. Beitollahi, *Microchemical Journal* **150** (2019) 104085. https://doi.org/10.1016/j.microc.2019.104085

[41] M. Montazarolmahdi, M. Masrournia, A. Nezhadali, *Chemical Methodologies* **4** (2020) 732-742. https://doi.org/10.22034/chemm.2020.113388

[42] H. Karimi-Maleh, F. Karimi, Y. Orooji, G. Mansouri, A. Razmjou, A. Aygun, F. Sen, *Scientific Reports* **10** (2020) 11699. https://doi.org/10.1038/s41598-020-68663-2

[43] M. M. Foroughi, H. Beitollahi, S. Tajik, A. Akbari, R. Hosseinzadeh, *International Journal of Electrochemical Science* **9** (2014) 8407. http://www.electrochemsci.org/papers/vol9/91208407.pdf

[44] M. Motahharinia, H. Zamani, H. Karimi-Maleh, *Chemical Methodologies* **5** (2021) 107-113. https://doi.org/10.22034/chemm.2021.119678

A. L. Nejad

J. Electrochem. Sci. Eng. **12(6)** (2022) 1041-1059

[45] H. Beitollahi, H. Mahmoudi Moghaddam, S. Tajik, *Analytical Letters* **52(9)** (2019) 1432-1444. https://doi.org/10.1080/00032719.2018.1545132

[46] S. Saghiri, M. Ebrahimi, M. Bozorgmehr, *Chemical Methodologies* **5** (1999) 234-239. https://doi.org/10.22034/chemm.2021.128530

[47] M. Bijad, H. Karimi-Maleh, M. Farsi, S.-A. Shahidi, *Journal of Food Measurement and Characterization* **12** (2018) 634-640. https://doi.org/10.1007/s11694-017-9676-1

[48] H. Peyman, H. Roshanfekr, A. Babakhanian, H. Jafari, *Chemical Methodologies* **5** (2021) 446-453. https://doi.org/10.22034/chemm.2021.135266

[49] A. Moghaddam, H. Zamani, H. Karimi-Maleh, *Chemical Methodologies* **5** (2021) 373-380. https://doi.org/10.22034/chemm.2021.135727

[50] A. Shamsi, F. Ahour, *Advanced Journal of Chemistry A* **4** (2020) 22-31. https://dx.doi.org/10.22034/ajca.2020.252025.1215

[51] F. Tahernejad-Javazmi, M. Shabani-Nooshabadi, H. Karimi-Maleh, *Talanta* **176** (2018) 208-213. https://doi.org/10.1016/j.talanta.2017.08.027

[52] H. Beitollahi, S. Tajik, F. G. Nejad, M. Safaei, *Journal of Materials Chemistry B* **8(27)** (2020) 5826-5844. https://doi.org/10.1039/D0TB00569J

[53] M. Abrishamkar, S. Ehsani Tilami, S. Hosseini Kaldozakh, *Advanced Journal of Chemistry A* **3** (2020) 767-776. https://dx.doi.org/10.22034/ajca.2020.114113

[54] H. Beitollahi, F. G. Nejad, Z. Dourandish, S. Tajik, *Environmental Research* **214** (2022) 113725. https://doi.org/10.1016/j.envres.2022.113725

[55] S. Cheraghi, M.A. Taher, H. Karimi-Maleh, *Journal of Food Composition and Analysis,* **62** (2017) 254-259. https://doi.org/10.1016/j.jfca.2017.06.006

[56] P. M. Jahani, F. G. Nejad, Z. Dourandish, M. P. Zarandi, M. M. Safizadeh, S. Tajik, H. Beitollahi, *Chemosphere* **302** (2022) 134712. https://doi.org/10.1016/j.chemosphere.2022.134712

[57] S. Azimi, M. Amiri, H. Imanzadeh, A. Bezaatpour, *Advanced Journal of Chemistry A* **4** (2021) 152-164. https://dx.doi.org/10.22034/ajca.2021.275901.1246

