**Nanoparticles-based sensors for detection of thiourea in hydrometallurgical operations**

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The use of species such as thiourea, thiosulphate or cyanide ions is strongly linked to the electroplating, electrowinning, and electrorefining of metals, as well as to mining activities. Given the environmental importance of these pollutants it is relevant to achieve a more rational use consolidating a competitive industry with the introduction of effective environmental management. The development of suitable sensors for use in production processes, as well as those aimed at monitoring effluents, contributes to better use and re-use of hazardous reagents.

In this work, novel and easy-to-use colorimetric and electrochemical thiourea (TU) screen-printed sensors based on immobilized polyvinylpyrrolidone-stabilized silver nanoparticles (PVP-AgNPs) are presented. These sensors are aimed for its direct application in a) leaching solutions of waste of electrical and electronic equipment, containing significant thiourea and copper amounts, and b) copper electrorefinery baths, where thiourea is added as an additive in small amounts.

Quantitative analysis was carried out by adding different thiourea amounts into synthetic solutions simulating the electrolytic bath, and the leaching solutions. For the colorimetric sensor the absorption changes of the surface plasmon resonance band (SPRB) were monitored by UV–Vis spectrophotometry. A linear correlation between the absorbance change and thiourea concentration was obtained, ranging from 0.125 to 1 mgL-1. Our technique has the advantage of working in acidic media containing high concentrations of ions, such as Cu2+.

For the electrochemical sensor, 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. The charge-transfer resistance, calculated from Randles modified equivalent circuit from the spectra, was plotted versus thiourea concentration, showing excellent linear correlation (R2=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 were: 9% for measurements in the absence of TU, less than 5% for 0.250–0.750 gL-1 and 13% for 1 gL-1). Affinity between thiourea and cations such as Cu2+ or Fe3+ could affect the performance of this sensor (Akeneev et al. 2005, Ratnarathorn et al. 2012), and for this reason the charge transfer resistance values as a function of thiourea concentration were evaluated in a bath containing Cu(II), Fe(III) and trace amounts of gold and silver. The results 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) /(gL-1), R2=0.975 and detection limit of 0.143 gL-1.

The effect of different experimental conditions during the nanoparticle synthesis was analyzed and the system of immobilized PVP-AgNPs was characterized by Field Emission Scanning Electron Microscopy (FESEM). The proposed systems provide simple, economical, easy-to-handle and rapid measurement tools for monitoring hydrometallurgical processes for optimizing the reconditioning of thiourea solutions, reducing its environmental impact (Tashdjian et al. 2013, Pedre et al. 2015).

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