



Tuneable properties of boron-doped diamond working electrodes and their advantages for the detection of pesticides

Zuzana Kramplová^a, Adriana Ferancová^{b,*}, Tibor Maliar^a, Andrea Purdešová^{a,*}

^a Institute of Chemistry and Environmental science, University of Ss. Cyril and Methodius in Trnava, Faculty of Natural Sciences, Nám. J. Herdu 2, 917 01 Trnava, Slovak Republic

^b Unit of Measurement Technology, Kajaani University Consortium, University of Oulu, Kehräämöntie 7, 87400 Kajaani, Finland

ARTICLE INFO

Keywords:

Boron-doped diamond electrode
Pesticides
Electrochemical properties
Electrochemical determination
Potential window

ABSTRACT

Boron-doped diamond (BDD) is a versatile carbon material widely utilized in electroanalysis for detecting various organic compounds. In comparison to commonly employed carbon electrode materials, BDD possesses interesting and unique properties. This review article explores important role of adjustable - tuneable BDD characteristics, including boron concentration, sp^3/sp^2 carbon ratio, and surface treatments, in the electrochemical determination of pesticides. Through an intricate interplay of these properties, BDD's performance in term of sensitivity, selectivity, and resistance to fouling can be optimized. Notably, the exceptional potential window of BDD electrodes extends the detection capabilities into regimes where other materials falter due to oxygen evolution reactions. Furthermore, in the reduction potential range, BDD electrodes (BDDE) offer a safer alternative to toxic mercury-based electrodes.

Despite the considerable progress, gaps remain in understanding the comprehensive effects of tuneable BDDE properties on pesticide analysis. Comparative studies exploring the interplay between these properties and their impact on detection, particularly in multianalyte systems and under challenging conditions, are crucial. Addressing issues related to matrix interference and fouling would contribute significantly to the development of robust pesticide sensors. This review provides insights into the critical role of BDD's properties in pesticide detection and highlights avenues for future research.

1. Introduction

Pesticides are nowadays common contaminants of the environment. The role of pesticides is to eliminate pest species; therefore, they are made from toxic chemicals. Such chemicals are often toxic to humans or other organisms that are not pesticides' target species. Therefore, pesticides must be well controlled, detected and analysed in the environment which also helps in their further remediation.

Conventional methods for the detection of pesticides have historically relied on techniques such as gas chromatography, liquid chromatography, mass spectrometry, and enzyme-linked immunosorbent assays (ELISA). While these methods have been effective in identifying and quantifying pesticides in various samples, they come with several shortcomings [1]. Firstly, these techniques often require complex and time-consuming sample preparation procedures. Additionally, many conventional methods are expensive and require specialized equipment and expertise, making them less accessible for routine pesticide

monitoring, particularly in resource-limited settings. Moreover, these techniques are usually laboratory-based and are not suitable for *on-site* and *real-time* measurements.

In contrast, electrochemical sensor methods offer several distinct advantages for pesticide detection. These sensors are designed to be cost-effective, portable, and easy to use, making them suitable for on-site and point-of-care applications [2]. Rapid analyses, instrumentation of small size and portable, make them ideal for the real time measurements in the field. Common materials for the construction of electrochemical sensors are metals (e.g., platinum or gold) as well as carbon materials, such as glassy carbon, pyrolytic graphite, and carbon nanomaterials. Frequent problem of these sensors, especially in the determination in a real matrix (such as water, soil), is the potential window and fouling of the surface with target analyte, reaction products or matrix interferences, that negatively affects the analytical performance of the sensor-based methods [3,4]. The fouling of electrode surface during the electroanalysis is one of the main obstacles in the development of

* Corresponding authors.

E-mail addresses: adriana.ferancova@oulu.fi (A. Ferancová), andrea.purdesova@ucm.sk (A. Purdešová).

<https://doi.org/10.1016/j.jelechem.2023.117846>

Received 17 August 2023; Received in revised form 29 September 2023; Accepted 7 October 2023

Available online 11 October 2023

1572-6657/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

sensors for the continuous and autonomous measurements in the field applications [5]. Moreover, there is also need of the multianalyte detection of pesticides and requirements of ultra-low detection limits and high selectivity, which are driving the development of advanced electrode materials, electrode surface treatments or modifications [4,6].

Boron-doped diamond (BDD) became a very interesting material for the preparation of electrochemical sensors. BDD combines the unique properties of pure diamond, such as complete C-sp³ hybridization and tetrahedral bonding, with the high electrical conductivity after p-doping with a boron [7]. Other advantages of BDD important also for the detection of pesticides include good chemical stability in acidic, alkaline, or organic media, good biocompatibility, extremely high overpotential for the oxygen evolution reaction, a wide potential window in aqueous electrolytes, as well as low background current. Thanks to these properties BDD electrodes have been used in number of applications including electroanalysis, electrosynthesis, and electrochemical degradation of organic contaminants [8–13].

Boron concentration, sp³/sp² ratio, and surface properties, that can be controlled during or after the preparation of BDD, have significant effect on the final electrochemical properties of BDD. They have been widely studied and discussed in several authoritative reviews [14,15]. Recently, there has also been a growing interest in tailoring BDD properties for specific applications, such as the detection of pesticides using BDD electrodes. Notably, the Czech research groups has specifically examined the impact of boron concentration and surface treatment, on the electrochemical detection of pesticides [16–20]. Additionally, other research groups have explored the effects of BDD surface treatment, modification of either the BDD surface or electrolyte, and their influence on pesticide detection [21–23]. This review article emphasizes the role of BDD properties (boron concentration, sp² carbon impurities, surface treatment, and modification) in pesticide detection. The preparation methods for BDD have been extensively described elsewhere [7,9,24–26] and will not be reviewed here.

2. BDD properties and electrochemical determination of pesticides

Natural diamond carbon is sp³ hybridized, resulting in complete tetrahedral bonding. This is the reason for unique mechanical and thermal properties of diamond [7]. However, its wide band gap leads to high electrical resistivity, making it unsuitable for use as an electrode material on its own. To enhance diamond's conductivity, it is necessary to introduce charge carriers through a process of doping [27], which transforms it into a suitable electrode material. Depending on the type of dopant used, diamond become either p-type or n-type semiconductor [24,28]. Donors such as phosphorus, nitrogen, and sulphur are employed as n-type dopants, while boron, as an acceptor, serves as the p-type dopant. For electroanalytical purposes, doping diamond with boron as a charge acceptor is the most common practice [29]. Additionally, boron doping is easier compared to some other dopants [30]. The boron content is one of the critical factors influencing the electrochemical properties of boron-doped diamond electrodes. Another important factors are the content of non-diamond sp² carbon (sp³/sp² ratio), and surface termination, which can also be alternated after the synthesis of BDD [28].

Although the tuneable properties of boron-doped diamond electrodes (BDDEs) play a crucial role for their electrochemical performance and analytical applications, we have noticed a limited number of comparative investigations that have been conducted to comprehensively understand the individual contributions of these properties in the determination of pesticides. Therefore, our review aims to provide insights into pesticide analysis using BDDEs, identify knowledge gaps, and emphasize the importance of future comparative studies to unravel the intricate interplay between BDD's tuneable properties and their impact on the determination of pesticides.

2.1. Boron doping level

Due to the higher density of electronic states formed within the bandgap of BDD, an increase in boron concentration enhances the diamond's conductivity [31]. Boron dopant concentration in the diamond is typically expressed as “ppm” (the concentration of boron in the gas phase relative to the carbon source), as a “% of boron to carbon” in the gas phase, or as the “number of boron atoms per cm³” in the solid phase [29]. Common boron concentrations in BDD range from 500 to 10 000 ppm (10¹⁹ – 10²¹ B atoms per cm³), corresponding to BDD electrode resistivity between 5 and 100 mΩ (or conductivity 0.2 – 0.01 S) [26]. Thus, the electrical properties of BDD can be adjusted by the boron concentration, resulting in BDD having either semiconductor (~10¹⁷ atom cm⁻³) or semi-metallic conductivity (~10²⁰ atom cm⁻³) [32]. For clarification, authors use various terms in this context. Some authors refer to moderately doped diamonds ([B] < 10²⁰ cm⁻³) or heavily doped diamonds ([B] > 10²¹ cm⁻³) [33], or highly (B1 = 1.5 × 10¹⁹ < [B] < B2 = 3 × 10²⁰ cm⁻³) and heavily ([B] > B2 = 3 × 10²⁰ cm⁻³) boron doped films, where the latter exhibits metallic conductivity [34]. In addition, normally doped (1%) BDD and low-doped (0.1%) BDD [35], as well as lightly doped (1000 ppm) [36], or BDD-low (1000 ppm; NA = 8 × 10¹⁷ B cm⁻³), BDD-moderate (5000 ppm; NA = 1.5 × 10¹⁹ B cm⁻³), and BDD-high (10000 ppm; NA = 2 × 10²⁰ B cm⁻³) have also been mentioned [37].

A higher boron doping concentration not only impacts the conductivity of BDDE but also leads to an increased amount of oxygen on the surface of as-grown BDD. This results in varying electron affinities, with negative and positive affinities observed for lightly and highly doped electrodes, respectively [31,38,39]. These electron affinities influence the manner in which electrons are either attracted to or repelled from the electrode surface, consequently affecting electrochemical reactions occurring on the BDD surface.

