

## آنالیز الکتروشیمیایی بنتازون باقیمانده در عصاره گیاه مریم گلی با استفاده از الکترواد اصلاح شده با $ZnFe_2O_4$ نشسته بروی نانوذرات گرافن

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تاریخ دریافت: ۲۴ مرداد ۱۳۹۷ تاریخ پذیرش: ۲۸ شهریور ۱۳۹۷

## Electroanalysis of Bentazon Residues in *Salvia Officinalis* Extract Essential Oils Using $ZnFe_2O_4$ Anchored on Reduced Graphene Oxide Nanoparticles Modified Electrode

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Received: 15 August 2018

Accepted: 19 September 2018

DOI: 10.30473/ijac.2018.37828.1122

### چکیده

اسانس گیاه مریم گلی که در معرض علف کش بنتازون قرار گرفته بود، استخراج شد و محتوای علف کش آن با استفاده از روش الکتروشیمیایی آنالیز شد. بدین منظور، الکترواد خمیر کربن با استفاده از نانوکامپوزیت روی-فریت/گرافن که از روش حلال گرمایی سنتز شده است، اصلاح شد. مشخصه‌یابی و مورفولوژی نانوذرات با استفاده از روش‌های XRD، FT-IR و FE-SEM انجام شد. تحت شرایط بهینه آزمایشی، الکترواد اصلاح شده یک سیگنال قوی برای اکسیداسیون بنتازون در پتانسیل +۰/۹۵ ولت نسبت به الکترواد مرجع Ag/AgCl ایجاد کرد. جریان آندی بنتازون به صورت خطی با غلظت این علف کش در محدوده ۰/۱ تا ۲۰ میکرومولار (حد تشخیص ۰/۰۷ میکرومولار) ارتباط داشت. کاربرد عملی الکترواد اصلاح شده با استفاده از آنالیز الکتروشیمیایی بنتازون باقی مانده در اسانس استخراج شده‌ای که گیاه آن در معرض سه دوز مختلف علف کش قرار گرفته بود، ارزیابی شد و نتایج معقولی بدست آمد.

### واژه‌های کلیدی

باقیمانده بنتازون؛ آنالیز الکتروشیمیایی؛  $ZnFe_2O_4$ /گرافن/اکسید احیاء شده؛ الکترواد خمیر کربن؛ نمونه‌های عصاره گیاه.

### Abstract

Essential oil of bentazon- treated plants were extracted and herbicide content analyzed by electrochemical method. For this propose, carbon paste electrode was modified using  $ZnFe_2O_4$  anchored on reduced graphene oxide which synthesized by solvothermal approach. The nature and morphology of nanoparticles were characterized using XRD, FT-IR and FE-SEM image. Under optimal experimental condition, modified electrode produces powerful oxidation signal for bentazon at +0.95 V (vs. Ag/AgCl). The anodic current was increased linearly with bentazon concentration in the range of 0.1 - 20.0  $\mu\text{mol L}^{-1}$  with a detection limit of 0.07  $\mu\text{mol L}^{-1}$ . The practical usage of modified electrode was evaluated by electro analysis of extracted bentazon residues at three applied doses which revealed reasonable results.

### Keywords

Bentazon Residues; Electroanalysis;  $ZnFe_2O_4$ / Reduced Graphene Oxide; Carbon Paste Electrode; Essential Oil Samples.

### 1. INTRODUCTION

Bentazon is a selective herbicide used to control broadleaf weeds cause increase the crop yield [1]. It used as post-emergence herbicide [2] of some medicinal plants. Among the medicinal plants, *Salvia* is one of the most important types which is

native to Europe and parts of Asia. Weed control of herbal medicine is important for its production. However, bentazon residual in extracts of medicinal herbs could have adverse effects on human health. Recently, analytical methods such