[58] M. Miraki, H. Karimi-Maleh, M. A. Taher, S. Cheraghi, F. Karimi, S. Agarwal, V. K. Gupta, *Journal of Molecular Liquids* **278** (2019) 672-676. https://doi.org/10.1016/j.molliq.2019.01.081

[59] H. Beitollahi, S. Tajik, H. K. Maleh, R. Hosseinzadeh, *Applied Organometallic Chemistry* **27(8)** (2013) 444-450. https://doi.org/10.1002/aoc.3001

[60] J. Mohanraj, D. Durgalakshmi, R. A. Rakkesh, S. Balakumar, S. Rajendran, H. Karimi-Maleh, *Journal of Colloid and Interface Science* **566** (2020) 463-472. https://doi.org/10.1016/j.jcis.2020.01.089

[61] S. Tajik, H. Beitollahi, F. G. Nejad, K. O. Kirlikovali, Q. Van Le, H. W. Jang, R. S. Varma, O. K. Farha, M. Shokouhimehr, *Crystal Growth & Design* **20(10)** (2020) 7034-7064. https://doi.org/10.1021/acs.cgd.0c00601

[62] H. Sadeghi, S. Shahidi, S. Naghizadeh Raeisi, A. Ghorbani-HasanSaraei, F. Karimi, *Chemical Methodologies* **4** (2020) 743-753. https://doi.org/10.22034/chemm.2020.113657

[63] X. Liu, *International Journal of Electrochemistry* **2011** (2011) 986494. https://doi.org/10.4061/2011/986494

[64] S. Tajik, H. Beitollahi, F. G. Nejad, I. S. Shoaie, M. A. Khalilzadeh, M. S. Asl, Q. Van Le, K. Zhang, H. W. Jang, M. Shokouhimehr, *RSC Advances* **10(62)** (2020) 37834-37856. https://doi.org/10.1039/D0RA06160C

[65] H. Karimi-Maleh, M. Sheikhshoaie, I. Sheikhshoaie, M. Ranjbar, J. Alizadeh, N. W. Maxakato, A. Abbaspourrad, *New Journal of Chemistry* **43(5)** (2019) 2362-2367. https://doi.org/10.1039/C8NJ05581E

[66] Y. Orooji, P. N. Asrami, H. Beitollahi, S. Tajik, M. Alizadeh, S. Salmanpour, M. Baghayeri, J. Rouhi, A. L. Sanati, F. Karimi, *Journal of Food Measurement and Characterization* **15(5)** (2021) 4098-4104. https://doi.org/10.1007/s11694-021-00982-y

[67] L. C. Fajardo, A. I. B. Tamayo, A. M. E. Guas, *Journal of Electrochemical Science and Engineering* **11** (2021) 247-261. https://doi.org/10.5599/jese.1005

[68] F. G. Nejad, M. H. Asadi, I. Sheikhshoaie, Z. Dourandish, R. Zaimbashi, H. Beitollahi, *Food and Chemical Toxicology* **166** (2022) 113243. https://doi.org/10.1016/j.fct.2022.113243

[69] S. A. Alavi-Tabari, M. A. Khalilzadeh, H. Karimi-Maleh, *Journal of Electroanalytical Chemistry* **811** (2018) 84-88. https://doi.org/10.1016/j.jelechem.2018.01.034

[70] B. Kamble, K.M. Garadkar, K.K. Sharma, P. Kamble, S. Tayade, B.D. Ajalkar, *Journal of Electrochemical Science and Engineering* **11** (2021) 143-159. https://doi.org/10.5599/jese.956

[71] I. Amar, A. Sharif, M. Ali, S. Alshareef, F. Altohami, M. Abdulqadir, M. Ahwidi, *Chemical Methodologies* **4** (2020) 1-18. https://doi.org/10.33945/SAMI/CHEMM.2020.1.1

[72] H. Karimi-Maleh, C. Karaman, O. Karaman, F. Karimi, Y. Vasseghian, L. Fu, A. Mirabi, *Journal of Nanostructure in Chemistry* **12** (2022) 429-439. https://doi.org/10.1007/s40097-022-00492-3