In general, electrochemical and electroanalytical properties of BDDEs were reported to be enhanced with an increase in the doping level. BDDEs with higher doping levels contain more surface-active sites that improve the electron transfer, electrode conductivity, and thus the reversibility of electrochemical reactions. A negative shift of the peak potentials with an increase in the doping level was also observed, indicating easier oxidation of the analytes [17]. BDD electrodes with higher boron doping levels usually offer higher sensitivities and lower detection limits (LODs) [29]. However, a very high concentration of boron can also have a negative effect on the electroanalytical properties. Trouillon et al. showed that boron-saturated BDD (5%) possesses similar properties to glassy carbon electrode, and a narrower potential window was observed than that of 0.1% BDD [40]. Authors also concluded that highly doped BDDEs with high electroactivity are more susceptible to the fouling than BDDEs with lower doping level.

Commonly used BDDEs for the detection of pesticides have doping level over 1000 ppm, mostly 8000 ppm (Table 1.). Several studies investigating the effect of boron doping level on the determination of pesticides or pesticide precursors can be found. Schwarzová-Pecková et al. studied the effect of BDDE doping level from 500 ppm to 8000 ppm on the voltametric signal of 2-aminobiphenyl [16]. Their results confirmed faster kinetics at electrodes with higher doping level. For semiconductive electrodes (500 ppm – 1000 ppm), they observed only small differences in the electrochemical currents, but significant differences were observed for electrodes with higher doping levels and metallic conductivity (2000 ppm – 8000 ppm). Authors also observed a negative shift of the peak potential with an increase in doping level. Similar results were also obtained for cresols [17]. The slopes of concentration dependences in the linear range were lower for BDDEs with semiconducting properties (500 ppm – 1000 ppm), but the standard deviations of peak heights were also lower than those obtained on BDDEs with metallic conductivity. Therefore, authors concluded that all studied BDDEs have comparable properties from an analytical point of view.

Table 1

Boron doping level, electrochemical method, peak potentials and analytical performance obtained at BDDEs used for the determination of pesticides and their precursors.

Analyte	Boron doping level	Electrochemical method	Peak potential (V)	Linear concentration range ($\mu\text{mol/L}$)	Limit of detection ($\mu\text{mol/L}$)	Ref.
diuron	8000 ppm	DPV	1.24	1.0–9.0	0.035	[11]
2,4-D			1.49	1.0–9.0	0.12	
tebuthiuron			1.74	2.5–22.5	0.34	
2-amino-biphenyl	500 ppm	DPV	0.72	0.25–50	0.72	[16]
	1000 ppm		0.71		0.48	
	2000 ppm		0.707		0.80	
	4000 ppm		0.709		0.48	
	8000 ppm		0.71		0.21	
o-cresol	500 ppm	DPV	~1.08	3–100	1.05 / 1.01*	[17]
	1000 ppm		~1.1		1.16 / 1.07*	
	4000 ppm		~1.05		2.67 / 2.58*	
	8000 ppm		~1.03		2.63 / 2.97*	
p-cresol	500 ppm	DPV	~1.17	3–100	1.25 / 0.69*	[17]
	1000 ppm		~1.08		1.37 / 1.06*	
	4000 ppm		~1.07		0.74 / 1.30*	
	8000 ppm		~1.03		0.61 / 1.52*	
terconazole	10 000 ppm	DPV	~0.5	0.2–4 (1st peak)	0.40	[18]
				1–4 (2nd peak)	0.87	
azoxystrobin	n.s.	DPV	~1.4	0.3–200	0.008	[19]
difenoconazole	1000 ppm	DPV	~1.75	0.1–40	0.049	[20]
formetanate	8000 ppm	SWV	1.1	0.498–17	0.37	[21]
triclosan	1000 ppm	SWV	0.67	3.5×10^{-3} –3.5	7.9×10^{-3}	[22]
dinoterb	1000 ppm	SWV	1.22	3.121×10^{-3} –3.12	9.16×10^{-3}	[23]
methomyl	n.s.	DPV/SWV *	~1.7	(5–410) / (66–420) *	1.2 / 19*	[41]
chlorothalonil	8000 ppm	SWV	–1.07	0.12–4.0	0.04	[42]
itraconazole	0.1%	SWV	0.59**	7.9×10^{-3} –1.2**	1.79×10^{-3}	[43]
posaconazole			0.55**	5.7×10^{-3} –0.844**	7.78×10^{-3}	
picloram	8000 ppm	SWV	~1.6	6.7–67	0.39	[44]
carbaryl	0.1%***	DPV	0.74	1–6	0.07	[45]
paraquat			–0.80	0.2–1.2	0.01	
carbaryl	n.s.***	DPV	1.35	–	1.18×10^{-3}	[46]
paraquat			–0.89		1.21×10^{-3}	
dichlorvos	n.s.***	DPV	–	0.1×10^{-3} –10	1.50×10^{-6}	[47]
fenitrothion					4.40×10^{-6}	
carbendazim	n.s.***	SWV	1.2	0.672–11.2	0.196	[48]
methoxyfenozide	n.s.	SWV	1.5	0.50–70	0.14	[49]
2,4,6-trichlorophenol	n.s.	SWV	0.66	1.93–21.23	0.15	[50]
pirimicarb	8000 ppm	DPV	0.97	2.0–219	1.24	[51]
fenthion	8000 ppm	SWV	1.27	0.25–10	0.08	[52]
thiabendazole	8000 ppm	SWV	1.4	0.498–11.2	0.127	[53]
daminozide	1000 ppm	DPV	1.5	21–17.4	2.19	[54]
clomazone	1000 ppm	SWV	~1.6	1–100	0.21	[55]
maneb	1000 ppm	DPV	~0.7	0.08–3	24×10^{-3}	[56]
bentazone	1000 ppm	DPV	1.07	2–100	0.5	[57]
pethoxamid	1000 ppm	SWV	1.35	3–100	1.37	[58]
azametiphos	1000 ppm	SWV	1.7	2–100	0.45	[59]

2,4-D = 2,4-dichlorophenoxyacetic acid; n.s. = not specified; DPV = differential pulse voltammetry; SWV = square-wave voltammetry.

* DPV/SWV; ** potential vs. saturated calomel electrode (SCE); ***surface modifier.

2.2. Electrochemical pretreatment of BDD surface

Like other types of electrode materials, BDD also requires specific surface treatments to ensure its unique analytical performance. Electrochemical pretreatment of the BDD surface includes cathodic or anodic pretreatment. These processes involve subjecting the BDD electrode to either cathodic or anodic potential in appropriate electrolyte. The potentiostatic method is mostly applied for this purpose; however, cyclic voltammetry has also been used. The methods for pretreating the BDDE surface, including conditions and electrolytes used before determining pesticides, are summarized in Table 2.

Both cathodic and anodic pretreatments offer valuable tools for tailoring the surface properties of BDDEs to meet the specific analytical needs of pesticide detection.

Cathodic treatment: During cathodic treatment, the BDDE is exposed to a cathodic potential in the appropriate electrolyte. One of the primary effects of cathodic pretreatment of BDD is the creation of a hydrogen-terminated (H-terminated) surface, altering the electrochemical characteristics of the electrode and making the BDD surface

hydrophobic [14,60]. It has been demonstrated that cathodic treatment enhances the reversibility of electrochemical responses and electron transfer kinetics for the ferro/ferricyanide redox couple on BDDE [61]. However, the degree of BDD surface hydrogenation decreases over time when exposed to atmospheric oxygen. Authors have also observed that BDDEs with higher doping levels (2000 and 8000 ppm of boron) lose hydrogen from the surface more slowly than moderately doped BDDEs (300 and 800 ppm of boron). Therefore, authors recommend performing cathodic treatment just before electrochemical measurements to ensure an H-terminated BDD surface.

Cathodic treatment of BDDE can remove organic contaminations from the electrode surface, and if a decrease in sensitivity and reproducibility is observed during measurement, cathodic treatment can be extended or followed by mechanical polishing [42,43]. Cathodic treatment prior to the determination of pesticides is mostly performed potentiostatically but in few cases, cyclic voltammetry was also used (see Table 2).

Anodic treatment: Anodic treatment involves the applying an anodic potential to the BDD electrode in an appropriate electrolyte

Table 2

Pretreatment methods applied to the BDDEs prior the determination of pesticides.

