

Preparation of Silver Nanoparticles-Based Sensors for the Electrochemical Detection of Thiourea in Leaching Solutions of Waste Electrical and Electronic Equipment

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Abstract

Waste of electrical and electronic equipment is an interesting secondary resource of base and precious metals. Particularly the use of thiourea-leaching in acidic medium was proposed for noble metals recovery. In this work, a novel and easy-to-use electrochemical sensor was developed, aimed to test thiourea from leaching solutions containing significant thiourea and copper amounts. The sensor was constructed using silver nanoparticles (AgNPs) deposited on screen-printed electrodes. Its performance was studied in a synthetic leaching solution; changes in the overall surface charge of AgNPs resulting in changes in the charge-transfer resistance for the copper ions were evaluated by electrochemical impedance spectroscopy.

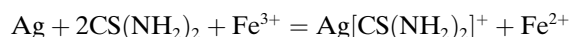
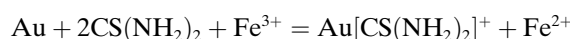
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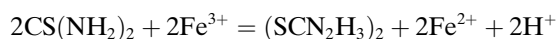
1 Introduction

Among the waste generated from the electric and electronic equipments (WEEE), wasted printed circuit boards (WPCB) are important components because of the high metal content. WEEE can contain up to 61 % metals (Cu, Sn, Fe, Pb, Au, Ag and Pd), 21 % plastics, 5.4 % glass and other materials used as resin reinforcing fibers, making the recycling difficult [1]. Particularly the gold recovery from the used WPCBs has received the most attention, because its concentration (300–350 mg/kg) from WPCBs is generally 100 times higher than that of gold ore [2]. Pyrometallurgical, hydrometallurgical and physical-mechanical processes have been proposed for the recycling of WEEEs. Hydrometallurgical processing of WEEEs involves the acid leaching treatment using oxidizing and complexing reagents [1]. Particularly the use of sulfuric acid (less corrosive and hazardous than nitric or hydrochloric acid) and thiourea (as complexing reagent with high affinity for noble metals) has been frequently proposed, where thiourea (TU) shows a fast kinetic reaction with gold and silver, less environmental impact compared to cyanide, and causes lower operating costs comparing to the thiosulfate method, because a much lower leaching reagent quantity is required. Besides, other disadvantages of thiosulfate are the oxidation of the reagent and the preferred leaching of copper, the major component of WPCBs, high cost of the reagent, and difficulty in the re-

covery process [3]. As thiourea is not stable under alkaline conditions, the complexing reaction with the noble metals takes place usually in acidic conditions, using ferric ions as the oxidant:



Nevertheless, thiourea is easily oxidized by ferric ions in acidic solutions, producing formamidine disulfide:



Formamidine disulfide is not stable in acidic solutions and decomposes producing elemental sulfur and cyanamide:



The final products may be elemental sulfur and urea [4]. Thiourea is also lost by the formation of other stable metal complexes.

The optimum thiourea concentrations, depending on the waste material to be leached, lie between 3 to 24 g L⁻¹ [4–7]. Some studies revealed that the critical factor for thiourea consumption was the leaching potential or ferric

sulfate concentration [4], but it is well-known that also the presence of copper ions has a deleterious influence on this leaching system, enhancing the thiourea consumption and affecting the reaction kinetics [8]. Copper ions not only degrade thiourea producing elemental sulfur (passivation leads to low gold extraction yields), but also catalyses thiourea oxidation by ferric ions.

Taking into account the growing number of publications of metals recovery from WEEEs and WPCBs using thiourea leaching, the dosage and control of thiourea in real time has become an imperative for the more rational use, reducing consumption and promoting reuse of its solutions. Thiourea, a representative of the family of the thio-amides, and their derivatives, is used in various areas of industry, from electroplating, copper electrorefining to agriculture where it is used as fungicide, herbicide, rodenticide. It is also used as reagent for spectrophotometric determination of metals. Thiourea is less toxic than cyanide but it is still a toxic substance, dangerous for its effects on carbohydrate metabolism, carcinogenic, potentially allergenic, showing in addition inhibitory effects on nitrification in soils and water [9–11]. Several methods have been employed in the determination of thiourea: Raman spectroscopy [12], mass spectrometry [13], FTIR [14], HPLC [15] and electrochemical methods such as thiourea oxidation on copper electrodes in basic medium, or its oxidation on electrodes of graphite, Au or Pt, in acidic medium [10,11,16]. The most commonly used non-enzymatic analytical methods are based on colorimetric measurements, following the reaction of analytes with chromophores, or the metal-complexing ability [9], but many studies are based on conductivity measurements for the detection of a variety of molecules [10]. These methods are hardly suitable for directed measurements in industrial matrices due to high ionic concentration, colored solutions and/or extreme pH values. Among the reported papers, most of them focus on waste water samples and determined thiourea in pure water at low concentration [9,11,13,15], or included measurements in acidic medium [10,12] or in basic medium [11]. Only few works carried out experiments with thiourea and metal ions in the same solution. Reference [15] works with a solution of thiourea concentration from 2 to 300 mgL⁻¹ and copper from 0 to 50 mgL⁻¹. Neither of the referred papers reported measurements at pH and concentrations of metal ions close to the typical conditions of leaching baths.

