

1-1-2015

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## Reduction behavior of fenoxaprop-p-ethyl and its voltammetric determination

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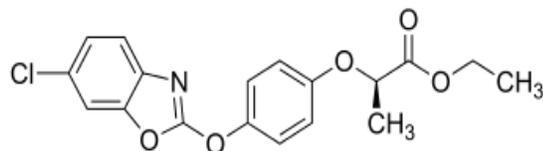
Received: 16.01.2014 • Accepted: 29.06.2014 • Published Online: 23.01.2015 • Printed: 20.02.2015

**Abstract:** The reduction behavior of fenoxaprop-p-ethyl (FNX) was studied on a hanging mercury drop electrode. FNX showed 2 reduction peaks at about  $-0.7$  V and at about  $-0.9$  V versus Ag/AgCl/3.0 M KCl in Britton–Robinson buffer at pH 4.8. Both reductions were irreversible and adsorption was effective. The reduction peaks were assigned to the reduction of C=N to CH–NH and the reduction of C=O to CH–OH. Square-wave voltammetry has been proposed and validated for quantification of FNX in different samples. The linear working range was established as  $0.30$ – $15.0$   $\mu$ M. Limit of detection and limit of quantification were calculated as  $0.07$   $\mu$ M and  $0.24$   $\mu$ M, respectively. The proposed method was successfully applied for the determination of FNX in tap water, river water, and plant samples with recoveries between 95.7% and 99.6% showing a relative standard deviation of less than 15%.

**Key words:** Fenoxaprop-p-ethyl, electrochemical behavior, voltammetric determination

### 1. Introduction

Fenoxaprop-p-ethyl (FNX), chemically known as (R)-2-[4-(6-chlorobenzoxazol-2-yloxy)phenoxy]propionic acid ethyl ester (Scheme), is used as a herbicide and belongs to the class of aryloxyphenoxypropionates. Members of this class are considered selective and systematic herbicides. They are absorbed by plants to interfere with the production of fatty acids by inhibition of acetyl coenzyme-A carboxylase, which is needed for plant growth. These herbicides are used to inhibit the growth of unwanted annual and perennial grasses between crops including barley, soybean, wheat, wild oat, tomato, cotton, and potato.<sup>1,2</sup>



**Scheme.** Chemical structure of FNX.

Since the Environmental Protection Agency and Cancer Assessment Review Committee (CARC) classified these chemicals as carcinogenic to humans,<sup>3</sup> the determination of their concentration levels in crops and environmental samples is of great importance. According to the literature, mainly chromatographic methods coupled with mass spectrometry after different kinds of extraction such as immersed solvent microextraction,<sup>4</sup> single-drop microextraction,<sup>5</sup> liquid–liquid extraction,<sup>6,7</sup> microwave-assisted solvent extraction,<sup>8</sup> dispersed liquid–liquid microextraction,<sup>9</sup> and solid-phase extraction<sup>10</sup> were proposed for the determination of FNX and

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its related compounds. Besides chromatographic methods, flow injection spectrophotometry<sup>11,12</sup> and acid hydrolysis followed by spectrophotometric determination<sup>13</sup> were also developed for its determination.

Electroanalytical methods are widely used not only for quantitative determination of a variety of organic and inorganic substances but also to evaluate many physical, chemical, and redox characteristics of species, and to propose plausible mechanism pathways for reduction and oxidation processes. They are further used to determine the adsorption-diffusion parameters of molecules. The evaluation of such parameters is also of great interest for biologically and environmentally important species as these parameters are useful for the study of distribution, metabolism, and pharmacological, toxicological, and pharmacokinetic properties of drugs and poisons.<sup>14–16</sup> So far, a wide range of applications of voltammetric methods have been reported in the literature to determine environmentally and biologically relevant substances.<sup>14–25</sup> Although FNX has an electroactive moiety there has been no detailed study about its electrochemical behavior to date.