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as HPLC and GC have been upgraded for tracing of bentazon residue at low levels in complex environmental matrices [3-5]. The great benefit of separation method is ability to minimize interferences. Since bentazon exhibit poor UV absorbance and low volatility [6], this detection method suffers adequate sensitivity and requires time for sample preparation steps. Electroanalytical methods offer advantages such as ease of use, speed, economical and good accuracy. The electro active amino group in bentazon structure makes it potent oxidizable species. During the oxidation of bentazon the products were adsorbed at the electrode surface and causes acute poisoning of electrode surface [7]. Carbon paste electrodes (CPE) with possibility to renew of electrode surface can be the good candidate in solving electrode poisoning problems. In particular, they offer favorable signal-to-noise characteristics and diversity in the way of surface modification. Nano materials have begun to integrate to electrochemical sensors because of their ability to enhancement of electrochemical signals.  $ZnFe_2O_4$  nanoparticles (NPs), a spinel-like structure mixed transition-metal oxides, are receiving growing attention in nanotechnology [8-9]. The addition of Zn to the pure hematite and formation of  $ZnFe_2O_4$  improve the magnetic and conductive properties of spinel [10]. As an allotrope of carbon, graphene is a sheet of carbon atoms with just one atom thick. The graphene sheet contains  $-OH$  and  $-COOH$  groups which enable graphene to be ideal support for interaction with metal and metal oxide nanoparticles [11-12]. The aim of this work is to develop a sensitive electrochemical method for bentazon determination which can use in the routine monitoring of herbal essential oil matrix. We fabricated  $ZnFe_2O_4$  NPs anchored on reduced graphene oxide modified paste electrode which generate powerful oxidation signal to bentazon and able to determine tolerance of this herbicide in *Salvia* essential oil. The information about bentazon resistance also helps to efficient weed control of this herbicide from agricultural fields. To our knowledge there is no report on determination of herbicide residual in essential oil of medicinal plants.

## 2. EXPERIMENTAL

The Autolab PGSTAT101 with NOVA software (Ecochemie, Utrecht, The Netherlands), and the three-electrode system consist of an Ag/AgCl reference electrode, a Pt counter electrode and the  $ZnFe_2O_4$  / reduced graphene oxide /CPE as the working electrode were used for electrochemical analysis. pH meter (Model 744, Metrohm, Switzerland) was used for pH measurement. The

structural and morphological studies were investigated by XRD (Holland Philips Xpert, X-ray diffractometer with Cu-K $\alpha$  radiation) and FE-SEM (Hitachi S-4160, Japan). FT-IR analysis was recorded using a JASCO FT-IR 680 plus spectrometer. An ultrasonic water bath (Elma, E30H) was used to disperse the nanoparticles in solution. Liquid bentazon 480 SL was prepared from Shanghai (China). Other analytical reagents were purchased from Merck (Darmstadt, Germany). Phosphate buffer solutions (0.10 mol L $^{-1}$ ) with various pH (3 to 8) values were prepared. Pure graphite powder (particle size <50  $\mu$ m, Merck Millipore) and paraffin (d = 0.88 kg L $^{-1}$ , Merck) were used for the preparation of paste electrodes. Deionized water was used to prepare all the solutions.

### 2. 1. Synthesis of $ZnFe_2O_4$ NPs/ reduced graphene oxide

Graphene oxide (GO) was synthesized according to modified Hummers method [13].  $ZnFe_2O_4$  NPs/ reduced graphene oxide was synthesized by solvothermal method [14]. The solution of 1 mg mL $^{-1}$  of GO in ethylene glycol was prepared and ultrasonicated for 1 h. Then, the solution containing 0.002 mol FeCl $_3 \cdot 6H_2O$  and 0.001 mol of ZnCl $_2$  in 10 mL of ethylene glycol was made and mixed to former solution. The resulting solution was stirring for 2 h and then 0.6 g urea was introduced into mixture and stirring again for 30 min. The final mixture was transferred to Teflon container steel autoclave and heated to 200  $^{\circ}$ C for 12 h. After filtering, the product was washed with DI water / ethanol (1:1, v/v) and dried in oven at 50  $^{\circ}$ C for 12 h. Preparation of carbon paste modified electrode was according to previous reported procedure [15]. The contents of modified electrode were 30 mg of nanocomposite, 500 mg of graphite powder and 0.3 mL paraffin oil.

