



Detection of thiourea from electrorefining baths using silver nanoparticles-based sensors



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ABSTRACT

A novel and easy-to-use colorimetric thiourea (TU) sensor based on immobilized polyvinylpyrrolidone-stabilized silver nanoparticles (PVP-AgNPs) is reported. The new sensor is aimed for its direct application in copper electrorefining baths. Quantitative analysis was carried out by adding different thiourea amounts into a synthetic bath and monitoring the absorption changes of the surface plasmon resonance band (SPRB) by UV–Vis spectrophotometry. A linear correlation between the absorbance change and thiourea concentration was obtained, ranging from 0.125 mg/L to 1 mg/L. Our technique has the advantage of working in acidic and high ionic concentrated solutions as those used in electrorefining baths. The influence of the nanoparticles synthesis conditions on the thiourea sensing was analyzed; particularly, the effect of using different silver concentrations and the same amount of borohydride ions as reducing agent ($[Ag^+]/[BH_4^-]$ ratios of 2:1, 8:1, 10:1 and 20:1 during the synthesis). The proposed system provides a simple, economical, easy-to-handle and rapid measurement tool for monitoring hydrometallurgical processes for optimizing the reconditioning of thiourea solutions, reducing its environmental impact.

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1. Introduction

The development of suitable sensors for use in production processes, as well as those aimed at monitoring effluents; contributes to a better use and re-use of hazardous reagents such as thiourea. The use of thiourea is strongly linked to the leaching, electroplating, and electrorefining of metals, and particularly the electrorefining of copper is a powerful process for production on a large scale. On the other hand, copper electrodeposition as an inexpensive and versatile bottom-up approach to the building up of nanostructures for electronics has several advantages over other routes [1]. In both cases, the control of film properties such as surface morphology, resistivity and brightness has been accompanied by the use of additives such as cyanide, thiourea, benzotriazole, and nicotinic acid (brighteners and roughness controllers), polyethylene glycol (suppressor) and mercapto compounds (accelerators) [2–5].

In the particular case of thiourea, its role in copper electrodeposition in refinery baths is mainly related to grain formation and grain size distribution, but the associated chemical and electrochemical mechanisms are still not completely understood [6].

In the copper electrorefining bath, thiourea is consumed by reactions with components of the electrolyte (complexation, hydrolysis, etc.), and partially captured by the metallic deposit, thus thiourea concentration varies continuously. The optimal concentration, depending on the quality of the deposit to be obtained, varies from 3 to 10 ppm. The dosage and control of thiourea content for the refining process has become a key variable for obtaining high-quality copper, but the constant addition rates do not guarantee an optimum in thiourea concentration. Thiourea is potentially toxic, affects the carbohydrate metabolism and is carcinogenic and allergenic, showing in addition inhibitory effects on nitrification in soils and water [7–9]. Therefore, it is desirable to be able to measure the thiourea content using a simple and rapid determination method, in order to reduce its consumption and to improve the quality of the obtained deposits. Various methods have been employed for thiourea analysis: Raman spectroscopy [10], mass spectrometry [11], FTIR [12], UV/Vis [8,13,14], HPLC [15], and electrochemical methods (thiourea oxidation on copper electrodes in

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basic medium, or on electrodes of graphite, Au or Pt, in acidic medium) [7,9]. Most works focus on diluted wastewater samples [8,9,11,15], or include measurements in acidic [7,10] or basic medium [9]. Only few works include experiments with thiourea and metal ions in the same solution. Rethmeier et al. [15] work with solutions of thiourea in a concentration range from 2 to 300 mg/L, and copper from 0 to 50 mg/L. In a previous study, we reported a thiourea sensor for a range of 0.133–1 g/L in a synthetic leaching solution, containing 10 g/L Cu^{2+} as copper sulfate, and 45 g/L H_2SO_4 [16]. Neither of the referred papers reported measurements at pH, metal ions and thiourea concentrations close to the typical conditions of electrorefining baths.

The use of silver and gold nanoparticles as colorimetric sensors has received a great deal of attention because of the color changes associated with the surface plasmon resonance band (SPRB), which is very sensitive to a number of parameters, such as particles size and shape, adsorbed species (stabilizer), medium dielectric properties, and the distance between particles [8]. Spherical silver nanoparticles (AgNPs) in solution appear brown due to their intense SPRB at ~ 400 nm [17]. Aggregation induces an electric dipole–dipole interaction and coupling between the plasmons of neighboring particles, causing the color to change. Based on this principle, AgNPs-based sensors can be used as measurement tools. Most of the studies on cation sensing (e.g., Li^+ , K^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , and Hg^{2+}) focused on gold particles, and, less attention received the use of AgNPs, in spite of the fact that AgNPs exhibit higher extinction coefficients than AuNPs of the same size, allowing detection with lower metal consumption, and that their preparation is more economical [8]. Changes in the SPRB have been successfully used for the detection of analytes such as proteins [18], other ligands and compounds [19–21], and metal ions [22–26].

