

## Volta metric Behavior of Mesotrione using Silver/Amalgam Electrode

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**ABSTRACT:** Volta metric behavior of mesotrione using silver/amalgam electrode we examined in this paper. Mesotrione belongs to the triketone group of herbicides. It is used against weeds in corn and operates by inhibition of 4-hydroxyphenyl piruvate in plants. There is little information about mesotrione as its presence in the market is short. For its wider application in the future, it is important to know details of its chemical characteristics and redox processes, including biogeochemical transformation and migration after application to agricultural land, which could contribute to its more efficient and safe application. The technique of cyclic voltammeter with conventional three-electrode cell and electrochemical workstation was used for the investigation of electrochemical behavior of mesotrione. Cyclic voltamograms of mesotrione were recorded at pH values 6, 8, 10 and 12. Several peaks were obtained at certain values of the potential and they were attributed to the reduction of two carbonyl groups (in position 1 and 3 of cyclohexane ring), the third carbonyl group and nitro group. The maximum current value was at pH 12.

**Key words:** Pesticide, Mesotrione, Cyclic Voltammeter, Volta metric behavior, Silver/Amalgam electrode

### INTRODUCTION

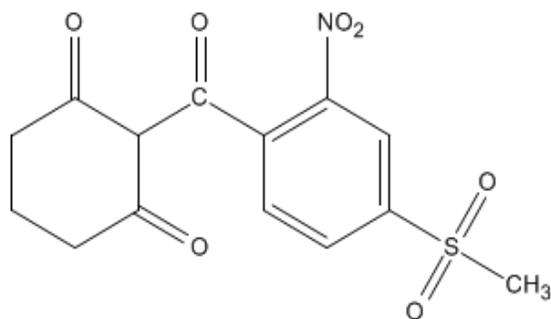
Agricultural production currently, and increasingly, depends on the use of pesticides (Jimenez and Navas, 1997). Pesticides, the most cost-effective means of pest and weed control, allow the maintenance of current yields and so contribute to economic viability. Concern about the environmental impact of repeated pesticide use has prompted research into environmental fate of these agents, which can emigrate from treated fields to air, other land and water (Arias-Estevez, *et al.*, 2008); Pesticides are one of the main organic pollutants. Groundwater pollution with inorganic and organic pollutants is a serious problem in the supply of drinking water (Roßknecht *et al.*, 2001). Today, with the development of industry and agriculture, traces of pesticides are increasingly present in the water, both surface and groundwater. The waste water concentrations of pesticides may be in mg/L, while surface water and groundwater contain µg/L (Goldstein *et al.*, 1993). Key objective for modern pesticide research is to discover new products that control the widest possible range of weed species, as flexibly possible (Edmunds, 2007). Mesotrione is a new selective herbicide used against annual grasses and broadleaf weeds in corn. It belongs to benzoylcyclohexane-1,3-dione (triketone) group of herbicides. The chemical

structure of the triketones is typically based around the 2-benzoyl or 2-heteroaroyl cyclohexane-1,3-dione template (Prysbilla, 1988). Mesotrione has been launched on the American and European markets by Syngenta in 2001, under the brand name CALLISTO® (Mitchell *et al.*, 2001). Syngenta has a long history of research in triketone herbicides, from their original discovery in 1977 through to the present day (Hellyer and Lassak, 1968). Mesotrione works by inhibition of 4-hydroxyphenylpiruvate deoxygenize (HPPD) in plants (Mitchell *et al.*, 2001). Mesotrione is applied during plant development from the first shoots to the V8 stage of development (when plant contain maximum of 8 sheets). The maximum dose of application is 0.15kg/ha (Kotkar and Srivastava, 2008). Typical use rates for mesotrione range from 0.1 to 2.25 kg/ha when applied pre-emergence, and 0.7-1.50 kg/ha for post-emergence applications (Wichert *et al.*, 1999). Mesotrione is entering the plant through leaves or roots. The symptoms are bleaching of leaves, followed by tissue necrosis. It is classified as toxicologically dangerous for the environment, but there is little information about its impact (Hawkes *et al.*, 2001) as its presence in the market is short (in Europe since 2001). Due to its wider application, it is important to know details of its chemical characteristics and redox

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processes, including biogeochemical transformation and migration after application to agricultural land, which could contribute to its more efficient and safe application (Erdogdu *et al.*, 2007).