[73] A. Dehno Khalaji, *Chemical Methodologies* **4(1)** (2020) 34-39. https://doi.org/10.33945/SAMI/CHEMM.2020.1.3

[74] S. Mafi, K. Mahanpoor, *Eurasian Chemical Communications* **2(1)** (2020) 59-77. http://dx.doi.org/10.33945/SAMI/ECC.2020.1.7

[75] H. Karimi-Maleh, R. Darabi, M. Shabani-Nooshabadi, M. Baghayeri, F. Karimi, J. Rouhi, C. Karaman, *Food and Chemical Toxicology* **162** (2022) 112907. https://doi.org/10.1016/j.fct.2022.112907

[76] S. Tajik, H. Beitollahi, F. G. Nejad, Z. Dourandish, M. A. Khalilzadeh, H. W. Jang, R. A. Venditti, R. S. Varma, M. Shokouhimehr, *Industrial & Engineering Chemistry Research* **60(3)** (2021) 1112-1136. https://doi.org/10.1021/acs.iecr.0c04952

[77] M. Rohaniyan, A. Davoodnia, S. Beyramabadi, *Chemical Methodologies* **4** (2020) 285-296. https://doi.org/10.33945/SAMI/CHEMM/2020.3.6

[78] E. Naderi; N. Akbarzadeh-T; T. Kondori; A. Tahkor, *Eurasian Chemical Communications* **2(2)** (2020) 265-271. http://dx.doi.org/10.33945/SAMI/ECC.2020.2.12

[79] S. Sarli; N. Ghasemi, *Eurasian Chemical Communications* **2(3)** (2020) 302-318. http://dx.doi.org/10.33945/SAMI/ECC.2020.3.2

[80] S. Tajik, Y. Orooji, Z. Ghazanfari, F. Karimi, H. Beitollahi, R. S. Varma, H. W. Jang, M. Shokouhimehr, *Journal of Food Measurement and Characterization* **15(4)** (2021) 3837-3852. https://doi.org/10.1007/s11694-021-00955-1

[81] F. Raoufi, H. Aghaei, M. Ghaedi, *Eurasian Chemical Communications* **2(2)** (2020) 226-233. https://dx.doi.org/10.33945/SAMI/ECC.2020.2.8

[82] S.S. Mohammadi, N. Ghasemi M. Ramezani, *Eurasian Chemical Communications* **2(1)** (2020) 87-102. https://dx.doi.org/10.33945/SAMI/ECC.2020.1.10

[83] B. Baghernejad, M. Rostami Harzevili, *Chemical Methodologies* **5(2)** (2021) 90-95. https://doi.org/10.22034/chemm.2021.119641

[84] Z. Hoseini, A. Davoodnia, A. Khojastehnezhad, M. Pordel. *Eurasian Chemical Communications* **2(3)** (2020) 398-409. http://dx.doi.org/10.33945/SAMI/ECC.2020.3.10

[85] S. Tajik, Y. Orooji, F. Karimi, Z. Ghazanfari, H. Beitollahi, M. Shokouhimehr, R. S. Varma, H. W. Jang, *Journal of Food Measurement and Characterization* **15(5)** (2021) 4617-4622. https://doi.org/10.1007/s11694-021-01027-0

[86] N. Ahmadi, A. Ramazani, S. Rezayati, F. Hosseini, *Eurasian Chemical Communications* **2(8)** (2020) 862-874. http://dx.doi.org/10.22034/ecc.2020.108366

[87] M. Alidadykhoh, H. Pyman, H. Roshanfekr, *Chemical Methodologies* **5(2)** (2021) 96-106. https://doi.org/10.22034/chemm.2021.119677

[88] M. Ozdal, S. Gurkok, *ADMET and DMPK* **10** (2022) 115-129. https://doi.org/10.5599/admet.1172

[89] S. Staroverov, S. Kozlov, A. Fomin, K. Gabalov, V. Khanadeev, D. Soldatov, I. Domnitsky, L. Dykman, S.V. Akchurin, O. Guliy, *ADMET and DMPK* **9** (2021) 255-266. https://doi.org/10.5599/admet.1023

