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Gold recovery from copper anode slime by means of magnetite nanoparticles (MNPs)

R. Ranjbar a, ⁎, M. Naderi a, H. Omidvar a, Gh. Amoabediny b, c

a Department of Mining and Metallurgical Engineering, Amir-Kabir University of Technology, 424, Hafez Avenue, P.O. Box 15875–4413, Tehran, Iran
b Department of Chemical Engineering, School of Engineering, University of Tehran, Tehran 14174, Iran
c Research Center for New Technologies in Life Science Engineering, University of Tehran, Tehran, Iran

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A B S T R A C T

Despite cyanidation currently being the conventional gold recovery process, researchers are looking for alternative methods for the recovery of gold from its sources without using cyanide. The current work attempts to study the recovery of gold from copper anode slime by means of a novel process utilizing magnetite nanoparticles (MNPs). In this process, MNPs were first synthesized by the co-precipitation method, and the characterization of the product was then carried out using the X-ray diffraction (XRD), transmission electron microscopy (TEM), and vibration sample magnetometer (VSM) methods.

Thiourea solution was employed as leachant. All the gold content of copper anode slime was dissolved in thiourea solution and a positive complex of gold and thiourea was obtained as a result. At a pH value higher than the pH of point of zero charge (PZC), the nanoparticles (NPs) were added to the gold solution. The gold complex adsorbed on the NPs due to their negative surface charge. At the last stage, ammonia was added to the gold-attached NP suspension and gold was consequently precipitated in metallic form. The results obtained from the method indicate the high efficiency of the method for the recovery of gold from copper anode slime.

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1. Introduction

In the conventional method of copper extraction from its ores and secondary source, at the electrowinning stage, only copper and electropositive metallic impurities such as iron, zinc, and lead are solved as ions and deposited on anode. At the above mentioned stage, impurities such as gold, silver, selenium, and tellurium, which are known as the anode slime, remain intact and fall down as the anode corrodes gradually (Abdollahy and Shafaei, 2004). However small quantity of these metals is present in the slime, and the recovery of gold from slimes, waste water, and other sources.

Activated carbons are carbonaceous materials with a well-developed porous structure consisting of hydrophobic graphene layer surface and hydrophilic surface functional groups. These characteristics turn them into efficient adsorbents, catalysts, and catalyst supports (Bansal et al., 1988; Jia and Demonopolous, 2003). Hydrometallurgical processes have been employed by many researchers for extraction of gold from anodic slime (Elkin and Tremblay, 1964; Hoffmann, 1991; Morrison, 1963; Rice, 1988; Subramanian et al., 1980). Another research work was conducted as green technology to recover gold from non-metallic secondary sources. The method employed in the research was based upon heating the scrap material along with using an “eco-friendly” or a “green” reagent (Syed, 2006).

Nowadays, NPs, nanomembranes, and nanopowders are used for detection and removal of chemical and biological substances including metals (e.g. cadmium, copper, lead, mercury, nickel, and zinc), nutrients (e.g. phosphate, ammonia, nitrate, and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins), viruses, bacteria, parasites, and antibiotics (Tiwari et al., 2008). Their size-dependent physical and chemical properties prove efficient in various useful technologies (Kim et al., 2007).

It has been reported that metal ions such as lead, chromium, copper, silver, and mercury can be removed/collected from diluted aqueous solutions using TiO2 NPs (Park et al., 2005). Some other studies focused on separation of iridium ions from aqueous solutions and indium (III).
from environmental samples by nano-Al₂O₃ and nano-sized titanium dioxide respectively (Zhang et al., 2009, 2012). A few researchers focused their studies on the recovery or extraction of gold from wastes or copper anode slimes. One of such studies employed ZnO nanopowders for collection of gold from wastewater (Park et al., 2005).

In recent years, magnetite nanoparticles (MNPs) have gained an increasing interest because of their potential applications; instances include their uses for cell separation (Jing et al., 2007), magnetic resonance imaging (Lee et al., 2006), drug delivery systems (Neuberger et al., 2005), protein separation (Gu et al., 2006), and cancer treatments through hyperthermia (Ito et al., 2003).

