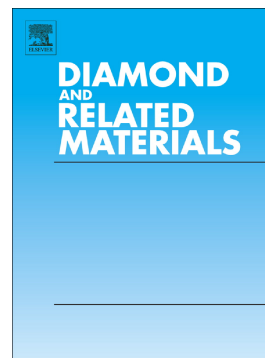# Accepted Manuscript

Boron-doped diamond electrode — A prestigious unmodified carbon electrode for simple and fast determination of bentazone in river water samples

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# Boron-doped diamond electrode – a prestigious unmodified carbon electrode

# for simple and fast determination of bentazone in river water samples

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**Abstract.** Bentazone (BZ) is selective contact-past herbicide with suspected reproductive toxicity potential for human due to possible contamination of ground and surface waters. This work presents simple, rapid, sensitive and accurate determination of bentazone at unmodified boron-doped diamond electrode, using differential pulse voltammetry in Britton-Robinson buffer (pH 4, oxidation peak at 1.0 V). Under optimized DPV conditions linear calibration curve was obtained for range of 2 to 100 μM, with a detection limit of 0.5 μM. The effect of possible interfering agents is negligible, confirming good selectivity of the method. The method was successfully applied to determination of bentazone in spiked river water samples. This electrochemical determination of bentazone represents a favorable alternative to other used time-consuming and expensive analytical techniques and procedures.

## 1. INTRODUCTION

Bentazone, 3-Isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide, is synthetic compound from thiadiazine chemical family. It is selective contact-past herbicide, absorbed through the leaves and it damages plants which are unable to metabolize this compound [1]. EPA has classified this chemical as a "Group E" as it is found to be non-carcinogenic to animals [2], but it is important to note that there are no studies about toxicity of bentazone on humans. It is confirmed that ingestion of bentazon cause fevers, kidney failure, tachycardia, dyspnea and hyperthermia [3]. Bentazone is quickly metabolized and degraded by pesticide resistant plants and by animals, and its metabolites, 6-hydroxybentazone and 8-hydroxybentazone, are not as toxic as parent compound [4]. Bearing in mind high water solubility and low soil adsorption characteristics, the major problem may arise in leaching of this chemical under conditions of extreme rainfall [4-6]. Once, out of the plants range, in soil, the possibility of bentazone degradation is considerable and it easily could contaminate groundwaters and impact on surface river waters. It was reported that bentazone was one of the most frequently detected pollutants in ground and surface European waters [7, 8].

Since Bentazon is widely applied herbicide, monitoring and determination of bentazone in ground and surface waters and in cultivated areas where it is used is of high significance. GC and LC methods [9], HPLC [10, 11] and combined and tandem techniques such as LC-MS/MS [12] and LC-ESI-MS/MS [13] were used for the determination of bentazone. All these determinations were time consuming and required expensive chemicals, equipment and sample preparation. Electrochemical techniques exhibit advantage over the aforementioned techniques in low-cost apparatus, fast and simple determination especially when it is performed at unmodified electrodes. Prior sample preparation often is not necessary for good selectivity of the method.

The idea of this work was to determine bentazone at unmodified boron-doped diamond electrode, as a relatively new electrode material with favorable characteristics. Nowadays, boron doped diamond electrode is widely investigated unmodified ("green") electrochemical sensor, exhibiting numerous advantages such as negligible adsorption phenomenon, very low background current and one of the widest linear ranges, requires no additional reagent costs and manipulation steps to increase determination characteristics of some different groups of compounds [14-19]. BDDE is quite resistant to surface contamination and poisoning which was a limiting factor for previous determination of this compound on bare glassy carbon electrode [20]. In order to solve this problem, a few researchers reported bentazone determinations or interaction studies at modified GC or CPE electrodes with polymeric film of a manganese phthalocyanine complex, multiwalled carbon nanotubes with β-cyclodextrin incorporated in a polyaniline film and polypirrole or polyaniline conducting polymers [21-23].