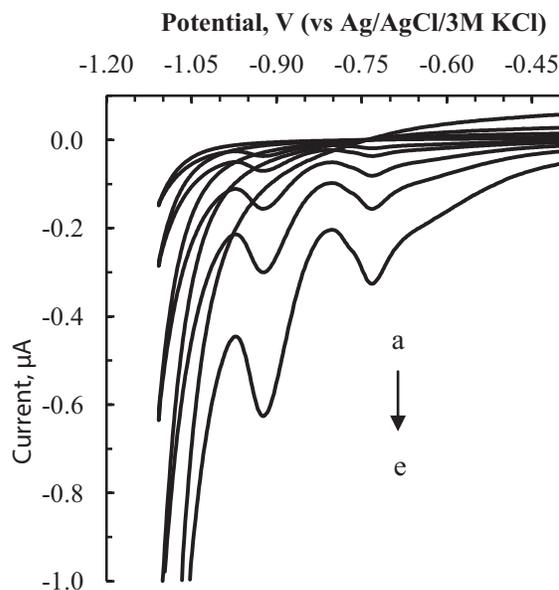
This study investigated the reduction behavior of FNX on a hanging mercury drop electrode (HMDE). Besides investigating its adsorption–diffusion characteristics, tentative reduction mechanisms were further proposed. In addition, this study also aimed to develop a novel, rapid, and simple voltammetric method for the direct determination of FNX in water samples and crops.

## 2. Results and discussion

### 2.1. Cathodic behavior of FNX on a HMDE

The electrochemical behavior of FNX on a HMDE was studied by using cyclic voltammetry (CV), square-wave voltammetry (SWV), and constant potential bulk electrolysis (BE).

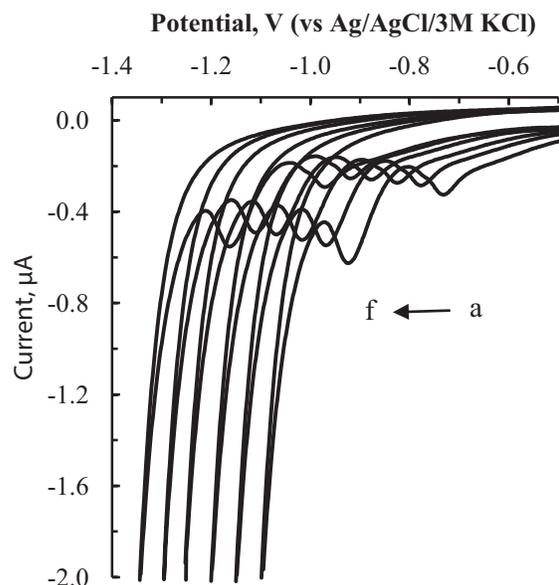
In CV studies a voltammetric baseline and potential window were established for blank BR. Then standard FNX solution was added to the cell. Based on these measurements 2 reduction peaks were investigated. The first reduction peak was at around  $-0.7$  V and the second one at around  $-0.9$  V. These peaks disappeared when only BR was scanned and the peak current increased linearly with increasing FNX concentration (Figure 1). This result suggests that these peaks belong to the reduction of FNX on the HMDE.



**Figure 1.** CVs of FNX solutions at different  $C_{FNX}$  (in mM a: blank, b: 0.05, c: 0.12, d: 0.24, e: 0.50) in BR of pH 4.8 and scan rate = 0.10 V/s.

### 2.1.1. Effect of pH

Electrochemical studies were conducted. First of all the effect of pH was investigated between the values of 1.8 and 10.8. Figure 2 shows that potentials of both reduction peaks shifted to more negative values with increasing pH from 1.8 to 6.8.



**Figure 2.** CVs of FNX solutions at different pHs (a: 1.8, b: 3.0, c: 4.0, d: 4.8, e: 5.9, f: 6.8) in BR,  $C_{FNX} = 0.50$  mM, scan rate = 0.10 V/s.