Analyte	BDDE treatment	Ref.
diuron; 2,4-D; tebuthiuron	CT (-500 mA cm ⁻² (-2.0 V), 30 s) in 0.5 M H ₂ SO ₄	[11]
2-aminobiphenyl	AT (+2.4 V, 20 min) in 0.1 M H ₂ SO ₄ ; re-oxidation after each set of experiments at +2.4 V; 10 min Activation at beginning of day at +2.4 V 180 s in 0.1 M H ₂ SO ₄ ; activation between measurements at +2.4 V, 30 s in sample solution	[16]
o-cresol p-cresol	Daily AT (+2.4 V, 5 min) in 0.5 M H ₂ SO ₄ ; between measurements activation in sample solution (+2.4 V, 1 min)	[17]
terconazole	AT (+2.4 V, 20 min) in 0.5 M H ₂ SO ₄ and 5 min in supporting electrolyte before series of measurements; between measurements activation at +2.4 V, 5 s in measured solution	[18]
azoxystrobin	CT by 20 CV scans (-1.75 V to +2.5 V) in electrolyte; BDDE surface even oxidized in the air	[19]
difenoconazole	AT by 20 CV scans (+2.2 V to -1.0 V) in 0.1 M HNO ₃ at the beginning of day	[20]
formetanate	AT (+3.0 V, 30 s) followed by CT (-3.0 V, 60 s) in 0.5 M H ₂ SO ₄	[21]
triclosan	CT (-1.5 V; once per day 180 s, between measurements 60 s) in 0.5 M H ₂ SO ₄	[22]
dinoterb	CT (-1.6 V; once per day 180 s, between measurements 60 s) in 0.5 M H ₂ SO ₄	[23]
methomyl	Daily and between measurements AT (+3.0 V, 120 s) followed by CT (-3.0 V, 240 s) in 0.5 M H ₂ SO ₄	[41]
chlorothalonil	AT (+3.0 V, 10 min) followed by CT (-3.0 V, 10 min) in 0.5 M H ₂ SO ₄ ; if needed CT was extended in 30 s	[42]
itraconazole posaconazole	CT by CV (-2.9 V to 0.3 V); in case of adsorbed analyte mechanical polishing	[43]
picloram	AT (+400 mA cm ⁻² ; 50 s) in 0.5 M H ₂ SO ₄ ; stabilization of electrode surface by 20–25 CV (0.0 V to +1.8 V)	[44]
methoxyfenozide	Mechanical polishing before measurement of new sample	[49]
2,4,6-trichlorophenol	AT (+3.0 V; 60 s) followed by CT (-3.0 V; 60 s) in 0.5 M H ₂ SO ₄	[50]
pirimicarb	AT (+3.0 V; 5 s) followed by CT (-3.0 V; 60 s) in 0.5 M H ₂ SO ₄	[51]
fenthion	AT (+3.0 V; 10 min) followed by CT (-3.0 V; 10 min); if needed CT repeated for 30 s	[52]
thiabendazole	Before new set of measurements AT (+3.0 V; 30 s) followed by CT (-3.0 V; 60 s) in 0.5 M H ₂ SO ₄	[53]
daminozide	AT (+2.0 V; 10 s) followed by CT (-2.0 V; 10 s) followed by AT (+2.0 V; 10 s)	[54]
maneb	AT (+2.0 V; 180 s) followed by CT (-2.0 V; 180 s) in 1 M H ₂ SO ₄	[56]
bentazone	AT (+2.0 V, 180 s) followed by CT (-2.0 V, 180 s) in 0.5 M H ₂ SO ₄	[57]
pethoxamid	AT (+2.0 V, 180 s) followed by CT (-2.0 V, 180 s) in 0.5 M H ₂ SO ₄	[58]
azametiphos	AT (+2.0 V, 180 s) followed by CT (-2.0 V, 180 s) in 1 M H ₂ SO ₄	[59]

AT = anodic treatment; CT = cathodic treatment; CV = cyclic voltammetry.

solution. This process leads to the formation of an oxygen-terminated (O-terminated) BDD surface with hydrophilic properties [14,60]. Duo et al. reported an enhancement in reproducibility after anodic treatment, which also led to the reduction of sp² sites [62]. This reduction resulted in a deterioration of electron transfer kinetics, where sp² sites serve as transfer promoters. Authors also observed an increase in the irreversibility of redox probes with the strength of the anodic treatment.

In some cases, anodic treatment can be performed *in situ*, i.e., in sample solution, which is advantageous when oxidation intermediates of the analyte (e.g. *p*-cresol) tend to passivate the electrode surface [17]. Thus, anodic pretreatment also serves as the regeneration of the electrode surface. This electrode was then successfully applied as the amperometric detector for HPLC.

Several authors have compared the effect of BDD treatments on the electron transfer kinetics and the determination of pesticides or

pesticide precursors. Fischer et al. compared anodically treated (O-BDD) and cathodically treated (H-BDD) BDDEs for the determination of terconazole [18]. Authors reported similar electron transfer kinetics for all studied electrodes. However, O-BDD was the most suitable electrode for their studies because its anodic treatment could be performed *in situ* and directly in the measured solution, while H-BDD required *ex situ* treatments.

Different methods of electrochemical BDDE treatment were also investigated in the work of Šešlovská et al. [19]. Particularly, they compared potential cycling, cathodic potentiostatic treatment, and anodic potentiostatic treatment. Authors showed that cathodic treatment of BDD caused an increase in the background current and a narrowing of the potential window in the determination of difenoconazole. The best results were obtained using potential cycling finalized at a positive potential (from +2.2 V to -1.0 V), leading to an O-terminated surface. This was performed only once a day (before first measurement) without the need for additional treatment. In contrast, potential cycling finalized at the negative potential (between -1.75 V and +2.5 V) was reported to be the best option for BDDE regeneration. Such treatment leads to H-terminated surface. However, due to the rapid and easy oxidation of the BDDE surface by atmospheric oxygen, authors assumed that the determination of azoxystrobin was finally performed on the O-terminated surface [20].

Some authors also used subsequent anodic and cathodic treatment before the determination of pesticides. In such a case, the aim of anodic treatment was to clean the BDDE surface, while in the following cathodic treatment, the BDDE surface was changed to H-terminated. Some authors describe this procedure as “cleaning and activation” of the BDD surface [41]. Ribeiro et al. compared the behavior of BDDE after subsequent treatments (first anodic, then cathodic treatment) and BDDE without any treatment [21]. Authors showed that without any treatment, the separation of electrochemical signals of the ferro-/ferricyanide redox couple was almost two times higher than that observed on treated BDDE. Therefore, subsequent BDD treatment was used for the determination of formetanate.

It is important to highlight that neither cathodic nor anodic pretreatment is universally superior; however, both have significant analytical consequences. On one hand, cathodic treatment of BDD surface leads to:

- a hydrophobic surface that can show improved sensitivity towards hydrophobic pesticides;
- reduced fouling, which can be advantageous in the analysis of complex samples; however, this is also advantage of anodic treatment [63]
- enhanced reproducibility caused by formation of well-defined surface with fewer active sites;
- enhanced conductivity and electrochemical activity towards some redox species [64].

On the other hand, anodic treatment of the BDD surface leads to:

- a hydrophilic surface, making it more amenable to interactions with polar or hydrophilic pesticides, but also more susceptible to fouling. However, it can also be a powerful method to remove a fouling layer *in situ* [17];
- lower conductivity, which is considered to be caused by a decrease in sp² impurities [26];
- enhanced electrostatic interactions caused by the presence of charged functional groups, which can promote the electrostatic interactions between the BDD surface and charged pesticides but also charged fouling species.

The choice between cathodic and anodic treatment of BDDEs depends on various factors, such as the analyte's properties, the sample matrix, and the desired analytical outcomes. Therefore, proper

optimization of pretreatment conditions is critical to achieving the best results in pesticide analysis using BDDEs.

2.3. Chemical modification of BDDE surface

In the previous section, we explored the properties of BDDEs subjected to electrochemical pretreatments that induce hydrogenation or oxidation of the BDD surface. While these electrochemical approaches have their merits, various additional modifications have been developed to further expand the utility of BDDEs (Table 3). Chemical modification represents an additional way for enhancing the versatility of BDDEs, particularly for the development of BDD-based biosensors and the study of biological molecules [65–69]. Unlike electrochemical termination, which alters the surface through the application of controlled potential, chemical modification involves molecular alterations. In this section, we describe the chemical modification developed for tailoring BDD surfaces for pesticide determination.

Methods for the chemical modification of BDDEs are similar to those used for other electrode materials, e.g. chemical or physical adsorption, covalent bonding, electrodeposition [65]. Prior to chemical modification, BDD is often subjected to cathodic or anodic treatment to create a suitable surface termination. Particularly, a hydrogen-terminated BDD surface is reported to be convenient for forming amine- or carboxyl-terminations and for straightforward modification with organic molecules [66]. As an example of attachment of organic molecules, one can mention the interaction of H-terminated BDDE with surfactants in the electrolyte [22,23]. While the BDDE itself was not directly modified by surfactant, authors expect that, due to hydrophobic interaction between the H-terminated BDDE and the hydrophobic tail of cetyltrimethylammonium bromide (CTAB), hemimicelles were formed at the BDDE surface during measurement. Finally, the positively charged hydrophilic end of CTAB at the BDDE surface was oriented towards the bulk electrolyte, creating an attractive environment for the adsorption of negatively charged triclosan [22] or dinoterb [23]. This was also confirmed through comparison with sodium dodecylsulfate (SDS), a surfactant oppositely charged compared to CTAB. In that case, the presence of SDS caused a decrease in the electrochemical signals of triclosan [22].

Electrochemical deposition as another modification method can be advantageously employed for the modification of the electrode surface with inorganic materials, such as carbon nanomaterials or metal nanoparticles. For instance, graphene and silver nanoparticles were electrochemically deposited onto the surface of BDDE for pesticide determination [45,46]. Graphene was electrochemically deposited at -1.3 V on the BDDE surface to increase the active surface area. The resulting electrode, BDDGR, was further modified by silver particles using cathodic deposition from an AgNO_3 solution [46]. This synergistic combination of Ag particles, graphene, and BDD allowed for much lower detection limits for carbaryl and paraquat than those achieved with

BDDE or graphene-modified BDDE.