[90] S. Tajik, H. Beitollahi, H. W. Jang, M. Shokouhimehr, *Talanta* **232** (2021) 122379. https://doi.org/10.1016/j.talanta.2021.122379

[91] F. G. Nejad, S. Tajik, H. Beitollahi, I. Sheikhshoaie, *Talanta* **228** (2021) 122075. https://doi.org/10.1016/j.talanta.2020.122075

[92] M. Shahsavari, M. Mortazavi, S. Tajik, I. Sheikhshoaie, H. Beitollahi, *Micromachines* **13(1)** (2022) 88. https://doi.org/10.3390/mi13010088

[93] S.S. Moshirian-Farahi, H.A. Zamani, M. Abedi, *Eurasian Chemical Communications* **2(9)** (2020) 702-711. https://dx.doi.org/10.33945/SAMI/ECC.2020.6.7

[94] S. Tajik, H. Beitollahi, Z. Dourandish, P. Mohammadzadeh Jahani, I. Sheikhshoaie, M. B. Askari, M. Shokouhimehr, *Electroanalysis* **34(7) (**2022) 1065-1091. https://doi.org/10.1002/elan.202100393

[95] T. Eren, N. Atar, M. L. Yola, H. Karimi-Maleh, *Food Chemistry* **185** (2015) 430-436. https://doi.org/10.1016/j.foodchem.2015.03.153

[96] S. Tajik, A. Lohrasbi-Nejad, P. Mohammadzadeh Jahani, M. B. Askari, P. Salarizadeh, H. Beitollahi, *Journal of Food Measurement and Characterization* **16(1)** (2022) 722-730. https://doi.org/10.1007/s11694-021-01201-4

[97] M. Payehghadr; Y. Taherkhani; A. Maleki; F. Nourifard, *Eurasian Chemical Communications* **2(9)** (2020) 982-990. https://dx.doi.org/10.22034/ecc.2020.114589

[98] S. Tajik, M. B. Askari, S. A. Ahmadi, F. G. Nejad, Z. Dourandish, R. Razavi, H. Beitollahi, A. Di Bartolomeo, *Nanomaterials* **12(3)** (2022) 491. https://doi.org/10.3390/nano12030491

[99] A. Hosseini Fakhrabad; R. Sanavi Khoshnood; M.R. Abedi; M. Ebrahimi, *Eurasian Chemical Communications* **3(9)** (2021) 627-634. https://dx.doi.org/10.22034/ecc.2021.288271.1182

[100] M. Pirozmand, A. Nezhadali, M. Payehghadr, L. Saghatforoush, *Eurasian Chemical Communications* **2(10)** (2020) 1021-1032. http://dx.doi.org/10.22034/ecc.2020.241560.1063

[101] T. Girish, J.G. Manjunatha, P.A. Pushpanjali, N. S. Prinith, D. K. Ravishankar, G. Siddaraju, *Journal of Electrochemical Science and Engineering* **11** (2021) 27-38. https://doi.org/10.5599/jese.934

[102] M. R. Aflatoonian, S. Tajik, B. Aflatoonian, M. S. Ekrami-Kakhki, K. Divsalar, I. Sheikh Shoaie, Z. Dourandish, M. Sheikhshoaie, *Eurasian Chemical Communications* **2(4)** (2020) 505-515. https://dx.doi.org/10.33945/SAMI/ECC.2020.4.8

[103]   H. Pyman, H. Roshanfekr, S. Ansari, *Eurasian Chemical Communications* **2(2)** (2020) 213-225. https://dx.doi.org/10.33945/SAMI/ECC.2020.2.7

[104]   H. Karimi-Maleh, A. F. Shojaei, K. Tabatabaeian, F. Karimi, S. Shakeri, R. Moradi, *Biosensors and Bioelectronics* **86** (2016) 879-884. https://doi.org/10.1016/j.bios.2016.07.086

[105]   M. R. Aflatoonian, B. Aflatoonian, R. Alizadeh, R. Abbasi Rayeni, *Eurasian Chemical Communications* **2(1)** (2020) 35-43. https://dx.doi.org/10.33945/SAMI/ECC.2020.1.4