Among the various NPs, nanomagnetites are particularly appealing for the above-mentioned purposes and due to two main reasons: 1. they behave superparamagnetically and present a relatively high magnetic saturation and high magnetic susceptibility and biocompatibility; and 2. in comparison to the magnetic transition metals such as cobalt, iron and nickel (Ferreira et al., 2010), they are less sensitive to oxidation. In a research work, mesoporous silica-coated magnetite nanoparticles (SCMNPs) have been used for a highly efficient removal and recovery of Hg from water; in this work, the size of nanomagnetites was around 50 nm, and a maximum efficiency of about 90% was reported (Hakami et al., 2012). In another research work, adsorption of arsenic and chromium by mixed magnetite and maghemite NPs from aqueous solution with efficiency of about 96–99% under controlled pH conditions was reported (Chowdhury and Yanful, 2010). Another work was also carried out for on the removal of dichromate anions; in this work, the size of magnetite NP was about 10 nm (Ozcan et al., 2009).

The current research work employs MNPs for gold recovery. MNPs were synthesized through the co-precipitation method, and then were coated by the method introduced by Stöber et al. (1968). TEM, XRD, and VSM were further used to characterize the synthesized NPs. Next, NPs were used to adsorb the positively charged complex of gold and thiourea obtained by dissolving gold in thiourea solution. In the last step, the desorption and regeneration tests were carried out utilizing ammonia so as to investigate whether this new type of adsorbent was appropriate and efficient for the recovery of metallic gold.

The novelities of this work, which might be of more interest, are first the high potential of such nanoparticles for gold recovery even at very low concentrations; second their reproducibility after several recycling periods, and third the introduction of a new method for gold recovery from copper anode slime and other sources with an efficiency of 100%.

2. Experimental

2.1. Materials

The copper slime utilized for the test was obtained from the National Sarcheshmeh Copper Company in Iran. All chemicals used in the preparation were procured from Merck (Germany).

2.2. Synthesis of MNPs

The procedure applied for the preparation of SCMNPs was of two stages: first, the synthesis of the magnetite (Fe₃O₄) nanoparticles (MNPs) and then the application of silica coating.

MNPs were first prepared using a slightly modified version of the co-precipitation method, introduced by Kang et al. (1996). According to this method, 10.81 g of FeCl₃·6H₂O and 3.97 g of FeCl₂·4H₂O were dissolved in water and HCl solution (37%), respectively. The resultant solutions were then added to deoxidized ammonia aqueous solution under vigorous stirring. The black precipitate, or MNPs, were rinsed several times by means of a magnet, and were dispersed in deionized water. Coating was then performed as per a slightly modified version of a common method introduced by Stöber et al. (1968). In this method, 100 ml ethanol (pure), 5 ml deionized water, 8.5 ml ammonium hydroxide (28%), and 1.5 ml TEOS were stirred for 30 min in 40°C. The resultant substance was a milky solution. Then, 1 g of nanoparticles was added to silica and stirred for 1 h so as to coat the magnetite core by silica. Finally, the coated nanoparticles were rinsed and dispersed in deionized water. It is worth to note that Silica-coating is appropriate at normal atmosphere. X-ray diffraction (XRD), transmission electron microscopy (TEM), and vibration sample magnetometer (VSM) were further used to characterize the synthesized MNPs.

2.3. Gold–thiourea solution

Leaching of gold in the copper anode slime is affected by some elements such as silver, iron, and selenium. Therefore, copper anode slime was first washed by concentrated nitric acid (65%). 10 ml of

![Fig. 1. XRD results for NPs.](image1)

![Fig. 2. TEM images for MNPs: A) magnetite B) SCMNPs.](image2)
3. Results and discussion

3.1. Characterization of MNP

The crystal structure, morphology, and magnetic properties of the NPs were characterized by XRD, TEM, and VSM, respectively. The XRD pattern was obtained using a Rigaku RINT-2000 diffractometer using CuKα radiation (λ = 1.5418 Å). The pattern obtained for the observed peaks was the same as the standard pattern for magnetite (JCPDS 19-629); this indicates the inverse spinel structure of the MNP (Fig. 1).

TEM images for MNP and SCMNP were obtained using a Philips, EM 208 instrument at 100 kV acceleration voltage. According to the TEM images obtained for MNP (Fig. 2a) and SCMNP (Fig. 2b), it can be concluded that the NPs are almost spherical with average diameters of around 8 and 15 nm, respectively (determined by a statistical measurement and averaging 50 particles, with particle size distribution of about 1.2).

