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Ag recovery from copper anode slime by acid leaching at atmospheric pressure to synthesize silver nanoparticles



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ABSTRACT

In this paper, recovery of silver from anode slime of Sarcheshmeh copper complex in Iran and subsequent synthesis of silver nanoparticles from leaching solution is investigated. Sarcheshmeh anode slime is mainly consisted of Cu, Ag, Pb and Se. Amount of Ag in the considered anode slime was 5.4% (by weight). The goal was to recover as much as possible Ag from anode slime at atmospheric pressure to synthesize Ag nanoparticles. Therefore, acid leaching was used for this purpose. The anode slime was leached with sulfuric and nitric acid from room to 90 °C at different acid concentrations and the run which yielded the most recovery of Ag was selected for Ag nanoparticles synthesis. At this condition, Cu, Pb and Se are leached as well as Ag. To separate Ag from leach solution HCl was added and silver was precipitated as AgCl which were then dissolved by ammonia solution. The Ag nanoparticles are synthesized from this solution by chemical reduction method by aid of sodium borohydride in the presence of PVP and PEG as stabilizers. The synthesized Ag nanoparticles showed a peak of 394 nm in UV–vis spectrum and TEM images showed a rather uniform Ag nanoparticles of 12 nm.

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1. Introduction

In electrorefining of copper, some metals are accumulated in the byproduct anode slime, which is an important source for recycling and recovery of these metals [1]. In this paper, copper anode slime of Sarcheshmeh copper complex was used, which is located in south east of Iran. Sarcheshmeh anode slime is characterized by higher amount of Ag, Se, Pb and Cu compared to other metals with very low amount of Au. The price of anode slime is mainly determined by its Ag and Au while Pb and Se are also important in some cases [2]. Therefore, there is interest in studying methods for recovery of these metals from anode slime. Impurities must also be removed from anode slime before recovery of valuable metals like Ag. Some metal nanoparticles such as silver and gold in the particle size range of less than 100 nm to 6 μm, are also of great industrial importance in the circuit industry for the manufacture of conductor thick film pastes. In particular, silver paste compositions are used in front end metallization of photovoltaic cells, actuators and plasma displays [3]. Spherical silver nanoparticles made by precipitation methods are one of the ways for silver supply for

these applications. The size distribution of these nanoparticles is controlled by synthesis method and process parameters such as concentration, temperature, method of reactants addition and growth inhibitor component [4–8].

The methods of leaching copper anode slime usually use sulfuric acid in the presence of oxygen and Fe³⁺ as oxidant to improve oxidation ability of sulfuric acid. In usual method, high pressure air at high temperature is used to reach satisfactory recovery of metals resulting in high recovery of Cu and poor Ag recovery. This method of metals recovery is usually performed in an autoclave. However, leaching of copper anode slime at atmospheric pressure at low and high temperatures also gives moderate Cu and poor Ag recovery and addition of oxidizing agents like MnO₂ and NaCl could not improve the recovery of Ag [9]. It is also possible to recover substantial amount of copper by first using high temperature sulfuric acid and subsequent feeding copper anode slime to an autoclave. An alternative method for processing of copper anode slime is wet chlorination where chlorine solution removes almost all of metals in the anode slime but recovery of silver is poor in this case as AgCl precipitates. In this case Au can be recovered due to formation of soluble complexes with Cl⁻ [10,11]. In some cases hydrochloric acid is used for oxidizing metals together with other oxidants like chlorine, H₂O₂ or NaClO [12]. A way to recover Ag is

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nitric acid, thiourea or thiosulfate leaching of anode slime [13–16]. Leaching with KOH can remove As and Sb [17].

Yavuz and Ziyadanogullari studied recovery of gold and silver from copper anode slime [18]. The slime contained Cu, Te, Se in addition to Ag and Au. To this aim pressure leaching with sulfuric acid in an autoclave removed Cu. selenium and tellurium were extracted by Na_2SO_3 or Na_2S solutions and the remained selenium was removed by roasting. They found that if the roasted samples are leached first with concentrated sulfuric acid in an autoclave at 350 °C under 800 kPa oxygen pressure, and then with 0.1 M sulfuric acid and then 3 M NH_3 , most of the silver can be dissolved. Gold were recovered by thiourea leaching.

An article by Hait et al. described role of MnO_2 and NaCl in sulfuric acid leaching of copper anode slime [9]. They found that at atmospheric pressure leaching recovery of Cu with sulfuric acid is low and addition of MnO_2 is beneficial for leaching of copper, selenium and tellurium. A combination of MnO_2 and NaCl was also investigated giving even higher recoveries of these metals and gold removal but not successful for removing Ag. Chen and Dutrizac have also studied slime leached with NaCl addition and the main difference in the leach residue was found to be that silver mainly occurs as silver chloride instead of sulfate, although silver sulfate is also insoluble in sulfuric acid [19]. They indicated that during O_2 – H_2SO_4 pressure leaching, significant amounts of Cu, Ni, Se, and Te are solubilized with the subsequent formation of Ag_2SO_4 , Ag_2Se in solid phase. However, at atmospheric pressure sulfuric acid leaching is not a suitable choice for Ag recovery and other leaching agents must be used. Amer studied processing of anode slime obtained from an Egyptian copper electrorefining plant [13]. The anode slime was characterized by high concentrations of copper, lead, tin and silver. The proposed hydrometallurgical process consisted of two leaching stages for the extraction of copper (H_2SO_4 – O_2) and silver (thiourea– Fe^{3+}).