The goal of this work is to develop novel electroanalytical method for detection of bentazone using unmodified and green electrochemical sensor and to present its simple, fast, accurate and sensitive determination at BDDE. Experimental conditions accompanied with effect of possible interfering compounds were investigated and optimized in order to achieve best analytical characteristics. After procedure developing, proposed approach was successfully applied for estimation of bentazone content in the surface water samples.

## 2. MATERIAL AND METHODS

### 2.1 Reagents

Bentazone was used as received from Sigma-Aldrich. The stock solution (1 mM) was prepared in freshly distillated methanol. All electrochemical studies of bentazone were done in Britton-Robinson (BR) buffer solutions [16]. Ultra pure water (18 MΩ cm) obtained from Millipore Simplicity 185 and analytical reagent grade chemicals were used throughout the experiments.

### 2.2 Apparatus and electrochemical measurements

All electrochemical measurements (cyclic, differential pulse and square wave voltammetry) were performed on PalmSens 3 potentiostat/galvanostat/impedance analyzer with PSTrace software (PalmSens BV, Netherlands). Three-electrode system in the electrochemical cell was consisted from Ag/AgCl (1M KCl) reference electrode and platinum wire counter electrode (CH Instruments, USA) while working electrode was boron-doped diamond electrode (Windsor Scientific Ltd, Slough, Berkshire, United Kingdom) embedded in a polyether ether ketone (PEEK) body with an inner diameter of 3 mm, a resistivity of 0.075 Ω cm and a boron doping level of 1000 ppm (as declared by the supplier). At the beginning of the working day, BDD electrode was anodically pretreated (+2 V) in 0.5 M sulfuric acid followed by cathodically pretreatment (-2 V), in order to get rid of impurities and renew hydrogen terminated surface, respectively. Both processes were done for 180 s. Before every measurement, the electrode was slightly polished with piece of cotton.

The pH measurements were done on Hanna Instruments pH meter with combined glass electrode. All experiments were done at room temperature.

*2.3 Preparation of river water samples*

Water samples were collected from Serbian rivers Ibar (Kosovska Mitrovica) and Timok (near Bor) in brown glass bottles and stored in fridge at 5 $^0$C. The river water samples were used for electrochemical measurements, almost without any prior preparation. The samples were filtered through syringe filter to remove suspended particles and spiked with a certain amount of standard bentazone solution in optimal BR buffer (pH 4). After homogenation, 1 mL of river water sample was added to 9 mL of BR buffer pH 4 and determination of bentazone was carried out by differential pulse voltammetry. The concentration of this compound was calculated from calibration curve.

## 3. RESULTS AND DISCUSSION

*3.1. Electrochemical behavior of bentazone at BDDE and influence of pH*

In order to get insight in redox process of bentazone at BDDE, the cyclic voltammogram (CV) of 100 μM of bentazone at pH 4 was recorded in wide potential range of -1.5 to 2 V (Fig.1). As can be seen, the CV obtains only one well defined irreversible oxidation wave in area of 1-1.2 V. The similar electrochemical behavior was observed by other authors using unmodified glassy carbon electrode [20, 23], while modification of GCE with PANI-β-CD/MWCNT film produces one more anodic wave at on higher potential, originated from adsorbed form of bentazone [23]. It is obvious that CV voltammogram in presence of 0.1 mM of bentazone at BDDE (compared with corresponding voltammograms obtained for baseline in