The size reduction results in an increase in superparamagnetic properties (Rice, 1988). In the current paper, the least particle size for obtaining the best magnetic properties was achieved by optimizing the conditions of synthesizing. It is significant that the important parameters including type of the base, reaction temperature, stirring speed and time were set in away to have the desired characteristics for the obtained MNP. The magnetic behavior of the synthesized MNP was characterized using a vibrating sample magnetometer (VSM). Fig. 3 presents the results confirming the above statements. As shown in Fig. 3, the curves for both MNP and SCMNP exhibit zero remanence and coercivity, demonstrating superparamagnetic property of these particles. Besides, it can be concluded that they are sufficient for magnetic separation with a conventional magnet due to their high magnetic saturation.

This property is suitable for industrial applications and is a significant finding on MNPs. A similar observation has been reported by Zhao et al. (2008).

Fig. 3 also shows that saturation magnetization of the Fe₃O₄ NPs is about 50 EMU/g at room temperature, while it is 40 EMU/g in the case of SCMNP.

This reduction is due to the presence of nonmagnetic silica layers on the magnetite particles. A similar magnetic behavior with the same amount of magnetization for MNPs, which have a similar diameter, has been reported by Mahdavian and Mirrahimi (2010).

The magnetically separated MNPs and SCMNP are not permanently magnetized, and can be re-dispersed without any signs of re-aggregation when the external magnetic field is removed. This property is due to the super-paramagnetic NPs. Both MNPs and SCMNP show similar characteristics. Because of the higher saturation magnetization for MNPs relative to SCMNP, and working in aqueous phase, it can be concluded that Fe₃O₄ NPs are most suitable for gold recovery from solution.

3.2. Anodic slime characterization

Table 1 presents the chemical composition of the delivered copper anode slime from the National Sarcheshmeh Copper Company before and after the washing process with nitric acid obtained by XRF and concentrated nitric acid was added to 5 g of copper anode slime, and the obtained mixture was then stirred for 15 min. As a result, gold and residual barite was deposited.

The gold and silver content of the residue was measured after leaching by atomic absorption spectroscopy (AAS), methyl iso-butylketone (MIBK), and XRF.

Leaching tests were carried out by thiourea in a 500-ml round bottomed flask. Mixing was performed by an adjustable speed stirrer. All of the experiments were carried out at ambient temperature. Thiourea powder, hydrogen peroxide (30%) (as the oxidizing agent), and sulfuric acid (98%) (for pH adjustment) were used for gold leaching with thiourea. In the next step, 5 g of the pretreated copper anode slime was added to the thiourea solution, and the resulting solution was then stirred for 24 h at 50 rpm. Finally, residue was removed from gold thiourea solution by filtration.

2.4. Gold adsorption on to NPs

At this step, MNPs were utilized for recovering gold from the gold-containing solution. Since the surface charge of the NPs changes by varying pH (Faraji et al., 2010), MNPs in ammonia solution were dispersed in order to obtain more negatively charged MNPs. NPs were then collected by applying a magnetic field. At the next step, 0.1 g of the negatively charged MNPs was stirred for 15 min using a mechanical stirrer. Gold-adsorbed MNPs were collected by applying a magnetic field. The resulting solution was then stirred for 15 min using a mechanical stirrer. Hence, metallic gold and MNPs were precipitated. At last, by applying a magnetic field, NPs were separated from the black sediment containing gold. After desorption process, MNPs were washed by an acidic buffer with pH 5 and water and then were re-used for gold adsorption process.

Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>CuO</th>
<th>SeO₂</th>
<th>Ag₂O</th>
<th>Sb₂O₃</th>
<th>BaO</th>
<th>PbO</th>
<th>SrO</th>
<th>Au</th>
<th>Re</th>
<th>IrO₂</th>
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</thead>
<tbody>
<tr>
<td>Before washing (wt %)</td>
<td>5.4</td>
<td>10.2</td>
<td>4.8</td>
<td>2.58</td>
<td>34.1</td>
<td>3.81</td>
<td>0.98</td>
<td>0.12</td>
<td>0.028</td>
<td>0.12</td>
</tr>
<tr>
<td>After washing (wt %)</td>
<td>0.128</td>
<td>0.42</td>
<td>0.2</td>
<td>3.72</td>
<td>64.7</td>
<td>3.81</td>
<td>1.62</td>
<td>0.12</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>After dissolved (wt %)</td>
<td>0.128</td>
<td>0.42</td>
<td>0.2</td>
<td>3.72</td>
<td>65</td>
<td>3.81</td>
<td>1.82</td>
<td>-0</td>
<td>0.04</td>
<td>0.12</td>
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Table 2
<table>
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<tr>
<th>pH</th>
<th>The amount of dissolved gold (ppm)</th>
<th>The percentage of dissolved gold (%)</th>
</tr>
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<tr>
<td>1.2</td>
<td>66</td>
<td>~100</td>
</tr>
<tr>
<td>1.4</td>
<td>66</td>
<td>~100</td>
</tr>
</tbody>
</table>