As many organic compounds used as pesticides mesotrione contains electro active groups and therefore the voltammeter could be used for mechanistic and analytical studies (Trojanowicz, 2002; Aprea *et al.*, 2002). For the investigation of electrochemical behavior of mesotrione we used the technique of cyclic voltammeter with conventional three-electrode cell and electrochemical workstation. The working electrode was Hg/Ag (silver/amalgam) electrode, platinum as auxiliary electrode and Ag/AgCl (3M KCl) as a reference electrode. During the experiment pH values of aqueous solution varied, while the constant concentration of mesotrione was maintained. Cyclic voltammograms were recorded by gradually increasing of scan rate.



**Fig. 1. Mesotrione: 2-[4-(methylsulphonyl)-2-nitrobenzoyl]-1-3-cyclohexandione**

## MATERIALS & METHODS

Mesotrione (95% purity) was supplied from Institute for plants, Belgrade, Serbia. Silver electrode was supplied from Austin, USA, and left to stand for 24 hours in mercury. Methanol, sodium chloride, potassium dihydrogen phosphate, sodium hydrogen phosphate, sodium hydrogen carbonate, sodium hydroxide, all of analytical grade purity, were obtained from Merck (Darmstadt, Germany). As supporting electrolytes in voltammeter measurements different pH solutions were used:  $\text{KH}_2\text{PO}_4/\text{NaOH}$  buffer,  $\text{NaHCO}_3/\text{NaOH}$  buffer and  $\text{Na}_2\text{HPO}_4/\text{NaOH}$  buffer.

Volta metric measurements were performed on electrochemical workstation CHI 760 (Austin, USA). CHI used software (Version 4.03). The three electrode system consisted of mercury buttoned silver electrode (Hg/Ag) (CHI 103) as working electrode, Ag/AgCl (3M KCl) as a reference electrode (CHI 221), and platinum wire as auxiliary electrode (CHI 111). All cyclic

voltammograms were recorded at scan rates: 25mV/s, 50mV/s, 100mV/s, 200mV/s, 300mV/s, 400mV/s, 500mV/s, 600mV/s, 700mV/s. For determination of pH value we used pH meter, model 744 with combined glass electrode and temperature sensor, Metrohm (Herisau, Switzerland).

Mesotrione solution (concentration of 0.006 mol/dm<sup>3</sup>) was prepared. The amount of 0.0041g of mesotrione (95% purity) was measured on analytical balance and dissolved in 2cm<sup>3</sup> absolute methanol. Then, 2cm<sup>3</sup> of supporting electrolyte was added, so that the concentration of mesotrione was 0.003 mol/dm<sup>3</sup>. Silver/amalgam electrode was prepared by leaving of the silver electrode for 24 hours in mercury. The mercury was adsorbed on the silver electrode and such electrode has a lifetime of a month. Afterwards the electrode was regenerated by polishing with powder of aluminum (0.05 $\mu\text{m}$ ). The electrode was rinsed with water and placed it in an ultrasonic bath. Finally we placed electrode in mercury to perform adsorption.

Based on earlier studies it was found that the most reproductive results (voltammograms with good separation of signals) were obtained using the Hg/Ag (silver/amalgam) electrode. We recorded all cyclic voltammograms at scan rates: 25mV/s, 50mV/s, 100mV/s, 200mV/s, 300mV/s, 400mV/s, 500mV/s, 600mV/s and 700mV/s, for pH values 6, 8, 10 and 12. Concentration of mesotrione in all experiments was 0.003 mol/dm<sup>3</sup>.

## RESULTS & DISCUSSIONS

The cycle voltammogram of mesotrione at pH 6 (0.1M phosphate buffer solution) was shown in Fig. 2. At the potential (E) of -0.838V to the Ag/AgCl electrode, well-defined cathode (reduction) peak was observed and it probably corresponded to the reduction of carbonyl group in position 1 and 3 of the cyclohexane ring. Two peaks were observed at the potential of -1.2355V and -1.3746V (signal 2 was weaker than the signal 3). They probably corresponded to the reduction of the third carbonyl group. At the potential of -1.5141V low intensity peak (signal 4) was observed which probably was the result of reduction of nitro group (Delamar *et al.*, 1997).

