



Studies on electrochemical recovery of silver from simulated waste water from Ag(II)/Ag(I) based mediated electrochemical oxidation process

K. Chandrasekara Pillai, Sang Joon Chung, Il-Shik Moon *

Department of Chemical Engineering, Suncheon National University, #315 Maegok Dong, Suncheon 540-742, Chonnam, Republic of Korea

ARTICLE INFO

Article history:

Received 22 May 2008

Received in revised form 15 July 2008

Accepted 15 July 2008

Available online 30 August 2008

Keywords:

Electrochemical deposition

Silver recovery

Mediated electrochemical oxidation process

Optimization of experimental conditions

Forced convection

ABSTRACT

In the Ag(II)/Ag(I) based mediated electrochemical oxidation (MEO) process, the spent waste from the electrochemical cell, which is integrated with the scrubber columns, contains high concentrations of precious silver as dissolved ions in both the anolyte and the catholyte. This work presents an electrochemical developmental study for the recovery of silver from simulated waste water from Ag(II)/Ag(I) based MEO process. Galvanostatic method of silver deposition on Ti cathode in an undivided cell was used, and the silver recovery rate kinetics of silver deposition was followed. Various experimental parameters, which have a direct bearing on the metal recovery efficiency, were optimized. These included studies with the nitric acid concentration (0.75–6 M), the solution stirring rate (0–1400 rpm), the inter-electrode distance between the anode and the cathode (2–8 cm), the applied current density (29.4–88.2 mA cm⁻²), and the initial Ag(I) ion concentration (0.01–0.2 M). The silver recovered by the present electrodeposition method was re-dissolved in 6 M nitric acid and subjected to electrooxidation of Ag(I) to Ag(II) to ascertain its activity towards Ag(II) electrogeneration from Ag(I), which is a key factor for the efficient working of MEO process. Our studies showed that the silver metal recovered by the present electrochemical deposition method could be reused repeatedly for MEO process with no loss in its electrochemical activity.

Some work on silver deposition from sulfuric acid solution of different concentrations was also done because of its promising features as the catholyte in the Ag(II) generating electrochemical cell used in MEO process, which include: (i) complete elimination of poisonous NO_x gas liberation in the cathode compartment, (ii) reduced Ag⁺ ion migration across Nafion membrane from anolyte to catholyte thereby diminished catholyte contamination, and (iii) lower cell voltage and hence lesser power consumption.

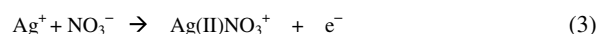
© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The mediated electrochemical oxidation (MEO) has been identified as one of the most promising future technologies by the United Nations Environmental Programme (GEF, 2004) for the ambient temperature destruction of toxic organic pollutants and waste streams including persistent organic pollutants and dioxins (Steele, 1990; Farmer et al., 1992; Bringmann et al., 1995; Galla et al., 2000; Sequeira et al., 2006; Balaji et al., 2007a,b,c,d; Matheswaran et al., 2007a,b,c; Kokovkin et al., 2007). Here a metal ion of high oxidation capacity, like Ag²⁺ ($E^0 = 1.98$ V (NHE)), Co³⁺ ($E^0 = 1.82$ V (NHE)), Ce⁴⁺ ($E^0 = 1.62$ V (NHE)), Mn²⁺ ($E^0 = 1.51$ V (NHE)) etc., is utilized as a mediator to oxidize the organic compound, and the oxidized form of the mediator is electrogenerated in a divided/undivided cell in a closed cycle. In particular, the Ag(II)/Ag(I) based

MEO system has been widely studied to destroy hazardous industrial waste (Steele, 1990; Farmer et al., 1992; Bringmann et al., 1995; Galla et al., 2000; Sequeira et al., 2006; Matheswaran et al., 2007a), and to decontaminate plastic waste (Fourcade et al., 2003), because of its high oxidation capacity at room temperature. In Ag(II)/Ag(I) based MEO system, Ag²⁺ is generated anodically from Ag⁺ in an aqueous nitric acid solution (Eqs. (1)–(3)) in a divided cell with Nafion membrane separator in between the anode and the cathode (Steele, 1990; Farmer et al., 1992; Bringmann et al., 1995; Galla et al., 2000; Sequeira et al., 2006; Matheswaran et al., 2007a).