### 2. 2. Plant material and growth condition

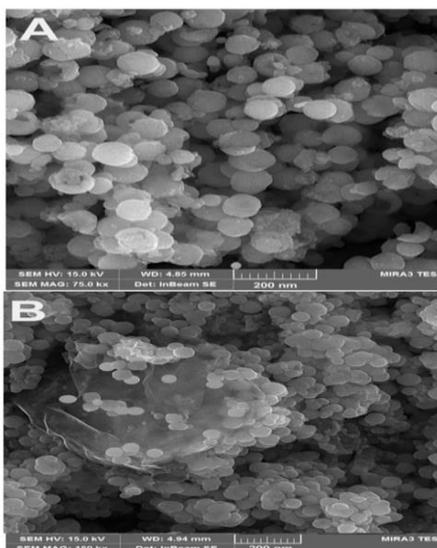
Greenhouse cultivation of *Salvia* carried out in Isfahan University of Technology (32' 43'E, 51' 31'N, Iran) during May–August, 2015. At first the seeds were sown in the outdoor sandy bed in March (2015). Then the seedlings were transplanting to pots at 4-6 leaf stage. The Sage was grown at a day/night cycle of 14/10 h, at 25/20  $^{\circ}$ C, and at a light intensity of 12000 LUX. Plants feed with NPK fertilizer (20-20-20+TE, 1 g L $^{-1}$ ) two times to avoid any nutrient deficit during growth period. The herbicides were applied post emergence at three different doses: 0.5X, 1X and 1.25 X where X (application of bentazon at 2 lit/ha, 48% SL, 1200 g a. i. ha $^{-1}$ ) is equal to the recommended dose that the factory

has proposed. The untreated plant (control) sprayed with distill water. The essential oil content at the 8-10 leaf stages was extracted by Clevenger methods using the Clevenger's apparatus. The essential oil was diluted with 25 mL methanol: pH 5 of PBS (5:25, v/v). The extraction yield of essential oil obtained by hydro-distillation from dried plant was 0.25% (w/w).

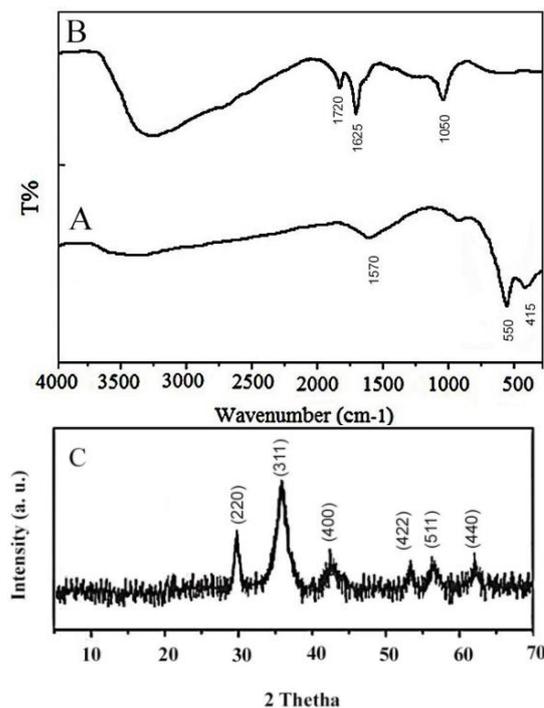
### 3. RESULT AND DISCUSSION

#### 3. 1. Characterization of $ZnFe_2O_4$ / Reduced Graphene Oxide Nano Composite

Fig. 1 display the FE-SEM image of  $ZnFe_2O_4$  (Fig.1A) and  $ZnFe_2O_4$  NPs/ reduced graphene oxide (Fig. 1B). The  $ZnFe_2O_4$  NPs have sphere-shaped with narrow size distribution and mean diameter about 100 nm. No aggregation between nanoparticles was seen. In  $ZnFe_2O_4$  NPs/ reduced graphene oxide the spinel anchored on the wave-like graphene sheets as substrate. The presences of reduced graphene induce the formation of  $ZnFe_2O_4$  NPs with smaller dimension (80 nm mean diameter). Fig. 2A shows FT-IR spectra of  $ZnFe_2O_4$  NPs/ reduced graphene oxide. Two peaks at 550 and 415  $cm^{-1}$  related to stretching vibration of Zn-O and Fe-O, respectively. The stretching vibration at 1570  $cm^{-1}$  can be assigned to carbon backbone. Compared to Fig. 2B (FT-IR spectra of GO), no peak was found for stretching bonds of -COOH and -OH group, indicate GO is reduced in nanocomposite. The XRD pattern of  $ZnFe_2O_4$  NPs/ reduced graphene oxide (Fig.2C) has six characteristic peaks at  $2\theta$  values of 30.0°, 35.0°, 42.0°, 53°, 56°, 62.0 which are matches well with  $ZnFe_2O_4$  Miller Indices of 220,311,400, 422, 511, 440, respectively.