The change in peak potentials with pH was explained by the participation of proton(s) in reduction mechanisms.<sup>14–17</sup> The shift of the peak potentials towards more negative values with increasing pH may be caused by a protonation step before the electron transfer.<sup>19–22</sup> In such mechanisms, the electroactive group was protonated before the electron transfer, which may be considered a classical acid catalyzed reduction. In these mechanisms the transfer of electron(s) needs much more potentials at higher pH<sup>14,16,22</sup> as we observed during the present study. Peak potentials are pH independent in neutral and alkaline solutions. When peak potentials for both reductions were plotted versus pH both potentials changed linearly with pH by obeying the following equations:

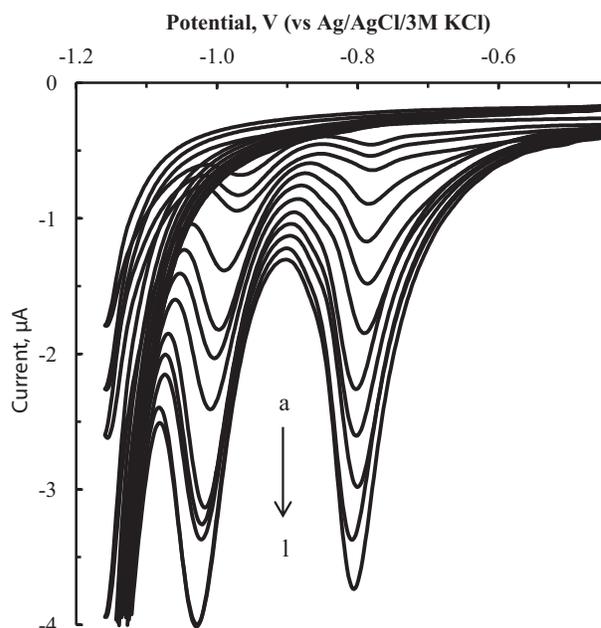
$$E_{pI}/V = -0.048pH - 0.71; R^2 = 0.9894 \quad (1)$$

$$E_{pII}/V = -0.052pH - 0.83; R^2 = 0.9962 \quad (2)$$

The ratio of the proton number to electron number was calculated by using the equations given in the literature<sup>14–16,21–25</sup> and it was concluded that in each reduction equal numbers of protons and electrons were involved. Peak current and peak shape were taken into account for the determination of the optimum pH as 4.8.

### 2.1.2. Effect of potential scan rate

After pH studies, the effect of the potential scan rate on peak potentials was evaluated for a FNX solution (0.5 mM in BR) at pH 4.8. Here, the potentials of both reduction peaks shifted to more negative potentials with increasing scan rate (Figure 3).



**Figure 3.** CVs of FNX solutions at different scan rates (a: 0.08, b: 0.09, c: 0.10, d: 0.20, e: 0.30, f: 0.40, g: 0.50, h: 0.60, i: 0.70, j: 0.80, k: 0.90, l: 1.00 V/s) in BR of pH 4.8,  $C_{FNX} = 0.50$  mM.

A change in peak potential with scan rate indicates an irreversible or quasireversible mechanism.<sup>15,19,21,26</sup> Since there is no oxidation peak on the reverse scan, irreversible reduction mechanisms might be proposed. The potential of the second reduction peak changes linearly with the logarithm of scan rate by obeying Eq. (3):

$$E_{pII}/V = 0.055 \log V - 0.98; R^2 = 0.9902 \quad (3)$$

The slope value of Eq. (3) was used to calculate the relation between the number of electron(s) in rate determining step ( $e$ ) and charge transfer coefficient ( $\alpha$ ). The value for  $e\alpha$  was around unity for the second reduction peak at about  $-0.95$  V. The charge transfer coefficient for ideal metallic electrodes was thought to be very close to 0.5.<sup>15,19,21,26</sup> Based on this, the participation of 2 electrons for the second reduction step is possible.