In this work, we present the use of an electrochemical system of disposable graphite electrodes manufactured by screen printing techniques [17]. This system is suitable to measure thiourea concentrations from acidic solutions (sulfuric acid 45 gL⁻¹), and in the presence of metal ions in quantities close to the typical ones found in WEEE leaching solutions (copper 10 gL⁻¹, gold 0.02 gL⁻¹ and silver 0.05 gL⁻¹) [6], and represents the first attempt to carry out direct measurements in a matrix of this industrial process.

The advantages of electrochemical methods are the simple signal processing, portability, quick response and

capability of measuring in complex and/or colored samples. A simple way for thiourea detection is capturing it at the electrode surface and observing the changes produced in the electron transfer process or in the capacitance by Electrochemical Impedance Spectroscopy (EIS) of this surface as transduction method. High affinity of thiourea for silver surface is used as sensor mechanism. The silver nanoparticles (AgNps) are synthesized and then suspended in a polymer matrix prepared from the interaction between a polyelectrolyte (polyallylamine) and a surfactant (sodium dodecylsulfate) [18,19], and this mixture is deposited on screen printed carbon electrodes. These electrodes are targeted for use in direct determinations in highly concentrated thiourea leaching tanks in presence of significant copper quantities. Copper ions were used to follow the chemical changes produced on the electrode surface; the analyte concentration was determined by the changes of the electron transfer process at the electrode surface.

2 Experimental

2.1 Apparatus and Reagents

Silver nitrate, polyvinylpyrrolidone K30 (PVP), copper sulfate and other reagents of analytical grade were used without further purification. All solutions were prepared with Milli-Q water. Visible absorption spectra were recorded on an Ocean Optics spectrophotometer. All experiments were performed at room temperature (25 ± 2 °C).

2.2 Synthesis of Silver Nanoparticles (AgNPs)

According to the specific needs for the electrodes, simple synthesis protocols [20,21] were modified, with the aim of using non-toxic and ready available water-soluble organic compounds as nanoparticle stabilizers. Silver(I) nitrate (AgNO₃) was used as the cation source, and sodium borohydride (NaBH₄) as the reducing agent. Polyvinylpyrrolidone (PVP) was the stabilizing reagent, preventing agglomeration and controlling growth. The synthesis was carried out by rapid addition of 10 mL of the borohydride solution (1 molL⁻¹ in 0.1 M NaOH) to 10 mL of the metal ion solution (0.20 M in water). Both solutions contained 0.02 g of PVP/mL, and the precipitation was carried out under sonication by ultrasonic bath. Stable dispersions of PVP-coated silver nanoparticles were obtained, still stable after more than eleven months of their synthesis.

2.3 Preparation of Sensor Electrodes

Silver nanoparticles were incorporated to the screen printed electrodes [17] by taking 20 μL of the PVP-covered AgNPs dispersion (1 × 10⁻¹ M Ag) prepared according to the procedure presented on Section 2.1. 20 μL of AgNPs dispersion were added to a solution containing

2 mL 1% sodium dodecylsulfate (SDS) solution and 1 mL of 0.04 mM poly(allylamine) (PA, $MW=65\,000$). Then, 8 μL of the resultant dispersion were applied on a 0.7 cm diameter screen printed electrode, and the solvent was left to evaporate at room temperature. The electrodes can be employed at least a week after their preparation and after 24 hours in freezer showing good reproducibility (standard deviation less than 10% without thiourea additions); stability during longer storage times is being studied. It is not possible to reuse the electrodes after they were exposed to the leaching bath.

The particles morphology and size, and the agglomeration degree once they are embedded in the electrode, were observed by scanning electron microscopy (SEM). Only for SEM characterization, the electrode samples were covered with gold before observation. The images were obtained using a FIB DUAL BEAM FEI HELIOS 600 NANOLAB scanning electron microscope (Netherlands), located at the IPICyT (San Luis Potosí).