At anode:

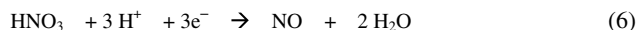
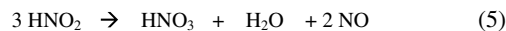
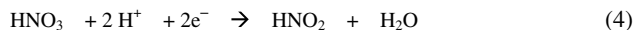


* Corresponding author. Tel./fax: +82 61 7503581.

E-mail addresses: kc_pillai@yahoo.com (K.C. Pillai), ismoon@suncheon.ac.kr (I.-S. Moon).

In the cathode compartment nitric acid is reduced following Vetter mechanism (Juttner et al., 2005) to NO through nitrous acid intermediate (Eqs. (4)–(6)) (Farmer et al., 1992; Sequeira et al., 2006).

At cathode:



The most common side reaction in the cathode compartment is the silver deposition (Eq. (7)), originating from silver ions migrated from anolyte to catholyte across



the Nafion separator. It is predominant and occurs in preference to direct nitric acid reduction at low acid concentrations, and this parasitic reaction is often suppressed by using higher concentrations of the acid ca. 6 M and above (Steele, 1990; Farmer et al., 1992; Bringmann et al., 1995; Galla et al., 2000). Thus, the process streams from the electrochemical reactors of Ag(II)/Ag(I) based MEO system typically contain high concentrations of precious silver as dissolved ions in both the anolyte (as univalent Ag^+ ions in major quantities along with small amount of highly unstable bivalent Ag^{2+} as $\text{Ag}(\text{II})\text{NO}_3^+$) and the catholyte (as Ag^+ ions). Therefore, it is necessary to develop new innovative methods of treating Ag(II)/Ag(I) based MEO wastewater effectively and economically, for silver recovery, before disposing the waste solution as effluent. In the present work electrochemical deposition method was investigated for the silver recovery from the Ag(II)/Ag(I) based MEO wastewater process. It may be mentioned here that the advantages of electrochemical approach, compared to several other chemical tools, have been well recognized for the recovery of metals in their metallic form from metal ion pollutants (Kusakabe et al., 1986; Hwang et al., 1987; Kongsricharoern and Polprasert, 1996; Beauchesne et al., 2005; Chen and Lim, 2005), because the electrochemical methods are relatively simple and clean; moreover, as the conversion of the response of a chemical reaction or a process into a measurable electronic signal is direct and precise in electrochemical methods (as current or potential), regulation and automation are easier to achieve with them in comparison to the chemical techniques.

The electrochemical deposition of silver has been intensely studied for the last several decades on the fundamental side covering various aspects, like kinetics and mechanism of deposition from various electrolytes and deposition baths on diverse substrates (polycrystalline and single crystal metals, semiconductors), nucleation and growth, etc., (Miranda-Hernández and González, 1997; Vandeputte et al., 1997; Márquez et al., 2003; Ramírez et al., 2004). Interestingly, in recent times advanced electrochemical strategies have been adopted in preparing supramolecular nano structures of silver as nano particles (Renado and Martinez, 2007), dendritic nano particles (Geddes et al., 2003), nano whiskers (Scholz and Hasse, 2005), nano rods (Qiu et al., 2005), and nano wire array electrodes (Aloisi et al., 1993; Krista et al., 2000; Tang et al., 2005).