**Fig. 1.** FE-SEM image of  $ZnFe_2O_4$  (A) and  $ZnFe_2O_4$  NPs/ reduced graphene oxide (B).

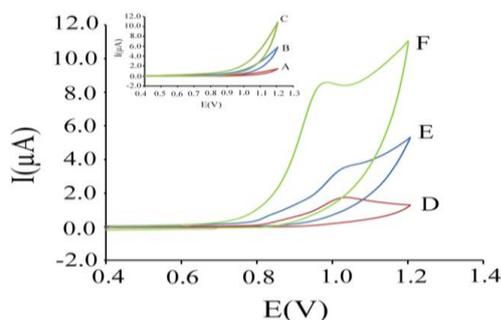


**Fig. 2.** FT-IR spectra of  $ZnFe_2O_4$  NPs/ reduced graphene oxide (A); pure GO (B) and XRD patterns of  $ZnFe_2O_4$  NPs/ reduced graphene oxide (C).

#### 3. 2. Electrochemical Behavior of Bentazon at the Surface of Modified Electrode

As mentioned previously in literature, the oxidation mechanism of bentazon is complex, consisting of irreversible one-electron transfer followed by a dimerization of the oxidation product [16]. The severe adsorption of product lead to poisoning and poor reproducibility. These problems can be solved using carbon paste electrodes with an easy renewable surface. In order to attain the maximum sensitivity, the oxidation current of bentazon was checked out in various pH values of the phosphate buffer solutions (pH = 3.0–8.0). The results showed that peak potentials were pH-independent in the interval from 3.0 to 8.0 occurred at  $E_p = +0.95$  V. Therefore it can be concluded that no proton was involved in oxidation mechanism of bentazon in this range. The maximum current obtained at pH 4.0. The width at half maximum of the bentazon peak current is  $W_{1/2} \sim 110$  mV, corresponding to an electrochemical reaction involving the transfer of one electron [17]. Figure 3 show cyclic voltammograms (CVs) of the PBS (pH 4.0) at (A) CPE ; (B)  $ZnFe_2O_4$ /CPE; (C)  $ZnFe_2O_4$  NPs/ reduced graphene oxide /CPE and 5  $\mu mol L^{-1}$  of bentazon ( 0.1 M PBS; pH=4.0) at (D) CPE; (E)  $ZnFe_2O_4$ /CPE and (F)  $ZnFe_2O_4$  NPs/ reduced graphene oxide /CPE. The potential scanned from 0 to 1.2 volt vs. Ag/AgCl electrode with scan rate of 50 mV/s in 0.1 M PBS (pH=4). At the bare

CPE (curve D), there was low oxidation current for bentazon, indicating that slow electron transfer process. The  $\text{ZnFe}_2\text{O}_4$ -modified /CPE cause about 1.5-fold increase in current response of bentazon than bare CPE due to nanometer dimensions of  $\text{ZnFe}_2\text{O}_4$  NPs. No reduction peak on reverses scan is observed for bentazon, which suggests that the electrochemical oxidation mechanism is irreversible. A further 4.1 times increase in oxidation current at  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide compare to CPE was seen. It can be ascribed to the higher available surface area which nanocomposite provide for bentazon oxidation. It is found that the background current of modified electrode is higher than that of the CPE. This is because  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide enhance the surface area of electrode, and because the charging current principally depends on the surface area of electrodes [18]. The real surface area of the bare and modified electrodes were calculated using Randles-Sevcik formula using  $1\text{mmol L}^{-1}$   $\text{K}_3\text{Fe}(\text{CN})_6$  as a probe in the  $0.1\text{mol L}^{-1}$  KCl electrolyte. From the slope of the  $I_{\text{pa}} - v^{1/2}$  relation, the real surface area was  $0.22\text{ cm}^2$  for the unmodified carbon paste electrode, and  $0.89\text{ cm}^2$  for  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide, which is 4.0 times greater than that for the CPE.

