Electrochemical sensor for thiourea focused on metallurgical applications of copper

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ABSTRACT

A simple and reliable device is presented for the direct monitoring of thiourea in copper electrorefinery baths as a tool for reconditioning of industrial baths, and so reducing its environmental impact. For this purpose, a screen-printed graphite electrode is modified with silver nanoparticles (AgNPs) contained in a polyelectrolyte-surfactant matrix. The AgNPs are able to adsorb the thiourea, improving the sensitivity of the electrode toward this analyte, even in the presence of usual additives (Avitone® and glue). The system allows the determination of thiourea in a range of 1–10 mg/L. A coupled electrochemical and IR analysis is proposed to evaluate the involved mechanism.

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1. Introduction

Thiourea (TU) is strongly linked to the electroplating, electrowinning, and electrorefining of metals, as well as to mining activities. During electrolysis in copper refinement, TU is consumed by reactions with electrolyte components (complexation, hydrolysis, and other reactions), and partially captured by the copper deposit on the cathode. Therefore, the concentration of TU varies continuously [1], with an optimal concentration from 3 to 10 mg/L, depending on the pursued type of deposit. This pushes to find reliable and rapid methods for determining TU contents under production conditions, in order to reduce its consumption and to improve the quality of the cathode deposit [1].

Thiourea is toxic, affects the carbohydrate metabolism and is carcinogenic and potentially allergenic, showing in addition inhibitory effects on nitrification in soils and water [2–5]. For this reason, it has become increasingly important to monitor TU and its derivatives [6]. Thus, appropriate methods for their determination in various media are worthy of development. Several methods for TU determination have been developed, such as Raman [7], FTIR

[8] and UV/Vis spectroscopies [9–12], mass spectrometry [13], and HPLC [14].

The direct oxidation of TU on different electrode surfaces was widely studied. On the one hand, on carbon-based electrodes, such as glassy carbon [15], conductive diamond [16], and graphite [1,17]; on the other, on metal-based electrodes (Cu, Ag, Au, Pt), showing a strong adsorption toward TU before the oxidation process [18–21].

Comparing to other methods, electrochemical techniques have some advantages in the development of sensors for the direct TU determination [22], such as simplicity, rapidity, high selectivity and sensitivity. Among electrochemical methods, thiourea oxidation on copper electrodes in basic medium, or its oxidation on different electrode surfaces (graphite, Au, Pt) in acidic medium, and based on changing of the copper cathode polarization potential, were proposed [1,23,24]. Most of the reported works focused on wastewater samples, determined thiourea at low concentrations and focus on the sample pH [1,6,7,11,13,14,16,22,23].

Recently, silver has begun to show its convenience to determine TU in copper electrorefining baths. Mozaffari et al. [19] used a highly uniform sputtered nanostructured silver film on carbon, obtained with a direct current magnetron sputtering system. Even though the system presents a low detection limit, its sensitivity is limited to control the bath composition. Another strategy was presented by our group using a simpler system that can be easily adapted to mass production of sensors [25], where silver

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nanoparticles were suspended in the presence of a surfactant and mixed with a polyelectrolyte, forming a stable suspension that can be applied on screen-printed graphite electrodes. The system was used on a sample where thiourea acts as a complexing agent, the electrode-solution interface of the AgNPs-modified screen-printed electrodes undergoes significant changes, which can be evaluated by impedance. In leaching baths, thiourea concentration is 1000 times higher than in the copper electrorefining process, where thiourea is used as an additive. Impedance is a very convenient technique when the analyte is not electroactive, for example in electrochemical immunoassays where an electrochemical probe has to be added. However, when its results are employed for quantification, the data require a complex treatment through an equivalent circuit adjustment. On the other hand, in reference [12] it was shown that the experimental conditions during the silver nanoparticules synthesis greatly affected their final characteristics, and their behavior in the presence of thiourea.

In the work presented here, we have reformulated and optimized the synthesis conditions of the AgNPs and the performance of the electrodes, allowing a direct quantification by square wave voltammetry, in this way thiourea can be directly and selectively oxidized and therefore its determination by square wave voltammetry should result in a peak current directly proportional to the analyte concentration, representing a simpler and direct method with focus on industrial applications.

