Int. J. Electrochem. Sci., 6 **(2011)** 5161 - 5171

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Monitoring of Photodegradation of Clothianidin, Nitenpyram and Imidacloprid Insecticides Using a Tricresyl Phosphate-Based Carbon Paste Electrode

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Received: 12 September 2011 / *Accepted:* 6 October 2011 / *Published:* 1 November 2011

A voltammetric investigation of two commercial neonicotinoid insecticides, *Clothianidin* (*Clo*) and *Nitenpyram* (*Nit*), was carried out and completed with the third one, *Imidacloprid* (*Imc*), from a previous study when using two different types of carbon paste electrodes made from graphite powder and silicone oil (SO-CPE) or tricresyl phosphate as the binder (TCP-CPE). For all substances of interest, the latter has been found superior with respect to the signal-to-noise characteristics and the overal electroanalytical performance. Subsequently, a new method employing the direct differential pulse voltammetry (DPV) and the TCP-CPE has been proposed for the determination of *Clo* and *Nit* at the low μg mL^{-1} concentration level; all the key parameters being applicable also to *Imc*. Finally, the procedure combining DPV with the TCP-CPE could be applied for the monitoring of the photolytic and TiO_2-assisted photocatalytic degradation of *Clo*, *Nit*, and *Imc* via their voltammetrically detectable disappearance, when the quantitative and kinetic data obtained have agreed well with the results of the reference HPLC/DAD measurements.

Keywords: neonicotinoids, (direct) differential pulse voltammetry, tricresyl phosphate-based carbon paste electrode, photolysis, TiO_2-assisted photocatalysis

1. INTRODUCTION

At present, the investigation on the photostability of insecticides represents a very dynamic area of various environmentally orientated studies mapping the impact of these organic pollutants in relation to possible photodegradation as one of the most effective ways of their ultimate removal from the nature [1]. Analytical procedures applied to this purpose are often quite complicated because of

numerous factors that have to be strictly controlled. Among others, it is a necessity to consider some interfering intermediates, considerable variations in pH of sample solutions to be analysed, or the presence of the photocatalyst (or its residua) which may negatively affect the monitoring of the concentration changes of the compounds of interest [2, 3]. Moreover, some problems can be associated with the transport of samples intended to analysed with well-established chromatographic methods that are usually inapplicable for direct field monitoring [1].

Today, neonicotinoids are one of the most important categories of insecticides introduced to the global market since the synthetic pyrethroids [4−6]. They are registered in more than 120 countries, being generally regarded as the most powerful insecticides for control of sucking insect pests like aphids, whiteflies, leaf- and plant-hoppers, thrips, some micro-Lepidoptera, or some other coleopteran pests [4−6]. Thus, massive and still expanding application of neonicotinoids requires also new analytical measurements that can be operated in very diverse samples, including the reliable monitoring of the photodegradation processes.

As mentioned above, the methods of choice for the determination of neonicotinoids are being based on high- and ultra-performance liquid chromatography (HPLC and UPLC) combined with the sensitive detection by a diode-array [7], mass spectrometry [7−10], or thermal-lens spectrometry [11]. As well known, voltammetric methods represent a convenient alternative method in the analysis of neonicotinoids. For such measurements, there are special procedures employing cyclic voltammetry (CV) [12], differential pulse polarography / voltammetry (DPP / DPV) [2, 13−20], or square-wave voltammetry (SWV) [21, 22]. Among these approaches, one can also find out an example on the monitoring of the photodegradation of some neonicotinoids described a couple of years ago [2]. Regarding this specific group of insecticides, the individual methods proposed for their determination have employed the mercury-based working electrodes [13−16, 21, 22] or detection units incorporating various unmodified and modified carbonaceous electrodes [12, 16−20].

The latter group of eventually suitable electrodes comprises also carbon paste electrodes (CPEs) whose employment for analysis of neonicotinoids has so far been described in some initial studies only [17−19], including a report recommending the tricresyl phosphate-based carbon paste electrode [23] for the determination of *Imidacloprid*, *Thiamethoxam*, and *Clothianidin*.

