Chemosphere 178 (2017) 249–258

Contents lists available at ScienceDirect

Chemosphere

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

High purity silver microcrystals recovered from silver wastes by eco-friendly process using hydrogen peroxide

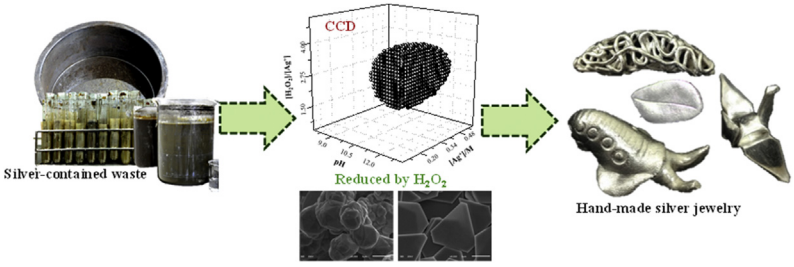
Harnchana Gatemala [a], Sanong Ekgasit [a], Kanet Wongravee [a, b, *]

[a] Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand
[b] Nanotec-CU Center of Excellence on Food and Agriculture, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330 Thailand

HIGHLIGHTS

- Simple, rapid, highly efficient, and environmentally friendly process for large scale silver recovery.
- The morphology of the recovered product can be easily controlled.
- The recovered silver microcrystals are in high purity (up to 99.99%).
- A direct usage of the recovered silver microcrystals as a raw material for wearable silver jewelry was explored.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 December 2016
Received in revised form
21 February 2017
Accepted 12 March 2017
Available online 14 March 2017

Handling Editor: Shane Snyder

Keywords:
Silver recovery
Hydrogen peroxide
Silver chloride
Silver microcrystal
Silver clay

ABSTRACT

A simple, rapid, and environmentally friendly process using hydrogen peroxide, was developed for recovering high purity silver directly from industry and laboratory wastes. Silver ammine complex, $[Ag(NH_3)_2]^+Cl^-$, derived from AgCl were generated and then directly reduced using H_2O_2 to reliably turn into high purity microcrystalline silver (99.99%) examined by EDS and XRD. Morphology of the recovered silver microcrystals could be selectively tuned by an addition of poly(vinyl pyrrolidone). The main parameters in the recovering process including pH, concentration of Ag^+ and the mole ratio of H_2O_2:Ag^+ were carefully optimized though the central composite design (CCD). The optimized condition was employed for a trial recovery of 50 L silver ammine complex prepared from a collection of silver-wastes during 3-year research on industrial nanoparticle production. The recovered silver microcrystals >700 g could be recovered with 91.27%. The remaining solution after filtering of the recovered silver microcrystals can be used repeatedly (at least 8 cycles) without losing recovery efficiency. Matrix interferences including Pb^{2+} and Cl^- play a minimal role in our silver recovery process. Furthermore, the direct usage of the recovered silver microcrystals was demonstrated by using as a raw material of silver clay for creating a set of wearable silver jewelries.

1. Introduction

Due to their unique physical and chemical properties, silver metal and silver salt are widely used as catalysts, antibacterial substances, sensors, photographic materials, batteries and as part of electronic devices in various industries as well as in agriculture

* Corresponding author. Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand.
E-mail address: kanet.w@chula.ac.th (K. Wongravee).

http://dx.doi.org/10.1016/j.chemosphere.2017.03.051
0045-6535/

and medicine productions. Recent reports have shown that silver is in great demand which is steadily increasing approximately 2–2.5% per annum (GFMS, 2015; Katrivanos, 2015). Because of the limited natural availability and diminishing of silver mineral, the cost of silver production is rapidly rising. Since the extensive applications of silver, industrial wastes containing silver were also dramatically increased. The releasing of silver as silver nanoparticles (AgNPs) or silver ion (Ag^+) from silver-contained wastes causes grave and irreparable to the environment and human health. The toxicity of AgNPs in zebrafish was reported to have the ecotoxicity in a concentration-dependent manner (Asharani et al., 2008). The Ag^+ ions have been reported that they can induce ion regulatory impairment and increase mortality in rainbow trout eggs (Guadagnolo et al., 2000). Therefore, an alternative economical sustainability criterion with the preservation of environmental assets is urgently required. A powerful recovery process is a promising protocol to regenerate silver from the industrial wastes. These have recently attracted much attention not only with respect to the environmental sustainability and reduction of production costs but also the energy saving aspects.

Several processes developed for recycling the silver-contained wastes involve disassembling the metal from the non-metal part followed by a leaching process using hydrometallurgical (chemical) (Akcil et al., 2015; Baláž et al., 1996; Gurung et al., 2013; Lee et al., 2011) which is preferred over bioleaching (Frías et al., 2002) especially from electronic waste. The final recovery step is the reduction of leachate by pyrometallurgical (Sathaiyan et al., 2006), chemical reduction (Chen and Lim, 2002; Lee and Fung, 1981), or electrochemical deposition (Chandrasekara Pillai et al., 2008; Chen and Lim, 2005; Chen et al., 2012). The most widely used process to recover silver from leachate is the cementation (galvanic replacement) which base metals such as aluminum and iron were employed as sacrificial metals(Aktas, 2010). This method is the cheapest process, however, the treatment of the remained solution might be required before releasing to the environments. Nevertheless, some recovery methods are costly, time consuming and require intensive labors. The addition of chemicals for precipitation and reduction in the processes generates large quantities of secondary wastes. Hence, an additional process for treating the secondary waste is required. The final product might be contaminated, therefore, the further purification is necessary. The direct usages of the recovered products have never been mentioned or explored as the morphology (size and shape) and purity of the recovered silver cannot be controlled. The modification and treatment of the recovered products substantially increase the recovery cost. As a result, silver recovery from wastes rarely achieves an economic scale. To overcome these problems, the development of low-cost, eco-friendly and shape-controlled silver recovery systems from wastes is strongly recommended.