The AgNPs are suspended in a polymer matrix prepared from the interaction between a polyelectrolyte (polyallylamine, PA) and a surfactant (sodium dodecylsulfate, DS) [26,27], and cast on the electrodes. Square wave voltammetry was successfully applied for the sensitive and direct quantification of TU in a Cu electrorefining bath, even in the presence of typical additives used in this industry. Since the particles remain stable, the sensors can be stored and easily transported. Scan rate dependence experiments combined with infrared spectroscopy (polarization modulation-infrared reflection adsorption spectroscopy, PM-IRRAS) were used to explore its response to thiourea and elucidate the involved mechanism.

The direct monitoring of thiourea in hydrometallurgical processes in a suitable concentrations range is demonstrated, which in turn optimizes its use and the reconditioning of baths and reduces its environmental impact.

2. Experimental

2.1. Apparatus and reagents

Silver nitrate (Quimicor), polyvinylpyrrolidone K30 (PVP) (Anedra), copper sulfate (Mallinckrodt), sulfuric acid (Carlo Erba), sodium borohydride (Aldrich) and other compounds were analytical grade reagents, and were used without further purification. Animal bone Glue (USACH) and AVITONE® (Dupont) were industrial grade reagents. All solutions were prepared with 18 MΩ resistivity water. All experiments were performed at room temperature ($25 \pm 2\,°C$). The particles morphology and size, and the agglomeration degree after their incorporation on the electrodes, were reported in a previous work [12]. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical device comprising a μAUTOLAB type III system. The system was run on a PC using GPS software. The SEM images were obtained using a FE-SEM Carl Zeiss NTS-SUPRA 40 at the Advanced Center for Microscopies (CMA, Universidad de Buenos Aires).

Spectroelectrochemical experiments (PM-IRRAS) were performed on a Thermo Nicolet 8700 (Nicolet) spectrometer equipped with a custom made external tabletop optical mount, a MCT-A

detector (Nicolet), a photoelastic modulator (PEM) (PM-90 with a II/Zs50 ZnSe 50 kHz optical head, Hinds Instruments, Hillsboro, OR), and a Synchronous Sampling Demodulator (GWC Instruments). A custom made Teflon electrochemical cell was coupled to the set-up to acquire in situ IR spectra. The IR window was a 1 inch (25.4 mm) CaF$_2$ equilateral prism (Harrick Scientific Technology). A Pt medal of approximately 1 cm diameter was polished with fine alumina ($0.05\,\mu m$) until mirror like reflection, sonicated in ethanol for 5 min, dried in a N$_2$ flow, ozonized for 15 min and modified with a layer of PA + DS with or without AgNPs. The modified medal was used as the working electrode, a Pt sheet as the counter electrode and an Ag/AgCl electrode as the reference. The potential was modified using a purpose built potentiostat (TeQ). The corresponding potential was applied for 5 min before acquiring each IR spectrum. Measurements were performed in solutions containing 20 mg/L TU and 1 mM H$_2$SO$_4$ in 18 MΩ resistivity water. All potentials were measured and reported with respect to an Ag/AgCl (3 M KCl) reference electrode. The IR spectra were acquired with the PEM set for a half wave retardation at 2200 cm^{-1}. The signal was corrected by the PEM response using a method described by Frey et al. [28]. Typically 1500 scans were performed and the resolution was set for 4 cm^{-1}. The angle of incidence was set to 60. The thickness of the thin layer of the electrolyte between the optical window and the gold electrode was typically set to 2.5 μm. The demodulation technique developed in Corn's laboratory was used in this work [29,30]. The absorbance of surface confined species in PM-IRRA spectra is given by

$$\Delta S = 2 \frac{|I_s - I_p|}{I_s + I_p}$$

where I_s and I_p are the intensities of s- and p-polarized light arriving to the detector.

2.2. Synthesis of silver nanoparticles (AgNPs)

As we previously reported [12], a solution containing polyvinilpyrrolidone (PVP, 20 g/L) and 0.2 M AgNO$_3$ was prepared, as well as a solution of PVP at pH 11 (adjusted with NaOH), containing 0.1 M NaBH$_4$ (molar ratio Ag$^+$:BH$_4^-$ 2:1). 2.5 mL of the AgNO$_3$ solution were placed in a sonic bath during 1 min, after which 2.5 mL of the NaBH$_4$ solution were added without stopping the sonication. A brown dispersion of nanoparticles was obtained with an average size of 20 nm. It was stored in the dark at −18 °C. The AgNPs were used as prepared, without any further surface modification treatment.