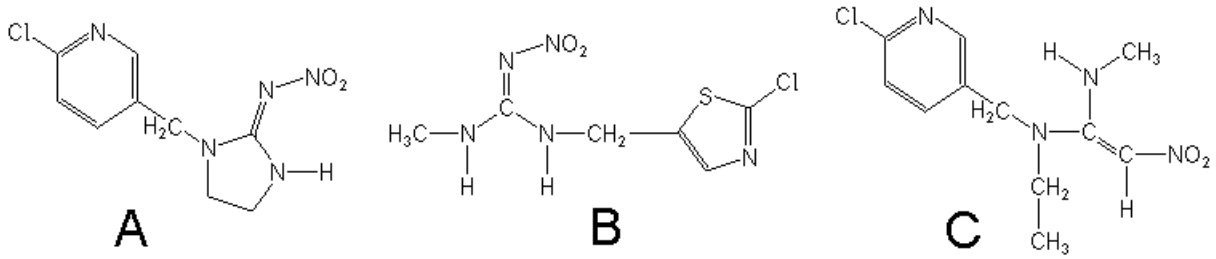

Figure 1. Chemical structures of the investigated neonicotinoids: (A) *Imc*, (B) *Clo* and (C) *Nit*.

In this work, the previous experience [17] with the determination of *Imidacloprid* (further abbreviated as "*Imc*", see Fig. 1A) has been adapted for voltammetric investigation of both

Clothianidin ("*Clo*", Fig. 1B) and *Nitenpyram* ("*Nit*", Fig. 1C). The voltammetric procedure — already described for *Imc* [17] and partially also for *Clo* [19] — was tested by means of monitoring the concentration changes of *Imc, Clo,* and *Nit* during their photolytic and TiO_2-assisted photocatalytic degradation, when using direct DPV in combination with the TCP-CPE and Britton–Robinson buffer (BRB, pH 7.0) as the supporting electrolyte.

2. MATERIALS AND METHODS

2.1. Chemicals and Solutions

All chemicals used were of analytical reagent grade and the solutions were prepared in doubly distilled water. Analytical standards (Sigma-Aldrich Laborchemikalien GmbH, Germany, PESTANAL®) of neonicotinoids were of 99.9% purity. The concentrations of the stock solutions were 162.3 and 176.0 μg mL^{-1} (6.5 x 10^{-4} mol L^{-1}) for *Clo* and *Nit*, respectively, and they were further diluted as required. BRB buffer solutions for voltammetric characterization and determination were prepared from a stock solution containing 0.04 mol L^{-1} phosphoric (Merck, Germany), boric (Merck) and acetic (Merck) acids, by adding 0.2 mol L^{-1} sodium hydroxide (Merck) to obtain the required pH value. For the preparation of the mobile phase in HPLC experiments, acetonitrile (J. T. Baker, Netherlands, purity 99.8%) and 0.2% phosphoric acid (made by diluting phosphoric acid (Centrohem, Serbia)) were used. In photocatalytic experiments, titanium dioxide, TiO_2 ("Degussa P-25", Degussa AG, Germany) was used as a model catalyst.

2.2. Apparatus

Voltammetric experiments were performed on an AUTOLAB PGSTAT12 electrochemical analyzer operated via GPES 4.9 software (Ecochemie, The Netherlands). The cell stand included a three-electrode system with a CPE as working, a saturated calomel electrode (SCE) (Amel, Italy) as reference, and a platinum (Amel) auxiliary electrode. All potentials are quoted vs. SCE reference electrode. Comparative HPLC measurements were performed using an Agilent 1100 liquid chromatograph (Agilent Technologies Inc., USA), Zorbax Eclipse XDB-C18 (250 mm × 4.6 mm, 3.5 μm) column, and DA-detector.

2.3. Procedures

Photodegradation. The solutions of the neonicotinoids (initial concentration 4.0 x 10^{-4} mol L^{-1}) were made in sterilized volumetric flasks. Aqueous solutions of the investigated neonicotinoids in absence of TiO_2 or in presence of TiO_2 (2.0000 g L^{-1}) were sonicated in the dark for 15 min before irradiation. The sonication was applied to improve homogenization of the samples and to make the dispersion of photocatalyst particles uniform, thus attaining the adsorption equilibrium in case of photocatalysis. Four different systems were made for all investigated compounds: in presence and

absence of TiO_2, both under natural insolation circumstances and in the dark. To ensure insolation conditions similar to the natural ones the photodegradation samples were kept under the natural day-night regime for one month (September 2009). All samples were hand-mixed daily. Aliquots for the analysis were taken in 1−5 day intervals in dependence of the type of compound and the procedure applied. The solutions were kept at ambient temperature.

