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Electrooxidation of thiourea and its square-wave voltammetric determination using pencil graphite electrode

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Abstract

The electrochemical properties of thiourea (TU) were investigated in pH range 2.0–12.0 by cyclic and square-wave voltammetry. The compound was irreversibly oxidized at a pencil graphite electrode in one or two oxidation steps which are pH-dependent. Based on the voltammetric peak for the second oxidation process of TU in phosphate buffer at pH 12.0, a square-wave voltammetric method was proposed for the determination of the compound in the range 6.3–30 μм, with a detection limit of 1.29 μм. The applicability to direct assays of wastewaters was also tested.

Keywords: cyclic voltammetry; pencil graphite electrode; square-wave voltammetry; thiourea; wastewater.

Introduction

Thiourea (TU) [$(H_2N)_2CS$)], together with its derivatives, is of great importance for various industrial applications such as rubber vulcanization (Puig et al. 1996), electrodeposition of copper and other metals (Fabricius et al. 1996, Juarez and Dutra 2000, De Oliveira and Carlos 2009), corrosion inhibitors (Gassa et al. 2002, Kuang et al. 2009), and also in agricultural industry as fungicides, herbicides and rodenticides (Perez-Ruiz et al. 1995, Ahmed 2001). It has also been used in the production of industrial cleaning agents (e.g., for photographic tanks, metal surfaces in general), pharmaceuticals (sulfathiazoles, thiouracils, tetramisole and cephalosporins), textile and dyeing auxiliaries, and synthetic resins (Xu et al. 1987, Arifoglu et al. 1992, Guibal et al. 2000, Hilson and Monhemius 2006).

TU and its derivatives can be regarded as representative sulfur-containing pollutants of soil and water, with toxic effects especially for nitrifying bacteria. Normally, it is not present in wastewater; however, it can become a serious problem for industrial wastewater treatment plants which utilizes the bacterial nitrification/denitrification process, especially when the wastewater comes from the industrial complexes. When its concentration of 76 μg l^{-1} is exceeded, nitrification bacteria are not able to degrade the ammonia to nitric acid and release of ammonia into the environment occurs (Raffaelli et al. 1997). Because of the absence of legal regulation limits for TU in wastewaters, the producers of TU-containing wastewater try to reduce its concentration below 1 mg l^{-1} (Rethmeier et al. 2001). Therefore, a fast and reliable method for the determination of TU in wastewater is strongly needed to keep this bacterial inhibitor under control (Raffaelli et al. 1997). Its high solubility in water and practically insolubility in nonpolar organic solvents make its extraction (e.g., solid-phase extraction) impossible. Moreover, most of the liquid chromatographic methods require organic eluents or have the disadvantage of long retention times. TU is relatively unvolatile and is not easily analyzed by gas chromatography, at least using common apparatus and columns. As an alternative, colorimetric methods are available but most of these are time-consuming or require toxic chemicals. However, it needs to be noted that few methods including spectrophotometry (Abbasi et al. 2009), reversed-phase high-performance liquid chromatography (Rethmeier et al. 2001) and atmospheric pressure ionization tandem mass spectrometry (Raffaelli et al. 1997) have allowed for the trace analysis of TU in wastewater, detection limits of 20, 2 and 1 μg l^{-1} being reported, respectively.

The electrochemistry of TU involves one or two electrooxidation processes at solid electrodes in aqueous media, depending on the oxidation conditions such as electrode material, the solution pH, and the applied potential. Its adsorption and oxidation on various electrode systems have been intensively studied in acidic media using electrochemical and spectroscopic techniques (Zakharov et al. 1971, Kirchnerova and Purdy 1981, Yan et al. 1996, Alodan and Smyrl 1998, Bolzán et al. 1999, 2001a,b, Zhang et al. 2001, Renner and Liddell 2002, Bolzán et al. 2004, Ghanem et al. 2006), whereas voltammetric experiments in alkaline media have been specifically performed for platinum, gold, silver and copper electrodes (Hepel and Bruckenstein 1987, Vandeberg and Johnson 1993, Lee et al. 1994, Lee and Yeo 2001, Manea et al. 2006). To the best of our knowledge, there is little information about the redox behavior of TU in alkaline media on carbon-based electrodes (Tulyupa and Losev 1986, Spataru et al. 2005).