2.3. Preparation of sensor electrodes

The used array consisted of one carbon (area = 0.65 cm^2) and one silver screen-printed electrode [31], which were used as working and reference electrodes, respectively. A stainless steel plate (1 cm × 2.5 cm) was used as the counter electrode. For the modification of graphite electrodes, 50 μL of the as prepared nanoparticles dispersion were added to 450 μL of a 1.1% sodium dodecyl sulfate (DS) solution. In a separate vial, a solution of polyallylamine (PA) 0.26% was adjusted with H$_2$SO$_4$ to a final pH of 7. Then, 250 μL of the latter solution were added to the AgNPs-DS suspension. The graphite electrodes were covered with 8 μL of this final suspension and dried at 50 °C for 30 min. Some electrodes were prepared with the PA, without adding NPs to the mixture (i.e., 500 μL of 1% DS + 250 μL of PA at pH 7). The electrodes can be employed a month after their preparation.

Completing the disposable system, silver screen-printed electrodes were treated with commercial bleach (sodium hypochlorite in basic medium, 55 g L^{-1} active chlorine) during 10 min and then rinsed with 18 MΩ resistivity water. The reproducibility and
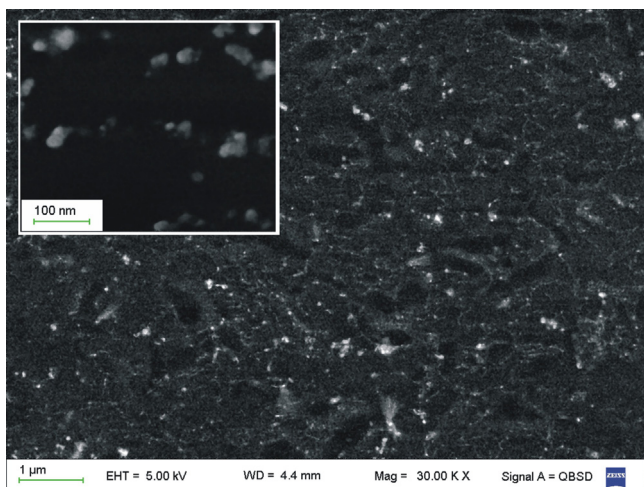
Fig. 1. FE-SEM image of the electrode surface modified with silver nanoparticles (AgNPs) dispersed in the polymeric matrix.

stability of these electrodes were studied and they resulted suitable as pseudo reference electrodes. In this work, all the potentials are stated vs. Ag/AgCl/KCl(3M).

3. Results and discussion

3.1. Sensor construction and response

Even though TU oxidation can be carried out on carbon electrodes [15,17], its sensitivity in the concentration range and pH used in electrorefinery baths is poor. This represents a severe drawback in the construction of sensors based on inexpensive graphite inks. A way to get around this problem is to modify the surface in such a way that a concentration process takes place. It is well known that metals like gold, platinum and silver are able to adsorb thiourea strongly. Based on previous works of our group [12,25], we incorporated AgNPs on screen-printed electrodes using a polyallylamine-dodecylsulfate mixture (PA + DS) as a matrix containing the nanoparticles. Fig. 1 shows a FEG-SEM image of silver nanoparticles (AgNPs) dispersed in the polymeric matrix.

These modified electrodes were tested in simulated copper refinery baths containing 0.65 M $CuSO_4$ (40 g/L Cu), 1.8 M H_2SO_4 (180 g/L), and between 0 and 20 mg/L TU. Cyclic voltammetries were carried out at 10 mV/s, scanning the potential between 0.8 and 1.5 vs. Ag/AgCl. We evaluated the performance of the AgNPs + PA + DS/graphite electrodes against bare graphite electrodes and PA + DS/graphite electrodes. In Fig. 2, the response for different concentrations of TU can be observed. As the bare and PA + DS/graphite electrodes show similar results, for the sake of clarity only results with PA + DS/graphite electrodes are presented for comparative purposes.

In Fig. 2a, the PA + DS/graphite electrode exhibits weak anodic peaks between 0.7 and 1 V for different TU concentrations, a behavior comparable to the reported in acidic media using graphite electrodes [1,17], while in Fig. 2b, the influence of AgNPs is observed showing a significant increase in the current response.