Preparation of CPEs. Carbon paste was made by intimate hand-mixing of CR 5 graphite powder (Graphite Týn, Czech Republic) with tricresyl phosphate (mixture of isomers, Sigma-Aldrich Chemie GmbH, Switzerland) or silicone oil (MV 8000, Lučební Závody, Czech Republic) as a pasting liquid. The detailed procedure of electrode preparation was described earlier [17].

Voltammetry on CPEs. In model systems neonicotinoids were measured in 5.00 mL of the solution of different concentration, to which 5.00 mL Britton–Robinson buffer was added. In the case of monitoring the photodegradation, the solutions for analysis were prepared from a mixture of photodegradation sample, BRB (pH 7.0) and doubly distilled water at a ratio of 1:1:2 (v/v). Scan rate in cyclic voltammetry was v_{CV} = 50 mV s^{-1}. Measurement parameters in DPV were as follows: the pulse amplitude, ΔE = 50 mV, pulse width, w = 50 ms, and the scan rate, v_{DPV} = 25 mV s^{-1} [17]. The deaerated solutions (nitrogen stream, 10 min) were measured without filtering, at ambient temperature.

HPLC/DAD. For comparative analysis, all aliquots were filtered through Millex 0.22 μm syringe filters. The mobile phase was a mixture of water (0.2% phosphoric acid) and acetonitrile (85:15, v/v). The reversed phase separation was performed at isocratic regime, the flow rate was 0.8 mL min^{-1}, and the column temperature was held at 25 °C. Neonicotinoids were detected at their main absorption maxima (270, 266, and 270 nm, respectively for Imc, Clo, and Nit). Concentration of the investigated compound was determined from the area of the corresponding peak.

3. RESULTS AND DISCUSSION

3.1. Voltammetric Investigation of Clo and Nit at Carbon Paste Electrodes

Similarly to *Imc* and *Thiamethoxam*, both *Clo* and *Nit* contain an electroactive nitro group (see again Figs. 1B and 1C) in their nitroguanidine / nitromethylene pharmacophores which can be readily reduced at the electrode.

Accordingly to the previous results concerning the electrochemical reduction of the nitro group-containing neonicotinoids at CPEs (*17−20*), both *Clo* and *Nit* have an irreversible reduction peak in cathodic region at potentials more negative than –1.0 V. Voltammograms were obtained for *Clo* and *Nit* in the range of pH 2.0-8.0 using CV and DPV techniques at both SO-CPE and TCP-CPE, in an effort to define the optimal pH-value for their determination. According to previous observations [17], the effect of oxygen dissolved in the sample solutions was suppressed by purging the solution with nitrogen (for 10 min) prior to measurements. Also, CPEs were subjected to potential cycling in

the range from −0.60 to −1.50 V (10 cycles) to stabilize the surface regime of the electrode given. As can be seen, Figs. 2A,B show no reduction peaks for the investigated compounds in solutions more acidic than pH 5.0. The increasing of the pH led to higher signal intensities and well-developed signals in neutral and slightly alkaline solutions (pH 7.0−8.0) at both electrodes. As expected, the increase of pH-value of the supporting electrolyte broadened the potential window of the working electrode in the cathodic range. On the other hand, the residual current was not affected significantly with the changes of the pH. Nitenpyram showed some deviation from this statement at pH 8.0 (Fig 2B).