Drop casting is a common method of electrode surface modification that is typically performed manually. It is a simple and rapid method often used for immobilizing modifiers from suspension [70]. Drop casting has also been employed for the modification of BDDE surface for pesticide detection. A suspension of nitrogen-doped porous carbon in water, along with a mixture containing acetylcholinesterase (AChE), was drop casted onto the BDDE surface [47]. The modified BDDE exhibited significantly lower electron transfer resistance than the unmodified BDDE, and the final AChE biosensor was successfully used for the amperometric determination of organophosphate pesticides based on the measurement of AChE inhibition. Additionally, a cathodically treated BDDE was modified with a suspension of multiwalled carbon nanotubes (MWCNT) in Nafion through drop casting [48]. MWCNT-BDDE was further modified with β -Cyclodextrin (β -CD) via cathodic electrodeposition. This electrode combined the advantages of a wide potential window of BDDE, a high surface area of nanomaterials, and the formation of inclusion complexes of β -CD with the analyte, significantly enhancing the sensitivity of adsorption stripping square wave voltammetric (SWV) method for the measurement of trace concentrations of carbendazim.

2.4. sp^3/sp^2 ratio

The sp^3/sp^2 carbon ratio is an important characteristic of BDD that significantly influences its electrochemical properties. This ratio essentially represents the ratio of pure sp^3 diamond to sp^2 carbon impurities, which are known to affect charge transfer kinetics between redox species, the operating potential window, and the background current [14,29].

The sp^2 carbon content can be controlled either during the preparation of BDD or later through electrode treatment, such as chemical treatment or electrochemical polarization [28,62]. A comprehensive study of the electrochemical properties of normally (1%) and low-doped (0.1%) BDD films was conducted by Xu et al. [35]. They controlled the sp^2 content during the preparation of BDD by varying the temperature and hydrogen flow rate. Authors demonstrated that an increased sp^2 carbon content in normally doped BDD enhanced electron transfer kinetics. However, for low-doped BDD films, the electron transfer kinetics decreased with an increase of sp^2 content. Authors attributed the behavior of low-doped BDD to several factors, including a greater abundance of surface oxygen and reduced carrier density. Rehacek et al. reduced the sp^2 content of completed BDD (considered as normally doped, $\sim 10^{19}$ B cm^{-3}) through wet chemical treatment [28]. They observed an enhancement in the electrochemical activity of the ferro-/ferricyanide redox couple after the BDD film treatment, despite an increase in its electrical resistance by 50 Ω . This observation is in contrast with findings in [35]. Authors in ref. [28] mentioned that the wet chemical treatment of BDD (especially strong acid or alkali at high

Table 3
Modification of BDDEs for the determination of pesticides.

Analyte	Modification of BDD	Electrochemical method	Linear concentration range ($\mu\text{mol/L}$)	LOD ($\mu\text{mol/L}$)	Ref.
carbaryl paraquat	Graphene oxide deposited electrochemically at -1.2 V (vs. SCE) for 60 s	DPV	1–6 0.2–1.2	0.07 0.01	[45]
carbaryl paraquat	Graphene oxide deposited electrochemically at -1.2 V (vs. SCE) for 60 s in presence of 0.1 M KClO_4 ; Ag particles deposited electrochemically on BDDGR at -1.2 V (vs. SCE) for 30 s. Electrode stabilized in acetate buffer by 15 CV cycles	DPV	–	1.18×10^{-3} 1.21×10^{-3}	[46]
dichlorvos fenitrothion	Mixture of nitrogen-doped porous carbon and AChE dropped on BDDE and dried	DPV	0.1×10^{-3} –10	1.5×10^{-6} 4.4×10^{-6}	[47]
carbendazim	10 CV scans (-0.4 V to $+1.2$ V) in 0.1 M H_2SO_4 followed by drop casting of MWCNT in ethanol and Nafion and dried; β -CD deposited electrochemically at -0.2 V for 120 s in Britton-Robinson buffer pH 4. Activation of modified electrode: 10 CV scans (-0.4 V to $+1.2$ V)	SWAdSV	0.672–11.2	0.196	[48]

SWAdSV = square-wave adsorption stripping voltammetry.

temperatures) leads to an oxygen-terminated surface. Therefore, in this case, one can expect the effect of several factors on the ferrocyanide electron transfer kinetics, not solely dependent on the sp^3/sp^2 ratio.

Unfortunately, no studies specifically focused on the determination of pesticides in relation to the sp^3/sp^2 ratio can be found. On the other hand, some authors have investigated the effect of sp^3/sp^2 ratio on the electrochemical degradation of pesticides [71,72]. In these studies, BDD with low level of sp^2 impurities is considered a “non-active” anode due to weak interaction with $\bullet OH$ radicals [71]. Such material leads to the complete degradation of pesticides [73]. In contrast, BDD with a high content of sp^2 impurities behaves as an “active anode”. sp^2 sites support the formation of molecular oxygen and thus direct electrochemical conversion/oxidation on the surface, resulting in the formation of various intermediates [59,74,75]. However, based on these studies, we can only estimate the effect of sp^3/sp^2 ratio on the electrochemical determination of pesticides. Several authors have compared BDDEs, as representative of sp^3 -carbon, with other carbon electrode types representing sp^2 -carbon materials concerning pesticide detection [17,18]. These research works can also make some insights into the reactivity and performance of BDD electrodes for pesticide determination.

Fischer et al. compared the electrochemical behavior of terconazole on glassy carbon (GC), pyrolytic graphite (PG) electrodes, and BDD electrodes [18]. Interestingly, the authors observed similar electron transfer kinetics and only small differences in terconazole peak potential at all studied electrodes. However, the comparison of GCE, PGE and carbon paste electrode (CPE) with BDDE for the detection of cresols demonstrated much lower resistance of sp^2 carbon materials to fouling with reaction products compared to what was observed on BDDE [17].

From the available research, some tentative conclusions can be drawn:

- sp^2 carbon materials (such as GCE) can exhibit higher electron transfer than BDDE, and a higher content of sp^2 carbon in BDDE usually results in faster electron transfer reactions. This can potentially be beneficial for the determination of pesticides (e.g increase of sensitivity);
- if BDDE contains a higher sp^3/sp^2 ratio, after certain pretreatment (e.g. electrochemical), the electron transfer properties can be improved, potentially enhancing electrode performance in pesticide determination. This also confirms the interconnected nature of BDD properties;
- sp^2 carbon forms adsorption sites for reaction intermediates. This was also confirmed for BDDs with a lower sp^3/sp^2 ratio. Such a BDD surface is more hydrophilic and susceptible to fouling with organic molecules, which may be a disadvantage in the analysis of pesticides [5,76,77].

2.5. Tuneable BDD properties: Summary of interplay and synergy

The interplay between tuneable properties of BDD electrodes, particularly boron concentration, sp^3/sp^2 ratio and surface termination, is a complex phenomenon that affects the electrochemical behavior and performance of the electrodes. Understanding this interplay and their synergistic effects is crucial for optimizing BDD electrodes for the determination of pesticides and other analytes. Following considerations and summaries are derived from the references reviewed within previous chapters.

- **Boron concentration** within the diamond lattice determines electrical conductivity and band gap. Higher boron concentration increases the conductivity and lowers the band gap, enhancing the electron transfer rate and hydroxyl radical generation. However, excessive boron introduces defects and impurities to the diamond structure, which can degrade the quality and stability of the electrode.
- **The sp^3/sp^2 ratio** affects the surface morphology and the electrocatalytic activity of the electrode. A higher sp^3/sp^2 ratios usually lead

into smoother and more uniform surfaces, reduced background current and the fouling tendency of the electrode. A higher sp^3/sp^2 ratio also means a higher overpotential for oxygen evolution and a higher electrocatalytic activity for hydroxyl radical generation.

- **Surface termination**, achieved through hydrogen or oxygen bonding, influences the surface chemistry and wettability. Hydrogen termination creates a hydrophobic and inert surface, which can increase the potential window and decrease the adsorption of organic molecules on the electrode. Oxygen termination creates a hydrophilic and reactive surface, which can enhance the electron transfer rate and increase the adsorption of polar molecules on the electrode.

The BDD properties affect each other in various ways and can have a synergistic effect on the electrochemical properties of BDD electrode:

- Boron concentration and sp^3/sp^2 ratio are inversely related, but a moderate boron concentration can also increase the sp^3/sp^2 ratio by enhancing diamond film crystallinity and reducing the grain boundaries.
- Boron concentration and surface termination are also inversely related, but a moderate boron concentration can also increase the surface termination by enhancing the surface roughness and porosity of the diamond film.
- sp^3/sp^2 ratio and surface termination are directly related, as increasing the sp^3/sp^2 ratio can increase the surface termination of the BDD electrode.