A wide oxidation peak, in the range from 1 to 1.3 V, is consistent with the reported values for different oxidation mechanisms [15,16]. The nature of the environment plays an important role in the oxidation process [15]; in this case, the interaction between TU and the silver nanoparticles contained in the polymer matrix modifies the charge transfer to the electrode, improving the response of the electrode as a thiourea sensor. Fig. 3 shows the current response as a function of TU concentration for PA + DS/graphite electrode,
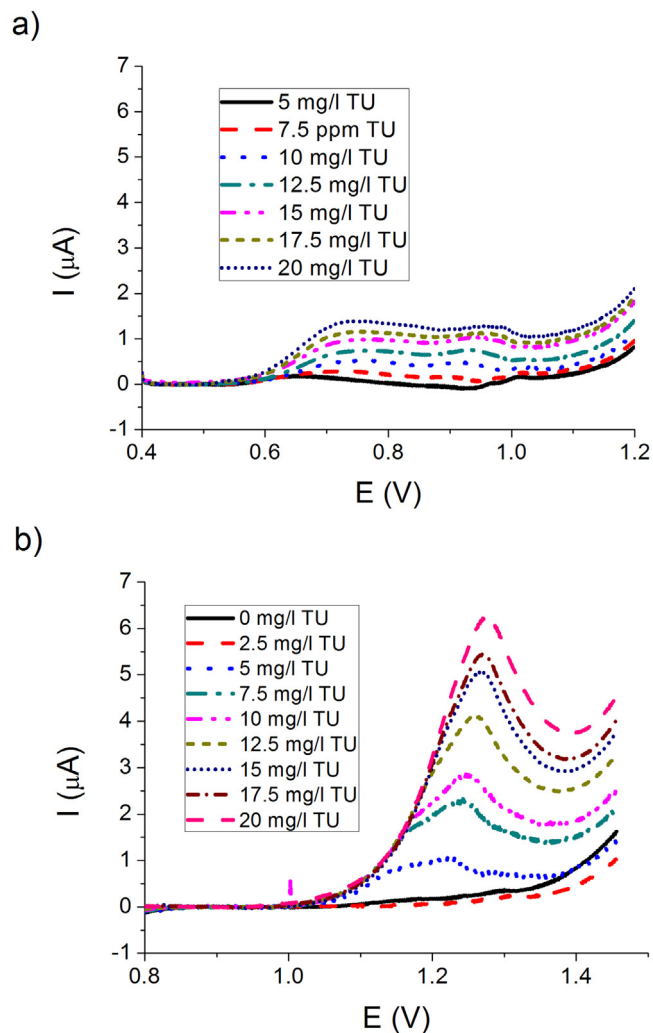

Fig. 2. Voltammograms of solutions (0.65 M $CuSO_4$, 1.8 M H_2SO_4) at different TU concentrations (0 to 20 mg/L in steps of 2.5 mg/L). Electrodes: (a) PA + DS/graphite, (b) PA + DS + AgNPs/graphite. Scan rate: 10 mV/s. All potentials are given vs. Ag/AgCl.
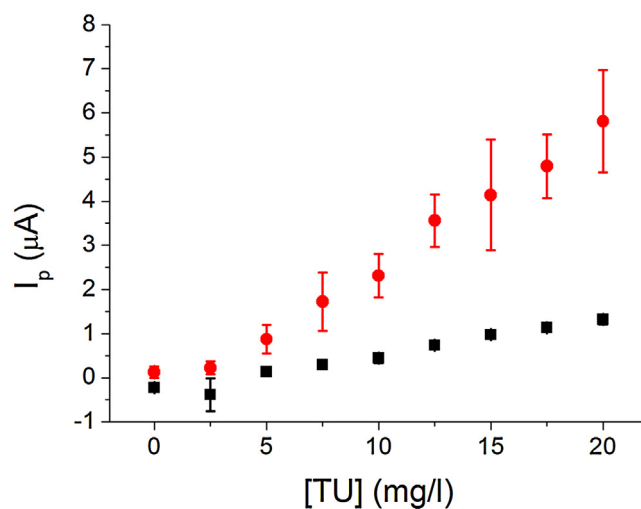