The surface modification is an important issue regarding the use of metal nanoparticles as colorimetric sensors. The attachment of ligands onto the particles surface provides stability in different media, as well as functionality [22,26]. The advantages of colorimetric sensors include their easiness of use, where detection involves only a single step without requiring trained personnel; low cost, as only a small quantity of nanoparticles is needed to generate visible color changes due to the extremely high extinction coefficients; and that they only require a portable UV–Vis spectrometer for localized SPRB extinction detection. Despite these advantages, the colorimetric applications usually involve mass transport through a liquid environment of the analyte to the AgNPs surface, and thus, the stability of AgNPs in solution is important. Challenges associated with nanoparticles aggregation-based colorimetric sensors cannot be overlooked, particularly in the nanoparticles preparation. In general, the synthetic procedure is simple, but size control is rarely achieved [27]. Another important factor involving AgNPs dispersions deals with their behavior following short- and long-term storage. Recently, a colorimetric method based on AgNPs aggregation for the thiourea detection was reported [8]. The method shows an impressive low detection limit and a linear relationship with thiourea concentration working in a pH range from 3 to 9; however, the electrorefining baths present a more aggressive medium, lower pH, high ion concentration and other additives, which could affect the nanoparticles stability in solution.

In this work, analytical determinations in this kind of medium were performed, and as a result, a sensitive sensor based on immobilized AgNPs is presented. The developed method coincides with the thiourea concentration range in electrorefining baths and is highly selective in the presence of other typical additives. The PVP-stabilized AgNPs are suspended in a polymer matrix prepared from the interaction between a polyelectrolyte (polyallylamine, PAA) and a surfactant (sodium dodecylsulfate, SDS) [28,29], and this mixture is deposited on cellulose acetate films; once the mixture is

dried, the particles remain stable and the sensors can be stored and easily transported. In contrast to the behavior observed for suspended AgNPs, here the nanoparticles aggregation by thiourea is impeded due to their immobilization. Instead, the detection principle used in the current device is based on the retardant effect of thiourea when AgNPs are exposed to the oxidation by ferric ions added to the sample. The work compares the behavior of the system first, when an aliquot of the AgNPs dispersion is added to the probe solution, and second, when the AgNPs are immobilized. The concentration ratio of silver:borohydride ions (2:1, 8:1, 10:1 and 20:1) during the nanoparticle synthesis was optimized, showing that an excess of silver improves the sensitivity of the method. The sensor proposed here shows a very good performance in a concentration range useful in electrorefining baths, even in the presence of other typical additives.

2. Experimental

2.1. Apparatus and reagents

Silver nitrate, polyvinylpyrrolidone K30 (PVP), copper sulfate, sulfuric acid, ferric nitrate and other compounds were analytical grade reagents, and were used without further purification. Glue and AVITONE® were industrial grade reagents. 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 ($25 \pm 2^\circ\text{C}$). The particles morphology and size, and the agglomeration degree after their incorporation on the strips, were observed by Scanning Electron Microscopy (SEM) using an ESEM FEI-QUANTA 200 and by Field Emission Scanning Electron Microscopy (FESEM) using a FIB DUAL BEAM FEI HELIOS 600 NANOLAB Scanning Electron Microscope (Netherlands), located at the IPICT (San Luis Potosí).

2.2. Synthesis of silver nanoparticles (AgNPs)

Based on the specific needs, simple synthesis protocols [30,31] were modified, with the purpose of using non-toxic and readily available reagents. Solutions of polyvinylpyrrolidone (PVP, 20 g/L) and 0.2, 0.85, 1.05 and 2.05 M AgNO_3 were prepared, as well as a solution of PVP of the same concentration and pH 11 (adjusted with NaOH), containing 0.1 M NaBH_4 . 2.5 mL of the corresponding 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. Brown dispersions were obtained. They were stored in the dark at -18°C . The AgNPs were used as prepared, without any further surface modification treatment. Nanoparticles synthesized via this technique have several desirable features, they are stabilized by the adsorbed PVP acting as a capping layer and are readily prepared in large quantities.