[106]   S. Mafi, K. Mahanpoor, *Eurasian Chemical Communications* **2(1)** (2020) 59-77. https://dx.doi.org/10.33945/SAMI/ECC.2020.1.7

[107]   F. G. Nejad, I. Sheikhshoaie, H. Beitollahi, *Food and Chemical Toxicology* **162** (2022) 112864. https://doi.org/10.1016/j.fct.2022.112864

[108]   H. Karimi-Maleh, H. Beitollahi, P. S. Kumar, S. Tajik, P. M. Jahani, F. Karimi, C. Karaman, Y. Vasseghian, M. Baghayeri, J. Rouhi, P. L. Show, *Food and Chemical Toxicology* **164** (2022) 112961. https://doi.org/10.1016/j.fct.2022.112961

[109]   A. Dinu, C. Apetrei, *Sensors* **20(9)** (2020) 2496. https://doi.org/10.3390/s20092496

[110]   S. Tajik, Z. Dourandish, F. G. Nejad, A. Aghaei Afshar, H. Beitollahi, *Micromachines* **13(3)** (2022) 369. https://doi.org/10.3390/mi13030369

[111]   A. Hojjati-Najafabadi, M. Mansoorianfar, T. X. Liang, K. Shahin, H. Karimi-Maleh, *Science of The Total Environment* **824** (2022) 153844. https://doi.org/10.1016/j.scitotenv.2022.153844

[112]   G. Erdoğdu, *Journal of Analytical Chemistry* **58(6)** (2003) 569-572. https://doi.org/10.1023/A:1024120320359

[113]   M. Arvand, M. Vaziri, M. A. Zanjanchi, *Journal of Analytical Chemistry* **68(5)** (2013) 429-435. https://doi.org/10.1134/S1061934813050043

[114]   A. Motaharian, F. Motaharian, K. Abnous, M. R. M. Hosseini, M. Hassanzadeh-Khayyat, *Analytical and Bioanalytical Chemistry* **408(24)** (2016) 6769-6779. http://dx.doi.org/10.1007%2Fs00216-016-9802-7

[115]   J. Ghodsi, A. A. Rafati, *Journal of Electroanalytical Chemistry* **807** (2017) 1-9. https://doi.org/10.1016/j.jelechem.2017.11.003

[116]   M. Khadem, F. Faridbod, P. Norouzi, A. Rahimi Foroushani, M. R. Ganjali, S. J. Shahtaheri, R. Yarahmadi, *Electroanalysis* **29(3)** (2017) 708-715. https://doi.org/10.1002/elan.201600293

[117]   D. Akyüz, A. Koca, *Sensors and Actuators B* **283** (2019) 848-856. https://doi.org/10.1016/j.snb.2018.11.155

[118]   F. Zahirifar, M. Rahimnejad, R. A. Abdulkareem, G. Najafpour, *Biocatalysis and Agricultural Biotechnology* **20** (2019) 101245. https://doi.org/10.1016/j.bcab.2019.101245

[119]   F. Tadayon, M. Jahromi, *Journal of the Iranian Chemical Society* **17(4)** (2020) 847-857. https://doi.org/10.1007/s13738-019-01819-8

[120]   T. Ghiasi, S. Ahmadi, E. Ahmadi, M. R. T. B. Olyai, Z. Khodadadi, *Microchemical Journal* **160** (2021) 105628. https://doi.org/10.1016/j.microc.2020.105628

[121]   O. K. Topsoy, F. Muhammad, S. Kolak, A. Ulu, Ö. Güngör, M. Şimşek, B. Ateş, *Measurement* **187** (2022) 110250. https://doi.org/10.1016/j.measurement.2021.110250

[122]   L. S. Porto, L. F. Ferreira, W. T. P. Dos Santos, A. C. Pereira, *Talanta* **246** (2022) 123477. https://doi.org/10.1016/j.talanta.2022.123477

A. L. Nejad

J. Electrochem. Sci. Eng. **12(6)** (2022) 1041-1059

[123] D. Grieshaber, R. MacKenzie, J. Vörös, E. Reimhult, *Sensors* **8(3)** (2008) 1400-1458. https://doi.org/10.3390/s80314000