The dependence of the signal height with the square root of scan speed at pH 6 is shown Figs 3, 4, 5 and 6. The linearity of  $i_p$  vs.  $v^{1/2}$  graphs indicates that the electrochemical reactions are diffusion controlled (Bard *et al.*, 2001). It indicated the quasi-reverse process. Better linearity in some cases indicated more reversible behavior of the system.

The cycle voltammogram of mesotrione at pH 8 is shown at Fig. 7. Supporting electrolyte was 0.1M phosphate buffer solution. At the potential of -1.0298V

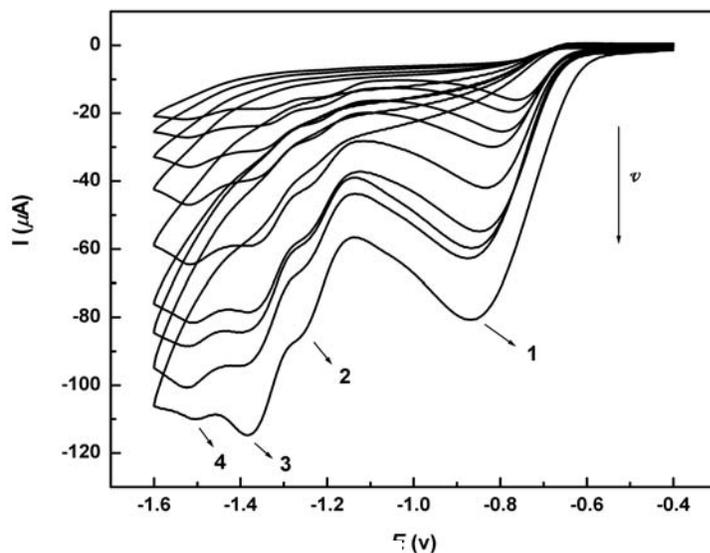


Fig. 2. Cycle voltammogram of mesotrione, 0.003 mol/dm<sup>3</sup>, in phosphate buffer, at pH 6