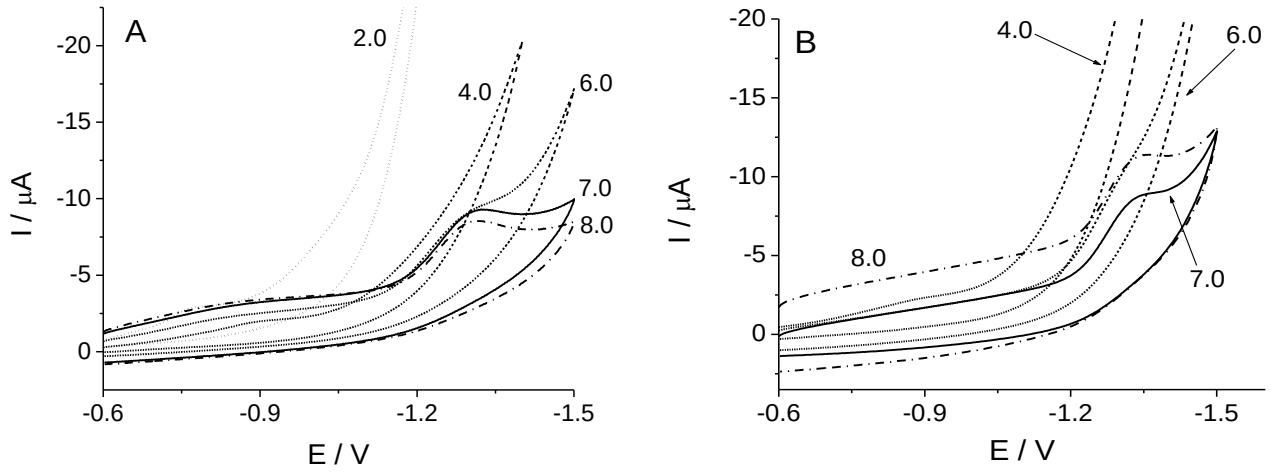

Figure 2. The influence of pH (the pHs of the solutions were indicated at the curves) on cyclic voltammograms of *Clo* (A) and *Nit* (B); c(*Clo*) = 27.05 µg mL^{-1} and c(*Nit*) = 29.33 µg mL^{-1}.

To avoid possible alkaline hydrolysis of the investigated compound and the used pasting liquid in case of TCP-CPE, the pH 7.0 was chosen for further investigations.

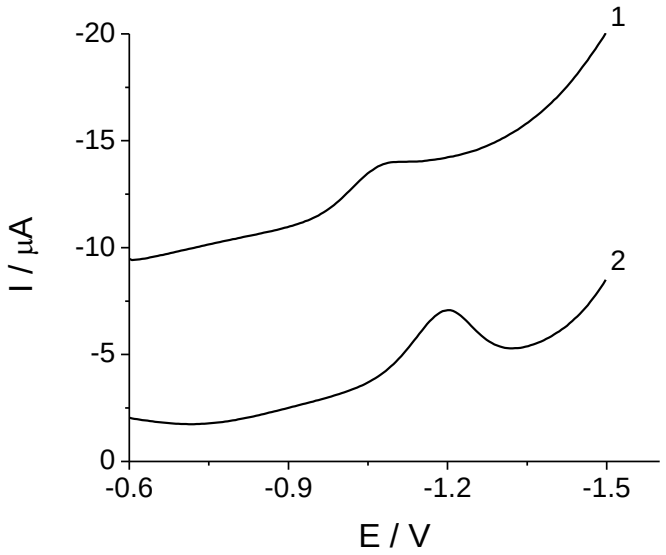

Figure 3. Comparison of differential pulse voltammograms of *Clo* at SO-CPE and TCP-CPE at pH 7.0; c = 27.05 µg mL^{-1}.

The comparison of the reduction signals for *Clo* (Fig. 3) and *Nit* at this pH show approximately 2.5 times higher intensities for the TCP-CPE in contrast to the SO-CPE, therefore, further investigations were performed with the TCP-CPE.

As shown earlier, the optimal measuring parameters in DPV analysis of neonicotinoids at CPEs were as follows: pulse amplitude, ΔE = 50 mV; pulse width, w = 50 ms; and scan rate, v_{DPV} = 25 mV s^{-1} [17]. The signal stability at TCP-CPE was checked by replicated recording of the DPV reduction signals for both *Clo* and *Nit* at 27.05 and 29.33 μg L^{-1} concentration level, respectively, in an interval of 30 min. No significant changes in the electrode properties were observed during measurements.