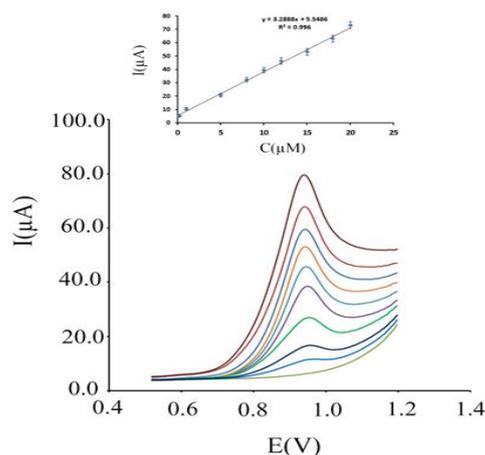


**Fig. 3.** Cyclic voltammograms of the PBS (pH 4.0) at (A) CPE ; (B)  $\text{ZnFe}_2\text{O}_4$ /CPE; (C) of  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide /CPE and  $5\text{ }\mu\text{mol L}^{-1}$  of bentazon in  $0.1\text{ M}$  PBS (pH=4.0) at (D)CPE;

(E) $\text{ZnFe}_2\text{O}_4$ /CPE and (F) of  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide /CPE.

### 3. 3. Electrochemical determination of bentazon.

Fig. 4. shows the DPVs (pulse amplitude of  $80\text{ mV}$ , pulse time of  $50\text{ msec}$  and the scan rate of  $60\text{ mV s}^{-1}$ ) from oxidation of various concentrations of bentazon at the  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide/CPE. The increase in peak current was linear with bentazon concentration and the corresponding equation was:  $I\text{ (}\mu\text{A)} = (3.258 \pm 0.12) C + (5.68 \pm 0.30)$  ( $R^2 = 0.9943$ ,  $n = 5$ ), where C is concentration of bentazon. The calibration graph was linear in the range of  $0.1\text{--}20.0\text{ }\mu\text{mol L}^{-1}$  with detection limit of  $0.07\text{ }\mu\text{mol L}^{-1}$  (at signal to noise ratio of 3). These two merits for proposed method were compared with other electrochemical techniques for determination of bentazon [5-6, 16]. Table 1 show the detection limit and linear dynamic range of proposed method is better than the other as given in the previous literature.



**Fig. 4.** DPVs of  $\text{ZnFe}_2\text{O}_4$  NPs/ reduced graphene oxide in  $0.1\text{ M}$  PBS (pH 5.0) containing bentazon . Inset: DPVs of a) blank; b)  $0.1$ ; c)  $1.0$ ; d)  $5.0$ ; e)  $8.0$ ; f)  $10.0$ ; g)  $12.0$ ; h)  $15.0$ ; i)  $18.0$ ; j)  $20\text{ }\mu\text{mol L}^{-1}$  of bentazon

**Table 1.** Comparison of LOD and linear dynamic range of recently published voltammetric methods with the proposed method for the determination of bentazon.

| Electrode  | Technique                      | Detection limit ( $\mu\text{mol L}^{-1}$ ) | Linear range ( $\mu\text{mol L}^{-1}$ ) | Reference       |
|--|--------------------------------|--|---|-----------------|
| Carbon Nanotube $\beta$ -Cyclodextrin                                | Cyclic voltammetry             | 1.6  | 10-80                                   | [16]            |
| Manganese acetate octakis-(2-diethylaminoethanethiol) phthalocyanine | Square wave voltammetry        | 0.25                                       | 50-750                                  | [6]             |
| Glassy carbon  | Square wave voltammetry        | 10   | 15.1-22.6                               | [5]             |
| $\text{ZnFe}_2\text{O}_4$ NPs/ reduced graphene oxide /CPE           | Differential pulse voltammetry | 0.07                                       | 0.1-20                                  | Proposed method |

### 3. 4. Interference studies

Since the essential oils contain high percentage of hydrocarbon and oxygenated monoterpenes, the effect of possible interfering biomolecules (existed in essential oil of *Salvia*) on oxidation signal of bentazone were investigated. Based on reported articles [19] the major constituents of essential oils from numerous *Salvia* species are p-cymene (11.9%) and c-terpinene (7.3%). DP voltammograms of bentazon in the presence and absence of these two interferences (at one fold level of p-cymene and c-terpinene) were almost the same. Therefore the modified electrode is sufficiently selective and could be applied for the determination of bentazon in essential oil of *Salvia*.