absence of bentazone) is characterized with current density increase at potential above 1.5 V due to easier supporting electrolyte oxidation. The effect of pH on electrochemical oxidation of bentazone at BDDE was examined and CVs of tested compound in BR buffers pH ranged from 2-9 were depicted in Fig 2. There was no linear dependence observed between changes in pH of the supporting electrolyte and obtained oxidation potentials for bentazone. By increasing the pH in presence of bentazone, the "raising" of baseline appeared at the lower potential values and became the limiting factor for determination of this compound at pH above pH 7. Hence, high and well-defined peak on pH 4 was chosen for further examinations.
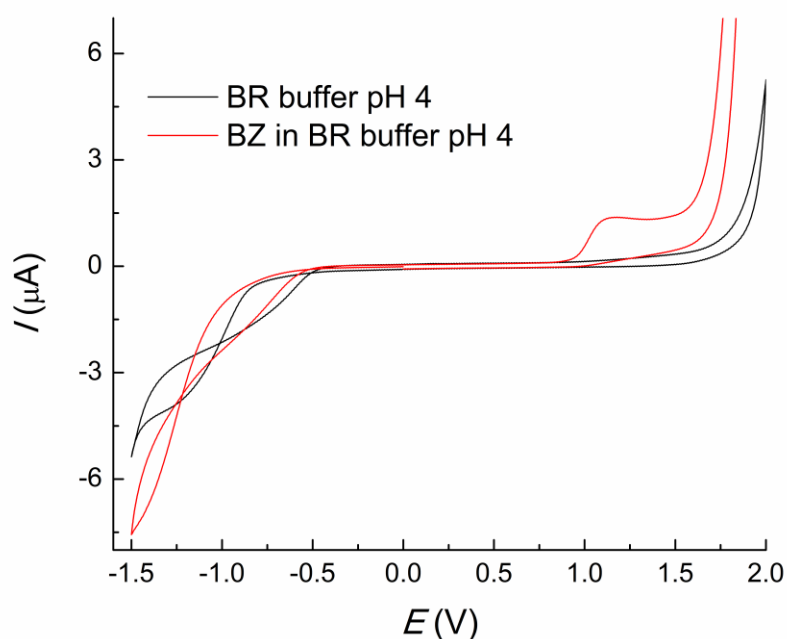


**Figure 1.** Cyclic voltammogram of 100 μM of bentazone at BDDE in BR buffer solution pH 4 (with baseline for comparison); scan rate of 50 mV/s
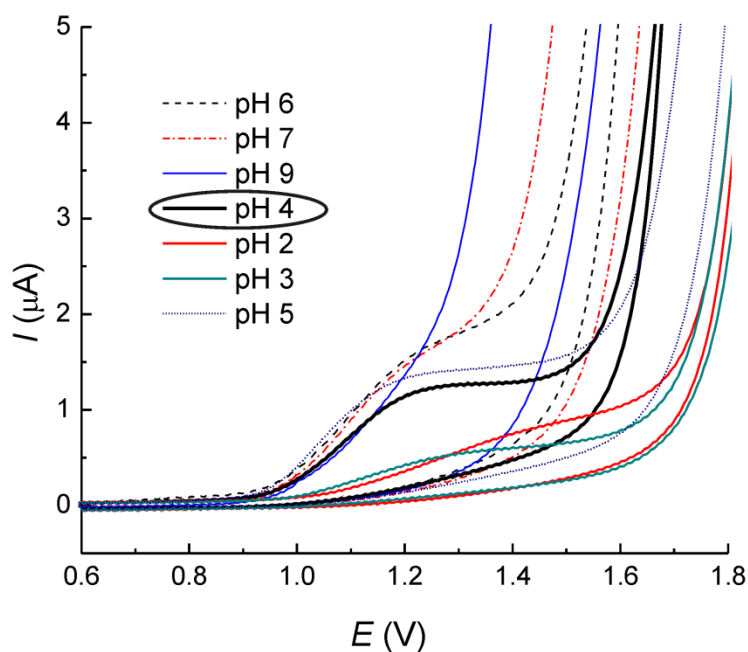
**Figure 2.** Cyclic voltammograms of 100 µM of bentazone at BDDE in BR buffer solution with different pH values; scan rate of 50 mV/s

Based on this study, it can be suggested that oxidation process of bentazone at BDDE proceeds on nitrogen on tertiary amine (Sch. 1) and the suggested mechanism corresponds to one-electron transfer followed by slow chemical step, probably dimerization of oxidation product These conclusions are in accordance with previously reported data [20, 22, 23].