By studying the effect of the potential scan rate on the peak current, the current of both reduction peaks changed linearly with scan rate according to the following equations:

$$i_{pI}/\mu A = -2.09V(V/s) - 0.03; R^2 = 0.9966 \quad (4)$$

$$i_{pII}/\mu A = -2.80V(V/s) - 0.29; R^2 = 0.9905 \quad (5)$$

The linear dependency of peak current to potential scan rate is one of the indications of an adsorption-controlled mechanism.<sup>14-26</sup> The logarithm of the peak current for both reductions was plotted with respect to the logarithm of scan rate and the relations follow the given equations:

$$\log i_{pI}/\mu A = 1.29 \log V(V/s) - 5.59; R^2 = 0.9954 \quad (6)$$

$$\log i_{pII}/\mu A = 0.95 \log V(V/s) - 5.68; R^2 = 0.9904 \quad (7)$$

Slope values for the relation between the logarithm of peak current and the logarithm of scan rate were close to theoretical values for adsorption-controlled mechanisms. Finally, the relation between peak current and the square-root of scan rate was investigated and peak currents showed no linear behavior towards the square-root of scan rate. According to scan rate studies both reductions might have adsorption-controlled mechanisms.

### 2.1.3. Constant potential bulk electrolysis (BE) and the number of electron(s)

For the determination of the number of electrons involved in the processes, 2 different approaches were applied. The first bulk electrolysis (BE) was carried out at a constant potential of  $-0.9$  V for the first reduction and at  $-1.2$  V for both reduction steps. In BE experiments 25.0 mL of 0.10 mM FNX solutions was used. After the charge value of 0.39 C for the first BE carried out at  $-0.9$  V peak current of the first reduction decreased to 17% of its initial current and the second reduction peak had nearly its initial current. The second BE was carried out at  $-1.2$  V after the first reduction peak had disappeared and the peak current of the second reduction decreased to 15% of its initial current after reaching a charge of 0.89 C. According to Faraday's equation,<sup>15,19,21,26</sup> in each reduction there might be 2 electrons involved. According to our previous assumptions each reduction process consequently features 2-electron 2-proton transfers.

As a second approach, equations for CV measurements to adsorption-controlled mechanisms<sup>18,23</sup> were applied directly to calculate the number of electrons. These results confirmed that the number of electrons involved in each reduction mechanism was around 2.

Although the exact electrode mechanism was not determined by complementary analysis, conclusions about the electroactive centers could be drawn with similar structures.<sup>14–16,21–24</sup> As shown in the Scheme, there are mainly 4 reducible groups in the structure of FNX: etheric oxygens, a carbonyl group, azomethine in one 5-membered ring, and chlorine as a leaving group.<sup>14,19,21,22</sup> Taking all the experimental studies into consideration, reduction of the carbonyl group to its corresponding alcohol by 2 protons and 2 electrons in such a way like acid catalyzed reduction and reduction of the C=N group to CH–NH again by 2 protons and 2 electrons could be thought of as reduction mechanisms.

## 2.2. Voltammetric determination of FNX

In order to develop a voltammetric method for the determination of FNX, reduction peak currents were calibrated. Square-wave voltammetric (SWV) and differential pulse voltammetric (DPV) techniques were examined and the SWV method was found to be more suitable and reproducible than DPV.

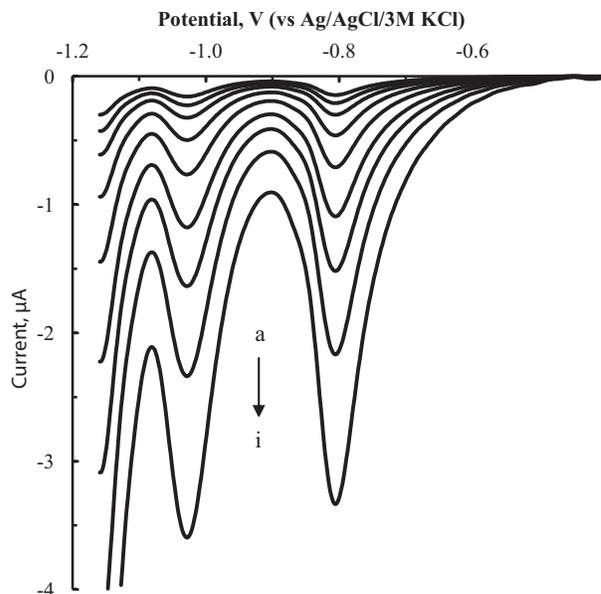
### 2.2.1. Optimization of variables

Experimental and instrumental variables were optimized. First, various electrolytes such as BR, phosphate, and acetate buffer solutions were examined. BR gave the highest peak current and better peak shapes than the other media. The analytical concentration of BR was optimized and 0.04 M was found to be the optimum value. Effects of pH were also investigated and the results were given above.