2.3. Preparation of colorimetric sensors

50 μL of the corresponding AgNPs dispersion were added to 450 μL of a 1.1% wt. sodium dodecyl sulfate (SDS) solution, and 0.250 mL of 0.26% polyallylamine (PAA), adjusted to pH 7 with H_2SO_4 , were added to the resulting mixture. 20 μL of the SDS-PAA-AgNPs suspension were placed on 1 cm-diameter circles on cellulose acetate films. In order to be able to subtract the absorbances of the substrate and the polymer mixture, “blank” strips were also prepared. For these we used 20 μL of a suspension prepared from 0.500 mL of a 1% SDS solution and 0.250 mL of the PAA solution adjusted to pH 7, as mentioned before. After this, the strips (Fig. 1) were dried at 50°C for half an hour. The strips can be stored at room temperature during a week after their

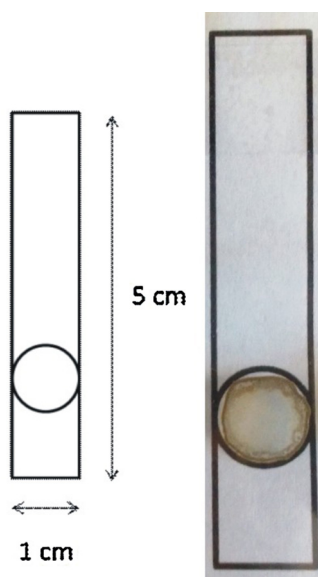


Fig. 1. Diagram/image of the AgNPs-test strip.

preparation. The absorbance data were taken after 12 min of the thiourea addition.

The measurements were carried out in an artificial electrorefining bath solution containing 0.45 M H_2SO_4 , 0.16 M CuSO_4 , which is a 1:4 dilution of the typical bath, with the addition of Fe(III) ions (as 1.8 mM $\text{Fe}(\text{NO}_3)_3$), and TU in different concentrations. In order to establish the blank of the absorption, “Blank” strips were immersed in the artificial bath solution without TU, employing a polystyrene cell of 1 cm of path length.

3. Results and discussion

3.1. Nanoparticles

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 (Fig. 2) for the silver dispersion (420 nm) exhibits a blue shift compared to the typical value for large particles (~ 440 nm) [22]. Fig. 2 also shows the SPR band of the AgNPs after dispersing them in the PAA + SDS solution ($[\text{Ag}^+]/[\text{BH}_4^-]$ ratio of 20:1 during the synthesis). The slight difference in both absorption bands could give a hint about some

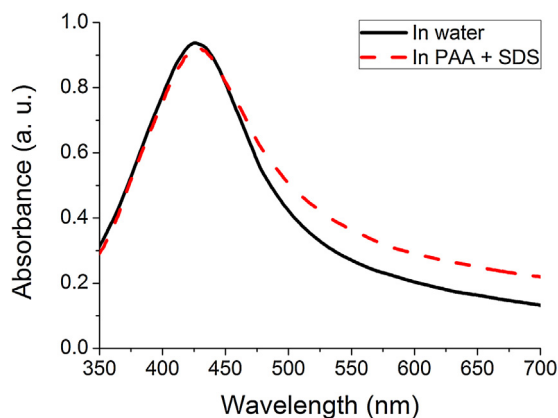


Fig. 2. Absorption spectra of silver nanoparticles dispersion showing the typical silver plasmon resonance band at 420 nm approximately. Black line: nanoparticles dispersion (as prepared, diluted 1:500), and red line: after dispersing them in the PAA + SDS solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

agglomeration as the nanoparticles interact with the polymeric mixture.

As we used different $\text{Ag}^+/\text{BH}_4^-$ concentration ratios (therefore, the amount of silver available for reduction varied for the different experiments), some statements must be made about the stoichiometry of the reaction. Two different kinds of reactions can occur simultaneously in an aqueous solution containing borohydride ions: these can act as a source of nucleophilic hydride H^- ions, which reduce the metal ions present, or the H^- nucleophilic moieties can be replaced by water molecules (hydrolysis) [27]. Therefore, the exact amount of BH_4^- ions remains unknown during the synthesis, and the stoichiometric ratio $\text{Ag}^+/\text{BH}_4^-$ is for this reason difficult to be controlled. Considering this, for the purpose of this research work, the employed silver concentrations of 0.2, 0.85, 1.05 and 2.05 M represent concentration ratios related to borohydride ions concentration of 2:1, 8:1, 10:1 and 20:1, respectively. Fig. 3a and b show the relationship between this ratio and the maximum of the associated surface plasmon resonance peak. In Fig. 3a the shape broadening and the position change of the SRPB maximum as the silver ions content increases indicates the broader size distribution and the presence of bigger particles. This is confirmed in Fig. 3b where the wavelength of the SRPB maximum for the particles (in both cases, dispersed and immobilized on the strips) is presented as a function of the $[\text{Ag}^+]/[\text{BH}_4^-]$ ratio during the synthesis. This is a consequence of the fact that the amount of