2.4 Electrochemical Impedance Spectroscopy (EIS) Measurements

Measurements of Electrochemical Impedance Spectroscopy (EIS) were carried out in a conventional three-electrode cell powered by an electrochemical device comprising $\mu\text{AUTOLAB}$ type III system. The system was run on a PC using GPES and FRA software. A stainless steel sheet was employed as counter electrode and a commercial Ag/AgCl electrode served as the reference. All the potentials reported in this work are versus Ag/AgCl electrode. Working electrodes were prepared according to the procedure presented on Section 2.3. The bath solution was an artificial leaching solution of 10 g L^{-1} of copper from copper sulfate, 45 g L^{-1} of sulfuric acid, and thiourea in concentration between 0 and 1 g L^{-1} . For EIS measurements a sinusoidal potential modulation of $\pm 10\text{ mV}$ amplitude in the 1 Hz–10 kHz frequency range, spaced logarithmically (9 per decade), was superimposed onto the formal potential of the redox, $\text{Cu}^{2+}/\text{Cu}^0$, 0 mV. The EIS results were analyzed by fitting the experimental impedance data to an electrical equivalent circuit model. The electrical equivalent circuit parameters were calculated by fitting the impedance function to the measure spectra with a nonlinear least-squares program, using Z-plot/Z-view for all measured frequencies. The criteria used to estimate the fitting were evaluated with chi-square value lower than 0.01. Three independent measurements were carried out for each reported concentration of thiourea and the results were fitted as it was previously described. Then the values for each electrical component were calculated as averaging the fitted values and the errors were estimated by their standard deviation.

In order to test the performance of the sensor in conditions closer to industrial samples, thiourea concentration was measured as described previously, in solutions of 10 g L^{-1} of Cu(II), 45 g L^{-1} of sulfuric acid, 2.5 g L^{-1} of Fe(III) as nitrate, 0.02 g L^{-1} of gold and 0.05 g L^{-1} of

silver (added in the form of citrate-stabilized nanoparticles, they are synthesized according to [22] and [9], respectively).

3 Results and Discussion

3.1 Synthesis of Silver Nanoparticles

Figure 1a shows the absorption spectrum of silver nanoparticles dispersion after the synthesis, and the diameter distribution histogram from SEM image of the prepared silver nanoparticles is showed in Figure 1b. The inset of Figure 1b shows the particles.

UV/Vis spectroscopy is useful to study the possible presence of quantum-confined effects on silver nanomaterials. In this case, the peak in the absorption spectra for the silver dispersion (400 nm) exhibits a noticeable blue