Hydrogen peroxide (H_2O_2) is well-known as a strong oxidizing agent, however, it can be an efficient reducing agent under an alkaline condition (Chen et al., 2009, 2010; Cui et al., 2012; Gatemala et al., 2015; Nootchanat et al., 2013; Parnklang et al., 2013). The reducing capabilities of H_2O_2 were demonstrated elsewhere (Chen et al., 2009, 2010; Cui et al., 2012; Parnklang et al., 2013). From our previous studies, we have observed that H_2O_2 can act not only as a reducing agent but also a shape transformation agent for promoting the growth of silver nanoplates (AgNPls) (Parnklang et al., 2013, 2015; Wongravee et al., 2013). Using of H_2O_2 as a reducing agent in the silver recovery process is considered as an attractive treatment process because it is eco-friendly process and low cost of operation. H_2O_2 was also reported to be used for improving the leaching efficiency of silver from ore or silver contained-waste (Sun et al., 2015). The leaching rate was increased with an increase of H_2O_2 concentration but leaching efficiency is eroded by the decomposition of H_2O_2 catalyzed by metal oxide (Jiang et al., 2004). The prominent advantages of using H_2O_2 are: (i) it does not generate toxic products (it decomposes to oxygen and water), (ii) the process can be performed under ambient condition, (iii) the process is inexpensive, straightforward, and fast, (iv) it has high recovery efficiency and generates highly pure silver crystals. Bas et al. reported the using of H_2O_2 as an oxidizing agent to recover silver from the X-ray film processing effluents (Bas et al., 2012). The concentration of H_2O_2 is the most significant parameter for recovery process which can be improved by an increase of pH. Moreover, an addition of ethylene glycol can enhance the recovery efficiency due to its H_2O_2-stabilization effect. Mahdizadeh et al. recovered silver from radiographic film processing effluents in similar protocol. The optimum conditions of the recovery process were determined by using response surface method (Mahdizadeh et al., 2014).

The objective of this work is to develop an eco-friendly process and to evaluate its efficiency for recovering high purity silver microcrystals from AgCl using H_2O_2 as a reducing agent under ambient condition. By turning precipitated AgCl (equation (1)) into silver ammine complex ($[Ag(NH_3)_2]^+$) (equation (2)), it should be noted that an adequate ammonia might be required to turn all the precipitated AgCl into silver ammine complex. Then, the silver ammine complex can directly be reduced into silver microcrystals by H_2O_2 (equation (3))(David, 2010). The reaction is simultaneously occurred according to the positive redox potential. Furthermore, this reaction gives non-harmful products which are metallic silver (Ag^0), ammonia, oxygen and water.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \quad (1)$$

$$AgCl(s) + 2NH_4OH(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq) + 2H_2O(l) \quad (2)$$

$$2[Ag(NH_3)_2]^+(aq) + H_2O_2(aq) \rightarrow 2Ag(s) + 4NH_3(aq) + 2H_2O(l) + 1/2O_2(g);\ E_0^{cell} = 0.227\ V \quad (3)$$

In this work, the morphology and recovery efficiency could be tuned by pH, concentration of Ag^+ and mole ratio of H_2O_2:Ag^+. To evaluate the recovery efficiency, the experiments were systematically performed using central composite design (CCD) approach, and the optimal conditions were determined by 3D-response surface plot. This determined condition was employed for recovering silver (>700 g) in 50 L silver ammine complex collected from silver waste during 3-year research on industrial silver nanoparticle production. The repeatability of the remaining solution after filtering of recovered silver microcrystals was revealed in order to access an eco-friendly process. The process was further developed for economical applications by using tap water (high Cl^- content) in the entire process. Furthermore, the recovery efficiency was further monitored when a contaminated ion (e.g. Pb^{2+}) interferes in the recovery process. According to high purity of silver microcrystals, we present the direct usages of these silver microcrystals for fabricating wearable silver jewelries.

2. Material and methods

2.1. Reagents and materials

Silver nitrate ($AgNO_3$, ≥99% purity), sodium chloride (NaCl, ≥99% purity), sodium hydroxide (NaOH, ≥99% purity), nitric acid (HNO_3, 65% w/v), ammonium hydroxide solution (NH_4OH, 25% w/w), sodium borohydride ($NaBH_4$, ≥98.0% purity) and hydrogen peroxide solution (H_2O_2, 30% w/w) were purchased from Merck®. Poly(vinyl pyrrolidone) (PVP, $M_w \approx 360{,}000$) was purchased from Aldrich. All chemicals are analytical grade and used as received.