From the electroanalytical point of view, few studies have been made on this compound. This is mainly because the use of noble metal electrodes for most sulfur compounds is limited because of the loss of electrode activity caused by accumulation of sulfurous adsorbates and surface oxides (Polta and Johnson 1986). Nevertheless, the alumina modified platinum electrode has been used for the determination of TU in real samples within the concentration range of 1.9–228 mg l^{-1} (Nematollahi and Rafiee 2003). In an early report, the use of glassy carbon (GC) and other carbon materials was demonstrated by linear sweep voltammetry and TU could be determined from concentrated acids to solutions of pH 5.0 (Kirchnerova and Purdy 1980). It has been shown that graphite electrodes can be used in the range of 1.0–30.0 mg l^{-1} for determining TU in solutions of copper refinery electrolytes (Akeneev et al. 2005). Recently, the oxidation of TU at boron-doped diamond (BDD) electrode was investigated in acidic, neutral and alkaline media. Based on the anodic peak for the first oxidation step in acidic media, a voltammetric method was proposed for TU determination in the range of 0.31–76.1 mg l^{-1} (Spataru et al. 2005). Amperometric determinations of TU were also successfully carried out on platinum and gold electrodes (Polta and Johnson 1986, Vandeberg et al. 1992, Lee et al. 1994, Lee and Yeo 2001, Akeneev et al. 2005), and copper oxide-copper electrode (Manea et al. 2006). By contrast, mercury electrodes allowed the use of differential pulse polarography (Smyth and Osteryoung 1977) and adsorptive stripping voltammetry (Starà and Kopanika 1984) for trace determination of TU in urine, with detection limits of 1 μg l^{-1} and 2.5 ng l^{-1}, respectively.

This paper, to our knowledge, is the first report on the possibility of determination of TU in wastewater coming from the sewage system by a voltammetric technique, after having made a more detailed study of the electrochemical oxidation of this compound (especially in alkaline media) over previously reported studies. The proposed method is based on the use of renewable and minimal cost pencil graphite (PG) electrode. PG electrode, a relatively new type of carbon electrode, has been the focus of great interest, especially in the field of sensitive and simple monitoring of toxic compounds, owing to its outstanding electrochemical features: high electrochemical reactivity, good mechanical rigidity, low cost, low technology and ease of modification. In the both economic and environmental sense, PG electrode, as disposable after use, in combination with field-based experiments can be much more attractive than the electrodes commonly used in the laboratory because of avoiding the need for extensive time delays, and considerable risk of contamination or loss of analyte of interest (Bond et al. 1997).

Materials and methods

Reagents and chemicals

Thiourea (TU, 99.9%) was from Sigma (Germany) and was used as received. TU stock solutions of 1 mg ml^{-1} (ca. 13 mM) were prepared in water and stored under refrigeration. All other chemicals (analytical grade) were obtained from Sigma or Aldrich (Germany). Four supporting electrolytes, namely acetate (0.1 M, pH 4.8), phosphate (0.1 M, 3.0 and 12.0), Britton-Robinson (0.1 M, pH 2.0, 6.0 and 9.0) and Tris (0.1 M, pH 7.0) buffer solutions containing 20 mM NaCl were used for preparing TU standard solutions.

Ultra pure water, purified by a Milli-Q system from Millipore (France), was used to prepare the solutions. All experiments were carried out at room temperature of the laboratory.

Apparatus

Electrochemical measurements were performed using a μAutolab type III electrochemical system (EcoChemie, The Netherlands) driven by a GPES software version 4.9 in connection with a personal computer. The raw voltammograms of differential pulse voltammetry (DPV) and square-wave voltammetry (SWV) were treated using Savitzky and Golay filter (level 2) and a moving average baseline correction (peak width: 0.01 V) of the GPES software. The electrode system consisted of a PG working electrode, an Ag/AgCl/3M NaCl reference electrode (Model RE-1, BAS, USA), and a platinum wire counter electrode. The pH values of solutions were measured using a WTW inoLab pH 720 m with a combined electrode (glass-reference electrodes).