Fig. 3. Current response (I_p) vs. thiourea concentration using the experimental results presented in Fig. 1. Black squares: PA + DS/graphite (at 0.95 V vs. Ag/AgCl); red circles: PA + DS + AgNPs/graphite (at 1.25 V vs. Ag/AgCl). Each determination is the average of three independent electrodes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
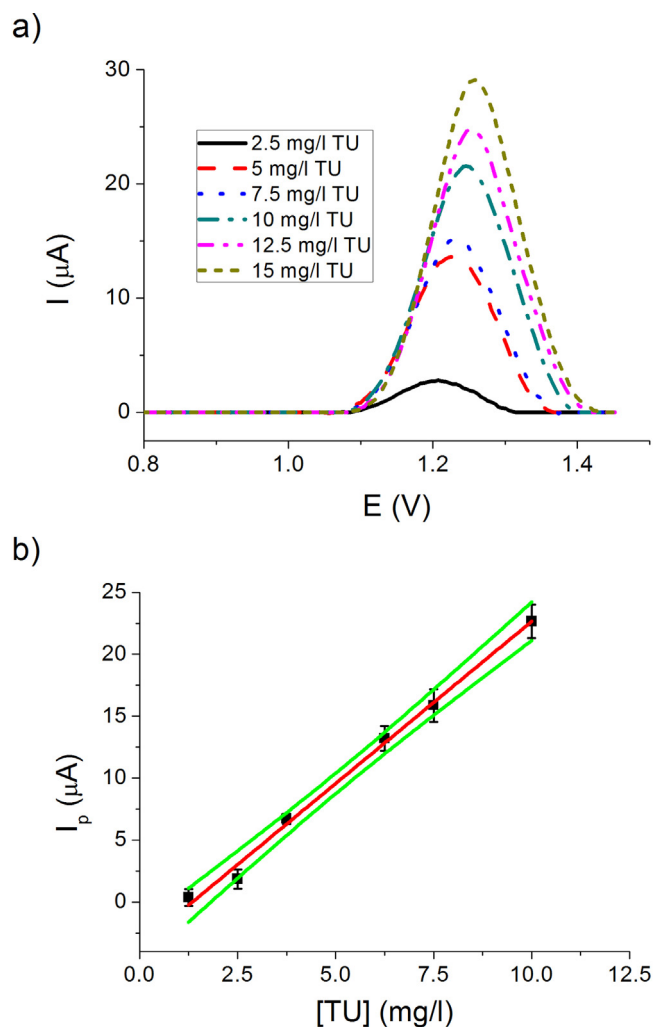
a)

b)

Fig. 4. (a) Square wave voltammetries of TU in simulated electrorefinery baths containing 0.65 M CuSO$_4$ and 1.8 M H$_2$SO$_4$. The electrodes were incubated in the bath for 5 min before the measurements. Frequency: 25 Hz, Step voltage: 5 mV, Amplitude 20 mV. All potentials are given vs. Ag/AgCl, (b) Thiourea calibration curve. Each determination corresponds to the average of three independent measurements at 1.25 V.

measured at 0.95 V vs. Ag/AgCl), and of PA + DS + AgNPs/graphite electrode, measured at 1.25 V vs. Ag/AgCl) yielding in this case a sensitivity of (0.32 ± 0.01) μA L/mg.

To improve the signal generation, measurements by square wave voltammetry (SWV) were performed (Fig. 4a). Modified electrodes were incubated in a copper electrorefinery bath of a given TU concentration during 5 min at open circuit, prior to the measurement. The incubation period is related to the involved mechanism of TU reaction in this system and will be discussed below. Blank experiments carried out in unmodified graphite electrodes, and electrodes modified with a layer of PA + DS, show negligible changes. The optimization of the different variables involved in this technique (frequency: 25 Hz, step voltage: 5 mV; amplitude voltage 20 mV) allows a sensitivity increase up to 8 times yielding a sensitivity of (2.6 ± 0.1) μA L/mg and a detection limit of 1.3 mg/L TU (Fig. 3b). For the calibration line shown in Fig. 4b, each determination corresponds to the average of three independent measurements, error bars represent the standard deviation of each. It can be observed that we obtained a good reproducibility. Also, the standard deviations for three independent measurements were 0.98 and 1.36 μA for 5 and 10 mg/L of TU respectively employing fresh electrodes. With the same batch of electrodes, two
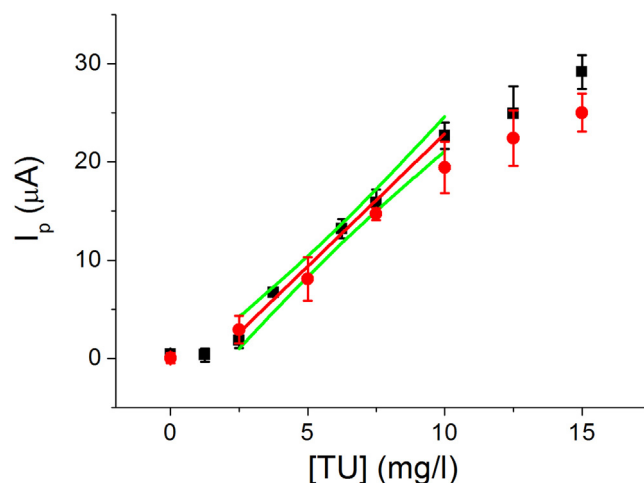

Fig. 5. Comparison of the current response obtained in the presence (red circles) and in the absence (black squares) of additives (Avitone® and glue, each in a concentration of 3 mg/L). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

independent measurements were made at ten day intervals for one month, without significant differences among the results. The standard deviations obtained for the average, including all measurements, were 0.91 and 1.80 μA for 5 and 10 mg/L of TU respectively. These results show that it is possible to employ the electrodes, during a month after their preparation.