The variations in peak currents and shape with instrumental conditions such as frequency (f), scan increment ( $\Delta E_i$ ), pulse height ( $\Delta E_a$ ), and pulse width ( $E_w$ ) were investigated for 3.0  $\mu$ M FNX. As a result, the optimum instrumental parameters were found as follows: f = 25 Hz,  $\Delta E_i = 3$  mV,  $\Delta E_a = 65$  mV, and  $E_w = 0.01$  s.

After the optimization step, calibration studies were performed. In the calibration step currents were measured as a function of FNX concentration in quintuplicate under the optimized conditions and the average

of these 5 serial measurements was used as a peak current. Variations in peak current and shape are given in Figure 4.



**Figure 4.** SWVs of FNX solutions for different  $C_{FNX}$  (in  $\mu\text{M}$ ; a: 0.3, b: 0.5, c: 0.9, d: 1.4, e: 3.0, f: 4.6, g: 6.5, h: 10.0, i: 15.0) in BR of pH 4.8.

### 2.2.2. Method validation

The applied method was validated by investigating the following parameters: linearity range, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision, reproducibility, and repeatability.<sup>14,16</sup>

Linearity was checked by preparing standard solutions at 15 different concentration levels between 0.10  $\mu\text{M}$  and 30.0  $\mu\text{M}$ . Five serial measurements were taken for each concentration and subsequent to evaluation of Q-test for 95% confidence level; the average was used as a peak current of related concentration. Figure 4 shows that the peak current changed linearly with FNX concentration in the range of 0.30  $\mu\text{M}$  to 15.0  $\mu\text{M}$  by obeying the following equations:

$$i_{pI}/\mu\text{A} = (0.16 \pm 0.002)C_{FNX(\mu\text{M})} + (0.10 \pm 0.004); R^2 = 0.9982 \quad (8)$$

$$i_{pII}/\mu\text{A} = (0.13 \pm 0.004)C_{FNX(\mu\text{M})} + (0.02 \pm 0.003); R^2 = 0.9940 \quad (9)$$

The good linearity of the calibration graphs and the negligible scatter of the experimental points are clearly evident from the determination coefficient ( $R^2$ ) given in Eqs. (8) and (9).

LOD and LOQ values were calculated from the electro-reduction peak current using the following equations:  $\text{LOD} = 3s/m$  and  $\text{LOQ} = 10s/m$  ( $s$  is the standard deviation of intercept and  $m$  is the slope of calibration curve)<sup>14,16</sup> and  $\text{LOD} = 0.07 \mu\text{M}$  and  $\text{LOQ} = 0.24 \mu\text{M}$  as given in Table 1.

Repeatability and reproducibility for peak current and peak potential were examined by interday and intraday measurements using FNX solutions with the same concentrations. For interday measurements, the same FNX solution was used and 5 measurements were obtained at different times. The relative standard deviation was calculated for peak current and peak potential. For intraday measurements FNX solutions were

prepared by the same manner each day and 5 measurements were made on 5 consecutive days. The relative standard deviation was calculated for peak current and peak potential. Results for both interday and intraday measurements are given in Table 1. The proposed method shows a coefficient of determination ( $R^2$ ) higher than 0.99 for both peaks. The repeatability and reproducibility of peak current and peak potential were satisfactory.

**Table 1.** Regression data of the calibration curve.

Regression parameter	Peak 1	Peak 2
Linearity range/ $\mu\text{M}$	0.30–15.0	0.30–15.0
Slope of calibration curve/( $\mu\text{A}/\text{mol}$ )	0.16	0.13
Intercept/ $\mu\text{A}$	0.10	0.02
Standard deviation (SD) of regression/ $\mu\text{A}$	0.035	0.052
SD of slope/( $\mu\text{A}/\text{mol}$ )	0.002	0.004
SD of intercept/ $\mu\text{A}$	0.004	0.003
Limit of detection (LOD)/ $\mu\text{M}$	0.08	0.07
Limit of quantification (LOQ)/ $\mu\text{M}$	0.25	0.24
Determination coefficient/ $R^2$	0.9983	0.9940
Within-day repeatability of peak current*, (% RSD)	7.29	7.52
Between-day repeatability of peak current*, (% RSD)	13.23	13.28
Within-day repeatability of peak potential*, (% RSD)	4.85	2.69
Between-day repeatability of peak potential*, (% RSD)	6.73	4.03