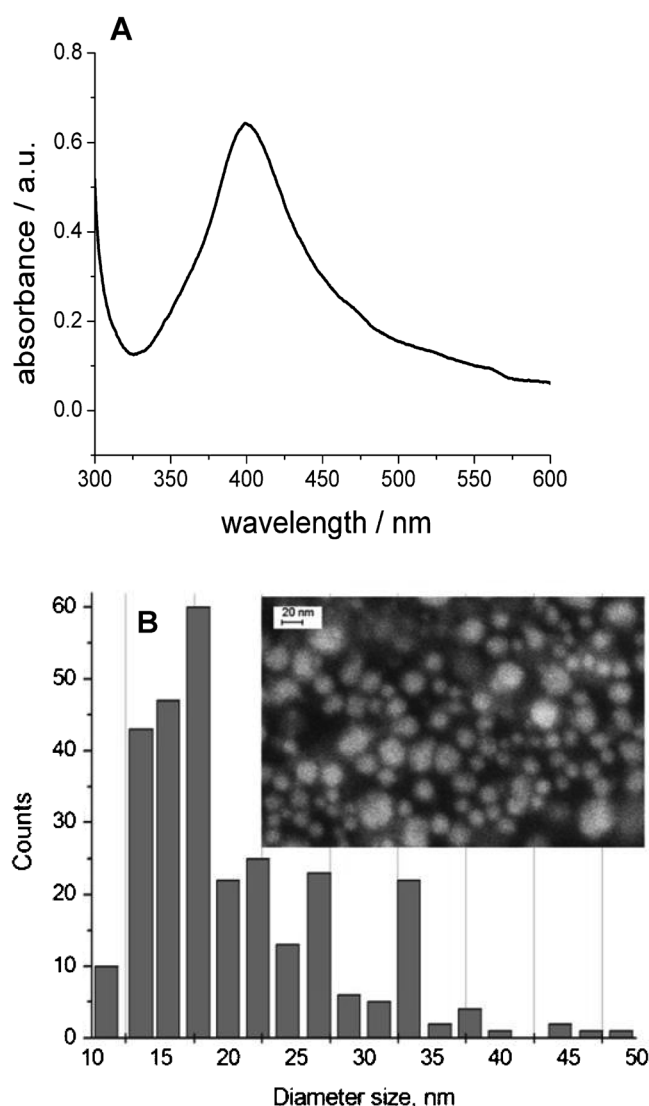


Fig. 1. a) Absorption spectra of silver nanoparticles dispersion showing the typical silver plasmon resonance band at 400 nm. b) Diameter distribution histogram for prepared AgNPs from SEM image (Inset).

shift compared to the bulk value (~ 440 nm). Excitations of conduction electrons in noble metal particles are known as particles plasmons, Mie plasmons or surface plasmons [23]. Silver particles have a strong and sharp plasmon band in the visible region whose shape and position are susceptible to surface adsorption, and therefore the particle formation and adsorption effects can be followed spectrophotometrically [24].

The position and shape of the plasmon absorption of silver nanoparticles are strongly dependent on the particle size and the surface adsorbed species [23]. An absorption band at 440 nm corresponds normally to the plasmon peak associated with relatively large spherical silver particles [25]. In this case, the main peak in the absorption spectra for the silver dispersion (400 nm) exhibits a noticeable blue shift compared to the bulk value. The silver particles present spherical morphology, their size vary between 5 and 22 nm, average size 20 nm, apparently with bimodal distribution. Bimodal size distribution by silver nanoparticles was attributed to their highly reactive surface by Green et al. [26].

3.2 Electrochemical Detection of Thiourea

Working electrodes were prepared as described above, by mixing the nanoparticles dispersion and a polymeric matrix. Figure 2 shows a FEG-SEM image of silver nanoparticles (AgNPs) dispersed in the polymeric matrix.

For the analytical determination of thiourea, the electrodes were immersed in a three-electrode cell containing a synthetic leaching solution of 10 gL^{-1} of copper from copper sulfate, 45 gL^{-1} of sulfuric acid, and thiourea in concentrations equal to: 0, 0.250, 0.500, 0.625, 0.750 and 1 gL^{-1} (see Figure 3). For each concentration three EIS

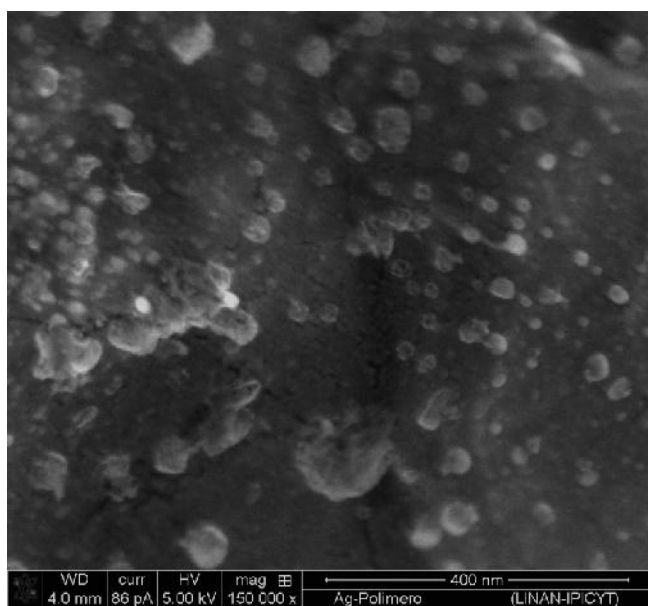


Fig. 2. FEG-SEM image of silver nanoparticles (AgNPs) dispersed in the polymeric matrix.