It is well known that the electrochemical bonding to boron-doped diamond works on H-terminated and oxidized surfaces. Cathodic pretreatment of BDDE at a negative potential in an acidic environment leads to H-terminated and successfully regenerated the electrode surface [17]. This positively charged surface promotes one electron transfer and oxidation of bentazone

and allowed repeatable reactions over extended periods of time. Adsorption of the bentazone anions (which are predominant at pH 4 [23]) on BDDE surface is more difficult in comparison to glassy carbon electrode due to well known adsorption resistivity because of lack of adsorption sites. On that way, BDDE represent convenient carbon material for determination of BZ, and it is confirmed by further analytical experiments.
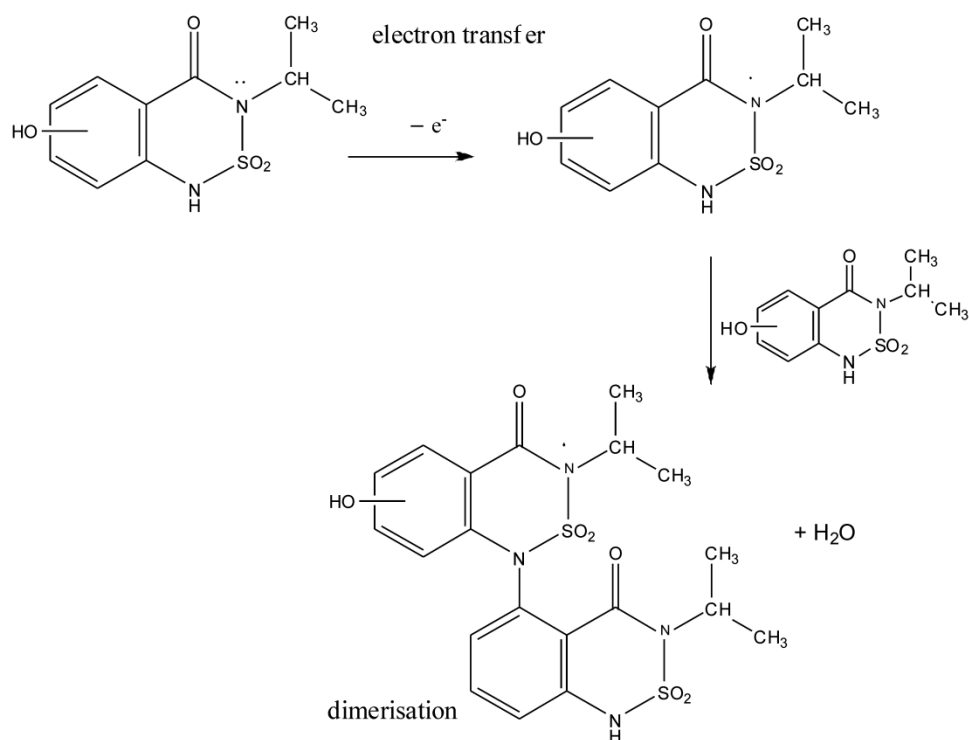


**Scheme 1.** The suggested mechanism of oxidation of bentazone

*3.2 The effect of scan rate on electrochemical behavior of bentazone*

Rate determining step of the oxidation reaction of 100 μM bentazone in BR buffer at pH 4 using BDDE was studied by recording CVs at different scan rates. It is evident that peak

current of BZ linearly increases with increase of the square root of the scan rate (Fig.3), while regression line of log I *vs* log v exhibited slope of 0.56 (not depicted graph), a very close value to theoretically expected slope of 0.5 for purely diffusion controlled process [24]. Hence, mass transport in diffusion layer during the oxidation reaction of bentazone (rate determining step) was primarily determined by diffusion and adsorption or other interaction reactions at surface of BDDE were negligible. The equations which described the linear dependences were:

$$I\,(\mu A) = -0.24 + 0.26 \times v^{1/2}\,(mV/s)^{1/2} \quad (R = 0.994) \tag{1}$$

$$\log I\,(\mu A) = -0.75 + 0.56 \times \log v\,(mV/s) \quad (R = 0.995) \tag{2}$$