\*relative standard deviation for 5 serial measurements

In order to evaluate the applicability of the proposed method to water and crop samples, FNX was examined in tap water, river water, and crop samples. As shown in Table 2, mean results for tap water samples were between 97.5% and 99.6% (with RSD values around 12.0%). The average recoveries for river samples were around 95.7% and 97.2% with RSD values less than 10.0% (Table 3).

**Table 2.** Recovery of FNX from tap water samples.

	Value spiked, $\mu\text{M}$	Values calculated/ $\mu\text{M}$	Recovery*/%	RSD**/%
Peak 1	0	ND	–	–
	0.95	0.80, 0.82, 0.93, 1.02, 1.06	$97.5 \pm 15.1$	12.5
	5.50	4.8, 5.1, 5.3, 5.6, 6.2	$98.2 \pm 12.0$	9.9
Peak 2	0	ND	–	–
	0.95	0.79, 0.84, 0.96, 1.05, 1.09	$99.6 \pm 16.9$	13.7
	5.50	4.7, 5.2, 5.3, 5.7, 6.3	$98.9 \pm 13.4$	11.0

\*value = average  $\pm$  ts/ $\sqrt{N}$  ( $N = 5$  and at 95% confidence level), \*\*relative standard deviation for 5 serial measurements, ND: not determined

As shown in Table 4, FNX sprayed crop samples contained about 3  $\mu\text{M}$  FNX. As stated in the sample preparation section, FNX sprayed crops were diluted 20 times during the washing process and washing residue was diluted 8 times with BR. This means that the FNX that was removed from the crop samples was diluted totally 160 times during the washing and preparation process. The concentration of FNX that was sprayed before on a leaf of a crop was calculated to be about 0.48 mM. This experimental value is very close to actual value of 0.50 mM stated in the sample preparation section.

In conclusion, detailed electrochemical characteristics of FNX on a HMDE were studied for the first time to date. The redox properties and electrochemical parameters of this compound might be of crucial importance

in evaluating its physicochemical and toxicological properties. Determinations of environmentally relevant molecules in different samples are also of great importance. In this study, a simple voltammetric method was presented that requires neither sophisticated instrumentation nor tedious extraction processes for determination of FNX used as herbicide.

**Table 3.** Recovery of FNX from river water samples.

	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	Recovery <sup>d</sup> , %	RSD <sup>e</sup> , %
Peak 1	0.95	0	0.88	97.2 ± 10.7	8.9
		0.55	1.45		
		0.85	1.55		
		2.55	3.81		
		6.85	7.92		
Peak 2	0.95	0	0.82	95.7 ± 8.3	7.0
		0.55	1.56		
		0.85	1.72		
		2.55	3.25		
		6.85	7.77		

<sup>a</sup> level of commercial FNX solution prepared,  $\mu\text{M}$ , <sup>b</sup> level of standard FNX solution added to A,  $\mu\text{M}$ , <sup>c</sup> calculated level of FNX by proposed method total in A and B,  $\mu\text{M}$ , <sup>d</sup> value = average  $\pm$  ts/ $\sqrt{N}$  (N = 5 and at 95% confidence level), <sup>e</sup> relative standard deviation for 5 serial measurements

**Table 4.** Recovery of FNX from crop samples.

	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>e</sup>	RSD <sup>f</sup> , %
Peak 1	1.15	0	4.00	2.85	3.09 ± 0.23	5.9
		0.25	4.32	2.92		
		0.55	4.80	3.10		
		2.15	6.52	3.22		
		4.25	8.74	3.34		
Peak 2	1.15	0	3.85	2.70	3.04 ± 0.25	6.6
		0.25	4.34	2.94		
		0.55	4.82	3.12		
		2.15	6.49	3.19		
		4.25	8.65	3.25		