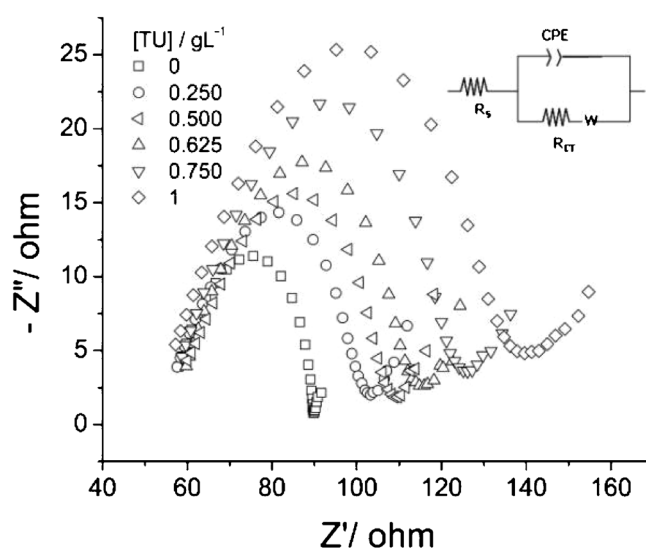


Fig. 3. Impedance spectroscopy of modified electrode, in artificial leaching bath solution as redox probe. Frequency range: 1 Hz–10 kHz, at the formal potential of the redox probe, 0 mV. The amplitude of the alternative voltage was 10 mV.

measurements were carried out, and different electrodes were employed in each measurement.

According to Wang and col., the reason why PVP protects the silver nanoparticles is the chemical interaction of PVP with silver through the N atom with formation of a protection layer [21]. In solution the adsorption of thiourea on the surface of citrate-stabilized AgNPs leads to the replacement of the original stabilizer and increased the van der Waals attractive forces among these TU-coated AgNPs, leading to aggregation of AgNPs [9]. In our system, PVP-stabilized AgNPs are immobilized into the polymeric matrix and the adsorption of thiourea on the surface of AgNPs changes the overall surface charges and the electric properties of the polymeric layer, which are evidenced by changes in charge-transfer resistance of the electrode.

The impedance spectra of Figure 3 were recorded within a frequency range of 1 Hz–10 kHz, at the formal experimental potential of the redox probe, $\text{Cu}^{2+}/\text{Cu}^0$, 0 mV. The amplitude of the alternative voltage was 10 mV; 9 points per frequency decade were taken with logarithmic distribution. The Randles modified equivalent circuit was used to fit the impedance spectroscopy and to determine electrical parameter values for each experiment. The equivalent circuit includes the following electronic elements. R_s is the electrolyte resistance between the working and the reference electrodes. R_{ct} is the charge transfer resistance, a manifestation of two effects: the energy potential associated with the oxidation event at the electrode and the redox species barrier reaching the electrode due to electrostatic repulsion or steric hindrance. A constant phase element (CPE) that simulates non-ideal behavior of the capacitor can be modeled as a series by combining the surface modification capaci-

Table 1. Theoretical fitting values.

[TU] (g L ⁻¹)	R_s (Ω)	R_{CT} (Ω)	CPE (S s ^{<i>n</i>})	<i>n</i>	W (Ω)
0	57 ± 4	34 ± 3	$7.5 \times 10^{-05} \pm 4 \times 10^{-06}$	0.76 ± 0.01	0.6 ± 0.1
0.250	54 ± 5	45 ± 2	$1.7 \times 10^{-04} \pm 2 \times 10^{-05}$	0.67 ± 0.02	0.16 ± 0.02
0.500	54 ± 3	52 ± 2	$1.33 \times 10^{-04} \pm 5 \times 10^{-06}$	0.72 ± 0.01	0.16 ± 0.09
0.625	57 ± 2	58 ± 2	$1.46 \times 10^{-04} \pm 2 \times 10^{-06}$	0.70 ± 0.01	0.15 ± 0.03
0.750	56 ± 3	70 ± 3	$1.19 \times 10^{-04} \pm 2 \times 10^{-06}$	0.69 ± 0.01	0.11 ± 0.01
1	55 ± 1	78 ± 10	$1.1 \times 10^{-04} \pm 2 \times 10^{-05}$	0.69 ± 0.03	0.11 ± 0.04

tance and double layer capacitance. A value of *n* between 0.5 and 1, associated with *CPE*, indicates a rough electrode. The Warburg impedance (*W*) represents the diffusion of the electroactive species to the electrode. The fitted values of these elements for different thiourea concentrations are listed in Table 1. The solution resistance R_s presents similar values for all experiments showing the good reproducibility in the building of electrochemical system. Significant differences were observed for the charge transfer resistance R_{ct} . The R_{ct} increased from (34 ± 3) Ω to (78 ± 10) Ω , indicating the energy barrier of the redox species Cu²⁺ reaching the electrode was incremented.