It was also observed that peak currents were slightly shifted to more positive potential values with increasing of the scan rate, which supports the assumption about irreversibility of the process.
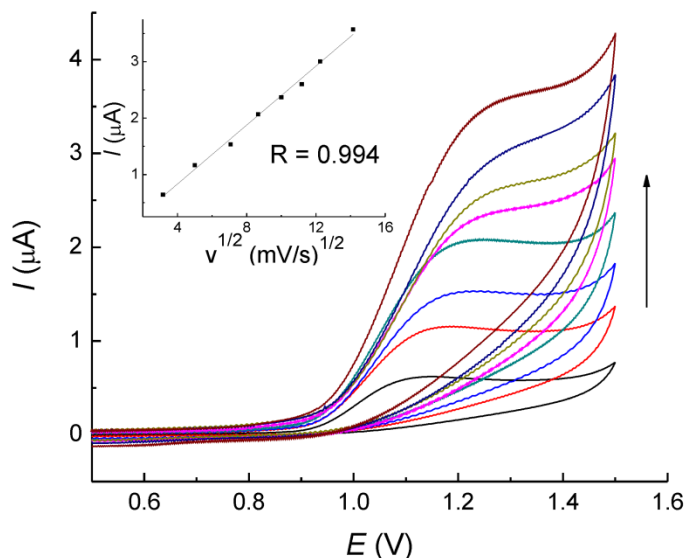
**Figure 3.** Cyclic voltammograms of $1 \times 10^{-4}$ M BZ at BDDE in BR buffer solution at pH 4, at various scan rates (10, 25, 50, 75, 100, 125, 150, 200 mV/s); inset figure: present dependence of the peak current *vs* $v^{1/2}$

*3.3 Development of the electroanalytical method*

DPV and SWV are the most frequently used electrochemical techniques in electroanalysis of biologically active compounds and environmentally important molecules [25]. Due to that, both techniques were tested and compared toward detection of BZ. Before techniques comparison important parameters for both methods were optimized. All these experiments were done in BR buffers at pH 4 containing 100 μM of BZ using BDD electrode.

Each of examined experimental parameters was varied in turn systematically while others were kept constant. The studied DPV parameters were: pulse amplitude from 10 to 200 mV and pulse time in the range of 5 to 75 ms (Fig. S1). The peak current rises with increasing of pulse amplitude, while different shape and height of peak current is obtained at a certain pulse time value. The optimized values for DPV, based on best shaped or highest peak, were pulse amplitude of 150 mV and pulse time of 10 ms. For SWV technique, the square wave frequency was varied from 10-50 Hz while pulse amplitude was changed from 20 to 70 mV and potential step (scan increment) was changed in the range 2-5 mV (data in supplementary material, Fig S2). It was found that best analytical response with this method was obtained at the frequency of 30 HZ, pulse amplitude of 50 mV and potential step of 5 mV, taking into account oxidation peak current and peak shape.

Analytical curves were constructed by using both of investigated techniques and validation parameters of determinations were summarized in Table 1. Both techniques present similar results. The SWV is faster technique but, in this case, the slight advantage may be given to DPV due to wider linear range, better correlation coefficient, and especially limit of detection and repeatability. The repeatabilities of the proposed methods were evaluated by three replicate DPV/SWV measurements under optimal operating conditions. The limit of detection (LOD) was calculated from corresponding calibration curves, obtained for bentazone quantification using both techniques, using the equation LOD=$3\sigma_{intercept}$/slope, where $3\sigma_{intercept}$ is 3 times standard deviation of intercept divided by slope.