The use of SWV results in better baselines and well-defined peaks. Although the linear response range is reduced, the sensor is still useful for use in baths of copper electrorefineries, in contrast to other works (see Table 1), where only a chromatographic method complies with the required linear range [14].

The response of the proposed system to the presence of typical additives (Avitone® and glue, each in a concentration of 3 mg/L) was analyzed (Fig. 5).

It can be observed in Fig. 5 that the presence of these products has a negligible effect on the current response.

3.2. Involved mechanism

Previous works on the electrochemical oxidation of TU on graphite and metal electrodes indicate that TU is adsorbed with different strength on these types of surfaces [1,15–21]. In order to establish the best conditions for the assay, the adsorption process on our system was studied. Cyclic voltammograms at different scan rates were carried out measuring TU directly when the electrode is introduced in the bath or allowing an incubation step of 5 min. The voltammograms were carried out by triplicate, a new electrode and fresh bath were used for each determination. In Fig. 6, the trend for I_p vs. scan rate is presented for both cases. For the direct measurements, without incubation (Fig. 6a), an erratic behavior is observed; while in the case of 5 min incubation (Fig. 6b, black squares), at slow scan rate, a linear trend can be observed, indicating that the oxidation process involves an adsorption step. Also, the magnitude of the current obtained after incubation is larger and more reproducible, for example at 20 mV s^{-1} it practically fourfolds. This indicates that a concentration process is occurring inside the film. This is confirmed by another experiment (Fig. 6b, red circles), in which the electrodes are incubated for 5 min in TU, rinsed, and measured in a bath without TU, showing the same peak currents.

This behavior can be understood taking into account the interactions of TU with the silver nanoparticles, since blank experiments using electrodes modified only with PA + DS do not show this behavior. The observed oxidation process is an irreversible one,

Table 1
Determination of TU in acidic media and/or high ions concentration.

| No	Sensitivity	Linear Range	Tested solution	Detection method	Ref.
1	(33 ± 4) a.u. L/mg	0–1 mg/L	Acidic medium and copper ions	UV–vis	[12]
2	$(41 \pm 4)\,\Omega$ L/g	0.250–1 g/L	Acidic medium and copper ions	EIS	[25]
3	$(0.33 \pm 0.04)\,\mu A$ L/mg	4–4000 μM	Acidic medium	Cyclic voltammetry	[16]
4	–	2–304.5 mg/L	Copper ions	Reversed phase HPLC	[14]
5	–	3–20 g/L	Acidic medium	Raman spectroscopy	[7]
6	(0.07 ± 0.01) peak area L/mg	60–80 mg/L	Acidic medium	FTIR	[32]
7	2.5 arb. units L/mg	0.05–2 mg/L	Acidic medium and copper ions	Cyclic voltammetry	[1]

a)

