ARTICLE IN PRESS

Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Combined oxidative leaching and electrowinning process for mercury recovery from spent fluorescent lamps

Cihan Ozgur [a], Sezen Coskun [b,*], Ata Akcil [c], Mehmet Beyhan [a], Ismail Serkan Üncü [d], Gokhan Civelekoglu [a]

[a] *Department of Environmental Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey*
[b] *Egirdir Vocational School, Suleyman Demirel University, TR32500 Egirdir, Isparta, Turkey*
[c] *Mineral-Metal Recovery and Recycling Research Group, Mineral Processing Division, Department of Mining Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey*
[d] *Department of Electrical and Electronic Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey*

ARTICLE INFO

Article history:
Received 30 September 2015
Revised 30 January 2016
Accepted 21 March 2016
Available online xxxx

Keywords:
Mercury recovery
Electrowinning
Leaching
E-waste
Spent fluorescent lamps

ABSTRACT

In this paper, oxidative leaching and electrowinnig processes were performed to recovery of mercury from spent tubular fluorescent lamps. Hypochlorite was found to be effectively used for the leaching of mercury to the solution. Mercury could be leached with an efficiency of 96% using 0.5 M/0.2 M NaOCl/NaCl reagents at 50 °C and pH 7.5 for 2-h. Electrowinning process was conducted on the filtered leaching solutions and over the 81% of mercury was recovered at the graphite electrode using citric acid as a reducing agent. The optimal process conditions were observed as a 6 A current intensity, 30 g/L of reducing agent concentration, 120 min. electrolysis time and pH of 7 at the room temperature. It was found that current intensity and citric acid amount had positive effect for mercury reduction. Recovery of mercury in its elemental form was confirmed by SEM/EDX. Oxidative leaching with NaOCl/NaCl reagent was followed by electrowinning process can be effectively used for the recovery of mercury from spent fluorescent lamps.

1. Introduction

Waste of electrical and electronic equipment commonly known as e-waste includes various forms of all electric and electronic apparatus which are at the end of its life. Some e-wastes such as televisions, computer monitors and fluorescent lamps contain Hg (mercury) (Bhutta et al., 2011; Garlapati, 2016). Due to the toxic effect of mercury, the disposal of e-wastes together with municipal wastes causes environmental problems in the landfill areas. Mercury is essential to the operation of fluorescent lamps. Distribution of electrical and electronic waste was determined in EU Directive 2002/96. Spent lamps were calculated 1.7% of total electrical and electronic wastes as the 5B lighting equipment e-waste group by European Union in 2005 (Erust et al., 2013; EU Directive 2002/96). E-waste stream is very fast growing in the modern world (Huang et al., 2009; Behnamfard et al., 2013) and these wastes should to be designed considering their recycle and reuse potential (Petter et al., 2014; Sahin et al., 2015). Though the lighting industry has achieved significant reductions in mercury content, the mercury is still an important component for the working of fluorescent lamps (NEMA, 2002; Tunsu et al., 2015). When the spent fluorescent lamps are improperly discarded, mercury may contaminate soil and water resources and it can be harmful to the humans and other organisms. Therefore, the recovery of mercury from spent fluorescent lamps would reduce the amount of waste, thus reducing the potential environmental risks (Durão et al., 2008; Coskun and Civelekoglu, 2014, 2015).

Hydrometallurgy process called as leaching had been widely applied for metal recovery from electronic wastes because of its' flexible and energy-saving characteristics (Kinoshita et al., 2003; Lai et al., 2008). However, acidic-leaching was usually applied to obtain high mercury yields in the studies (Rey-Raap and Gallardo, 2013; Tunsu et al., 2014), potential health risks and environmental impacts of using acidic reagents should be considered. In addition, acidic reagents used in the process caused to extraction of other metals (e.g., Al, Mn, Cu, Zn and Cd) solution and it may lead to reduce the efficiency of mercury leaching (Kalb et al., 1999; Coskun and Civelekoglu, 2014, 2015). Therefore, oxidative sodium hypochlorite (NaOCl)/sodium chloride (NaCl) was selected and conducted as oxidative leaching solution to extract mercury as Hg(II) complex as mercury tetra chloride, $HgCl_4^{2-}$ according to Eq. (1) (Twidwell and Thompson, 2001).

$$Hg_{(solid)} + HOCl + 3Cl^- \rightarrow HgCl_4^{2-}{}_{(aqueous)} + OH^- \quad K_f = 5.0 \times 10^{15} \qquad (1)$$

---

* Corresponding author.
E-mail address: sezencoskun@sdu.edu.tr (S. Coskun).

http://dx.doi.org/10.1016/j.wasman.2016.03.039
0956-053X/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article in press as: Ozgur, C., et al. Combined oxidative leaching and electrowinning process for mercury recovery from spent fluorescent lamps. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.03.039

In order to recovery of mercury from the leaching solution, it needs to be reduced to its elemental state (Hg^0). After oxidative leaching, mercury can be recovered as a Hg^0 from the leachate by suitable separation processes such as cementation, ion exchange, solvent extraction, biodegradation/bioreduction, heterogeneous photocatalysis, electrowinning and hybrid use of these processes (Cui and Zhang, 2008; Bussi et al., 2010; Chaturabul et al., 2015). The electrowinning technology was successfully applied electroplating process to recover heavy metals from concentrated leaching solutions (Vegliò et al., 2003). This process is attractive due to its versatility, energy efficiency, simple equipment, easy operation, and low operation cost (Jüttner et al., 2000; Meunier et al., 2006; Lai et al., 2008). However, little information is available about recovery of mercury using electrowinning from spent fluorescent lamps. The dissolved mercury in leachate can be recovered by cathodic reduction according to Eq. (2). On the other hand, mercury agglomerating may occur at the electrode surfaces. This may lead to Hg_2Cl_2 precipitation according to Eq. (3). When the solution pH goes down below 4, Hg_2Cl_2 is formed (Hummer et al., 2006). Therefore, neutral pH (pH of 7) condition was provided for electrowinning experiments in the current study

$$HgCl_4^{2-}{}_{(aqueous)} + 2e^- \rightarrow Hg^0 + 4Cl^- \qquad (2)$$

$$Hg^0 + Hg^{2+} + 2Cl^- \rightarrow Hg_2Cl_{2(s)} \qquad (3)$$

In the present study, electrowinning process was applied for convert mercury to its metallic state after oxidative (hypochlorite) leaching of mercury from spent tubular fluorescent lamps. The optimal process conditions for high efficiency of recovery were identified.