The effect of this interplay on pesticides detection also depends on the sample characteristics, such as the type, concentration, and matrix of the pesticides, as well as the detection technique, potential, and electrolyte used. However, synergistic effects can be summarized as follows:

- A moderate to high boron concentration, a high sp^3/sp^2 ratio, and optimal surface termination improves the conductivity, stability, reactivity, selectivity, and sensitivity of BDD electrode for various electrochemical applications.
- A high boron concentration, a high sp^3/sp^2 ratio, and hydrogen-terminated surface can extend the potential window and decrease the background current on BDD electrode for direct and sensitive detection of pesticides by voltammetric techniques.
- A moderate to high boron concentration, a high sp^3/sp^2 ratio, and oxygen-terminated surface can synergistically enhance the generation of hydroxyl radicals on BDD electrode for efficient and selective degradation of pesticides by anodic oxidation.

3. Voltammetric potential limits

The potential range available for the determination of an analyte varies across different types of electrodes, and it is crucial to consider this aspect when selecting a sensor for an application. We find it important to emphasize this factor in a separate chapter, as the tuning of the BDDE properties discussed earlier can influence the final potential range where BDD's surface redox processes do not significantly interfere with the electrochemical signals of the pesticides.

In comparison to electrodes made of other materials, BDDEs exhibit a wide potential window in aqueous solutions without water decomposition (3–3.5 V) [27]. This can be attributed to the strong inhibition of interaction between water molecules and the BDDE surface [78]. In non-aqueous solutions, the potential range reported is even larger (5–7.5 V) [27]. This is a significant advantage of BDDEs, particularly in the determination of organic compounds like pesticides, whose oxidation or reduction signals often appear at very positive or negative potentials. The peak potentials of pesticides observed in the reviewed works can be found in Table 1. It is evident that the majority of voltammetric signals used for the quantification of pesticides appear at potentials between 1.0 and 1.7 V, where determining these compounds with other electrode

materials (e.g., gold or various types of carbon) would be very challenging or impossible due to the oxygen evolution. Fig. 1A shows the comparison of potential limits across various types of electrodes.

Several research groups have investigated the effect of tuneable BDD properties on the voltametric potential limits. Schwarzová-Pecková et al. studied the effect of boron concentration on the potential window in different aqueous solutions [16]. They found that the available potential range decreases with an increase in boron concentration, particularly for low-doped diamonds (500–2000 ppm). The potential limit on the anodic side was also found to be less sensitive to boron concentration than on the cathodic side. Authors concluded that in the case of metallic type of BDEs (2000 – 8000 ppm), the evolution of oxygen is more influenced by pH and type of solution than by the boron content (Fig. 1B). For higher doping levels, the authors found the widest potential range and highest anodic potential limits in acidic solutions.

Salazar-Banda et al. also concluded that in low-doped BDD, the hydrogen and oxygen adsorption is more restricted due to the lack of active sites [79]. Similar observations were published by Trouillon et al. [40]. Specifically, for BDD doped with 0.1% and 1% boron, the anodic potential limit in 0.5 M H₂SO₄ was higher than that in phosphate buffer. Additionally, the cathodic potential limit shifted positively with an increase in doping level, indicating easier adsorption of proton needed to initiate the hydrogen evolution.

The content of sp² carbon impurities was also found to be important for the available potential window of BDEs. For normally doped BDD (1% boron) films, an increase in sp² carbon narrowed the potential window, while for low-doped BDD (0.1% boron) films, the potential window was wider with an increase in sp² content [35]. This was explained by the difference in the structure of sp² carbon in normally and low-doped BDD. Authors also observed a more significant effect on

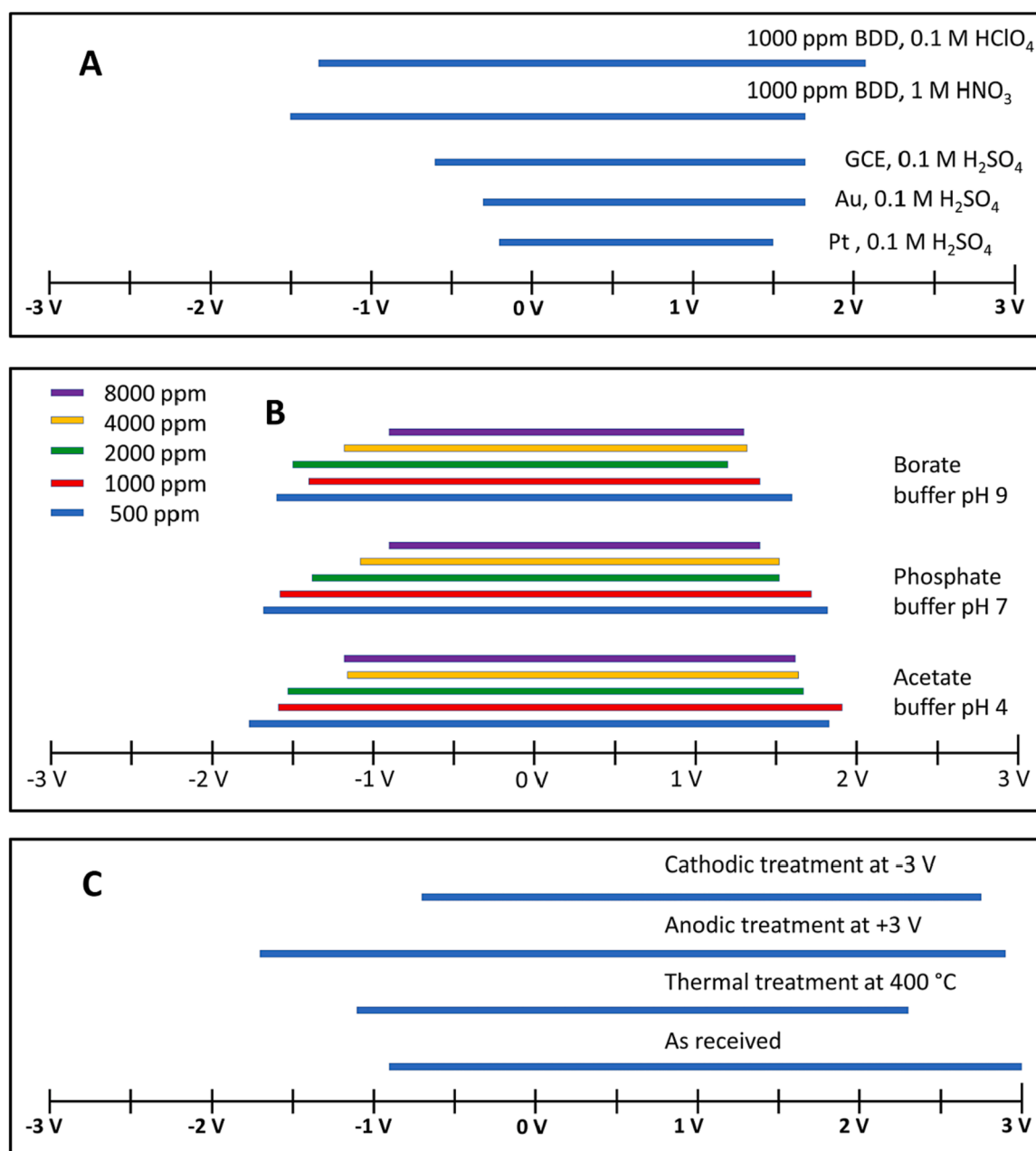


Fig. 1. Voltammetric potential limits: A – comparison at different electrode materials (1000 ppm BDD, 0.1 M HClO₄ according to [14], 1000 ppm BDD, 1 M HNO₃ according to [57], GCE, Pt and Au, 0.1 M H₂SO₄ according to [11]); B – effect of boron concentration and solution pH (according to [14]); C – effect of surface treatment (800 ppm BDD, 0.5 M H₂SO₄, potentials is reported vs. hydrogen electrode “in the same solution”, according to [60]).

the cathodic potential limit, especially in the case of low-doped BDD. The potential window of BDDEs is also influenced by surface treatment. Salazar-Banda et al. compared the voltammograms of differently treated 800 ppm BDDE [61]. The widest potential window was observed for anodically treated BDDE while the narrowest potential window was exhibited by cathodically treated BDD (Fig. 1C). The difference of the cathodic potential limits observed on the studied BDDEs was more remarkable, while the anodic potential limit was very similar for cathodically and anodically treated as well as for as-received BDDE. It was confirmed that cathodic treatment of the BDD causes erosion of the BDD surface (microcracks and microcavities), which is beneficial for hydrogen evolution reactions but also narrows the potential window [79].

4. Conclusions

Pesticides, as common contaminants of the environment, require accurate and sensitive detection methods due to their toxic nature and potential harm to humans, animals and the environment. Electrochemical methods became the effective tools for the pesticide detection, and BDD have garnered attention as promising electrode material due to its unique characteristics. In this review article, we have explored the significant role of BDDE properties in the electrochemical determination of pesticides.

BDDEs possess exceptional characteristics, including high electrical conductivity after boron doping, good chemical stability, biocompatibility, and wide potential window. These characteristics can be altered either during the synthesis of BDD or prior to the application of electrodes and current research indicates the intricate interplay between tuneable properties of BDD, such as boron concentration, sp^3/sp^2 ratio, and surface treatment, and their impact the electrochemical properties and analytical performance of BDDE.