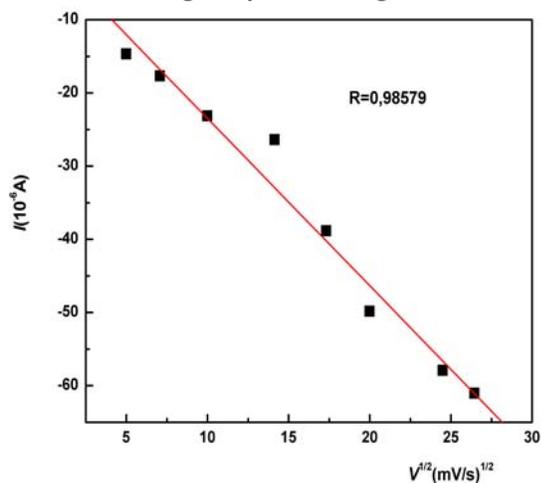


Fig. 3. Current dependence of the square root of scan speed (for peak 1) at pH 6

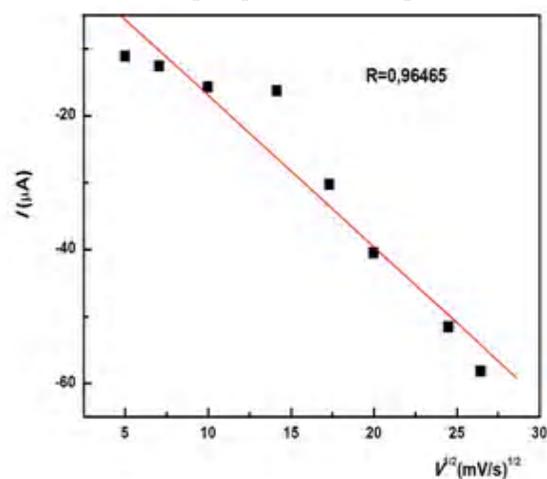


Fig. 4. Current dependence of the square root of scan speed (for peak 2) at pH 6

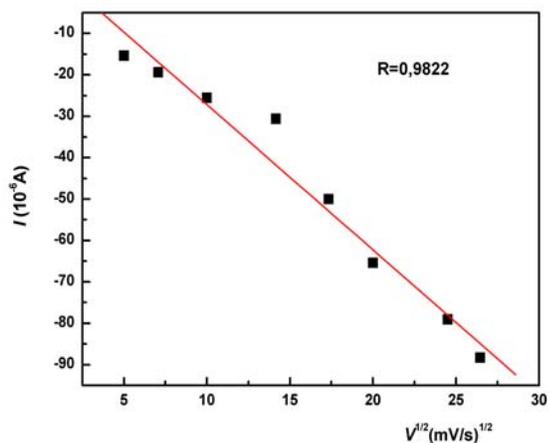


Fig. 5. Current dependence of the square root of scan speed (for peak 3) at pH 6

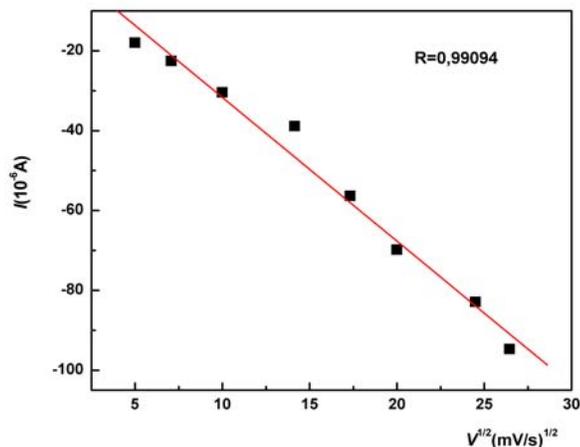


Fig. 6. Current dependence of the square root of scan speed (for peak 4) at pH 6

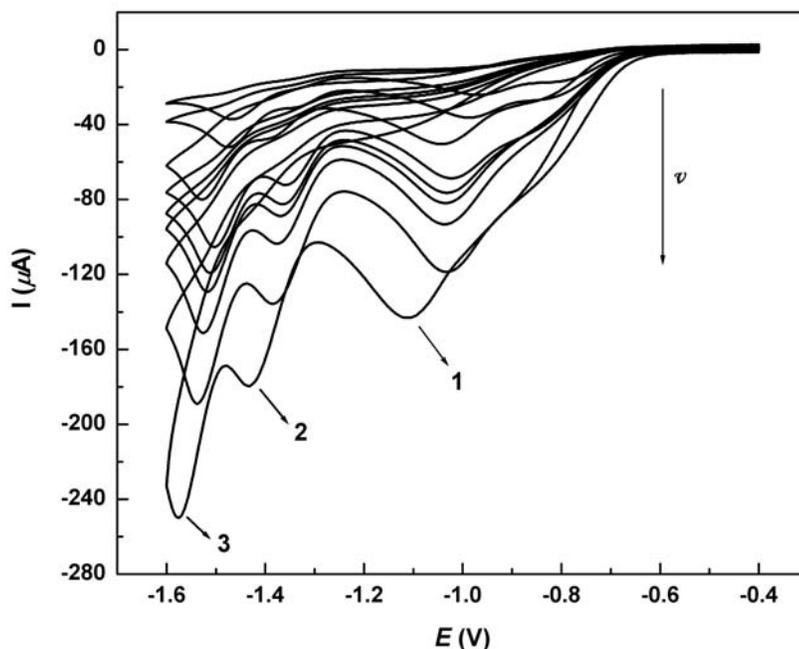


Fig. 7. Cycle voltammogram of mesotrione,  $3 \times 10^{-3} \text{ mol/dm}^3$ , in phosphate buffer, pH 8

expanding of cathode (reduction) peak was observed, and probably corresponded of the reduction of carbonyl group in position 1 and 3 of cyclohexane ring. Spreading of peaks rose from the differentiation of electrochemical reduction. At the potential of  $-1.3651 \text{ V}$  is observed peak (signal 2), which probably corresponded to the reduction of the third carbonyl group. On potential of  $-1.5102 \text{ V}$  is observed peak (signal 3), which probably comes from the reduction of nitro groups.

Figs 8, 9 and 10 were show the dependence of signal height with the square root of scanning speed (for comparing correction factors). It indicates the quasi-reverse process, but better linearity was observed indicating more reversible system behavior.