Fernández et al. presented a method for recovery of components of copper anode slime by combination of pyrometallurgical with hydrometallurgical method [17]. Arsenic and antimony, present in anode slimes, can be selectively and almost completely dissolved in 0.4 M KOH at 80 °C. After this extraction, alkaline roasting of anode slimes in the presence of K_2CO_3 , at 600 °C solubilizes Se (99%) and less than 2% As and 0.1% of Sb. After Se leaching, Cu and Te can be dissolved in 1.2 M HCl at 25 °C as well as in CuSO_4 – H_2SO_4 solution. The residue contains BaSO_4 , PbSO_4 , SiO_2 , Au, Ag and small amounts of Se, Cu and Te and can be smelted in order to obtain a bullion for Ag and Au recovery by the conventional electrorefining process. Luo et al. reported a method for treating anode slime in several operations, including removal of copper and nickel by leaching with dilute sulfuric acid, leaching of selenium, silver and tellurium with dilute HNO_3 (2–8 M), recovery and recycling of HNO_3 , selective solvent extraction of silver, and, finally, separation and recovery of selenium and tellurium from the Ag free solution by reduction with SO_2 under different conditions (acidities) [20]. The residues from the nitric acid leaching were collected for further processing to recover gold and other noble metals. Arai et al. studied Ag recovery from copper anode slime by leaching it with thiosulfate which acts as oxidizing agent [21]. It was found that electrolytic recovery of Ag from thiosulfate solution containing $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ can deposit silver with 99.8% purity.

In this paper, an experimental study was begun to recover almost all of silver from copper anode slime to synthesize silver nanoparticles. It examines effect of temperature and concentration for Ag leaching with two acids at atmospheric pressure, when Ag concentration in leach solution is monitored with time. The Ag concentration is reported for the purpose of comparing two acid performance in Ag leaching from copper anode slime and conditions of high Ag recovery was determined in terms of acid concentration and temperature. Silver nanoparticles are synthesized by

chemical reduction of silver in presence of polymer stabilizers at aqueous solution and rather uniform silver nanoparticles are formed. More detailed studies on kinetics of silver leaching from copper anode slime will be presented in upcoming papers.

2. Experimental

2.1. Leaching experiments

The chemicals used in this work were of reagent grade and supplied by Merck. Copper anode slime of Sarcheshmeh were ground with a lab scale mill. X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy were used for chemical analysis and mineralogy of copper anode slime. The morphology of anode slime was obtained by scanning electron microscope (SEM). The XRD, XRF, SEM and atomic absorption spectroscopy (AAS) equipment models were Phillips, ARL 8410, Phillips and Shimadzu, respectively. UV–vis spectroscopy and transmission electron microscopy (TEM) images were taken from silver nanoparticles to confirm their synthesis in solution and obtain their size and shape. Nitric acid was 65%, sulfuric acid 96%, hydrochloric acid 37%, sodium borohydride 96%, ammonia solution 25%, sodium citrate, polyvinylpyrrolidone (PVP) 40000 and polyethylene glycol (PEG) 5000–7000.

Experiments were carried out in a 600 mL glass vessel at atmospheric pressure and vessel contained 400 mL solution (also shown in [Supplementary data](#)). The anode slime to solution ratio was 1:10 and 40 g copper anode slime was used in each experiment. The solution was agitated with a magnetic stirrer at 1000 r/min and heated on a hotplate directly. Experimental solution temperature was 25, 40, 60 and 90 °C at different nitric acid and sulfuric acid concentrations. The change in Ag concentration during leaching was monitored by measuring Ag absorbance by AAS (after dilution). At selected time intervals (10 min), 5 mL of leaching solution was sampled from solution and filtered, 1 mL of this solution was diluted to 500 mL by distilled water and the diluted solution was analyzed by AAS to determine silver content in leaching solution. In order to eliminate mixing effect, stirrer speed was 1000 r/min which ensures complete mixing in leaching solution. In nitric acid leaching experiments, a reddish brown vapor was also observed above the solution in the beginning of leaching, indicating NO production. Some parts of solution was also evaporated during each leaching experiment causing the silver concentration change during leaching which is considered in silver concentration calculation. Volume change of solution is measured and reported in [Supplementary data](#). Volume change is noticeable at 60 and 90 °C.

Silver recovery is defined as the ratio of silver in leach solution at time t to initial silver in slime. In calculating the leaching recovery of silver (Recovery, %), a volume correction formula Eq. (1) was used; which includes correction factor to account for the volume losses due to sampling:

$$\text{Recovery}(\%) = \frac{(V - \sum v_i)C_{\text{Ag},i}}{m(\%wt/100)} \quad (1)$$

where V is the initial volume, mL of the solution; v_i the volume, mL of the sample i withdrawn each time; $C_{\text{Ag},i}$ the concentration of Ag in sample i , mg/L; m the mass of anode slime in g in leaching vessel and %wt the weight percent of Ag in anode slime. The procedure for calculating silver recovery is given in [Supplementary data](#).

2.2. Silver separation from leaching solution

To obtain silver, it must be separated from other metals presenting in leaching solution. There are many metals in the anode slime which are also recovered to the solution by acid leaching

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