Table 3
<table>
<thead>
<tr>
<th>pH</th>
<th>The remained gold in solution (ppm)</th>
<th>Absorbed gold (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>~0.01</td>
<td>0±1</td>
</tr>
<tr>
<td>1.4</td>
<td>~0.01</td>
<td>0±1</td>
</tr>
</tbody>
</table>

3.3. Gold containing thiourea solution characterization

Table 2 shows the amount of dissolved gold in the thiourea solution (dissolution efficiency) in ppm scale.

According to Farinha et al. (1992), the maximum amount of gold dissolved in thiourea solution can be obtained with thiourea to hydrogen peroxide ratio of 2 and pH value of between 1 and 1.5. The results obtained also confirm this fact that under the following leaching conditions, the gold contained in the copper anodic slime dissolved almost completely (99.99%) at CS(NH2)2/H2O2 = 60 (g/l)/30 (g/l) = 2. The tests were carried out at pH values between 1.2 and 1.4.

3.4. Adsorption process

Gold in thiourea solution is in the form of the Au(CS(NH2)2)2+ positive complex. The adsorption process involves coulombic attraction between the negatively charged NPs and the positive complex. Around the isoelectric point, Fe-OH is the dominating surface species for MNPs. However, the dominating sites can be altered in the presence of H+ and OH− ions from dissolved acids or bases. Under the pH(PZC), the dominating surface species changed to Fe-OH+2, and the surface charge of the particles became positive. Increasing pH above the isoelectric point caused formation of Fe-O− and a negative surface charge. Hence, after dispersing MNPs in ammonia, more negatively charged particles were obtained due to enhancement of hydroxide ions (Illés and Tombácz, 2006). The obtained pH(PZC) for MNPs was about 6 (Faraji et al., 2010; Ferreira et al., 2010). Thus, when MNPs were placed in ammonia solution, Fe−O− formed on the NP surfaces. Upon addition of MNPs to gold−thiourea solution, a layer of gold complex formed around the MNP surface, and this layer prevented dissolution of MNPs in the acidic solution. After adsorption, MBKB was carried out on the remaining thiourea solution to determine the percentage of gold adsorption. Table 3 presents the results obtained from the MBKB test. The effect of time was investigated as well, the results of which are shown in Fig. 4. It is notable that the adsorption amount of Au-cations on MNPs increases with time, and Au-cation concentration in the solution decreases until it disappears or is completely removed from the solution. This shows the high separation potential and efficiency of the synthesized superparamagnetic magnetite nanoparticles.

Morphology of gold on the surface of NPs was studied by TEM at 100 kv (Fig. 5).

TEM images show spherical NPs with an average diameter of around 25 nm, demonstrating adsorption of gold onto the magnetite.

3.5. Desorption study

At this step, for the desorption process, ammonia solution was added to the magnetite-gold NP suspension, and as a result, a black sediment containing gold and MNPs was deposited. The gold complex was stable in the pH range from 1 to 1.5, and therefore, by adding ammonia to NPs, pH reached a level of over 8, and the complex disassociated according to the following reaction. Therefore, gold along with other components was precipitated (Farinha et al., 1992; Hilson and Monhemius, 2006; Örgül and Atalay, 2002).

2Au(CS(NH2)2)2+ + 2OH− → Au + 2CS(NH2)2 + H2O + ½ O2.                  (1)

Thiourea can also be dissociated according to reaction 2.