The preparation of PG electrode has been described in the study of Wang et al. (2000). In brief, a Rotring® Pencil Model T 0.5 (Germany) was used as a holder for pencil leads (Tombo, Japan), which were purchased from a local bookstore. All leads had a total length of 60 mm and a diameter of 0.5 mm. Electrical contact to the lead was achieved by wrapping a metallic wire around the metallic part of the pencil. A total of 10 mm of lead was immersed in solution per measurement. Such length corresponds to an active electrode area of 15.9 mm^2. PG electrode surface was pretreated by applying a potential of +1.30 V for 30 s (in the case of cyclic voltammetric studies, +1.6 V for 60 s) in the blank supporting electrolyte without stirring, in order to increase the hydrophilic properties of the electrode surface through introduction of oxygenated functionalities, accomplished with oxidative cleaning. Each measurement was performed using a new pencil surface in a home-made 5-ml glass cell containing 4 ml of solution.

Procedure for real samples analysis

Wastewater samples were collected from the Sewage System of Yüzüncü Yıl University, Van, Turkey. All samples were filtered through filter paper (Whatman, No. 42) and stored in a refrigerator until used. Appropriate volume (1 ml) of the clear filtrate was transferred to voltammetric cell containing phosphate buffer (pH 12.0) and analyzed following the recommended procedure.

Results and discussion

This article is a part of our continuing studies on the electrochemical oxidation and determination of toxic compounds in the environment using PG electrode. The voltammetry of nicotine, 7,12-dimethylbenz[*a*]anthracene and benzo[*a*]pyrene has been described in very recent studies of our group (Levent et al. 2009, Keskin et al. 2010, Yardım et al. 2010).

Electrochemical behavior of TU on the PG electrode

Figure 1 shows the cyclic voltammograms of 1.3 mM TU solutions in a broad pH range (pH 2–12) at a scan rate of 100 mV s^{-1}. The voltammogram recorded at pH 2 within the potential range of 0 V to +1.6 V exhibits a broad and

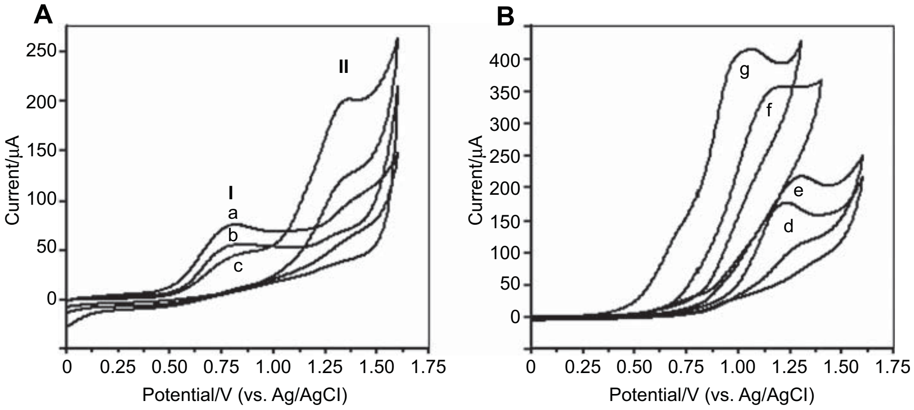

Figure 1 Cyclic voltammograms at different pH values. (A) (a) Britton-Robinson buffer pH 2.0, (b) phosphate buffer pH 3.0, (c) acetate buffer pH 4.8. (B) (d) Britton-Robinson buffer pH 6.0, (e) Tris buffer pH 7.0, (f) Britton-Robinson buffer pH 9.0, and (g) phosphate buffer pH 12.0. TU concentration, 1.31 mM; scan rate, 100 mV s^{-1}.

well-defined oxidation peak (denoted as I) at +0.75 V (Figure 1A, curve a). The compound could be further oxidized at higher potentials. However, the presence of the secondary process (presented as II) in the range of 1.25–1.50 V was less distinct, indicating that PG electrode behaves in a way similar to a GC electrode, in terms of the oxidation of TU in acidic media (Kirchnerova and Purdy 1981). However, the second oxidation step observed became more pronounced at BDD electrode (Spataru et al. 2005). It should be noted that this oxidation process occurred at approximately the same potential for both PG electrode and BDD electrode, whereas at PG electrode the first wave took place at approximately 250 mV more negative potential than that observed for BDD electrode. This was not surprising because the oxidation processes of sulfur-containing compounds (owing to their poor adsorption) require higher overpotentials at the diamond surface, compared to other carbon electrodes (Spataru et al. 2001, 2005). In the case of the graphite electrode, TU is oxidized giving only one anodic wave (Zakharov et al. 1973). The authors explained that the absence of the second wave resulted from the lack of adsorbed oxygen on this electrode.