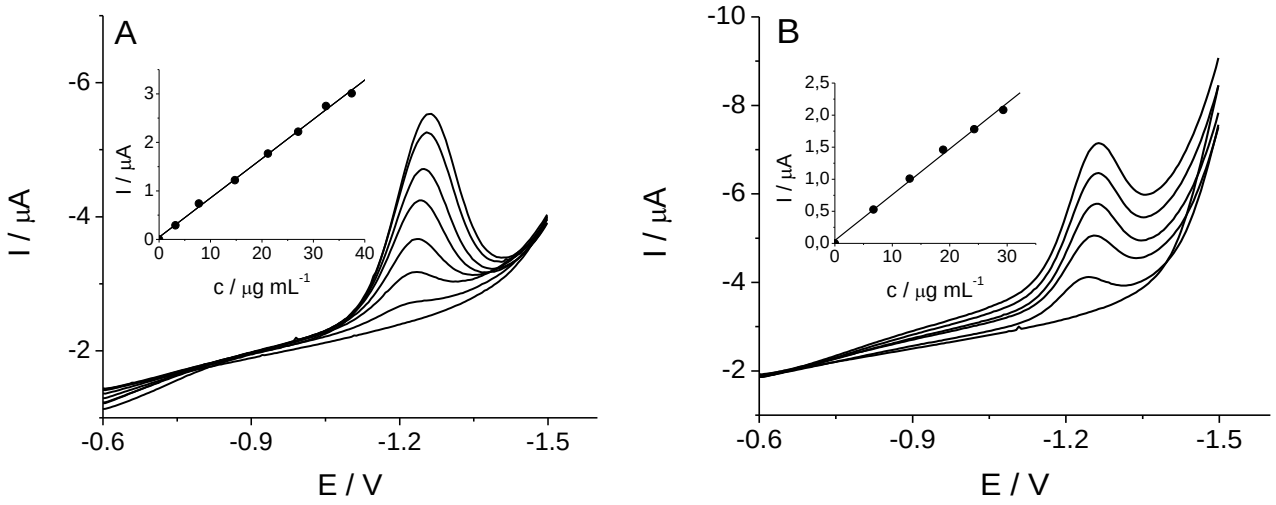

Figure 4. Differential pulse voltammograms recorded at the TCP-CPE for different concentrations of *Clo* (A) and *Nit* (B) at pH 7.0 together with the corresponding calibration plots.

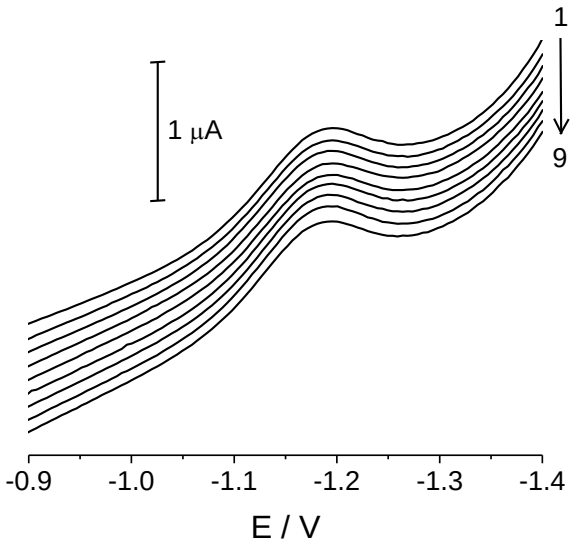

Figure 5. The reproducibility of the analytical signal of *Clo* in model solution at TCP-CPE at the concentration level of 7.73 μg mL^{-1}.

Under the optimal conditions, there is a linear relationship between the reduction peak height and neonicotinoid concentration over the range of 2.70−37.45 and 2.51−29.33 μg mL^{-1} for *Clo* and *Nit*, respectively (Fig. 4). The reproducibility of the proposed method was checked at relatively low concentration level (7.73 μg mL^{-1} for *Clo* (Fig. 5) and 6.72 μg mL^{-1} for *Nit*). The relative standard deviations (RSD) were 1.9 and 0.83%, respectively. The analytical parameters for the DPV determination of *Clo*, *Nit* and also for *Imc* [17] are summarized in Table 1.The detailed procedure of determination of *Imc* at TCP-CPE was given earlier [17]. A linear relationship between the reduction peak height and *Imc* concentration was obtained over the range of 1.73−30.0 μg mL^{-1} [17].

Table 1. Analytical parameters for the differential pulse determination of *Clo*, *Nit* and *Imc* at TCP-CPE. *r*: linear regression coefficient; LOD: limit of detection; LOQ: limit of quantitation.

Parameter	Compound		
	Clo	*Nit*	*Imi* [17]
Concentration interval [μg mL^{-1}]	2.70−37.45	2.51−29.33	1.73−30.0
Intercept [μA]	–0.0308	0.0452	–0.0769
Slope [μA mL μg^{-1}]	0.0803	0.0714	0.1268
r	0.999	0.998	0.999
LOD [μg mL^{-1}]	0.81	0.75	0.52
LOQ [μg mL^{-1}]	2.70	2.51	1.73
RSD [%] (*n* = 9)	1.9	0.83	1.4

3.2. Voltammetric monitoring of the photodegradation of Nit, Imc and Clo by using TCP-CPE

In this study, an attempt was made to use of the developed DPV method using TCP-CPE for the monitoring of the concentration changes of *Imc*, *Clo* and *Nit* during their photolytic and TiO_2-assisted photocatalytic degradation.

