



Selective recovery of gold on functionalized resins



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ABSTRACT

The functional resins containing guanylthiourea, 1-methylimidazole, 2-mercapto-1-methylimidazole, dipropylamine, 1,2-dimethylimidazole and 1-(3-aminopropyl)imidazole ligands were highly selective for the gold(I) and silver(I) from ammonia solution and they did not sorb ammine complexes of copper(II). The kinetics of gold(I) sorption on these resins was improved by immobilization of N,N-dimethylethanolamine ligands, which were responsible for increasing the hydrophilicity of the polymeric material. 1-Methylimidazole resins retained their capacity towards gold in five consecutive sorption/desorption cycles. All resins in cyanide form displayed high affinity towards gold(I) from ammoniacal solution (100 g/L NH₃·H₂O, 5.00 g/L (NH₄)₂SO₄). The sorption degrees of gold were 99.5%.

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1. Introduction

Gold is very rare and scattered precious metal, recovered from poor grade raw materials on an industrial scale by using hydrometallurgical methods, which are the only guarantee of the effective extraction of this metal. Hydrometallurgy of gold is mainly based on cyanide leaching of easily leachable ores in the presence of oxygen or air (Breuer et al., 2005; Cattrho and Koch, 1964; Hedley and Tabachnik, 1968; Miltzarek et al., 2002). This type of ores is exhausted, which is why gold is extracted now from refractory gold ores, where the gold is trapped in the copper sulfide minerals or other metals. Release of the gold grains from these ores requires a pretreatment (roasting, pressure leaching, bioleaching) before the actual cyanide leaching. An alternative solution, which does not require pre-treatment, is ammonia leaching of refractory ores in hydrothermal conditions under oxygen atmosphere. Ammonia is less toxic than cyanide, relatively inexpensive and easily regenerated by evaporation techniques (Han and Fuerstenau, 2000; Meng and Han, 1996). The use of ammonia leaching requires the development of selective and efficient methods for separation of gold complexes from ammoniacal solutions.

For the gold recovery from leaching solutions sorption on activated carbon (CIP method, called “carbon in pulp”) and sorption on polymeric resins (RIP method, called “resin in pulp”) are applied. Gold-selective resins have some distinct advantages over activated carbon for the

recovery of gold. Resins have potentially higher loading capacities and higher loading rates are less likely to be poisoned by organics, and do not require thermal regeneration. The main disadvantage of polymeric resins is that they are more expensive than activated carbon (Green et al., 2002).

Polymeric materials, ion-exchange resins, containing selective functional groups, and chelating resins are widely used in hydrometallurgy, especially for the separation of noble metal ions from various solutions (Parodi et al., 2008). Chelating polymers are characterized by the presence of reactive functional groups containing O, N, S and P donor atoms that are capable of forming complexes with metal ions. These materials are used when the concentration of metal ions in the solutions is small and the resins display preferential sorption towards chosen ions. The efficiency of the removal process depends on the process parameters (pH of the solution, ion concentration, contact time) and on the properties of the ion exchange/coordination resin (swelling, crosslinking degree, type and structure of immobilized ligand).

The gold-selective resins (MINIX and AURIX) were developed by Mintek and were used for the recovery of gold from cyanide leaching solutions. MINIX is a strong-base resin, which contains tributylamine as the functional group, while AURIX is a medium-base resin. They are reported to be styrene-divinylbenzene resin beads functionalized with guanidine functional group (Green et al., 2002).

The recent research on the selective metal ion removal has been widely carried out by using specific ligands in modified polymers in order to pre-concentrate the precious metal ions. Noble metals, especially gold, were loaded and recovered using: poly[4-vinylbenzyl(2-hydroxyethyl)sulfide] resin (Qu et al., 2006), guanidine resin