The influence of boron concentration on BDD's electrochemical performance has been relatively extensively investigated. Higher doping levels tend to enhance the electron transfer kinetics, sensitivity, and detection limits, leading to improved analytical performance. However, excessively high boron concentrations can negatively affect the electrode's properties and increase the susceptibility to fouling. Thus, the optimization of boron doping level for specific applications is needed. Electrochemical pretreatment of BDD surfaces, such as anodic and cathodic treatments, has been shown to significantly influence the electroanalytical behavior of pesticides. These treatments, along with potential cycling and surface modification, allow for the tailored tuning of BDD surfaces to enhance their sensitivity, selectivity. Electrochemical treatment can also regenerate the surface of BDDEs and increases the resistance to fouling which is important for the application of BDDEs as the detectors for liquid chromatography. The electrochemical pretreatment also alters the hydrophobicity of the BDDE surface and thus can be targeted to the pesticide of the interest. The sp^3/sp^2 carbon ratio has also been identified as a parameter affecting significantly the BDD's electrochemical properties. A higher sp^2 content generally leads to improved electron transfer kinetics and might potentially enhance the sensitivity for pesticide detection. However, as the effect of the sp^3/sp^2 carbon ratio on the determination of pesticides was not yet investigated we can only make the tentative conclusions on this parameter. Finally, we have emphasized the broad potential window of BDD electrodes, which permits the detection of pesticides at potentials where other electrode materials would face challenges due to oxygen or hydrogen evolution reactions. This characteristic of BDD further enhances its applicability for pesticide analysis. There is evident intricate relationship between mentioned BDDE characteristics, potential limits and electrochemical behavior that requires further investigations to fully comprehend its influence on pesticide determination.

While this review sheds light on the critical role of BDD properties in the pesticide detection, there remain opportunities for future research. There are gaps in the comparative studies of BDD-based sensors,

investigating the interplay between various tuneable properties and their influence on pesticide determination that would provide a deeper understanding of these relationships. Moreover, exploring BDD's application in multianalyte detection systems and addressing the challenges of matrix interferences and fouling would contribute to the development of robust and accurate pesticide sensors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

This study was realized with support of project KEGA 022UCM-4/2023. A. Ferancová thanks to Regional Council of Kainuu (Kainuun Liitto)/ ERDF for the financial support.

References

- [1] S. Ghosh, S.S. Alkafaas, C. Bormman, W. Apollon, A.M. Hussien, A.E. Badawy, M. H. Amer, M.B. Kamel, E.A. Mekawy, H. Bedair, The application of rapid test paper technology for pesticide detection in horticulture crops: a comprehensive review, *Beni-Suef Univ. J. Basic Appl. Sci.* 11 (2022) 73, <https://doi.org/10.1186/s43088-022-00248-6>.
- [2] N. Kalyani, S. Goel, S. Jaiswal, On-site sensing of pesticides using point-of-care biosensors: a review, *Environ. Chem. Lett.* 19 (2021) 345–354, <https://doi.org/10.1007/s10311-020-01070-1>.
- [3] R. Ramachandran, V. Mani, S.M. Chen, G. Gnanakumar, M. Govindasamy, Recent developments in electrode materials and methods for pesticide analysis - an overview, *Int. J. Electrochem. Sci.* 10 (2015) 859–869.
- [4] B.L. Hanssen, S. Siraj, D.K.Y. Wong, Recent strategies to minimise fouling in electrochemical detection systems, *Rev. Anal. Chem.* 35 (2016) 1–28, <https://doi.org/10.1515/revac-2015-0008>.
- [5] J. Berek, How to improve the performance of electrochemical sensors via minimization of electrode passivation, *Chemosensors* 9 (2021) 12, <https://doi.org/10.3390/chemosensors9010012>.
- [6] T. Vrabelj, M. Finšgar, Recent progress in non-enzymatic electroanalytical detection of pesticides based on the use of functional nanomaterials as electrode modifiers, *Biosensors* 12 (2022) 263, <https://doi.org/10.3390/bios12050263>.
- [7] J.H.T. Luong, K.B. Male, J.D. Glennon, Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications, *Analyst* 134 (2009) 1965–1979, <https://doi.org/10.1039/B910206j>.
- [8] C.H. Lee, Y.K. Lim, E.S. Lee, H.J. Lee, H.D. Park, D.S. Lim, Boron-doped diamond nanowire array electrode with high mass transfer rates in flow-by operation, *RSC Adv.* 8 (2018) 11102–11108, <https://doi.org/10.1039/C8RA01005F>.
- [9] P. Joshi, P. Riley, K.Y. Goud, R.K. Mishra, R. Narayan, Recent advances of boron-doped diamond electrochemical sensors toward environmental applications, *Curr. Opin. Electrochem.* 32 (2022), 100920, <https://doi.org/10.1016/j.coelec.2021.100920>.
- [10] S.T. McBeath, D.P. Wilkinson, N.J.D. Graham, Application of boron-doped diamond electrodes for the anodic oxidation of pesticide micropollutants in a water treatment process: a critical review, *Environ. Sci. Water Res. Technol.* 5 (2019) 2090–2107, <https://doi.org/10.1039/c9ew00589g>.
- [11] E.H. Duarte, J. Casarin, E.R. Sartori, C.R.T. Tarley, Highly improved simultaneous herbicides determination in water samples by differential pulse voltammetry using boron-doped diamond electrode and solid phase extraction on cross-linked poly(vinylimidazole), *Sens. Actuata. B: Chem.* 255 (2018) 166–175, <https://doi.org/10.1016/j.snb.2017.08.021>.
- [12] T.F. Mekonnen, L. Byrne, U. Panne, M. Koch, Investigation of chlorpyrifos and its transformation products in fruits and spices by combining electrochemistry and liquid chromatography coupled to tandem mass spectrometry, *Food Anal. Methods* 11 (2018) 2657–2665, <https://doi.org/10.1007/s12161-018-1245-7>.
- [13] Y. Einaga, Development of electrochemical applications of boron-doped diamond electrodes, *Bull. Chem. Soc. Jpn* 91 (2018) 1752–1762, <https://doi.org/10.1246/bcsj.20180268>.
- [14] Y. Einaga, J.S. Foord, G.M. Swain, Diamond electrodes: diversity and maturity, *MRS Bull.* 39 (2014) 525–532, <https://doi.org/10.1557/mrs.2014.94>.
- [15] N. Yang, S. Yu, J.V. Macpherson, Y. Einaga, H. Zhao, G. Zhao, G.M. Swain, X. Jiang, Conductive diamond: synthesis, properties, and electrochemical applications, *Chem. Soc. Rev.* 48 (2019) 157–204, <https://doi.org/10.1039/C7CS00757D>.
- [16] K. Schwarzová-Pecková, J. Vosáhlová, J. Berek, I. Sloufová, E. Pavlova, V. Petrák, J. Závazalová, Influence of boron content on the morphological, spectral, and

