Silver recovery from simulated photographic baths by electrochemical deposition avoiding Ag$_2$S formation

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ABSTRACT

Aiming at recovering silver from a simulated photographic wastewater, a study on electrochemical deposition with modulated current was developed. In cathodic potentials where hydrogen formation occurs, Ag$_2$S formation was noticed over the electrode due to parasitic reactions. Therefore, in a galvanostatic process, the electrodeposition would only be feasible if conducted under current control to avoid Ag$_2$S formation. An electrochemical flow reactor was used for silver electrodeposition under current control using a stainless steel plate. The modulated current values for the electrodeposition were calculated according to the limiting current kinetic control, applying the mass transfer coefficient calculated from experimental values of diffusion coefficient of silver ions and diffusion layer thickness. Silver electrodeposition was achieved at high efficiency rates, low energy consumption and without the presence of parasitic reactions. The highly negative potentials were avoided when the limiting current was applied and, consequently, sulfur sulfide was not formed over silver deposit. The modulated current electrodeposition of silver revealed to be a feasible process to recover silver from spent photographic baths.

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1. Introduction

Disposal of toxic materials from industrial wastewaters or any other sort of waste generated by human activities has grown exponentially in the last decades, drawing attention due to their impact on the environment and human settlements around these disposal sites. Severe legislation has been adopted in most countries regulating, monitoring and determining legal limits on concentration of these residues, as carbon monoxide emissions by cars, metallic ions from processing facilities and organic compounds generated by chemical plants.

Photographic, X-ray and cinema processing wastewaters constitute the main source of effluents containing silver. In these effluents, silver halide weights from 30% to 40% of the total solution weight, thus making clear that the removal of these species is important not only because of environmental concerns, but mainly due to economic reasons [1]. Although many techniques have been tested for silver recovery, such as cementation [2], adsorption using cationic resins or activated carbon [3], and precipitation [4], electrolysis has been preferred because high-purity silver is obtained, the fixer may be recycled, and silver concentration in the wastewater can be considerably reduced [5]. Recently, Condomitti et al. [6] reported a technique combining magnetically coated carbon particles and electrodeposition to recover silver from dilute solutions.

Since the primary reagent is the electron, the electrochemical technology is even more desirable nowadays due to its environmental compatibility. Furthermore, it is also very economically competitive, presenting a low cost solution besides both easy operation and maintenance procedures. However, the application of electrolysis for silver recovery faces some drawbacks regarding to the low current densities and its unsatisfactory operation for solutions with concentrations less than 200–500 ppm silver due to parasitic electrochemical reactions, leading to precipitation of silver sulfide [7].

Since 1837, the photographic process using fixing solutions based on silver halide (AgX) dissolution in ammonium or sodium thiosulfate solutions has been used by the photograph and X-ray industry [8]. The AgX dissolution in thiosulfates and thiocyanates is fast and no catalysts are necessary, being thermodynamically more stable in slight alkaline pH. The simplified mechanism of AgCl dissolution in sodium thiosulfate is shown in Eq. (1) [3].
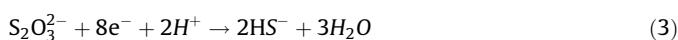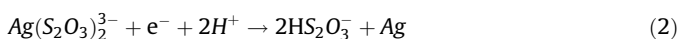
$$AgCl_{(s)} + 2Na_2S_2O_{3(aq)} \rightleftharpoons Na_3[Ag(S_2O_3)_2]_{(aq)} + NaCl_{(aq)} \qquad (1)$$
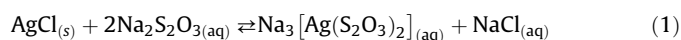
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Nomenclature

A	Membrane area [L^2]
C	Mass concentration [$M\,L^{-3}$]
C_b	Molar concentration in bulk of solution [$N\,L^{-3}$]
C_i	Molar concentration of "i" [$N\,L^{-3}$]
C_s	Molar concentration on surface [$N\,L^{-3}$]
D, D_{AB}	Diffusion coefficient [$L^2\,t^{-1}$]
E_{cell}	Cell potential [V]
I	Current [I]
i	Current density [$I\,L^{-2}$]
i_{lim}	Limiting current density [$I\,L^{-2}$]
k_m	Mass transport coefficient [$L\,t^{-1}$]
L	Membrane length [L]
M	Molecular weight [$M\,N^{-1}$]
N_D	Diffusive flux within boundary layer [$N\,t^{-1}\,M^{-1}$]
V_i	Volume "i" [L^3]
x	One-dimensional length [L]
z	Ion charge [$I\,t$]
β	Cell constant [L^{-2}]
δ	Boundary layer thickness [L]
ε	Current efficiency [–]
η	Energy consumption [$M\,T^{-2}\,L^{-1}$]
σ	Conductivity [$t^3\,I^2\,M^{-1}\,L^{-3}$]