At pH 3 the oxidation of TU exhibits similar behavior, although the height of both anodic peaks decreased (Figure 1A, curve b). In the solution pH of approximately 5, peak I became less evident, whereas the height of peak II was increased (Figure 1A, curve c). It was observed that peak I almost disappeared at pH values higher than approximately 5.0 (Figure 1B). Increasing the pH value up to 12.0 resulted in a cathodic shift of peak potential for peak II (except at pH 6.0).

The repetitive cyclic voltammogram of TU in phosphate buffer at pH 12 (most suitable media for analytical purposes) is presented in Figure 2. It is seen to be low background current of PG electrode in spite of clays and polymers present in pencil graphite.

Cyclic voltammetry revealed the absence of reverse waves within the potential range studied even if the scan rate was increased to 750 mV s^{-1}, thereby indicating an irreversible electrode process.

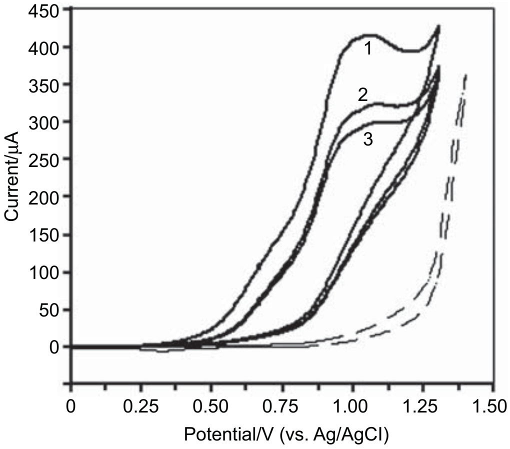

Figure 2 Multisweep cyclic voltammogram in phosphate buffer pH 12.0 in the absence (dashed line) and presence (solid line) of 1.31 mM TU. Scan rate: 100 mV s^{-1}; potential range: between 0 and +1.3 V. The numbers indicate the number of scans.

The effect of potential scan rate between 10 and 750 mV s^{-1} on the peak current and the peak potential of TU was also evaluated in phosphate buffer (pH 12.0). The anodic shifts in the peak potential of peak II together with the absence of cathodic wave confirmed the irreversibility of the oxidation process. A plot of logarithm of peak current vs. logarithm of scan rate gave a straight line with a slope of 0.56 (correlation coefficient: 0.996). The slope means that the process is predominantly controlled by diffusion, although it is partially coupled to weak adsorption in the whole scan rate range studied. Furthermore, a linear dependence of the peak current on the square root of the scan rate (correlation coefficient: 0.997) was found, demonstrating a diffusional behavior.

Although elucidating the mechanism of TU electrochemical oxidation is beyond the aim of this study, a short comment can be made. Considering previously reported data (Kirchnerova and Purdy 1981, Spataru et al. 2005) and results from our study, we can assume that the initial oxidation step (peak I) could be due to the one-electron transfer to yield $[(H_2N)_2(H_2N)_2C_2S_2]^{2+}$ dimer ion, *C,C′*-dithiodiformamidinium ion, through the formation of $[(H_2N)_2CS^{-}]^{+}$, TU-corresponding radical ion. The reaction pathway for this step can be written as follows:

$(H_2N)_2CS \rightarrow [(H_2N)_2CS^{-}]^{+}+e$
$2[(H_2N)_2CS^{-}]^{+} \rightarrow [(H_2N)_2(H_2N)_2C_2S_2]^{2+}$

The point concerning the peak II, which follows the initial oxidation of TU, is not yet completely clear. The studies of the electrooxidation taken place at more positive potentials revealed that the first electrooxidation product of this step has been described as diprotonated sulfenic acid (Kirchnerova and Purdy 1981), according to the reaction:

$[(H_2N)_2CS^{-}]^{+}+H_2O \rightarrow [(H_2N)_2CSOH_2]^{2+}+e^{-}$

that further decomposes, yielding a variety of products (including oxidation products) by a series of chemical and additional electrochemical steps depending on the experimental conditions (e.g., solution pH, applied potential and electrode material) (Kirchnerova and Purdy 1981, Yan et al. 1996; Garcia et al. 2006, Feng et al. 2008). According to the previous suggestions, a possible explanation could be provided by the fact that at higher potentials TU-corresponding radical ion is consumed both by dimerization and by reacting with water.