**Table 1.** Validation parameters of bentazone determination by SW and DPV technique at BDDE in BR solution at pH 4

| Validation parameters | SWV | DPV |
|---|---|---|
| Peak potential (V) | 1.04 | 1.07 |
| Linear range (μM) | 3-90 | 2-100 |
| Correlation coefficient, R | 0.993 | 0.998 |
| Intercept μA | 0.58 | 0.48 |
| Slope μA/ μM | 0.034 | 0.037 |
| Limit of detection-LOD (μM) | 1.2 | 0.5 |
| Peak current repeatability (RSD %) | 3.32 | 1.67 |

DPV voltammograms and corresponding calibration curve for bentazone determination, under above described optimized experimental conditions, are presented in Fig. 4. As can be

noticed from these measurements, in the presence of lower amount of BZ, the second oxidation

peak of BZ appears at higher potential value. Similar behavior was also reported earlier [23] and

this phenomenon is attributed to the oxidation of strongly absorbed form of bentazone. SWV

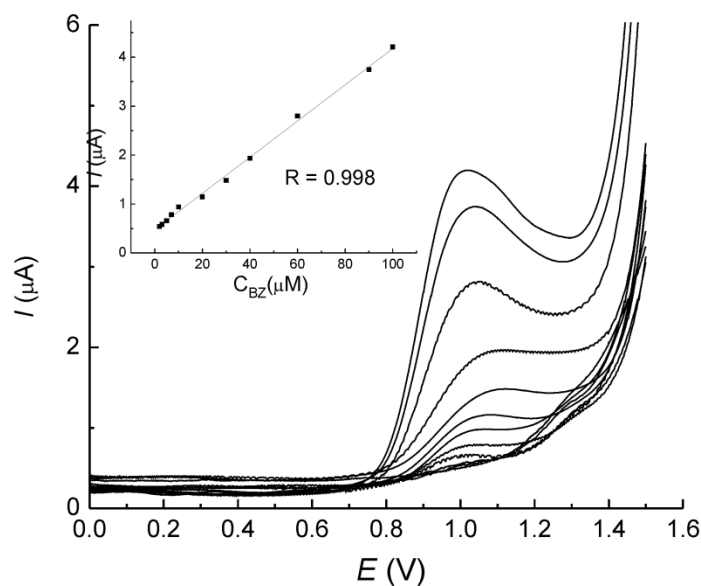voltamograms and corresponding calibration curve are presented in Fig. S3 (supplementary

material).



**Figure 4.** DP voltammograms of various concentrations (0, 1, 2, 3, 5, 7, 10, 20, 30, 40, 60, 90, 100 μM) of bentazone, in BR buffer at pH 4 at BDDE, under optimized experimental conditions; Corresponding calibration curve is in inset.

Contrary to reported determination of BZ on bare GCE, preparing the BDDE for each

measurement does not require the time-consuming electrochemical treatment after the usual

mechanical renewing of electrode surface or addition of some compound in order to prevent high

BZ adsorption at GC, e.g. surfactant triton [20]. Reproductive and accurate results were obtained by proposed simple and fast analytical procedure at unmodified BDDE and sensitivity of determination was improved (linear working range of 2-100 μM, LOD of 0.5 μM) comparing to reported methods on bare GCE (LOD was $10^{-5}$ M of BZ) [20] and even expensive and difficult to prepare PANI-β-CD/fMWCNT/GC modified electrode (the range of 10–80 μM, with a LOD of 1.6 μM) [23].

### 3.4 Interference study

In order to investigate selectivity of the developed method, different ions were added to 10 μM of bentazine in BR solution pH 4 and DPV measurements at BDDE were performed under optimized experimental conditions. The most of metal ions ($K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$) and anions ($NO_3^-$, $SO_4^{2-}$, $CO_3^{2-}$, $CH_3COO^-$) present in the 200-fold excess concentration produced change of signal of ±1.5-4.5%. If the signal change equal or higher than ±5 % is considered as a significant interference, then it could be concluded that studied ions negligible interfere in the determination of bentazone using proposed procedure.