The fixing baths also contain a large number of chemicals such as acids, preservatives, hardeners, and buffers. Therefore, the aqueous waste resulting from the photographic process is a complex solution, which typical composition was provided by Adani et al. [3]. The main components of the sodium sulfate solutions are Ag^+ (2050 mg L^{-1}), Na^+ (3050 mg L^{-1}), and K^+ (3500 mg L^{-1}). The silver electrodeposition reaction [9] shown in Eq. (2) will compete with thiosulfate reduction (Eq. (3)) and hydrogen evolution reaction (Eq. (4)), which constitute the main parasitic reactions occurring during silver electrodeposition.

$$Ag(S_2O_3)_2^{3-} + e^- + 2H^+ \rightarrow 2HS_2O_3^- + Ag \qquad (2)$$

$$S_2O_3^{2-} + 8e^- + 2H^+ \rightarrow 2HS^- + 3H_2O \qquad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (4)$$

At low concentrations, HS^- reacts according to the mechanism of Eq. (5), precipitating silver as Ag_2S.

$$HS^- + 2Ag(S_2O_3)_2^{3-} + 3H^+ \rightarrow Ag_2S + 4HS_2O_3^- \qquad (5)$$
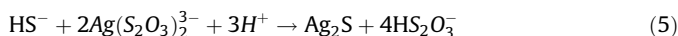
Using flat plate electrodes, many authors investigated the silver electrodeposition under galvanostatic and potentiostatic modes [10–12]. The influence of flow rate, current, and potential on silver removal rate were investigated and it can be concluded that, besides high mass transfer rates, the rigorous control of the potential was fundamental to obtain high current densities and silver electrodeposition to concentrations lower than 1.0 mg L^{-1} without the formation of Ag_2S.

In order to overcome mass transfer constraints and improve current efficiency, three-dimensional electrodes have been studied for silver electrodeposition. Packed bed of carbon particles [9] and reticulated vitreous carbon [13,14] has been used for this purpose. Although it is recognized that three-dimensional electrodes can satisfactorily be applied to recover metals from diluted solutions, the electrode potential control in these electrodes is not easy due to the irregular current and potential distribution inside the porous matrix [15,16].

In this work silver electrodeposition from a simulated sodium thiosulfate solution was investigated. In a first attempt, a three-dimensional cathode (reticulated vitreous carbon) was tested to carry out the electrodeposition, but the formation of Ag_2S and the difficulty of potential control during the electrolysis stimulated the search for new strategies to deposit silver and avoid Ag_2S formation: (*i*) an attempt to remove sulfur compounds by reducing the solution pH was tested and (*ii*) a potentiodynamic mode to supply a modulated current (maintaining the limiting current) was successfully tested.

2. Experimental

2.1. Electrolyte preparation

To mimic the real conditions found in a photographic wastewater, the solutions used in the voltammetric characterizations and for silver electrodeposition were prepared according to the silver concentration found in real wastewater. In this case, a wastewater sample from a photographic store was analyzed by flame atomic absorption spectrophotometry and the average concentration of 800 mg L^{-1} was achieved, along with a 7.3 pH and 35.8 mS cm^{-1} conductivity. This wastewater was a mixture of the spent photography fixer and the wash water. The average concentration of sodium thiosulfate in this mixture was estimated from literature. The value used in this work was 8.75 g L^{-1} [17,18].

The simulated wastewater was prepared by dissolving silver chloride in 8.75 g L^{-1} $Na_2S_2O_3$ solution. Sulfuric acid and sodium hydroxide were used to control the pH. The conductivity was adjusted adding sodium sulfate as supporting electrolyte, when necessary. All reagents were of analytical grade and deionized water was used to prepare the solutions.

2.2. Voltammetric and chronopotentiometric analyses

Cyclic voltammetries were performed in a typical three-electrode cell using 1.0 cm^2 and 1.5 cm^2 Pt foils as working and counter-electrode, respectively. Ag/AgCl 3.0 M KCl was used as reference electrode. The electrolytes used for voltammetry contained Ag^+ (from AgCl) in concentrations ranging from 10 to 1000 mg L^{-1} and 8.75 g L^{-1} $Na_2S_2O_3$. Potential was scanned at 50 mV s^{-1}.

Chronopotentiometric electrodeposition was performed using a 1.0 cm^2 Pt foil as working electrode. In this case, 3.0 mA was applied, giving an initial electrode potential of −0.7 V and the initial Ag^+ concentration was reduced to 374 mg L^{-1}, since Ag_2S formation occurs preferentially at low concentrations in the conditions studied in this work.

2.3. Silver electrodeposition on RVC

Fig. 1(a) shows a schematic representation of the experimental system used for silver electrodeposition. It was composed by: 1) electrolyte tank with maximum capacity of 5L; 2) centrifugal pump (Bomax, PX-NH40); 3) rotameter; 4) diaphragm valve for reactor flow rate control; 5) voltmeter for cell potential measurement; 6) electrochemical reactor; 7) power supply (Minipa, model 3003D) or potentiostat (Autolab, PGSTAT30); 8) thermostatic bath; 9) sphere valve for by-pass flow rate control, and 10) sphere valve for system drainage.

The electrochemical reactor used for silver electrodeposition (Fig. 1(b)) was built in acrylic. The electrolyte flowed upward in closed loop between reactor and the electrolyte tank. A polyethylene mesh covered with a polyamide fabric was placed between the