### 3. 5. Operational life time and reproducibility

The duration of ZnFe<sub>2</sub>O<sub>4</sub> NPs/ reduced graphene oxide /CPE high activity was checked by DPV using 5×10<sup>-7</sup> mol L<sup>-1</sup> of bentazon. The oxidation peak retained to 96 % of its primary value after two month and 89 % after six weeks. The modified electrode reproducibility defined as relative standard deviation from bentazon (5×10<sup>-7</sup> M) oxidation signals using four modified electrodes which calculated 3.7%.

### 3. 6. Analytical application

The results proved that the modified electrode was very sensitive and sufficiently selective toward bentazon therefore, it could be applied for the determination of this pesticide in essential oil samples. Average bentazon residues in essential oil of *Salvia officinalis* after 4-weeks treatment were determined. Essential oil was extracted and then diluted using 5 mL methanol and 25 mL PBS (pH=4.0) and then was directly transfer to electrochemical cell. Spike-and-recovery technique was applied for determination of bentazon. The recovery percentages were 94.9 and 97.0%, showing the appropriate analytical utility of fabricated electrode for practical analytical performance (Table 2). The bentazon was below detection limit of proposed method at applied dose of 0.5X. For proportion of labeled used rates of 1X and 1.25X with three replicate measurements the bentazon concentrations found as 0.15(μM) ±0.01 and 2.9(μM) ±0.2, respectively. Therefore, the proposed method could apply as a reliable procedure for the analysis of bentazon in essential oil matrix. Since the maximum allowable bentazon residue level in most types of food reported as 0.05 ppm [20], essential oil of *Salvia officinalis* at applied dose of 1X can be used as medicinal plants without negative effect from bentazon residue.

**Table 2.** Electrochemical determination of bentazon in sage essential oil after 4-weeks treatment.

| Applied dose | Added bentazon (μmol L <sup>-1</sup> ) | Found by proposed method <sup>a</sup> (μmol L <sup>-1</sup> ) | Recovery (%) |
|--------------|--|---|--------------|
| 1X           | -                                      | 0.15±0.01   | -            |
|              | 2.0                                    | 2.04±0.1  | 94.9         |
| 1.25X        | -                                      | 2.9±0.2   | -            |
|              | 5.0                                    | 7.67±0.9  | 97.0         |

<sup>a</sup>Average of three replicated measurements ± Standard deviation

## 4. CONCLUSION

ZnFe<sub>2</sub>O<sub>4</sub> NPs/reduced graphene oxide was synthesized by one-pot solvo-thermal approach. The nanocomposite modified electrode enhanced oxidation current of bentazon noticeably. The modified electrode was adequately selective toward bentazon determination in the presence major hydrocarbon constituents existed in extract of essential oil. Compared to previously reported electrochemical techniques, the proposed method has the lowest detection limit for bentazon determination. Furthermore the results of the electroanalysis can be valuable in routine analysis of bentazon residues in essential oil of plant for investigation of adverse effects on human health.

## Acknowledgements

The authors gratefully acknowledge support of this work by the Research Council of Payame Noor University.

## REFERENCES

- [1] C.M. Wu and C.Y. Wang, Physiological study on bentazon tolerance in inbred corn, *Weed Technol.* 17 (2003) 565–570.
- [2] J.M. Salman and B.H. Hameed, Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions, *J. Hazard. Mater.* 175 (2010) 133–137.
- [3] A. Fuhrmann, O. Gans, S. Weiss, G. Haberhauer and M.H. Gerzabek, Determination of bentazone, chloridazon and terbuthylazine and some of their metabolites in complex environmental matrices by liquid chromatography–electrospray ionization–tandem mass spectrometry using a modified QuEChERS method: an Optimization and validation study, *Water Air Soil Pollut.* 225 (2014) 1944.
- [4] G.M.F. Pinto and I.C.S.F. Jardim, Determination of bentazon residues in water by high-performance liquid chromatography: Validation of the method, *J. Chromatogr A*, 846 (1999) 369–374.