Herein, one should take into account that, during the photodegradation of the neonicotinoids, the pH can change significantly because of the acid formation [2, 24, 25]. Because of the high pH-dependence of the analytical signals it is necessary to adjust the pH of the investigated samples to the optimal value (pH 7.0) before analysis. Further on, the unfavorable adsorption of TiO_2 catalyst onto the electrode surface had to be considered. The experiments have shown that the addition of the BRB (pH 7.0) at a relatively high concentration causes the precipitation of the catalyst, thus hindering its adsorption onto the electrode surface. Thus, all measurements were performed in such dispersions, without filtering. The samples, prepared in this way (and described under “Procedures” section) were analysed directly after pH-adjusting.

As can be seen from the corresponding DPV signals and a kinetic curve in Fig. 6A, *Nit* decomposes rapidly in consequence of photolysis. It was found out that all the content of *Nit* disappeared after less than two weeks. In comparison to that, the photocatalytic degradation (Fig. 6B) is much faster – *Nit* could be degraded in less than three days. As seen from the corresponding

voltammograms, no electrochemical interferences occurred during the analysis, so it is assumed that the formation of the nitro group-containing intermediates was negligible.

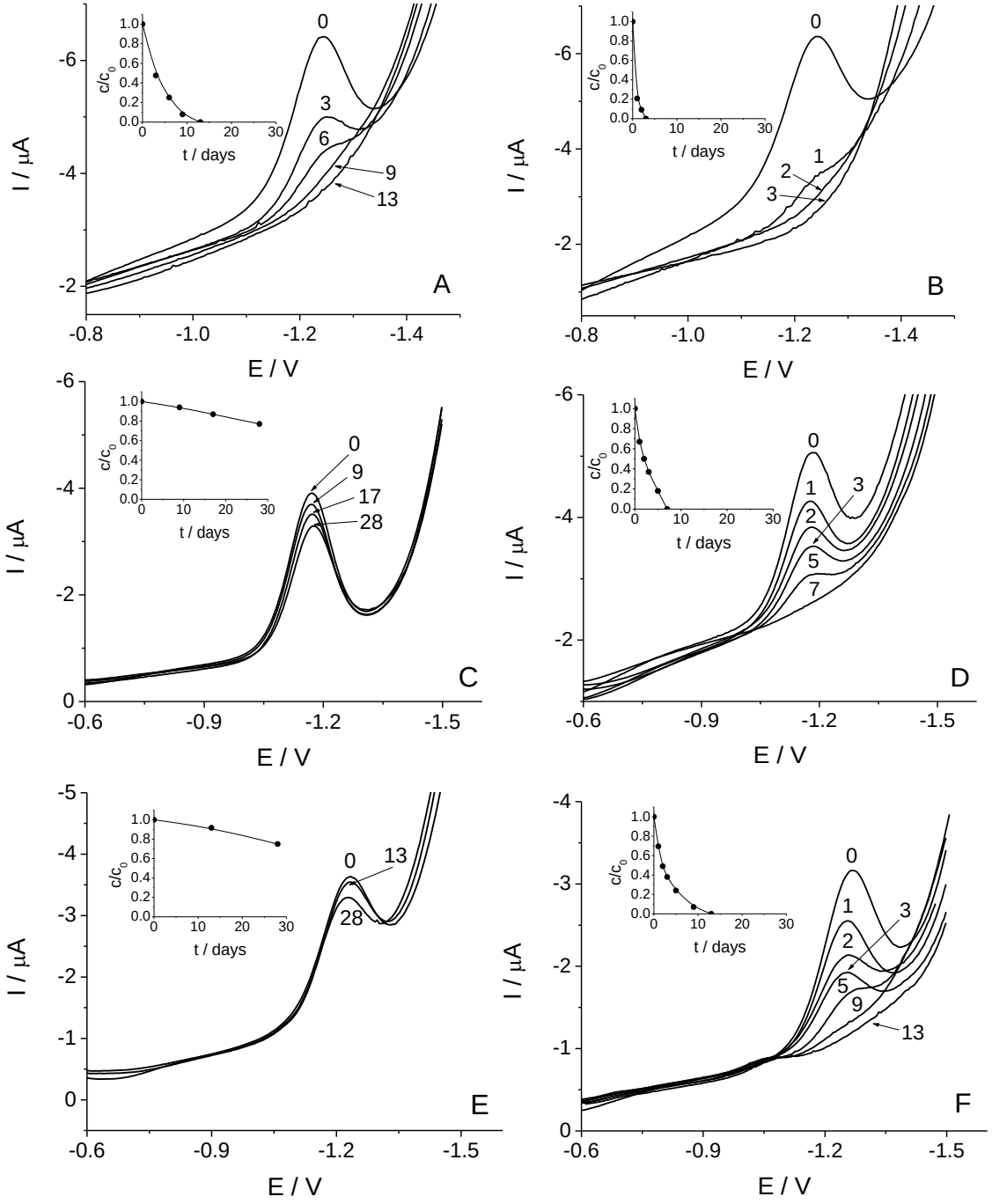

Figure 6. Differential pulse voltammetric monitoring of the photolytic (A, C, E) and photocatalytic (B, D, F) degradation of *Nit* (A, B), *Imc* (C, D) and *Clo* (E, F) together with corresponding kinetic curves; c(*Nit*) = 108.29 µg mL^{-1}, c(*Imc*) = 102.26 µg mL^{-1}, and c(*Clo*) = 99.87 µg mL^{-1}. Numbers on DPV curves indicate the days of the sampling.