b)
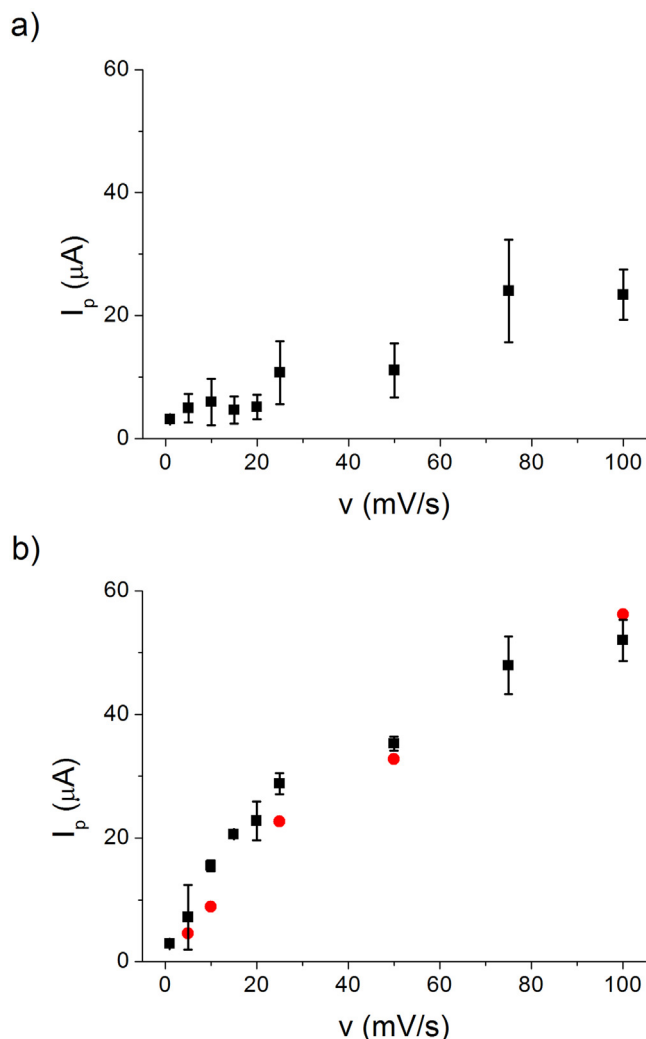
Fig. 6. Correlation between oxidation peak current of thiourea and scan rate. Voltammograms carried out: a) immediately after electrode immersion in a TU solution (0.65 M $CuSO_4$ and 1.8 M H_2SO_4), b) after 5 min incubation (black squares). Red circles correspond to electrodes incubated for 5 min in a TU-containing solution (0.65 M $CuSO_4$ and 1.8 M H_2SO_4), rinsed and measured in the same matrix without TU. (For interpretation of the references to colour in this figure legend and in the text, the reader is referred to the web version of this article.).

since in contrast to the reported in previous work [15], no reduction peaks related to the oxidized TU can be assigned. Fig. 7 shows two voltammograms at two different TU concentrations, scanning the electrode potential from −0.75 to 1.4 V. It can be observed that the only difference due to the different concentrations is the oxidation peak at 1.3 V, the other processes can be attributed to the oxidation-reduction process of the AgNPs and the proton reduction. The oxidation and reduction peaks about 0.5 V are only observable in presence of AgNPs. The proton reduction can be observed at potential lower than −0.5 V even in absence of TU.
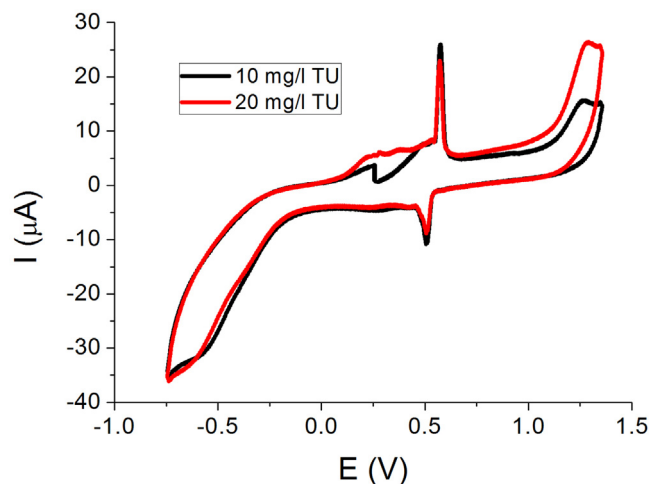

Fig. 7. Voltammogram of TU in 1.8 M H_2SO_4 solution at different concentrations: 10 ppm (black), 20 ppm (red). Scan rate = 25 mV/s. All potentials are given vs. Ag/AgCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Elucidating the mechanism of electrooxidation of TU is beyond the scope of the present work. However, the voltammetric patterns obtained could be explained by assuming the oxidation process in the following way:
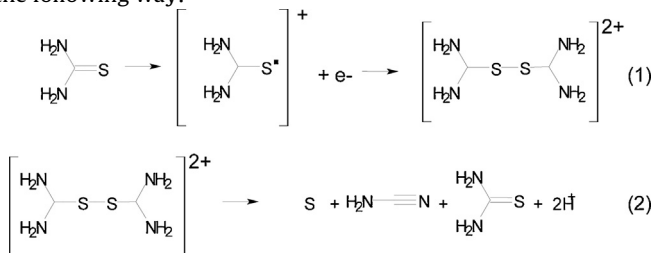
Eq. (1) stands for the oxidation process followed by the dimer formation, while Eq. (2) stands for the decomposition of the dimer. This last step differs from the results obtained by other authors, who observed a reduction peak at around 0 V for this species [15].