- electroanalytical characteristics of anodically oxidized boron-doped diamond electrodes, *Electrochim. Acta* 243 (2017) 170–182, <https://doi.org/10.1016/j.electacta.2017.05.006>.
- [17] J. Vosáhllová, J. Sochr, S. Baluchová, L. Švorc, A. Taylor, K. Schwarzová-Pecková, Comparison of carbon-based electrodes for detection of cresols in voltammetry and HPLC with electrochemical detection, *Electroanalysis* 32 (2020) 2193–2204, <https://doi.org/10.1002/elan.202060103>.
- [18] J. Fischer, J. González-Martín, P. Lochyński, H. Dejmková, K. Schwarzová-Pecková, M. Vega, Voltammetric study of triazole antifungal agent terconazole on sp^3 and sp^2 carbon-based electrode materials, *J. Electroanal. Chem.* 863 (2020), 114054, <https://doi.org/10.1016/j.jelechem.2020.114054>.
- [19] R. Šešlovská, M. Herynková, J. Skopalová, P. Kelšíková-Martinková, L. Janíková, P. Cankar, P. Bednář, J. Chýlková, Oxidation behavior of insecticide azoxystrobin and its voltammetric determination using boron-doped diamond electrode, *Electroanalysis* 31 (2019) 363–373, <https://doi.org/10.1002/elan.201800647>.
- [20] R. Šešlovská, K. Schwarzová-Pecková, R. Sokolová, K. Krejčová, P. Martinková-Kelšíková, The first study of triazole fungicide difenoconazole oxidation and its voltammetric and flow amperometric detection on boron doped diamond electrode, *Electrochim. Acta* 381 (2021), 138260, <https://doi.org/10.1016/j.electacta.2021.138260>.
- [21] F.W.P. Ribeiro, C.P. Sousa, S. Moraes, P. de Lima-Neto, A. Nunes Correia, Sensing of formate pesticide in fruits with a boron-doped diamond electrode, *Microchem. J.* 142 (2018) 24–29, <https://doi.org/10.1016/j.microc.2018.06.012>.
- [22] Y. Yardim, N. Alpar, Z. Şentürk, Voltammetric sensing of triclosan in the presence of cetyltrimethylammonium bromide using a cathodically pretreated boron-doped diamond electrode, *Int. J. Environ. Anal. Chem.* 98 (2018) 1226–1241, <https://doi.org/10.1080/03067319.2018.1537395>.
- [23] P.T. Pinar, S. Allahverdiyeva, Y. Yardim, Z. Şentürk, Voltammetric sensing of dinitrophenolic herbicide dinoterb on cathodically pretreated boron-doped diamond electrode in the presence of cationic surfactant, *Microchem. J.* 155 (2020), 104772, <https://doi.org/10.1016/j.microc.2020.104772>.
- [24] J.V. Macpherson, A practical guide to using boron doped diamond in electrochemical research, *PCCP* 17 (2015) 2935–2949, <https://doi.org/10.1039/C4CP04022H>.
- [25] J.E. Butler, Y.A. Mankelevich, A. Cheesman, J. Ma, M.N.R. Ashfold, Understanding the chemical vapor deposition of diamond: recent progress, *J. Phys. Condens. Matter* 21 (2009), 364201, <https://doi.org/10.1088/0953-8984/21/36/364201>.
- [26] A. Kraft, Doped diamond: a compact review on a new, versatile electrode material, *Int. J. Electrochem. Sci.* 2 (2007) 355–385.
- [27] K. Muzyka, J. Sun, T.H. Fereja, Y. Lan, W. Zhang, G. Xu, Boron-doped diamond: current progress and challenges in view of electroanalytical applications, *Anal. Methods* 11 (2019) 397–414, <https://doi.org/10.1039/C8AY02197J>.
- [28] V. Rehacek, I. Hotovy, M. Marton, M. Mikolasek, P. Michniak, A. Vincze, A. Kromka, M. Vojs, Voltammetric characterization of boron-doped diamond electrodes for electroanalytical applications, *J. Electroanal. Chem.* 862 (2020), 114020, <https://doi.org/10.1016/j.jelechem.2020.114020>.
- [29] O. Sarakhma, L. Švorc, A review on recent advances in the applications of boron-doped diamond electrochemical sensors in food analysis, *Crit. Rev. Anal. Chem.* 52 (2022) 791–813, <https://doi.org/10.1080/10408347.2020.1828028>.
- [30] E.A. Ekimov, V.A. Sidorov, E.D. Bauer, N.N. Mel'nik, N.J. Curro, J.D. Thompson, S.M. Stishov, Superconductivity in diamond, *Nature* 428 (2004) 542–545, <https://doi.org/10.1038/nature02449>.
- [31] J. Xu, Y. Yokota, S. Naoi, K. Nakata, Y. Einaga, Effect of doping level on the electrochemical reduction of CO_2 on boron-doped diamond electrodes, *Diam. Relat. Mater.* 86 (2018) 167–172, <https://doi.org/10.1016/j.diamond.2018.04.028>.
- [32] P.V. Nidheesh, G. Divyapriya, N. Oturan, C. Trellu, M.A. Oturan, Environmental applications of boron-doped diamond electrodes: 1. Applications in water and wastewater treatment, *Chem. Electro. Chem.* 6 (2019) 2124–2142, <https://doi.org/10.1002/celec.201801876>.
- [33] T. Watanabe, Y. Honda, K. Kanda, Y. Einaga, Tailored design of boron-doped diamond electrodes for various electrochemical applications with boron-doping level and sp^2 -bonded carbon impurities, *Phys. Status Solidi A* 211 (2014) 2709–2717, <https://doi.org/10.1002/pssa.201431455>.
- [34] A. Deneuville, C. Baron, S. Ghodbane, C. Agnès, Highly and heavily boron doped diamond films, *Diam. Relat. Mater.* 16 (2007) 915–920, <https://doi.org/10.1016/j.diamond.2006.12.057>.
- [35] J. Xu, Y. Yokota, R.A. Wong, Y. Kim, Y. Einaga Xu, Unusual electrochemical properties of low-doped boron-doped diamond electrodes containing sp^2 carbon, *J. Am. Chem. Soc.* 142 (2020) 2310–2316, <https://doi.org/10.1021/jacs.9b11183>.
- [36] N. Roy, Y. Hirano, H. Kuriyama, P. Sudhagar, N. Suzuki, K. Katsumata, K. Nakata, T. Kondo, M. Yuasa, I. Serizawa, T. Takayama, A. Kudo, A. Fujishima, C. Terashima, Boron-doped diamond semiconductor electrodes: efficient photoelectrochemical CO_2 reduction through surface modification, *Sci. Rep.* 6 (2016) 38010, <https://doi.org/10.1038/srep38010>.
- [37] P. Subramanian, S. Kolagatla, S. Szunerits, Y. Coffinier, W.S. Yeap, K. Haenen, R. Boukherroub, A. Schechter, Atomic force microscopic and raman investigation of boron-doped diamond nanowire electrodes and their activity toward oxygen reduction, *J. Phys. Chem. C* 121 (2017) 3397–3403, <https://doi.org/10.1021/acs.jpcc.6b11546>.
- [38] A.F. Azevedo, M.R. Baldan, N.G. Ferreira, Doping level influence on chemical surface of diamond electrodes, *J. Phys. Chem. Solid* 74 (2013) 599–604, <https://doi.org/10.1016/j.jpcc.2012.12.013>.
- [39] P. Kuang, K. Natsui, C. Feng, Y. Einaga, Electrochemical reduction of nitrate on boron-doped diamond electrodes: effects of surface termination and boron-doping level, *Chemosphere* 251 (2020), 126364, <https://doi.org/10.1016/j.chemosphere.2020.126364>.
- [40] R. Trouillon, D. O'Hare, Y. Einaga, Effect of the doping level on the biological stability of hydrogenated boron doped electrodes, *PCCP* 13 (2011) 5422–5429, <https://doi.org/10.1039/C0CP02420A>.
- [41] D.J.E. Costa, J.C.S. Santos, F.A.C. Sanches-Brandão, W.F. Ribeiro, G.R. Salazar-Banda, M.C.U. Araújo, Boron-doped diamond electrode acting as a voltammetric sensor for the detection of methomyl pesticide, *J. Electroanal. Chem.* 789 (2017) 100–107, <https://doi.org/10.1016/j.jelechem.2017.02.036>.
- [42] T.S. Lima, M.A. La-Scalea, C. Raminelli, F.R. Simões, E. Franco Jr, G. Dias da Silva, M.A. Salvador, P. Homem-de-Mello, H.P.M. de Oliveira, L. Codognoto, Voltammetric determination of chlorothalonil and its respective reduction mechanism studied by density functional theory, *J. Solid State Electrochem.* 23 (2019) 553–563, <https://doi.org/10.1007/s10008-018-4162-1>.
- [43] K. Mielech-Lukasiewicz, B. Starczewska, The use of boron-doped diamond electrode for the determination of selected biocides in water samples, *Water* 11 (2019) 1595, <https://doi.org/10.3390/w11081595>.
- [44] J.L.L. da Silva, V.B. dos Santos, C.A. Neves, J.P.I. de Souza, An ecologically correct electroanalytical method to determine the herbicide Picloram in Amazon waters using a miniaturized boron-doped diamond electrode and a 3D compact electrochemical cell, *Chem. Papers* 75 (2021) 1055–1067, <https://doi.org/10.1007/s11696-020-01357-1>.
- [45] A. Pop, F. Manea, A. Flueraş, J. Schoonman, Simultaneous voltammetric detection of carbaryl and paraquat pesticides on graphene-modified boron-doped diamond electrode, *Sensors* 17 (2017) 2033, <https://doi.org/10.3390/s17092033>.
- [46] A. Pop, S. Lung, C. Orha, F. Manea, Silver/graphene-modified boron doped diamond electrode for selective detection of carbaryl and paraquat from water. *Int. J. Electrochem. Sci.* 13 (2018) 2651–2660, <https://doi.org/10.20964/2018.03.02.2651-2660>.
- [47] M. Wei, S. Feng, Amperometric determination of organophosphate pesticides using acetylcholinesterase based biosensor made from nitrogen-doped porous carbon deposited on a boron-doped diamond electrode, *Microchim. Acta* 184 (2017) 3461–3468, <https://doi.org/10.1007/s00604-017-2380-3>.
- [48] M. Brycht, O. Vajdle, K. Sipa, J. Robak, K. Rudnicki, J. Piechocka, A. Tasić, S. Skrzypek, V. Guzvány, β -Cyclodextrin and multiwalled carbon nanotubes modified boron-doped diamond electrode for voltammetric assay of carbendazim and its corrosion inhibition behavior on stainless steel, *Ionics* 24 (2018) 923–934, <https://doi.org/10.1007/s11581-017-2253-0>.
- [49] K. Morawska, W. Ciesielski, S. Smarzewska, First electroanalytical studies of methoxyfenozide and its interactions with dsDNA, *J. Electroanal. Chem.* 882 (2021), 115030, <https://doi.org/10.1016/j.jelechem.2021.115030>.
- [50] E.D.P. Schwab, S.V. de Almeida, M.L. Felsner, E.G. de Castro, A. Galli, Determination of 2,4,6-trichlorophenol in beverages using voltammetry: optimization and validation studies, *Food Anal. Methods* 13 (2020) 1000–1007, <https://doi.org/10.1007/s12161-020-01716-4>.
- [51] T.M.G. Selva, W.R. de Araujo, R.P. Bacil, T.R.L.C. Paixão, Study of electrochemical oxidation and quantification of the pesticide pirimicarb using a boron-doped diamond electrode, *Electrochim. Acta* 246 (2017) 588–596, <https://doi.org/10.1016/j.electacta.2017.06.051>.
- [52] R.F. França, T. de Souza Lima, F.R. Simões, L. Codognoto, Electroanalytical determination of fenthion in *Passiflora alata* tincture samples, *Orbital: Electron. J. Chem.* 10 (2018) 92–97, <https://doi.org/10.17807/orbital.v10i2.1077>.
- [53] F.W.P. Ribeiro, R.C. de Oliveira, A.G. de Oliveira, R.F. Nascimento, H. Becker, P. de Lima-Neto, A.N. Correia, Electrochemical sensing of thiazendazole in complex samples using boron doped diamond electrode, *J. Electroanal. Chem.* 866 (2020), 114179, <https://doi.org/10.1016/j.jelechem.2020.114179>.
- [54] A. Usenko, J. Chýlková, R. Šešlovská, M. Sedláč, J. Vána, J. Bartáček, T. Mikysek, Voltammetric determination of daminozide and its degradation product N, Ndimethylhydrazine using a boron-doped diamond electrode, *J. Electroanal. Chem.* 904 (2022), 115857, <https://doi.org/10.1016/j.jelechem.2021.115857>.
- [55] S. Djurdjić, V. Vukojević, S. Jevtić, M. V. Pergal, B. B. Petković, D. M. Stanković, Herbicide clomazone detection using electroanalytical approach using boron doped diamond electrode. *Int. J. Electrochem. Sci.*, 13 (2018) 2791–2799. <https://doi.org/10.20964/2018.03.39>.
- [56] D.M. Stanković, Electroanalytical approach for quantification of pesticide maneb, *Electroanalysis* 29 (2017) 352–357, <https://doi.org/10.1002/elan.201600268>.
- [57] S. Jevtić, A. Stefanović, D.M. Stanković, M.V. Pergal, A.T. Ivanović, A. Jokić, B. B. Petković, Boron-doped diamond electrode — a prestigious unmodified carbon electrode for simple and fast determination of bentazone in river water samples, *Diamond Rel. Mater.* 81 (2018) 133–137, <https://doi.org/10.1016/j.diamond.2017.12.009>.
- [58] S. Jevtić, V. Vukojević, S. Djurdjić, M.V. Pergal, D.D. Manojlović, B.B. Petković, D. M. Stanković, First electrochemistry of herbicide pethoxamid and its quantification using electroanalytical approach from mixed commercial product, *Electrochim. Acta* 277 (2018) 136e142, <https://doi.org/10.1016/j.electacta.2018.05.004>.
- [59] V. Vukojević, S. Djurdjić, S., M. V. Pergal, A. Marković, J. Mutić, B. B. Petković, D. M. Stanković, First electrochemical investigation of organophosphorus pesticide azamethiphos and its quantification using electroanalytical approach. *Int. J. Environ. Anal. Chem.* 98 (2018) 1175–1185. doi: 10.1080/03067319.2018.1537394.
- [60] B.C. Lourencao, R.F. Brocenschi, R.A. Medeiros, O. Fatibello-Filho, R.C. Rocha-Filho, Analytical applications of electrochemically pretreated boron-doped diamond electrodes, *Chem. Electro. Chem.* 7 (2020) 1291–1311, <https://doi.org/10.1002/celec.202000050>.
- [61] G.R. Salazar-Banda, L.S. Andrade, P.A.P. Nascente, P.S. Pizani, R.C. Rocha-Filho, L. A. Avaca, On the changing electrochemical behaviour of boron-doped diamond