CS(NH2)2 = NH4+ + SCN−.                                                  (2)

Furthermore, thiourea can be hydrolyzed, and have reaction with H2O according to the following reaction:

CS(NH2)2 + H2O = = CO(NH2)2 + H2S.                                      (3)

Another reversible reaction that may occur is the formation of formamidine disulfide. Formamidine disulfide oxidizes to produce cyanamide, hydrogen sulfide, and elemental sulfur.

2CS(NH2)2 = = NH2(CSSCNH2)NH2 + 2H+ + 2e−.                             (4)

NH2(NH)CSCN(NH)NH2 = = NH2CSNH2 + Sulfinic compound                   (5)

Sulfinic Compound →CNH2 + S0.                                            (6)

Also, to confirm the elemental gold precipitation, XRD test was carried out on the residue: the results of the test without any noise filtration and numerical normalization are shown in Fig. 6. The XRD diffraction pattern shows two diffraction peaks related to gold which demonstrates pure gold particle precipitates. It can be concluded from the seven observed diffraction peaks emphasizing the magnetite structure that they are recovered without any change. Hence, they can be used for several times.

Finally, after washing the precipitate with deionized water, gold was separated from MNPs by applying a magnetic field. In fact, the XRD analysis of results shows that there are no metallic impurities besides gold. They also indicate the successful recovery of gold.

3.6. MNPs recycling

After desorption process, MNPs were separated from gold by applying magnetic field. MNPs were then washed by acidic buffer with a pH of about 5 as well as water to remove all impurities. The obtained recycled
products were used for separation of gold complex. The adsorption capacity \( (q_e, \text{mg g}^{-1}) \), i.e. the amount of gold adsorbed at equilibrium, was calculated by the following equation (Hakami et al., 2012):

\[
q_e = \frac{V(C_0 - C_e)}{m}
\]  

(7)

where \( C_0 \) is the initial gold concentration in solution (mg l\(^{-1}\)), \( C_e \) is the equilibrium concentration (mg l\(^{-1}\)) after adsorption, \( V \) is the solution volume (l) and \( m \) is the mass of NPs adsorbent (g). Fig. 7 presents the results pertaining to separation of gold. The results reveal that the recycled products have still preserved their capability for separation. The capacity of gold adsorption is reduced about 2–4% during each recycling period which may be due to gold complex or thiourea not being released from adsorption sites between cycles; this actually suggests the stability of superparamagnetic MNPs after separation and recycling procedure. It can also be concluded that the electrostatic (physical) bonding between gold complex and MNPs is the most important cause of easy separation of gold from the surface of MNPs and capacity retention of MNPs.

4. Conclusions

1. MNPs were prepared using the co-precipitation method, and the silica-coating process was carried out according to the Stöber method (1968). NP characterization suggested that the process produced a uniform structure and uniform properties. TEM images illustrated that the particle size for MNPs and SCMNPs was about 8 and 10 nm, respectively. Moreover, both of them show superparamagnetic properties according to their magnetization curves.

2. Due to various reasons such as higher saturation of magnetization of MNPs relative to SCMNPs, working in aqueous phase as well as economic reasons, it can be concluded that Fe\(_3\)O\(_4\) NPs are the most suitable and profitable method for the recovery of gold from the solution.

3. Gold solution was prepared using thiourea as solvent. Gold ions appeared in the solution in the Au(CS(NH\(_2\))\(_2\))\(^+\) form.

4. Gold adsorption onto the NPs occurred according to the electrostatic attraction between the negative charged MNPs and positive complex of gold.

5. Gold-attached MNPs were successfully prepared in an aqueous solution with pH control. In fact, this was achieved by using copper anode slime as Au source. Au ions attached the MNP surfaces as per the ionic surface charge force as well as the zeta potential or pH\(_{\text{zpc}}\) of the MNPs.

6. Au complex adsorbed on MNPs could be desorbed effectively using ammonia for increasing pH, and this is because of the low stability of gold complex in alkaline solution.

7. The capacity of gold adsorption was reduced about 2–4% during each recycling step and this shows the stability of MNPs after separation and recycling process.

8. The results suggest that MNPs can be an effective alternative to conventional adsorbents for the adsorption of gold complex from
its solution at high recovery efficiency of about 100% and in a very short time.

9. The advantage of MNPs is their ease of separation by an external magnetic field and possibility of simple recovery after washing with acidic aqueous solution and water. The method for synthesis of MNPs and gold collection process addressed in this work is viable for obtaining gold with high purity from anode slime and other secondary sources.

References