The decomposition of the dimer was also confirmed by infrared experiments. Fig. 8a shows the spectra of a Pt electrode modified in the same way as the graphite electrode and exposed to a 20 mg/L TU solution in 1 mM H_2SO_4. Spectra was taken at different applied potentials to establish the possible oxidation products of the TU. All spectra show strong absorption peaks corresponding to the polyallylamine adsorbed on the Pt electrode and to the DS dispersing the mixture, confirming the stability of the material adsorbed on the electrode. Fig. 8b is a zoom at ∼2300 cm^{-1} of the spectra in Fig. 8a. It shows the appearance at 1.2 and 1.6 V of a small peak at 2341 cm^{-1}. This peak (which is not observed in the spectra corresponding to the absence of AgNPs) is characteristic of cyanamide [33] (Eq. (2)). Other characteristic peaks of cyanamide appear in the ∼1500 cm^{-1} region and could not be observed in this work because of the presence of the peaks corresponding to the other compounds present
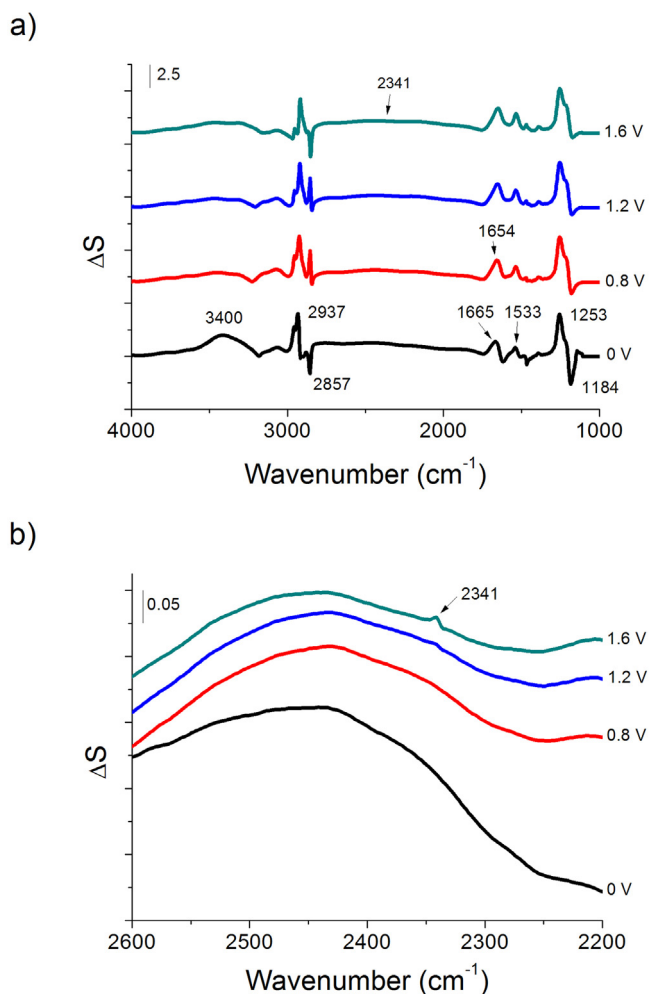
a)

b)

Fig. 8. a) PM-IRRA spectra of the modified Pt medal at different applied potentials. Medium: 20 mg/L TU in 1 mM H_2SO_4, (b) Zoom of a), all potentials are given vs. Ag/AgCl.

on the Pt medal in much higher concentration than cyanamide. In summary, PM-IRRAS shows the formation of cyanamide at 1.2 V or higher potentials, supporting the proposed mechanism.

4. Conclusions

An electrochemical method for the quantification of TU based in the modification of screen-printed graphite electrodes, with AgNPs supported in a polyelectrolyte-surfactant matrix, was developed. The AgNPs promote the adsorption of TU on the electrode surface, facilitating the electron transfer process, characterized by an irreversible oxidation. A proposed mechanism was supported by electrochemical and IR data.

The disposable sensors are able to determine TU in a typical electrorefinery bath, even in the presence of common additives, through linear and square wave voltammetries, with figures of merit according to the needs in the copper industry. In addition, since TU is strongly adsorbed on the AgNPs, the sensor can be introduced in the bath for a few minutes, rinsed, and the determination can be carried out independently.

The proposed system provides a simple and reliable measurement tool for the direct monitoring of thiourea in electrorefinery of copper allowing the reconditioning of baths and reducing its environmental impact.

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