<sup>a</sup> level of commercial FNX solution added to washing water of crops,  $\mu\text{M}$ , <sup>b</sup> level of standard FNX solution added to A,  $\mu\text{M}$ , <sup>c</sup> calculated level of FNX by proposed method,  $\mu\text{M}$ , <sup>d</sup> FNX level in washing water of crops in case of 100% recovery of added FNX,  $\mu\text{M}$ , <sup>e</sup> average FNX level in D (value = average  $\pm$  ts/ $\sqrt{N}$  (N = 5 and at 95% confidence level)), <sup>f</sup> relative standard deviation for 5 serial measurements

### 3. Experimental

#### 3.1. Apparatus

Voltammetric measurements were carried out using a Reference 3000 (Gamry Instruments, Warminster, PA, USA) electrochemical work station. The 3-electrode system consisted of working electrodes (hanging mercury drop electrode (HMDE); BAS CGME 1108, 0.0190 cm<sup>2</sup>, reference electrode (Ag/AgCl; 3 M KCl; MF-2052, RE-5B) and a Pt auxiliary electrode (BAS MW-1034) were used. All pH measurements were performed with

a Thermo Orion Model 720A pH ion meter featuring an Orion combined glass pH electrode (912600; Thermo Fisher Scientific). Double-distilled deionized water was supplied from Ultra-Pure Water System (ELGA as PURELAB Option-S). All measurements were performed at room temperature.

### 3.2. Reagents and solutions

FNX standard (with CAS number: 66441-23-4) was kindly purchased from Sigma-Aldrich. Stock solutions (5.0 mM) were prepared in ethanol (Merck KGaA, Darmstadt, Germany) and kept in the dark and below 4 °C. Working solutions of FNX were prepared by sufficient dilution of the stock solution with supporting electrolyte at optimum pH and used within the same day to avoid any possible decomposition. Phosphoric acid (Riedel-de-Haen, Honeywell Specialty Chemicals Seelze GmbH, Germany), boric acid (Riedel-de-Haen, Honeywell Specialty Chemicals Seelze GmbH, Germany), and acetic acid (Merck KGaA, Darmstadt, Germany) were used in the preparation of BR solution in which each component had an analytical concentration of 0.04 M. Double-distilled deionized water was used in the preparation of all the solutions. All chemicals were used as received.

### 3.3. Procedure

For voltammetric measurements, a known volume of FNX solution was pipetted into 8.0 mL of supporting electrolyte. Voltammetric measurements were carried out after degassing with argon for 15 min before the first measurement and 30 s between the successive measurements. Voltammograms were subsequently recorded by scanning the potential towards the negative direction.

A 3-electrode combination system for bulk electrolysis (BE) with mercury pool (ca. 60 cm<sup>2</sup>) as working electrode, coiled platinum wire as an auxiliary electrode (BAS MW-1033 (23 cm)) and a Ag/AgCl reference electrode (BAS MF-2052 RE-5B in 3.0 M KCl) was used. In BE studies 25 mL of 0.10 mM solutions was used.

### 3.4. Preparation of samples for analysis

Tap water samples were collected from the city of Amasya and used as collected; river water samples were collected from the Yeşilirmak river in Amasya and homogenized by filtration and centrifugation. Both tap and river water samples were analyzed by standard addition methods. Crops including tomato, barley, and wheat were subjected to spray of 25.0 mL of 0.5 mM FNX solution. After 24 h all the leaves of the crops were collected, washed with 500.0 mL of a mixture of ethanol and distilled water (v:v, 9:1) and carefully collected by keeping the volume of washing mixture as closely as possible to 500.0 mL. Afterwards 1.0 mL of washing water was added to 7.0 mL of a BR solution and the pH of the mixture was adjusted to the optimum value. Subsequently, the voltammetric measurements were carried out following the standard addition method.

### Acknowledgment

The authors are grateful for the financial support from the Scientific Research Unit of Amasya University (grant number: FMB-BAP-2013-0037).