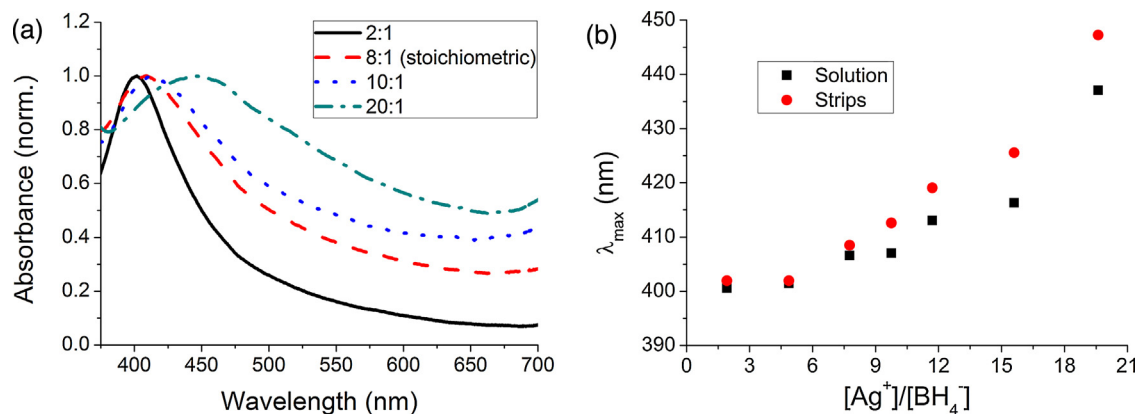


Fig. 3. (a) Spectra of the test strips (corrected for blank and normalized) at different $[\text{Ag}^+]/[\text{BH}_4^-]$ ratios. (b) Maximum of the associated SPRB of the AgNPs dispersions prepared at the different silver ions/borohydride concentration ratios, and of the corresponding cellulose acetate strips (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

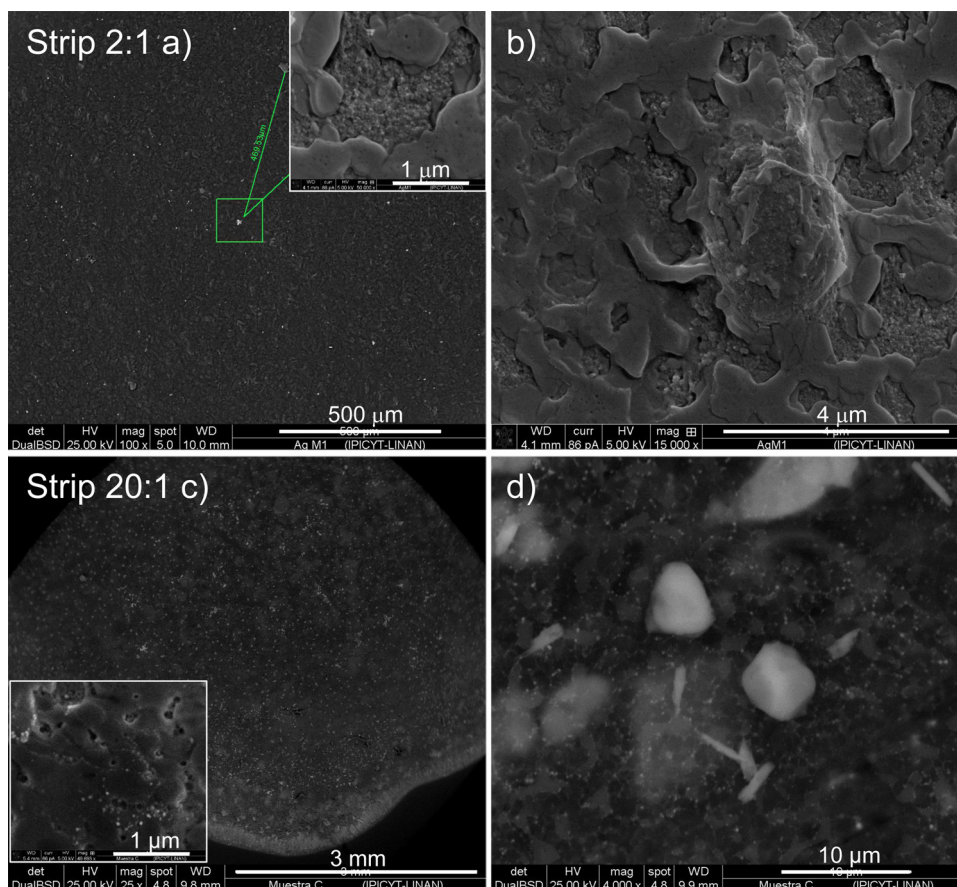


Fig. 4. SEM and FESEM micrographs of the as-prepared strips with AgNPs synthesized at 2:1 and 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ ratios. Figures a, c, c (inset) and d, backscattering detector. Figures a (inset) and b FESEM, secondary detector.