- surfaces with time after cathodic pre-treatments, *Electrochim. Acta* 51 (2006) 4612–4619, <https://doi.org/10.1016/j.electacta.2005.12.039>.
- [62] I. Duo, C. Levy-Clement, A. Fujishima, C. Comninellis, Electron transfer kinetics on boron-doped diamond Part I: Influence of anodic treatment, *J. Appl. Electrochem.* 34 (2004) 935–943, <https://doi.org/10.1023/B:JACH.0000040525.76264.16>.
- [63] R. Trouillon, Y. Einaga, M.A.M. Gijs, Cathodic pretreatment improves the resistance of boron-doped diamond electrodes to dopamine fouling, *Electrochem. Commun.* 47 (2014) 92–95, <https://doi.org/10.1016/j.elecom.2014.07.028>.
- [64] L. S. Andrade, G. R. Salazar-Banda, R. C. Rocha-Filho, O. Fatibello-Filho, (2011). Cathodic Pretreatment of Boron-Doped Diamond Electrodes and their Use in Electroanalysis. In *Synthetic Diamond Films* (eds. A. Wieckowski, E. Brillas and C. A. Martínez-Huitle). doi: 10.1002/9781118062364.ch8.
- [65] J. Svitková, T. Ignat, L. Švorc, J. Labuda, J. Barek, Chemical modification of boron-doped diamond electrodes for applications to biosensors and biosensing, *Crit. Rev. Anal. Chem.* 46 (2016) 248–256, <https://doi.org/10.1080/10408347.2015.1082125>.
- [66] Y. Yu, Y. Zhou, L. Wu, J. Zhi, Electrochemical biosensor based on boron-doped diamond electrodes with modified surfaces, *Intl. J. Electrochem.* (2012), 567171, <https://doi.org/10.1155/2012/567171>.
- [67] O. Matvieiev, R. Šeššová, L. Janíková, Modification of boron-doped diamond electrode and its applications, *Scientific Papers of the University of Pardubice, Series A* 27 (2021) 73–102. <https://hdl.handle.net/10195/78454>.
- [68] S. Szunerits, R. Boukherroub, Different strategies for functionalization of diamond surfaces, *J. Solid State Electrochem.* 12 (2008) 1205–1218, <https://doi.org/10.1007/s10008-007-0473-3>.
- [69] S. Szunerits, C. Jama, Y. Coffinier, B. Marcus, D. Delabouglise, R. Boukherroub, Direct amination of hydrogen-terminated boron doped diamond surfaces, *Electrochem. Commun.* 8 (2006) 1185–1190, <https://doi.org/10.1016/j.elecom.2006.05.023>.
- [70] A.K.S. Kumar, Y. Zhang, D. Li, R.G. Compton, A mini-review: how reliable is the drop casting technique? *Electrochem. Commun.* 121 (2020), 106867 <https://doi.org/10.1016/j.elecom.2020.106867>.
- [71] F.L. Souza, C. Saéz, M.R.V. Lanza, P. Cañizares, M.A. Rodrigo, The effect of the sp^3/sp^2 carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes, *Electrochim. Acta* 187 (2016) 119–124, <https://doi.org/10.1016/j.electacta.2015.11.031>.
- [72] S. Garcia-Segura, E. Vieira dos Santos, C.A. Martínez-Huitle, Role of sp^3/sp^2 ratio on the electrocatalytic properties of boron-doped diamond electrodes: a mini review, *Electrochem. Commun.* 59 (2015) 52–55, <https://doi.org/10.1016/j.elecom.2015.07.002>.
- [73] E. Brillas, Recent development of electrochemical advanced oxidation of herbicides. A review on its application to wastewater treatment and soil remediation, *J. Clean. Prod.* 290 (2021), 125841, <https://doi.org/10.1016/j.jclepro.2021.125841>.
- [74] D. Medeiros de Araújo, P. Cañizares, C.A. Martínez-Huitle, M.A. Rodrigo, Electrochemical conversion/combustion of a model organic pollutant on BDD anode: role of sp^3/sp^2 ratio, *Electrochem. Commun.* 47 (2014) 37–40, <https://doi.org/10.1016/j.elecom.2014.07.017>.
- [75] L.C. Espinoza, A. Henríquez, D. Contreras, R. Salazar, Evidence for the production of hydroxyl radicals at boron-doped diamond electrodes with different sp^3/sp^2 ratios and its relationship with the anodic oxidation of aniline, *Electrochem. Commun.* 90 (2018) 30–33, <https://doi.org/10.1016/j.elecom.2018.03.007>.
- [76] L.C. Espinoza, M. Aranda, D. Contreras, A. Henríquez, R. Salazar, Effect of the sp^3/sp^2 ratio in boron-doped diamond electrodes on the degradation pathway of aniline by anodic oxidation, *Chem. Electro. Chem.* 6 (2019) 4801–4810, <https://doi.org/10.1002/celec.201901218>.
- [77] Y. He, H. Lin, Z. Guo, W. Zhang, H. Li, W. Huang, Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants, *Sep. Purif. Technol.* 212 (2019) 802–821, <https://doi.org/10.1016/j.seppur.2018.11.056>.
- [78] H.B. Suffredini, S.A.S. Machado, L.A. Avaca, The water decomposition reactions on boron-doped diamond electrode, *J. Braz. Chem. Soc.* 15 (2004) 16–21, <https://doi.org/10.1590/S0103-50532004000100004>.
- [79] G.R. Salazar-Banda, A.E. de Carvalho, L.S. Andrade, R.C. Rocha-Filho, L.A. Avaca, On the activation and physical degradation of boron-doped diamond surfaces brought on by cathodic pretreatments, *J. Appl. Electrochem.* 40 (2010) 1817–1827. <https://www.doi.org/10.1007/s10800-010-0139-1>.