### References

1. Pornprom, T.; Mahatamnuchoke, P.; Usui, K. *Pest. Manag. Sci.* **2006**, *62*, 1109–1115.
2. Hajslova, J.; Pudil, F.; Jehlickova, Z.; Viden, I.; Davidek, J. *J. Chromatogr.* **1988**, *438*, 55–60.

3. United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (7510C).
4. Bagheri, H.; Es'haghi, A.; Es'haghi, A. *Int. J. Environ. Anal. Chem.* **2013**, *93*, 450–460.
5. Bagheri, H.; Dehghan, M.; Es'haghi, A.; Naderi, M. *Anal. Method.* **2013**, *5*, 4846–4851.
6. Lucini, L.; Molinari, G. P. *Quality Assurance and Safety of Crops & Foods* **2011**, *3*, 63–68.
7. Lucini, L.; Molinari, G. P. *Pest. Manag. Sci.* **2010**, *66*, 621–626.
8. Shehzad, F. U. N.; Shah, J.; Jan, M. R.; Muhammad, M. *J. Chem. Soc. Pakistan* **2012**, *34*, 1554–1559.
9. Li, S. Q.; Gao, P.; Zhang, J. H.; Li, Y. B.; Peng, B.; Gao, H. X.; Zhou, W. *J. Sep. Sci.* **2012**, *35*, 3389–3395.
10. Pythoglou, O.; Vryzas, Z.; Alexoudis, C.; Senseman, S. A.; Vassiliou, G. *Fresen. Environ. Bull.* **2012**, *21*, 3012–3017.
11. Shah, J.; Jan, M. R.; Muhammad, M.; Shehzad, F. U. N. *Toxicol. Environ. Chem.* **2011**, *93*, 1547–1556.
12. Shah, J.; Jan, M. R.; Muhammad, M.; Shehzad, F. U. N. *J. Brazil. Chem. Soc.* **2010**, *21*, 1923–1928.
13. Shah, J.; Jan, M. R.; Shehzad, F. U. N.; Muhammad, M. *J. Chem. Soc. Pakistan* **2010**, *32*, 537–541.
14. Pamuk, D.; Taşdemir, I. H.; Ece, A.; Canel, E.; Kılıç, E. *J. Brazil. Chem. Soc.* **2013**, *24*, 1276–1286.
15. Wang, J.; *Analytical Electrochemistry*; 2nd ed, Wiley–VCH: New York, NY, USA, 2000.
16. Zorluoğlu, S. L.; Taşdemir, I. H.; Ece, A.; Kılıç, E. *Can. J. Chem.* **2013**, *91*, 951–959.
17. David, I. G.; Badea, I. A.; Radu, G. L. *Turk. J. Chem.* **2013**, *37*, 91–100.
18. Tasdemir, I. H.; Akay, M. A.; Erk, N.; Kılıç, E. *Electroanalysis* **2010**, *22*, 2101–2109.
19. Bond, A. M.; *Broadening Electrochemical Horizons*; Oxford University Press: Oxford, UK, 2002.
20. Yardım, Y.; Sentürk, Z. *Turk. J. Chem.* **2011**, *35*, 413–426.
21. Brett, C. M. A.; Oliviera-Brett, A. M. *Electrochemistry, Principles, Methods and Applications*; 3rd ed., Oxford University Press: Oxford, UK, 1996.
22. Bard, A. J.; Stratmann, M.; Scholz, F.; Pickett, C. J. (Eds.) *Encyclopedia of Electrochemistry, 8*: Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2007.
23. Erdogan, D. A.; Taşdemir, I. H.; Erk, N.; Kılıç, E. *Collect. Czech. Chem. Commun.* **2011**, *76*, 423–442.
24. Lund, H.; Hammerich, O. (Eds.) *Organic Electrochemistry*; 4th ed. Marcel Dekker: New York, NY, USA, 2001.
25. Karakoç, O.; Nakiboğlu, N. *Turk. J. Chem.* **2013**, *37*, 712–720.
26. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; 2nd ed, John Wiley & Sons Inc: Hoboken, NJ, USA, 2001.