borohydride and PVP available, related to silver, diminishes. When borohydride is added to a solution containing an excess in silver ions, the formed metal nuclei are closer and aggregate [8]. Furthermore, the lower ratio of PVP to AgNO_3 causes a decrease in coverage and the nanoparticles become bigger [32]. Thus, larger particles are obtained, and in a wider sizes range. Besides, the red-shift of the SPRB observed for the immobilized AgNPs in Fig. 3b indicates the agglomeration due to the media change and the drying of the polymer suspension on the strips.

In order to get a better understanding of the influence of the AgNPs structure on the different spectroscopical responses, SEM and FESEM observations of the sensors containing Ag^+ and BH_4^- in

the ratios 2:1 and 20:1 were carried out. The first SEM micrograph of the as-prepared sensor, obtained using the dispersion prepared at a 2:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ ratio (Fig. 4a, backscattering detector), shows an almost homogeneous distribution of the particles all over the surface and the presence of some silver aggregates (bright spots). Fig. 4b and the inset of 4a show high magnification FESEM micrographs of the silver particles, where the narrow size distribution is evident. Fig. 4c shows a low magnification view of the as-prepared strip obtained using the dispersion prepared at a 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ ratio. The silver particles are well distributed on the surface. The micrograph in Fig. 4d shows, using the backscattering electrons detector, that big particles and “bright spots” in the surface of the

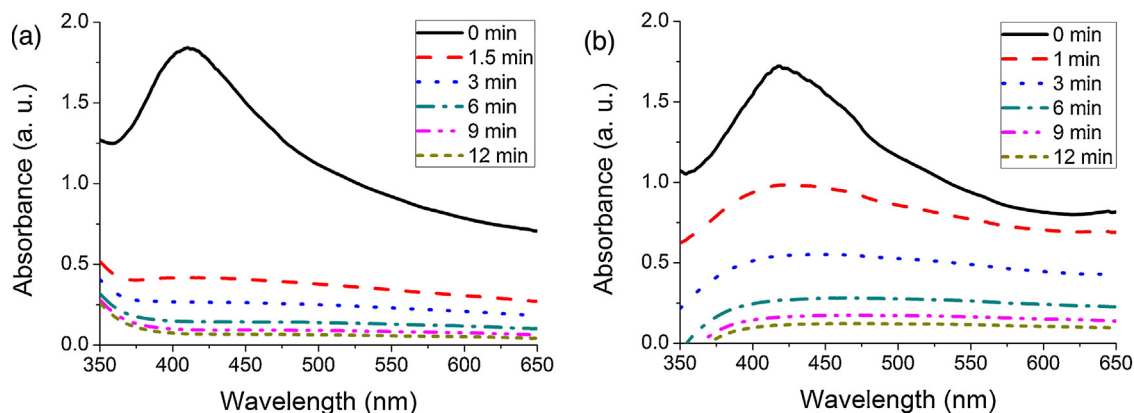


Fig. 5. Temporal evolution of the SPRB of 10 μl AgNPs dispersion in 2 ml of solution containing 0.45 M H_2SO_4 , 0.16 M CuSO_4 , 1.8 mM $\text{Fe}(\text{NO}_3)_3$. (a) 0 ppm TU and (b) 1 ppm TU.