Effects of presence of two common used herbicides, sulcotrione (SU) and mesotrione (MZ), (individually and synergetic) on electrochemical signal in mixed solutions where concentration of BZ was 7 μM, are shown in Fig. 5. Bentazone oxidation current without presence of these compounds were used as 100 % in calculations. Obviously, there is no significant change in peak current in 3-fold added concentration of SU or MZ, as well as in solution with mixed equal concentrations of all three herbicides. On the other hand, the significant interferences were noticed in a ratio 1:5 in BZ/SU and BZ/MS (not presented)

individually, and in mixed solutions in ratios 1:3:3 and 1:5:5 BZ/SU/MS solutions. Bearing in mind that recommended dose for sucotrione is less than 450 g/ha [23] and mesotrione is less than 200 g/ha [27] while for bentazone is much higher 1.0-2.2 kg/ha [28], in the case of contamination with all these herbicides, it is realistic to expect that bentazone can be found in much greater concentrations in real samples where the presence of the other herbicides will not interfere with BZ determination.
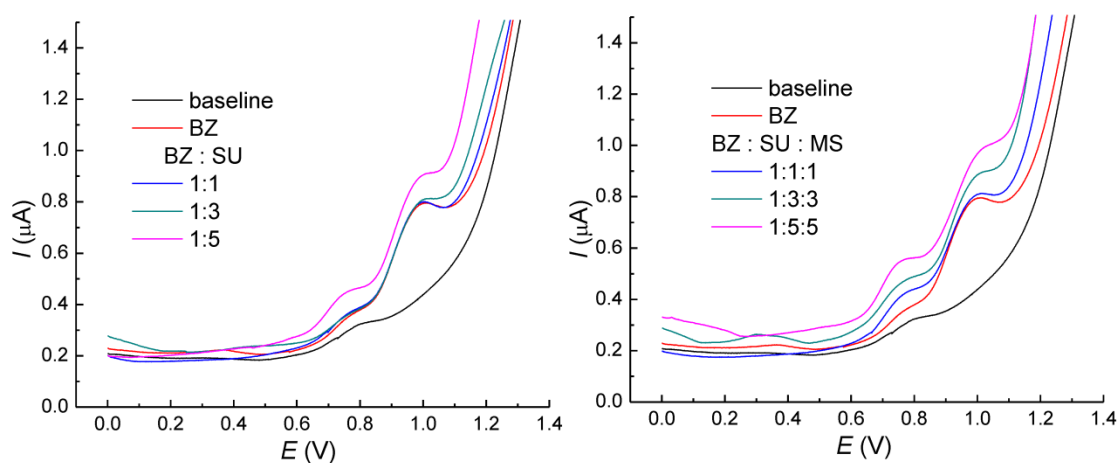


**Figure 5.** The influence of different concentration of sulcotrione and mesotrione on DPVcurrent obtained for BZ determination under optimized experimental conditions

*3.5 Applicability of the method in river water samples*

The proposed DPV method was employed for determination of bentazone in spiked river water samples. Rivers Timok (RW1) and Ibar (RW2) were chosen for collection of water samples due to the proximity of industrial plants and mines. Hence, the collected river water samples were possibly polluted with organic compounds and traces of heavy metals and

represent a good test for the applicability of the proposed method for bentazone determination. As can be seen (Fig. S4 and Table 2), the determinations of low concentration were the most affected by the matrix is polluted rivers, (recoveries of 108.3 and 106.7). Nevertheless, the results indicated the low effect of the tested solution matrix. Hence, from these measurements and recovery values, it can be concluded that proposed method is suitable for determination of this herbicide in river water samples.