- [5] C.W. Thorstensen, O. Lode, A.L. Christianse, Determination of bentazone, dichlorprop, and MCPA in different soils by sodium hydroxide extraction in combination with solid-phase preconcentration, *J. Agric. Food Chem.*, 48 (2000) 5829–5833.
- [6] E.M. Garrido, J.L. Costa Lima, C.M. Delerue-Matos and A.M. Oliveira Brett, electrochemical oxidation of bentazon at a glassy carbon electrode Application to the determination of a commercial herbicide, *Talanta* 46 (1998) 1131–1135.
- [7] I.A. Akinbulu and T. Nyokong, Characterization of polymeric film of a new manganese phthalocyanine complex octa-substituted with 2-diethylaminoethanethiol, and its use for the electrochemical detection of bentazon, *Electrochim. Acta* 55 (2009) 37–45.
- [8] Z. Shahnavaz, P.M. Woi and Y. Alias, Electrochemical sensing of glucose by reduced graphene oxide-zinc ferrosinels, *Appl. Surf. Sci.*, 379 (2016) 156–162.
- [9] D. Lu, Y. Zhang, S. Lin, L. Wang and C. Wang, Synthesis of magnetic ZnFe<sub>2</sub>O<sub>4</sub>/graphene composite and its application in photocatalytic degradation of dyes, *J. Alloys Compd.* 579 (2013) 336–342.
- [10] Y. Fu and X. Wang, Magnetically Separable ZnFe<sub>2</sub>O<sub>4</sub>-Graphene Catalyst and its High Photocatalytic Performance under Visible Light Irradiation, *Ind. Eng. Chem. Res.* 50 (2011) 7210–7218.
- [11] Q. Ke and J. Wang, Graphene-based materials for supercapacitor electrodes, *J. Materiomics* 2 (2016) 37-54.
- [12] D. Chen, H. Feng and J. Li, Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications, *Chem. Rev.* 112 (2012) 6027–6053.
- [13] S.D. Perera, R.G. Mariano, K. Vu, N. Nour, O. Seitz, Y. Chabal and K.J. Balkus Jr, Hydrothermal synthesis of graphene-TiO<sub>2</sub> nanotube composites with enhanced photocatalytic activity, *ACS Catal.*, 2 (2012) 949–956.
- [14] J.J. Shi, X.Y. Zhou, Y. Liu, Q.M. Su, J. Zhang and G.H. Du, One-pot solvothermal synthesis of ZnFe<sub>2</sub>O<sub>4</sub> nanospheres/graphene composites with improved lithium storage performance, *Mater. Res. Bull.* 65 (2015) 204-209.
- [15] M.d Fouladgar, Nanostructured Sensor for Simultaneous Determination of Trace Amounts of Bisphenol A and Vitamin B6 in Food Samples, *Food Anal. Method*, 10 (2017) 1507–1514.
- [16] V. Rahemi, J. M. P. J. Garrido, F. Borges, C.M.A. Brett and E.M.P.J. Garrido, Electrochemical Determination of the Herbicide Bentazone Using a Carbon Nanotube b-Cyclodextrin Modified Electrode, *Electroanalysis* 25 (2013) 2360–2366.
- [17] C.M.A. Brett and A.M. Oliveira-Brett, Electrochemistry, *Principles, Methods and Applications*, Oxford University Press, Oxford, UK 1993.
- [18] A.R. Rautio, O. Pitkanen, T. Jarvinen, A. Samikannu, N. Halonen, M. Mohl, J.P. Mikkola and K. Kordas, Electric Double-Layer Capacitors Based on Multiwalled Carbon Nanotubes: Can Nanostructuring of the Nanotubes Enhance Performance, *J. Phys. Chem. C.* 119 (2015) 3538–3544.
- [19] S.E. Sajjad and A. Ghannadi, Essential oil of the Persian sage, *Salvia rhytidea* Benth, *Acta Pharm.* 55 (2005) 321-326.
- [20] R.P. Pohanish, *Sittig's handbook of agriculture and chemicals*, second edition, William Andrew publishing, Norwich, NY, 2005