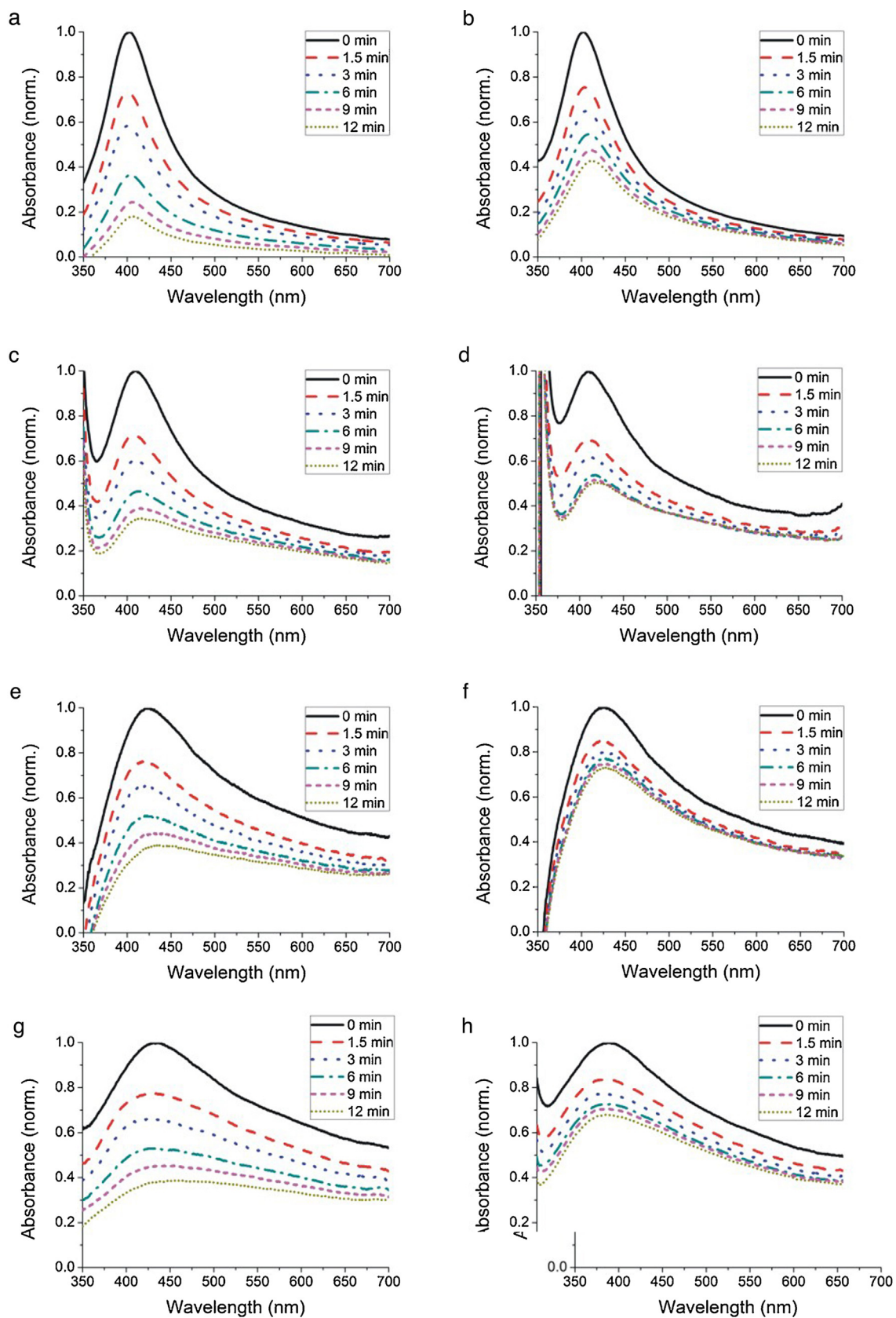


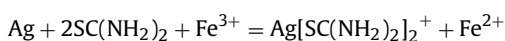
Fig. 6. Sequences of spectra as a function of time for different experimental conditions: (a) 2:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ in the absence of TU, (b) 2:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ and 1 mg/l TU, (c) 8:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ in the absence of TU, (d) 8:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ and 1 mg/l TU, (e) 10:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ in the absence of TU, (f) 10:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ and 1 mg/l TU, (g) 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ in the absence of TU, (h) 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ and 1 mg/l TU. In all cases, the H_2SO_4 , Cu^{2+} and Fe^{3+} concentrations were 0.45 M, 10 g/l and 1.8 mM, respectively.

strip are visible, suggesting a bimodal size distribution due to the excess of silver related to the amount of reducing agent. The small particles appear in both sensors to be well incorporated into the polymeric matrix.

These facts are of relevance for the interpretation of the spectroscopic results obtained during the strips characterization. The SEM images confirm the broader size distribution and the presence of bigger particles for the sensor 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$ ratio.

3.2. Colorimetric thiourea detection

It is well-known that Fe(III) is a good oxidizing agent during the leaching of metals (e.g. Ag, Cu, Au) in the presence of complexing agents (e.g. cyanide). Since Ag^+ ions are able to form a stable complex with thiourea in acidic conditions, we decided to investigate the changes produced in the AgNPs when they are exposed to a electrorefining bath to which Fe(III) ions are added. In these conditions the following reaction takes place:



Thiourea as a nucleophilic agent plays a dual role in the system, it stabilizes Ag^+ ions due to formation of a complex in solution, and has a strong affinity towards AgNPs, adsorbing on metallic Ag° via the S atom [8]. The Ag coverage by TU retards the oxidation reaction; therefore, the dissolution rate will depend on the interplay of these two processes.