The cycle voltammogram of mesotrione at pH 10 is shown in Fig. 11. On potential of  $-0.9867 \text{ V}$  was observed cathode (reduction) peak, which probably corresponds to the joint reduction of carbonyl group in position 1

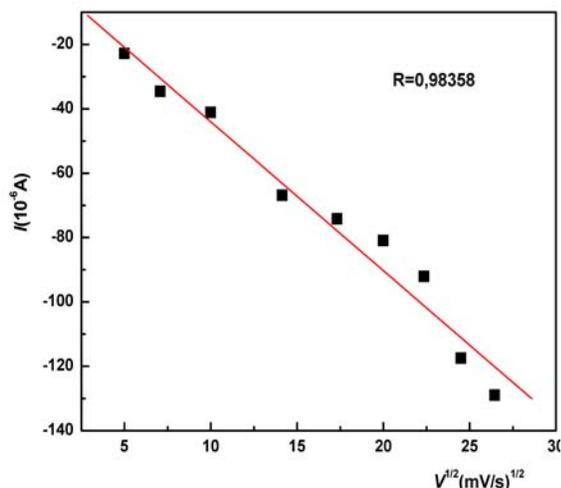


Fig. 8. Current dependence of the square root of scan speed (for peak 1) at pH 8

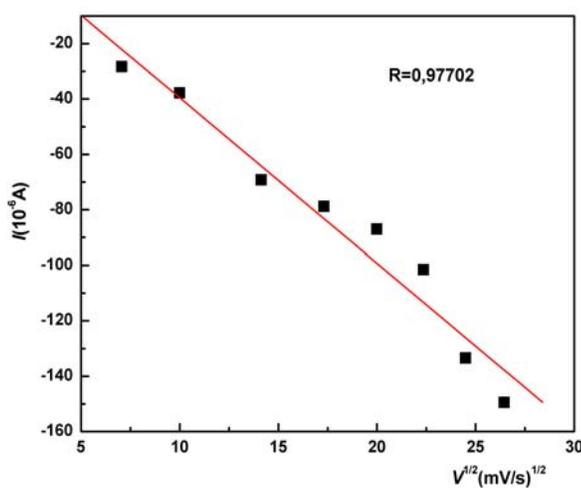


Fig. 9. Current dependence of the square root of scan speed (for peak 2) at pH 8

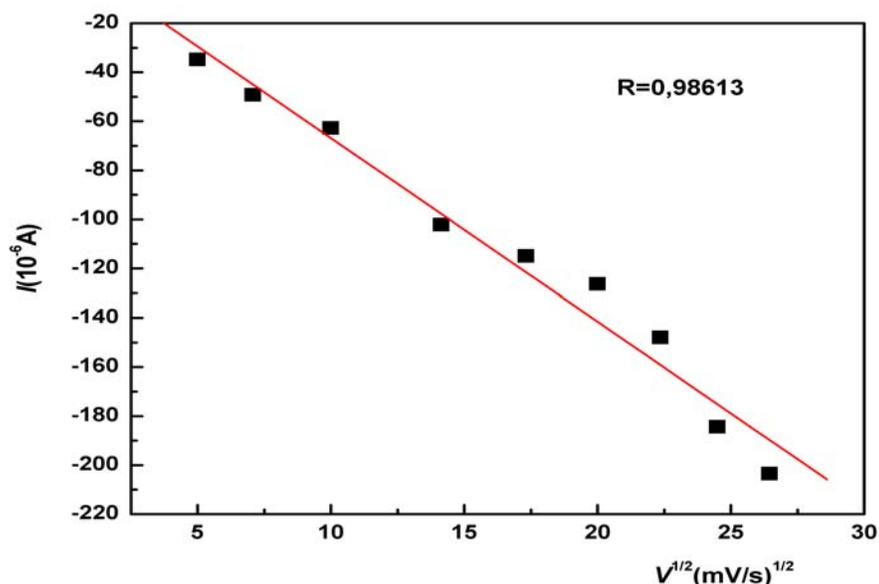


Fig. 10. Current dependence of the square root of scan speed (for peak 3) at pH 8