Proposed analytical method

To develop a voltammetric methodology for determining TU, square-wave (SW) mode, in connection with the moving average baseline correction approach, was selected because of the virtue of reducing the charging current to a maximum extent and increasing the sensitivity effectively. For the second oxidation step, the study of the effect of pH on the SW voltammograms within the pH range from 6.0 to 12.0 showed that the peak intensities reached a maximum at pH 12.0, as illustrated in Figure 3. Phosphate and Britton-Robinson buffer solutions yielded approximately the same results at the same pH; however, phosphate buffer was selected for further study because it not only gave the highest peak current but also gave the best peak shape. By contrast, the poorly resolved signal was obtained for the first oxidation step between pH values of 2.0 and 5.0 at low concentration of TU even in strong acidic media (data not shown). By considering the voltammetric peak for the second step of TU oxidation, unlike BDD electrode (Spataru et al. 2005), the SW voltammogram technique was applied in phosphate buffer at pH 12.0 for the remainder of the study.

The SWV parameters such as the frequency, step potential and pulse amplitude were evaluated and optimized. The dependence of the peak current on the frequency was studied between 10 and 120 Hz. The peak currents increased with frequency owing to the increase in the effective scan rate but the peak shape and baseline were distorted at frequencies higher than 50 Hz. This was attributed to the greater contribution of the capacitive current at higher frequencies. When the step potential was varied between 2 and 24 mV, a decrease in peak current was observed above 14 mV. Pulse amplitude was examined in the range from 5 to 60 mV. Peak currents increased with an increase in SW amplitude from 5 to 60 mV. However, the peak shape became wider at higher than 20 mV. Thus, the frequency of 50 Hz, the step potential of 14 mV and the pulse amplitude of 20 mV were selected for all subsequent studies.

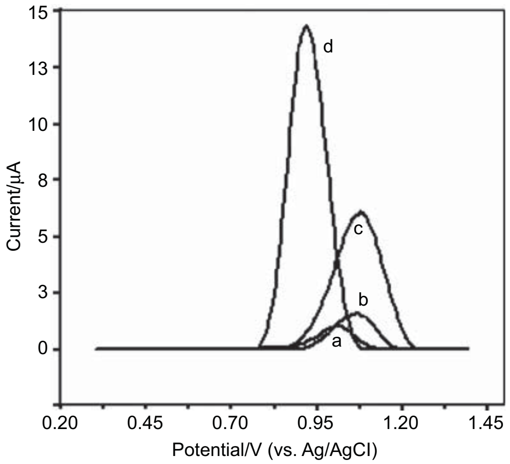

Figure 3 SW voltammograms at different pH values: (a) Britton-Robinson buffer pH 6.0, (b) Tris buffer pH 7.0, (c) Britton-Robinson buffer pH 9.0, and (d) phosphate buffer pH 12.0. TU concentration: 65.5 µM. SWV conditions: pulse amplitude, 25 mV, frequency, 25 Hz, step potential, 8 mV.

Under the optimum experimental conditions, the peak current at approximately +0.95 V varied linearly with TU concentration in the range of 6.3–30 µM (0.48–2.28 mg l^{-1}) and fitted the equation: i_p=0.359 C-1.231 with a correlation coefficient of 0.997, where i_p is peak current in µA and C is TU concentration in µM. Figure 4 presents SW voltammograms of TU in various concentrations and the insert shows the corresponding calibration plot. A variation of the TU concentration was found to have a slight influence on the peak potential. The peak potential shifted towards more negative values when the concentration was increased.