In solution this reaction occurs at a rate that can be easily followed; therefore, in the case of the dispersed AgNPs, a change in the surface plasmon band should be observed. In order to establish the best conditions for the use of this reaction in the detection of thiourea, Fe(III) ions (as 1.8 mM $\text{Fe}(\text{NO}_3)_3$), were introduced in an artificial electrorefining bath solution without thiourea, but containing 0.45 M H_2SO_4 , 0.16 M CuSO_4 , which is a 1:4 dilution of the typical bath. Its mixture with AgNPs induces significant absorbance changes in the surface plasmon resonance band (Fig. 5a). It is evident that the nanoparticles are susceptible to structural changes when exposed to this aggressive environment, showing dramatic effects on the extinction maximum. In this case, acidity and the presence of Fe(III) ions promotes oxidation of the PVP-stabilized AgNPs (Fig. 5a). The addition of thiourea (TU) led to an attenuated absorbance change of the AgNPs SPRB (Fig. 5b). As the TU concentration in the sample increases, a decrease in the absorbance change rate is observed. If the dispersed AgNP are exposed to TU in absence of Fe(III), their aggregation is also observed but the rate is smaller. The changes observed in the AgNPs when they are exposed either to Fe(III) or TU show that the surrounding PVP layer can be easily displaced, in a similar fashion that in the case of citrate protected AgNPs [8]. PVP is a polymeric surfactant used to stabilize the AgNPs during the synthesis, that adsorbs onto the surface of silver solid through O-Ag bonding but when the ratio of PVP to AgNO_3 decreases, it could cause a low coverage [32], and other species as Fe(III) or TU can replace them.

However, a different behavior is observed when the AgNPs are immobilized on the strips, their immersion in solution containing TU, and in the absence of Fe(III), does not produce significant differences in their spectra, showing that the strip environment does not allow the free movement of the AgNPs for aggregation; therefore, the addition of Fe(III) is necessary to generate a noticeable change.

In order to evaluate the behavior of the proposed method, a solution simulating a typical bath of a copper electrorefining plant was prepared. After that, $\text{Fe}(\text{NO}_3)_3$ was added to this dilution in a concentration of 1.8 mM. 2 mL-aliqouts of the resulting solution were taken in 1 cm-spectrophotometer cells. Having taken the absorbance of this system as zero, the strips were placed in the light path and the spectra were measured in the range between 350 and

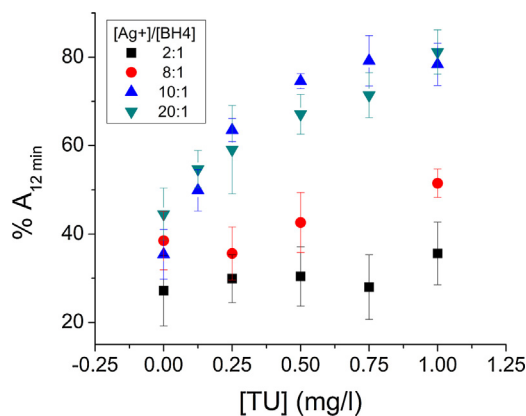


Fig. 7. Curves of remaining absorbance after 12 min vs. thiourea concentration for AgNPs synthesized with different $[\text{Ag}^+]/[\text{BH}_4^-]$ ratios. In all cases, the H_2SO_4 , Cu^{2+} and Fe^{3+} concentrations were 0.45 M, 10 g/l and 1.8 mM, respectively. Error bars correspond to standard deviation of three independent experiments.

700 nm. The measurements were performed at intervals of time and lasted 12 min (Fig. 6).

Similar experiments were performed for different thiourea concentrations. In all cases, the absorbance of the maximum at 0 min of exposure (A_0), and after 12 min exposure (A_{12}) were measured. Then the percentage of remaining absorbance was calculated as:

$$\%A_{12 \text{ min}} = \frac{100 \times A_{12}}{A_0}$$

and these results were plotted as a function of thiourea concentration (in a range of 0–1 mg/L), for the different $[\text{Ag}^+]/[\text{BH}_4^-]$ ratios. The results in Fig. 7 show that an excess of silver is necessary to increase the sensitivity of the system. When AgNPs synthesized in 0.607 M of excess of AgNO_3 are employed, a linear correlation is observed. The corresponding calibration curve is reported in Fig. 8.

Other additives (gelatin, glues, commercial reagents, etc.) are widely used, together with thiourea, in electrolytic refining of copper. With the purpose of a better emulsion of an electrowinning bath, 3 ppm of glue and 30 ppm of AVITONE® were added to the previously employed solution, getting a calibration with similar sensitivity than without additives (curve $y = (36 \pm 1)x + (54 \pm 1)$ in the corresponding units; $R^2 = 0.917$) in the same range of concentrations of thiourea (0–1 mg/l).