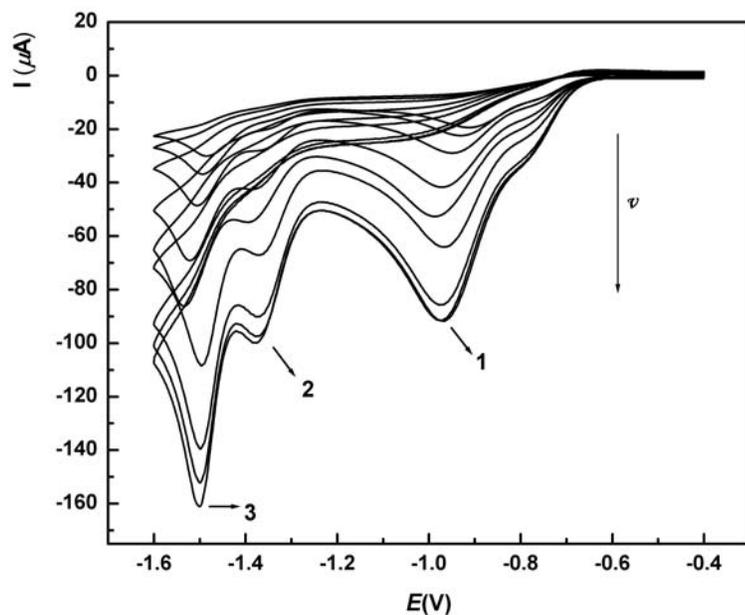


Fig. 11. Cycle voltammogram of mesotrione, 0.003 mol/dm<sup>3</sup>, in carbonate buffer, pH=10.

and 3 of cyclohexane ring. On potential of -1.3946V was observed another peak (signal 2), which probably comes from the reduction of the third carbonyl group. On potential of -1.5338V was observed third peak, which probably comes from the reduction of nitro groups. Due to differentiation of electrochemical reaction, obtained signals 1 and 2 had lower intensity. The dependence of the signal height with the square root of scanning speed is shown in Figs. 12, 13 and 14. It indicates the quasi-reverse process, but better

linearity was observed indicating more reversible system behavior.

The cycle voltammogram of mesotrione at pH 12 was shown in Fig. 15. Supporting electrolyte was 0.1M phosphate buffer solution. Cathode (reduction) peak was observed at the potential of -1.0416V and it probably corresponded to the reduction of carbonyl group in position 1 and 3 of the cyclohexane ring. The second peak (signal 2) at the potential of -1.4141V prob-

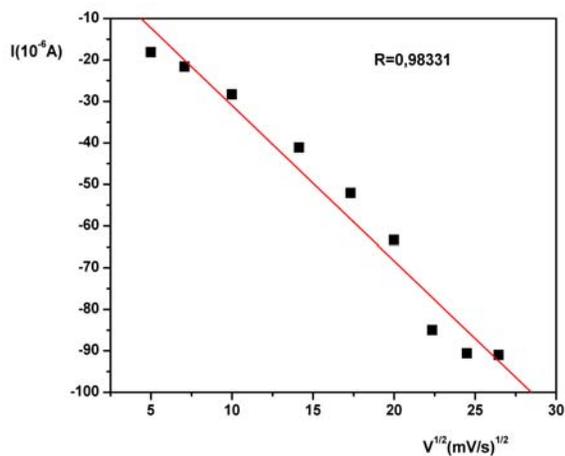


Fig. 12. Current dependence of the square root of scan speed (for peak 1) at pH 10

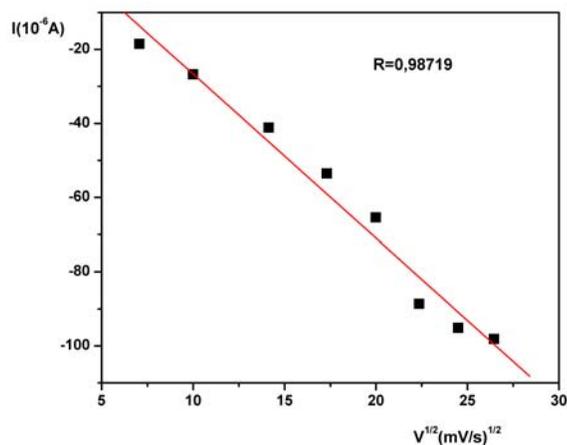


Fig. 13. Current dependence of the square root of scan speed (for peak 2) at pH 10