This behavior can be explained since silver in acidic media reacts with thiourea producing a cationic complex. This reaction could be generating a positive charged interface that electrostatically repels the positive charged redox probe, Cu²⁺, which would be responsible for the R_{ct} changes. R_{ct} is one of the elements most commonly used as indication of affinity binding for faradaic sensors [27]. We observed an increment in *CPE* values from 0 gL⁻¹ to 0.250 gL⁻¹ of thiourea, and then a tinny decrease. The reaction between silver nanoparticles and thiourea causes microscopic chemical inhomogeneities on the surface of electrodes changing locally the charge of the interface and the dielectric constant of the media, and both surface effects and inhomogeneous current distribution contribute to *CPE* behavior. The value of *n* presents a difference between the experiments with and without thiourea, but among experiments with thiourea the value of *n* remains almost constant (close to 0.70), associated with *CPE*, this value indicates a rough and inhomogeneous electrode. The Warburg impedance (*W*) represents the diffusion of the electroactive species to the electrode. The value of *W* is significantly higher in solution without thiourea in the studied range. This parameter could be affected by the formation of a copper-thiourea complex by changing the ion transport modes. Studies for thiourea concentration less than 0.250 gL⁻¹ and in solutions with different concentrations of copper are being carried out to clarify *CPE* and *W* behavior.

The charge-transfer resistance, calculated from Randles modified equivalent circuit from the spectra of Figure 3, was plotted versus thiourea concentration in Figure 4, showing excellent linear correlation ($R^2 = 0.932$ and detection limit 0.133 gL⁻¹), and very good reproducibility, employing different modified electrodes for each experiment. (standard deviation for 3 independent experiments

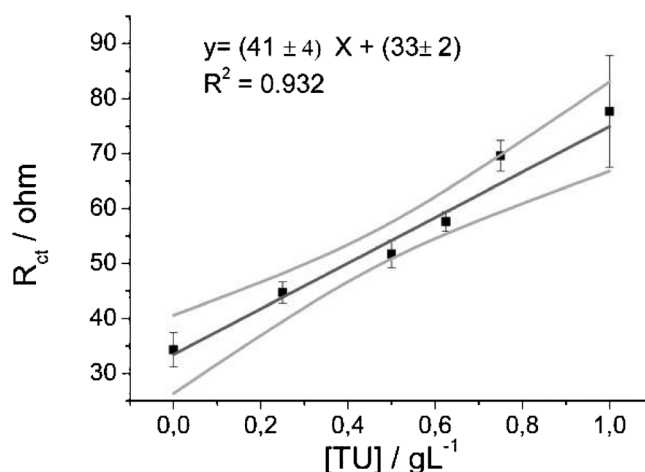


Fig. 4. Charge transfer resistance vs. thiourea concentration for modified electrodes with AgNPs dispersed in polymeric matrix. Error bars represent the standard deviation from 3 independent experiments. Linear fitting: black line, confident bands: grey lines.

were: 9% for 0 thiourea measurements, less than 5% for 0.250–0.750 gL⁻¹ and 13% for 1 gL⁻¹).

Affinity between AgNPs or thiourea and cations such as Cu²⁺ or Fe³⁺ could affect the performance of this sensor [10,28]. The charge transfer resistant values as function of thiourea concentration were evaluated in a bath containing Cu(II), Fe(III) and trace amounts of gold and silver were fitted for 0, 0.250, 0.500, 0.750 and 1 gL⁻¹ showing a linear correlation, too, with an average sensitivity of (34 ± 3) Ω /(g L⁻¹), $R^2 = 0.975$ and limit of detection of 0.143 gL⁻¹. Further work is in progress to evaluate the effect of the concentration of Fe³⁺ on the performance of the sensor to carry out measurements in industrial samples.

4 Conclusions

We have presented an electrochemical system consisting of a disposable graphite electrode manufactured by screen printing techniques, on which a polymer matrix with dispersed silver nanoparticles is deposited. Silver nanoparticles were synthesized from environmentally friendly reagents, enabling their industrial scale production with low environmental impact. The reproducibility on the construction of electrodes was satisfactorily evalu-

ated. The impedance response of the system was performed and the results were fitted by an equivalent circuit. From these electric elements we found that the charge transfer resistance was proportional to thiourea concentration even in presence of sulfuric acid, Cu(II) and Fe(III). This correlation in the presented synthetic leaching baths is the principle of the operation of the sensor and provides new opportunities in the development of effective environmental management measures in industrial processes.

This system is a novel, simple, nonexpensive and robust electrochemical method to monitor thiourea in the metal recovery industry in a suitable range of concentration for a leaching bath of WEEEs contributing to optimize and reduce the use of this hazardous substance.

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