The rate of the photolytic and photocatalytic decomposition of *Nit* followed first order and pseudo-first order kinetics, respectively (Fig. 7, lines 1,2). The corresponding rate constants for photolytic (k) and photocatalytic (k_{ap}) degradation obtained by DPV were in very good agreement with the data of the comparative HPLC/DAD method (Table 2).

In the case of *Imc* and *Clo*, approximately the 24% of the parent compound disappeared after one month of insolation (photolysis) (Figs. 6C,E). In the presence of TiO_2, the degradation became much faster, and *Imc* and *Clo* disappeared after less than two weeks (Figs. 6D,F), approximately 4 times slower then *Nit*. Similarly to *Nit*, the photolysis of *Imc* and *Clo* followed the first-order kinetics, while the photocatalysis pseudo-first order kinetics (Fig. 7, lines 3-6). Finally, as it is evident from Fig. 6F, during the photocatalytic degradation of *Clo*, a small signal of an electroactive intermediate appears at potential of –1.05 V. This potential is quite different from that for the reduction of *Clo*, being –1.26 V. In that way, it was possible to monitor the concentration changes of the parent compound in the presence of the electroactive degradation product. Similarly to the degradation of *Nit*, the comparative HPLC/DAD assay with *Imc* and *Clo* showed very similar kinetic data to the DPV measurements, confirming the fine performance of the voltammetric method proposed here for the monitoring of the photodegradation of *Nit*, *Imc*, and *Clo*.