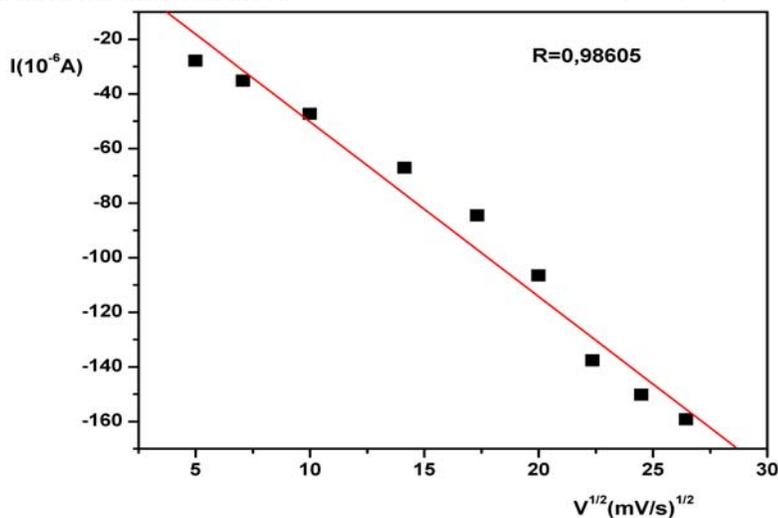


Fig. 14. Current dependence of the square root of scan speed (for peak 3) at pH 10

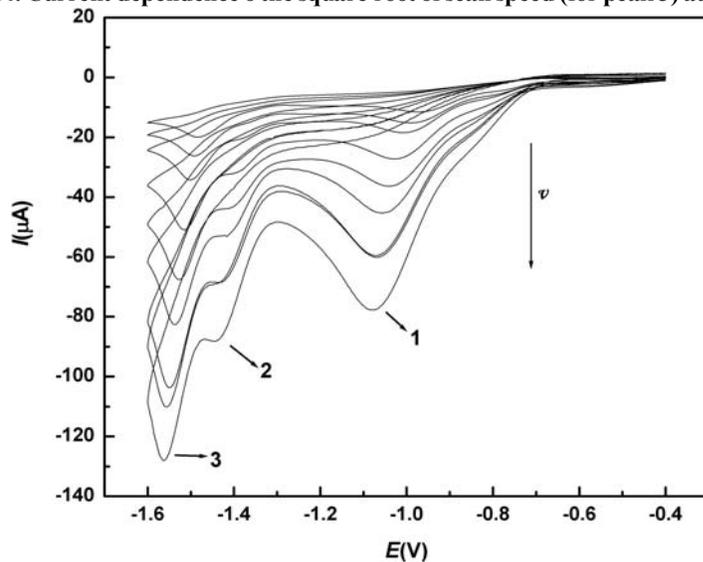


Fig. 15. Cycle voltammogram of mesotrione, 0.003 mol/dm<sup>3</sup>, in phosphate buffer, pH 12

ably came from the reduction of the third carbonyl group. At the potential of -1.5278V the third peak (signal 3), could be attributed to the reduction of nitro groups. Due to the differentiation of electrochemical reaction, obtained signals 1 and 2 had lower intensity.

The dependence of the signal height with the square root of scanning speed is shown at the Figs 16,

17 and 18. It indicates the quasi-reverse process, but better linearity was observed indicating more reversible system behavior.

On the basis of results obtained and from Fig. 19, it could be concluded that the maximum current value was at pH 12. All current values for pH 6, 8, 10 and 12 were shown in Table 1.

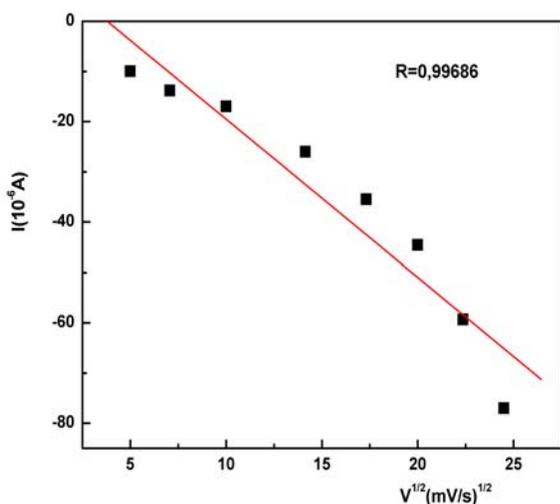


Fig. 16. Current dependence on the square root of scan speed (for peak 1) at pH 12