From the application point of view, the electrochemical silver deposition method is widely used in the industry for the removal and recovery of the valuable metal from waste and dilute solutions (Pollet et al., 2000; Reyes Cruz et al., 2002; Fourcade et al., 2003; Chen and Lim, 2005). Reyes Cruz et al. (2002) studied selective recovery of silver by electrodeposition from spent cyanide leaching solutions mimicking those used in hydrometallurgy industry,

which contained very small quantities of silver and gold but high quantities of copper, all in the form of cyanide species. Experiments in a batch electrochemical reactor with recirculation and with a reticulated vitreous carbon electrode indicated that silver at low concentration (10^{-4} M) was recovered without reducing Cu(I) in spite of large concentration difference ($[\text{Ag}(\text{CN})_3]^{2-} : [\text{Cu}(\text{CN})_4]^{3-} = 10^{-4} : 10^{-1}$). In a study by Fourcade et al. (2003), the overall electrochemical process of recovery of silver from “iodized silver derivatives”, dissolved or adsorbed on solid industrial waste or embedded in mineral matrices silica and alumina, was optimized. Chen and Lim (2005) studied the simultaneous electrochemical removal of silver, copper, lead and organic waste (humic acid and EDTA). The rates of recovery for the three metals were found to be slower under competing conditions than in a single metal ion bath, and the competitive metal recovery followed the order silver > lead > copper. A removal of 33–50% of HA and 40–50% of EDTA were also achieved depending on their initial concentration. Numerous work into the electrochemical recovery of silver from photographic baths were reported; for example, Pollet et al. (2000) studied the removal of silver from photographic processing model ‘fix’ solutions (dilute aqueous $\text{Na}_2\text{S}_2\text{O}_3/\text{NaHSO}_3$) with and without ultra sound in a specially designed electrochemical cell (SonoEcoCell) with a stainless steel cylinder electrode. It was reported that the rate constant for the disappearance of silver increased between 18 and 25 times at the maximum ultrasonic intensity of 107 W cm^{-2} depending upon the position of the ultrasonic probe with respect to the electrode.

This work presents the investigation of several experimental parameters including nitric acid concentration, stirring rate, inter-electrode distance, current density and Ag(I) concentration by studying galvanostatically the kinetics of silver deposition on Ti cathode in an undivided cell, in order to design an electrochemical deposition process for silver recovery from simulated nitric acid solution containing Ag(I) ion mimicking waste samples of Ag(II)/Ag(I) based MEO system. Recently, we have shown (Pillai et al., 2008) that the use of sulfuric acid, instead of customarily used nitric acid, as the catholyte in Ag(II)/Ag(I) based MEO process offers several advantages (*vide supra*). Thus, some silver deposition experiments from sulfuric acid were conducted in the present work at different acid concentrations. Our studies showed that the silver metal recovered by the present electrochemical deposition method could be reused repeatedly for MEO process with no loss in its electrochemical activity.

2. Experimental details

2.1. Materials

Silver(I) nitrate (99.8%) from Junsei Chemical Co. Ltd., Japan, nitric acid (60%) from Sam Chun Chemicals, Korea, and sulfuric acid (95%) from DC Chemicals Co. Ltd, Korea were used as-received. Mesh-type IrO_2 -coated-Ti and Ti electrodes of dimension $5\text{ cm} \times 8.5\text{ cm} \times 0.5\text{ cm}$, and mesh-type Pt-coated-Ti and Ti electrodes of dimension $10\text{ cm} \times 14\text{ cm} \times 0.5\text{ cm}$ were purchased from Wesco, Korea. The roughness factor of all the electrodes was 0.8. Nafion® 324 membrane was from Dupont, USA. All the solutions were made using water purified by reverse osmosis (RO) (Human Power III plus, Korea).

2.2. Apparatus

Electrochemical experiments were carried-out in a rectangular cell made of acrylic plates with groves cut along the sides to mount the electrodes at specific distance of separation between them. A mesh type IrO_2 -coated-Ti as the anode and a Ti as the cathode

Download English Version:

<https://daneshyari.com/en/article/4412903>

Download Persian Version:

<https://daneshyari.com/article/4412903>

[Daneshyari.com](https://daneshyari.com)