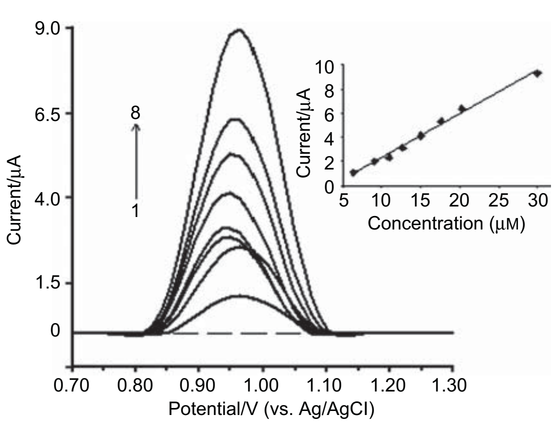

Figure 4 Successive additions of TU in phosphate buffer (pH 12.0) containing 20 mM NaCl. TU concentration: from 6.3 to 30 µM (1–8). Dashed line represents background current. Inset: the corresponding calibration plot. For operating conditions, see the text.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the following equations (Ermer and Miller 2005):

LOD=3 *s/m*; LOQ=10 *s/m*,

where *s* is the standard deviation of the peak current (three runs) of the concentration of the linearity range (15 μM) and *m* is the slope of the related calibration equation. LOD and LOQ were calculated as 1.29 μM (98.2 μg l^{-1}) and 4.3 μM (0.33 mg l^{-1}), respectively.

Although the linearity ranges of calibration plots could be expanded to approximately 30 times higher concentrations by the use of BDD electrode (Spataru et al. 2005), there is no significant difference between the analytical performances of PG and BDD electrodes, in terms of low concentration of the calibration curve (in micromolar concentration).

The precision of the method was established by repeated assays (n=13) using 15 μM solution of TU. The relative standard deviation was 3.48%.

To evaluate the selectivity of the proposed method, the influence of selected potential interfering compounds such as metal ions and organic molecules, which could accompany TU in real samples, was examined by analyzing synthetic sample solutions containing 15 μM of TU and various excess amounts of these species. At a 10-fold excess, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, CH_3COO^-, saccharin did not significantly influence the height of the peak currents, whereas Fe^{2+}, Fe^{3+}, Cu^{2+} and uric acid seriously interfered with TU assay at PG electrode. The peak heights were suppressed by ~50% and ~70% in the presence of uric acid and Cu^{2+}, respectively. Interference due to surfactants such as Tween 20 (nonionic), sodium dodecylsulfate (anionic) and hexadecyltrimethylammonium bromide (cationic) was also tested. At an approximately 35-fold excess, the peak heights decreased to ~70% of the initial value by the proposed method when nonionic was added to the sample solution, and almost disappeared with addition of anionic and cationic surfactants.

Because there is great interest in the monitoring of TU in wastewaters and in view of the almost adequate levels of the LOD of the proposed method (98.2 μg l^{-1}) and the toxicity limit (76 μg l^{-1}), the next step was to see if the proposed voltammetric method at PG electrode would also work in this rather complex medium. The samples were collected from the Sewage System of Yüzüncü Yıl University, Van, Turkey. No signal for TU was observed when the samples were analyzed by using the method described above, thus samples were spiked with known amounts of TU standard solutions. TU peaks were clearly displayed for reanalyzed spiked wastewater samples. Recovery of TU was calculated by comparing the concentration obtained from the spiked mixtures with those of the pure TU. The results are summarized in Table 1. Recovery of the spiked TU was also observed to be good in samples.

Table 1 Results obtained for TU analysis from spiked waste water samples.

Spiking concentration (μM)	Measured concentration[a] (μM)	Recovery (%)± RSD (%)
4.5	4.25	94.44±5.19
9.0	10.06	111.77±3.89
13.5	12.90	95.55±2.06

[a] Calculated using the calibration curve. Values reported are the average of three independent analyses of the same sample.

It is important to note that when the other coexisting substances at higher concentrations only change the sensitivity of the method, problems can be partially solved by using the standard addition method. However, the presence of TU at very low levels in real samples can be completely masked by the large number of other components present. In this case, it could require a minimal sample pretreatment, such as the addition of some reagents to eliminate the matrix effect.

Conclusion

The developed SWV procedure at PG electrode provides a convenient and efficient method for the assay of TU, which avoids the time-consuming multiple extraction and organic solvent consumed. It was found that the voltammetric response in alkaline media is suitable for analytical application. The possibility of applying the proposed method for the determination of TU in wastewaters was also tested. Because the maintenance of the inexpensive and renewable PG electrode in the field is easy, it is foreseen that such a method could be a key step to detect TU in environmentally important matrices by field-based voltammetry. The proposed voltammetric method for TU determination could also be useful in many different applications such as TU-containing pesticides, fruit juices, solutions used in leaching experiments, bleaching and toning solutions in photography.

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