2. Material and methods

2.1. Sample preparation and oxidative leaching tests

Spent fluorescent lamps were collected from hospitals, schools and factories in the city center of Isparta, Turkey. T8 and T12 linear (tubular) types of spent fluorescent lamps were selected for study owing to their high rate of consumption around the world (Coskun and Civelekoglu, 2015). These lamps also have higher mercury content than the other mercury-containing lamps such as T2, T5 and compact fluorescent lamps (CFLs) (Hu and Cheng, 2012). Each spent fluorescent lamp was manually dismantled under vacuum in laboratory. The oxidative leaching experiments were conducted on pulverized mixture samples of lamps (50–50% mixture of the T8 and T12 lamps) to simulate a realistic situation. Sample preparation method was described in detail by Coskun and Civelekoglu (2015).

To determine the initial mercury concentration of lamps, 20 g pulverized samples were extracted with 25 mL water and 25 mL aqua regia (HCl/HNO_3, v/v - 3/1) in polypropylene flasks using a magnetic stirrer at 200 rpm (Heidolph MR Hei-Tec 3001) at room temperature for 18 ± 2 h. Each sample was filtered through funnels using following the mixing stage. The initial mercury concentrations were determined using atomic absorption spectrophotometer (AAS) (PerkinElmer-FIMS 400, attached with flow injection automated system). NaOCl (6–14% active chlorine, Merck 105614) and NaCl (extra pure, Merck 106400) were used as chemical (oxidative) leaching reagents to extract mercury from pulverized lamp samples. The leaching tests were performed in 250 mL polypropylene flasks placed in temperature-controlled water baths (GFL 1086) with mechanical stirrers. During the leaching tests, the pH of the solutions was monitored using a digital pH meter (WTW multi, 340i). The solutions were filtered (20 μm, pure cellulose filter papers), and analyzed for their mercury content to quantify leaching efficiency. Each sample was diluted by a factor of 1:10 using nitric acid solution (pH = 2) to avoid the precipitation of metals and then stored at 4 °C for further analysis using AAS. Quantification of leaching efficiency was determined by comparing initial mercury concentration in extracted lamp sample solutions and final mercury concentration in filtered leaching solutions. All mercury analysis were based on Method 7471B (Mercury in solid or semisolid waste-manual cold vapor technique) from USEPA's "Test methods for evaluating solid waste-physical/chemical method" (SW-846) (USEPA, 1998).

2.2. Electrowinning tests

Leaching process was followed by electrowinning and oxidative leaching solution was used as electrolyte in this process. The reaction system was comprised of a 150 mL glass reactor with one graphite electrode (0.5 cm diameter, 6 cm length), acting as the cathode, one dimensionally stable anode (DSA®) (2 cm width, 5 cm length), which is made of titanium substrate with a thin layer of iridium oxide (IrO_2) acting as the anode of the electrolytic cell. A power supply (GW Instek GPR-1820 HD) that provides electric current (0–10 A and 0–18 V) was used to provide electric current. While the applied current was constant (e.g., 2, 4 or 6 A), the voltage value was varied from 7 to 12 V between the two electrodes during the experiments. All electrowinning tests were carried at room temperature and pH of 7. The pH values were adjusted using reagent grade NaOH and/or HCl solutions with different molar concentrations (0.2 M–0.5 M–1 M). The electrodes were connected parallel to the power supply and the mercury was analyzed with AAS.

Citric acid ($C_6H_8O_6$, Merck-818707) was added into filtered leaching solution as a reducing agent. The effects of the current intensity (A), citric acid amount (g/L), electrolysis time (min.) on process yield were evaluated on basis of 2^3 full factorial designs (Table 1) at 25 °C of temperature. The central point tests were used to evaluate the experimental error of electrowinnig process and therefore the SE (standard error) for the effects. The experimental matrix was designed according to Yates Algorithm (Montgomery, 1991).

The graphite electrodes were analyzed before and after of electrowinnig process by scanning electron microscope coupled with an energy-dispersive X-ray spectrophotometer (SEM/EDX) (FEI Quanta250 FEG) to investigate the elemental compositions.

3. Results and discussion

3.1. Leaching tests

Oxidative leaching tests were carried out to determine the optimal leaching conditions in terms of simultaneous mercury extractions. Mercury could be leached by NaOCl/NaCl reagent with an efficiency of 96% from real spent fluorescent lamps at 2-h contact time, 50 °C of temperature, pH 7.5 and 120 rpm agitation speed (Coskun and Civelekoglu, 2015). The addition of chloride ions

Table 1
Factors and levels investigated in electrowinning tests.

Code	Factor (variable)	Level		
		−1	0	+1
A	Current intensity (A[a])	2	4	6
B	Citric acid amount (g/L)	5	15	30
C	Electrolysis time (min)	30	60	120

[a] Ampère (A).

Please cite this article in press as: Ozgur, C., et al. Combined oxidative leaching and electrowinning process for mercury recovery from spent fluorescent lamps. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.03.039