[124] Z. Dourandish, S. Tajik, H. Beitollahi, P. M. Jahani, F. G. Nejad, I. Sheikhshoaie, A. Di Bartolomeo, *Sensors* **22(6)** (2022) 2238. https://doi.org/10.3390/s22062238

[125] I. G. Munteanu, C. Apetrei, *International Journal of Molecular Sciences* **22(23)** (2021) 13138. https://doi.org/10.3390/ijms222313138

[126] H. Karimi-Maleh, Y. Orooji, F. Karimi, M. Alizadeh, M. Baghayeri, J. Rouhi, A. Al-Othman, *Biosensors and Bioelectronics* **184** (2021) 113252. https://doi.org/10.1016/j.bios.2021.113252

[127] E. Cesewski, B. N. Johnson, *Biosensors and Bioelectronics* **159** (2020) 112214. https://doi.org/10.1016/j.bios.2020.112214

[128] P. Bollella, G. Fusco, C. Tortolini, G. Sanzò, G. Favero, L. Gorton, R. Antiochia, *Biosensors and Bioelectronics* **89** (2017) 152-166. https://doi.org/10.1016/j.bios.2016.03.068

[129] R. Monošík, M. Stred'anský, E. Šturdík, *Journal of Clinical Laboratory Analysis* **26(1)** (2012) 22-34. https://doi.org/10.1002%2Fjcla.20500

[130] Z. Ma, C. Meliana, H. S. H. Munawaroh, C. Karaman, H. Karimi-Maleh, S. S. Low, P. L. *Chemosphere* **306** (2022) 135515. https://doi.org/10.1016/j.chemosphere.2022.135515

[131] H. Beitollahi, S. Tajik, Z. Dourandish, K. Zhang, Q. V. Le, H. W. Jang, M. Shokouhimehr, *Sensors* **20(11)** (2020) 3256. https://doi.org/10.3390/s20113256

[132] V. S. Somerset, M. J. Klink, M. M. Sekota, P. G. Baker, E. I. Iwuoha, *Analytical Letters* **39(8)** (2006) 1683-1698. https://doi.org/10.1080/00032710600713834

[133] Y. D. T. de Albuquerque, L. F. Ferreira, *Analytica Chimica Acta* **596(2)** (2007) 210-221. https://doi.org/10.1016/j.aca.2007.06.013

[134] V. S. Somerset, M. J. Klink, P. G. Baker, E. I. Iwuoha, *Journal of Environmental Science and Health, Part B* **42(3)** (2007) 297-304. https://doi.org/10.1080/03601230701229288

[135] N. Zehani, S. V. Dzyadevych, R. Kherrat, N. J. Jaffrezic-Renault, *Frontiers in Chemistry* **2** (2014) 44. https://doi.org/10.3389/fchem.2014.00044

[136] M. Arvand, M. Dehsaraei, *Ionics* **24(8)** (2018) 2445-2454. https://doi.org/10.1007/s11581-017-2373-6

[137] N. Pajooheshpour, M. Rezaei, A. Hajian, A. Afkhami, M. Sillanpää, F. Arduini, H. Bagheri, *Sensors and Actuators B: Chemical* **275** (2018) 180-189. https://doi.org/10.1016/j.snb.2018.08.014

[138] S. Hassani, M. R. Akmal, A. Salek-Maghsoudi, S. Rahmani, M. R. Ganjali, P. Norouzi, M. Abdollahi, *Biosensors and Bioelectronics* **120** (2018) 122-128. https://doi.org/10.1016/j.bios.2018.08.041

[139] A. R. Zare, A. A. Ensafi, B. Rezaei, *Journal of the Iranian Chemical Society* **16(12)** (2019) 2777-2785. https://doi.org/10.1007/s13738-019-01741-z

[140] H. Khosropour, B. Rezaei, P. Rezaei, A. A. Ensafi, *Analytica Chimica Acta* **1111** (2020) 92-102. https://doi.org/10.1016/j.aca.2020.03.047