The FESEM micrograph in Fig. 9a shows the effect on the strip of the electrolyte solution containing acid, Cu(II) and Fe(III). The polymer seems degraded, and an important amount of AgNPs

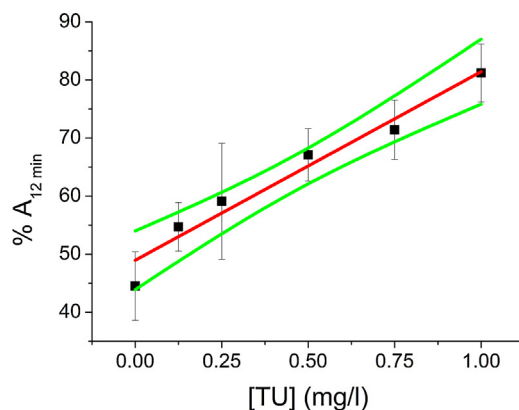


Fig. 8. Calibration curve for 20:1 $[\text{Ag}^+]/[\text{BH}_4^-]$. $y = (33 \pm 4)\%/\text{mg } x + (49 \pm 6)\%$; $R^2 = 0.955$. Solution: concentrations of H_2SO_4 , Cu^{2+} and Fe^{3+} were 0.45 M, 10 g/l and 1.8 mM, respectively. Error bars correspond to standard deviation of three independent experiments.

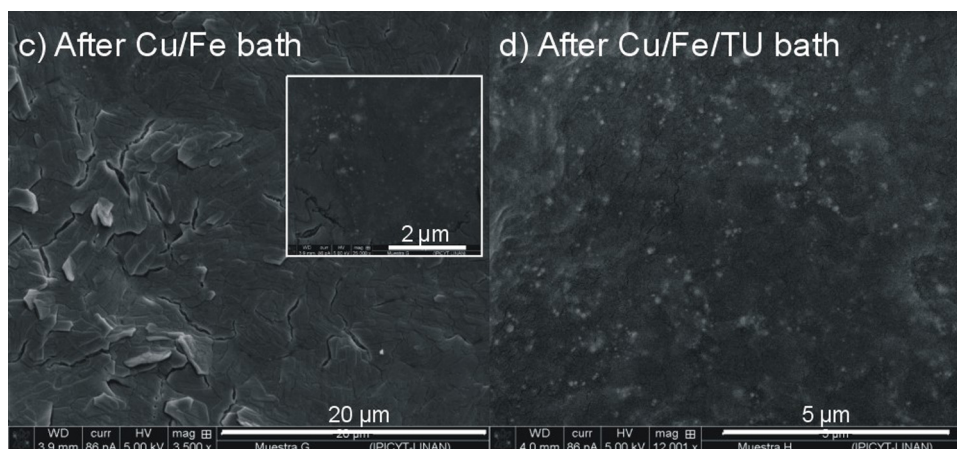


Fig. 9. FESEM micrograph of the as-prepared strip with AgNPs synthesized in 20:1 $[Ag^+]/[BH_4^-]$ solution after use in Cu/Fe and Cu/Fe/TU baths.

disappeared, the remaining particles appear as they were covered by the polymer, apparently acting as a protection against the aggressive medium. The micrograph 9b shows a view of the sensor after being contacted with a thiourea-containing bath. The thiourea seems to act as a protecting agent, as the presence of more AgNPs is evident. These results suggest that an important amount of AgNPs disappear rapidly from the sensor under the aggressive medium conditions, but some protection is offered by the thiourea molecules to impart sensitivity to the 20:1 strip.

4. Conclusions

We have presented a colorimetric thiourea (TU) disposable sensor, based on immobilized polyvinylpyrrolidone-stabilized silver nanoparticles (PVP-AgNPs), and its application on copper electrorefinery baths was studied. In this immobilized system the nanoparticles remain stable and the sensors can be stored and easily transported. The effect of different conditions of AgNPs synthesis was analyzed and the system of immobilized PVP-AgNPs was characterized by UV-vis and Scanning Electron Microscopy (SEM).

Quantitative analysis was carried out by adding different amounts of thiourea into a synthetic bath even in the presence of typical additives and monitoring the absorption changes of the surface plasmon resonance band by UV-vis spectrophotometry. A linear correlation between the absorbance change and thiourea concentration was obtained.

The proposed system provides a simple, economical, robust and rapid measurement tool for monitoring thiourea in hydrometallurgical processes in a suitable concentrations range, optimizing the use and reconditioning of thiourea solutions and reducing its environmental impact.

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