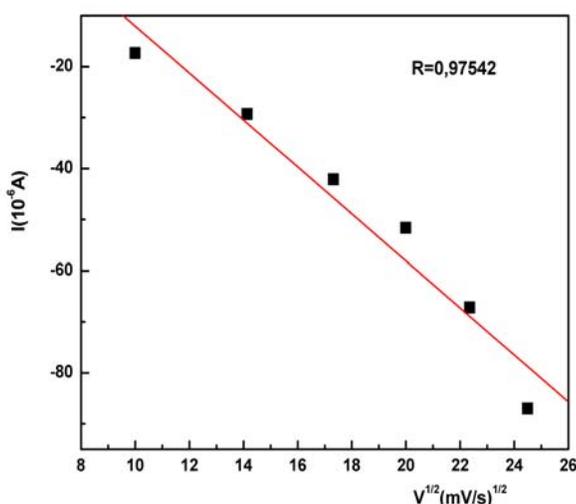


Fig. 17. Current dependence on the square root of scan speed (for peak 2) at pH 12

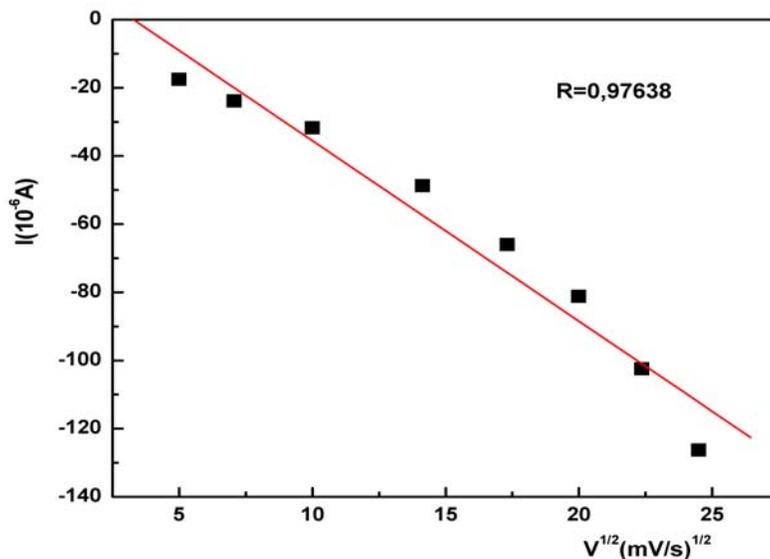


Fig. 18. Current dependence on the square root of scan speed (for peak 3) at pH 12

Table 1. Current peaks for pH values 6, 8, 10 and 12

pH	I (μA)
6	-21.5441
8	-33.2728
10	-29.9176
12	-38.3198

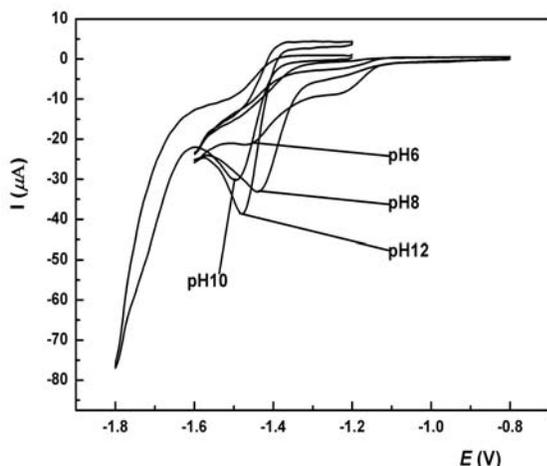


Fig. 19. Current dependence of the potential for signal 1 at pH values 6, 8, 10 and 12

## CONCLUSION

Mesotrione was electrochemically active at investigated pH (6, 8, 10 and 12). According to the classical theory of reversibility it is a typical irreversible system (absence of anodic oxidation signal), while dependence of peak intensity on the scan rate indicates the reversibility at lower speeds and quasi-reversibility at higher speeds. The maximum current value of 38,3198  $\mu\text{A}$  was obtained at pH 12. Absence of anodic peak should be investigated with the Hg/Ag microelectrode at higher polarization speeds. On the basis of results obtained can be based the electrochemical degradation of mesotrione remaining after the treatment in the environment. Dependence of signal intensity of the scan rate varied at different pH values. It indicated greater or lesser participation of chemical reactions in comparison to the electrochemical reactions. This conclusion was based on the shift of potential signal depending of the pH scale and scan rate. The resulting signals were attributed to the reduction of carbonyl group (in position 1 and 3 of cyclohexane ring), the third carbonyl group and nitro group.

## ACKNOWLEDGEMENT

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