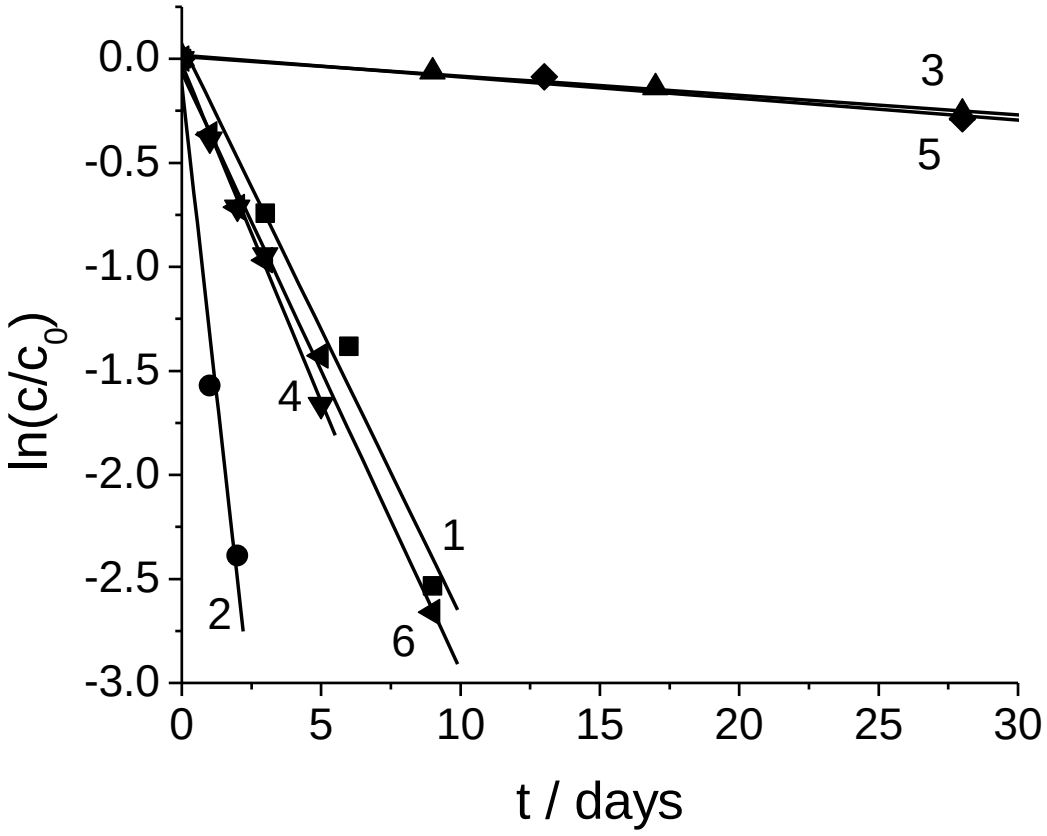

Figure 7. Comparison of the kinetics of the photolytic (1, 3, 5) and photocatalytic (2, 4, 6) degradation of *Nit* (1, 2), *Imc* (3, 4) and *Clo* (5, 6) monitored by DPV method. c(*Nit*) = 108.29 μg mL^{-1}, c(*Imc*) = 102.26 μg mL^{-1}, and c(*Clo*) = 99.87 μg mL^{-1}.

Table 2. Kinetic parameters obtained during differential pulse voltammetric and HPLC/DAD monitoring of photolytic and photocatalytic degradation of *Nit*, *Imc*, and *Clo*; c(*Nit*) = 108.29 μg mL^{-1}, c(*Imc*) = 102.26 μg mL^{-1}, and c(*Clo*) = 99.87 μg mL^{-1}. *r*: linear regression coefficient.

Kinetic parameters	Method	Compound		
		Nit	*Clo*	*Imi*
k_{ap} [1/day]	DPV	–1.19	–0.29	–0.32
		r = –0.984	*r* = –0.998	*r* = –0.998
	HPLC/DAD	–1.24	–0.31	–0.34
		r = –0.985	*r* = –0.995	*r* = –0.999
k [1/day]	DPV	–0.27	–0.0106	–0.0088
		r = –0.991	*r* = –0.977	*r* = –0.992
	HPLC/DAD	–0.26	–0.0104	–0.0094
		r = –0.997	*r* = –0.983	*r* = –0.994

4. CONCLUSION

It can be stated that the study described above has demonstrated the applicability of CPEs in combination with the (direct) cathodic voltammetry of the neonicotinoids *Clo* and *Nit*. The sensitivity of the voltammetric procedure was found to depend considerably upon the carbon paste mixture used, when the TCP-CPE type has exhibited better electroanalytical performance than SO-CPE with respect to the overall signal-to-moise characteristics for both insecticides analysed. Then, the DPV with the TCP-CPE in BRB (pH 7.0) has been found to be fairly applicable for the determination of both insecticides with the linear response within the concentration range of 2.70-37.45 *Clo* and 2.51-29.33 μg mL^{-1} *Nit* with the LOQ of 2.70 and 2.51 μg mL^{-1}, respectively.

Moreover, the voltammetric procedure with the TCP-CPE was also found to be effective for the monitoring of the concentration changes of *Imc*, *Clo* and *Nit* during their photolytic and TiO_2-assisted photocatalytic degradation. To the authors' knowledge, the method described herein is the first application of a CPE in electrochemical monitoring of the photodegradation process of commercially available and widely used organic pollutants.

Although commonly used chromatographic analyses provide undoubtedly richer information about the system examined, the voltammetric alternative with the TCP-CPE detection unit offers a rapid, simple, and inexpensive tool applicable to the basic screening and capable of quickly obtaining the actual concentration profile(s) of the insecticide(s) transformed during the photodegradation process.

ACKNOWLEDGEMENTS

Authors acknowledge financial support of the Ministry of Education and Science (Project No. 172012 and 172059), the Secretariat for Science and Technological Development of AP Vojvodina, Republic of Serbia (Grants No. 114-451-02011/2007-02) and CEEPUS II network (CII-CZ-0212-04-1011). The Czech authors would like to thank the financial support from the Czech Ministry of Education, Youth, and Sports (projects LC 06035 and MSM0021627502).

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