**Table 2.** Determination of bentazone in river water samples

| Samles | Spiked (μM) | Determined* (μM) | Recovery (%) |
|--------|-------------|------------------|--------------|
|        | 3.00        | 3.25             | 108.3        |
| RW1    | 9.00        | 8.81             | 97.9         |
|        | 24.00       | 22.5             | 93.75        |
|        | 3.00        | 3.20             | 106.7        |
| RW2    | 9.00        | 9.11             | 101.2        |
|        | 24.00       | 24.22            | 100.9        |

*Average of three replicate measurements

**CONCLUSION**

This work reports the electrochemical behavior of bentazone at unmodified boron-doped diamond electrode and development of differential pulse voltammetric method for bentazone

determination, successfully applied in river water samples. Proposed method has advantage over reported unmodified and some modified electrodes in terms of sensitive, rapid, repeatable, simple and non-expensive determination, with no electrochemical pretreatment and adsorption preventing additives. Also, there is no complicated preparation of electrode modifiers or time-consuming sample preparation. Hence, the boron-doped electrode proves to be a prestigious carbon material for electrochemical determination of bentazone.

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**Figure and scheme captions:**

**Scheme 1.** The suggested mechanism of oxidation of bentazone

**Figure 1.** Cyclic voltammogram of 100 μM of bentazone at BDDE in BR buffer solution pH 4 (with baseline for comparison); scan rate of 50 mV/s

**Figure 2.** CV profiles of 100 μM of bentazone at BDDE in BR buffer solution with different pH values; scan rate of 50 mV/s

**Figure 3.** Cyclic voltammetric profiles of $1\times10^{-4}$ M BZ at BDDE in BR buffer solution at pH 4, at various scan rates (10, 25, 50, 75, 100, 125, 150, 200 mV/s); inset figure: present dependence of the peak current *vs* $v^{1/2}$

**Figure 4.** DPV profiles of various concentrations (0, 1, 2, 3, 5, 7, 10, 20, 30, 40, 60, 90, 100 μM) of bentazone, in BR buffer at pH 4 at BDDE, under optimized experimental conditions; Insert figure present corresponding calibration curve.

**Figure 5.** The influence of different concentration of sulcotrione and mesotrione on current obtained for BZ determination under optimized experimental conditions
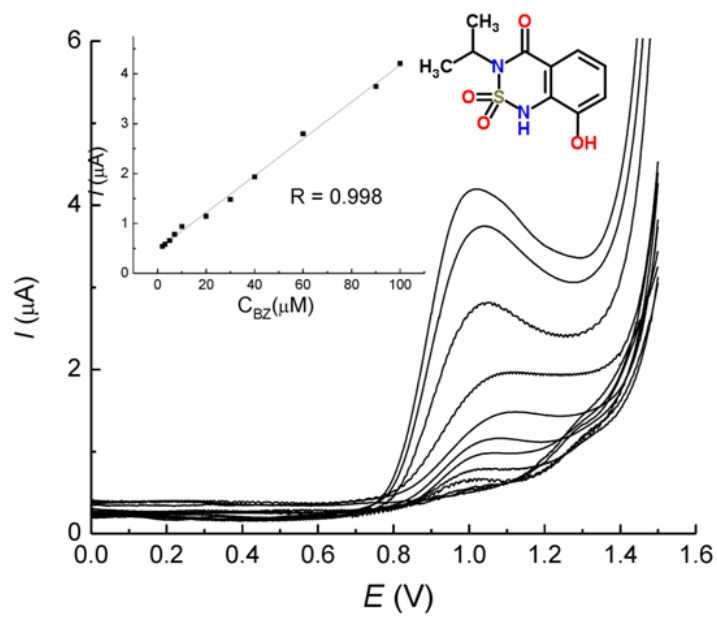
Graphical abstract

**Highlights:**

- Boron-doped diamond electrode was used for sensitive determination of bentazone

- Simple and fast analytical procedure with no electrochemical pretreatment and modification

- Lower detection limit compared to unmodified and some modified electrodes

- Applicable for the determination of this herbicide in surface water samples