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(Jermakowicz-Bartkowiak, 2005; Kolarz et al., 2004), resin containing calixpyrroles (Kaładkowski and Trochimczuk, 2006), bis(2-benzimidazolylmethyl)amine resin (Pramanik et al., 2004), resin containing benzimidazolylazo groups (Das et al., 1999), thiourea-based coordinating polymers (Zuo and Muhammed, 1995), resins with amino, thio and amino/mercaptane functionalities (Donia et al., 2005), resin containing 1,4-bis(imidazolylazo)benzene ligands (Pramanik et al., 2006), phosphine sulfide chelating polymers (Sanchez et al., 2001), resin containing carboxymethylphosphonate and methylenediphosphonate ligands (Trochimczuk, 2001). Polymers with functional groups containing sulfur atoms are very effective for the sorption of gold. The resin with amino/mercaptane ligands has the highest affinity towards Au(III) ions (439 mg Au/g of resin) (Donia et al., 2005). The polymeric resins with “soft” electron pair donor atoms in the macrocyclic calix[4]pyrrole[2]thiophene ligand also display extremely high sorptive ability towards gold (335 mg Au/g of resin) (Kaładkowski and Trochimczuk, 2006). The polymer with phosphonate groups can effectively remove AuCl_4^- complexes from hydrochloric acid solutions (130–166 mg Au/g of resin) and from solutions containing large quantities of Cu(II) (70 mg Au/g) (Trochimczuk, 2001).

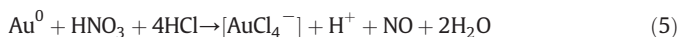
Our group had obtained novel resins containing different ligands: carboxyphosphonate, 1-methylpiperazine, ethylenediamine, dipropylamine, 1-methylimidazole, 2-mercapto-1-methylimidazole, 1,2-dimethylimidazole, 1-(3-aminopropyl)imidazole and different amino ligands, which were used for the gold recovery from ammonium buffer solutions (Piłśniak and Trochimczuk, 2006; Piłśniak and Trochimczuk, 2007; Piłśniak et al., 2009).

The aim of this work was to present the possibility of the gold sorption from a single and the multicomponent solutions on the vinylbenzyl chloride-divinylbenzyl copolymer functionalized with the aliphatic and aromatic amine. This paper was a continuation of our research that was focusing on preparing the new resins in order to improve gold sorption kinetics and increase the efficiency and selectivity of Au recovery.

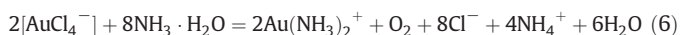
2. Experimental

2.1. Chemical reagents

The chemicals were Sigma-Aldrich products. The solution of gold in ammonium buffer was prepared by dissolving metallic gold in aqua regia. The solution of $[\text{AuCl}_4]^-$ was introduced into ammonium buffer solution (50.0 g/L $(\text{NH}_4)_2\text{SO}_4$, 100 g/L $\text{NH}_3 \cdot \text{H}_2\text{O}$). Experiment was carried out in autoclave under oxygen atmosphere (10–15 atm) and high temperature (120 °C). The preparation of gold solution could be described using the following reactions:



(Łętowski, 1975; Trzebiatowski, 1979)



(Lazarev and Kharlamov, 1987; Wozniak and Apostoluk, 2008; Xu et al., 1996)



The initial gold concentrations were 398.0 and 431.4 mg Au/L. These solutions were diluted twenty times with ammonium buffer (100 g/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, 5.00 g/L $(\text{NH}_4)_2\text{SO}_4$) in order to obtain the concentration of 19.90 or 21.57 mg Au/L and various concentrations of ammonia and ammonium sulfate.

The solutions of $\text{Au}(\text{NH}_3)_2^+$ containing 19.90 or 21.57 mg/L of gold and 100 g/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 5.00 g/L $(\text{NH}_4)_2\text{SO}_4$ were used in the sorption experiments.

The solutions of gold(I), silver(I) and copper(II) were prepared by dissolving a known amount of copper sulfate and silver nitrate in ammonium solution of gold.

The polymeric resins used in this work were prepared from the starting material: vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer. The polymeric support was obtained by typical suspension polymerization. The chloromethyl groups present in its structure served as a reactive place for the immobilization of a ligand. In an attempt to prepare resin with optimal properties, three starting materials with different morphologies (Table 1) (expanded gel, gel and porous) were used.

2.2. Methods of analysis

Water regain was measured using centrifugation method in which about 1 g of polymer swollen in water was placed in a column with filled-glass bottom and centrifuged at 3000 rpm for 5 min, weighted and dried at 80 °C for 24 h. After cooling in a desiccator, the polymer was weighted again. The water regain was calculated as $(m_w - m_d) / m_d$, where m_w is the weight of the swollen polymer after centrifugation, m_d is the dry weight of polymer.

Nitrogen content was determined using the Kjeldahl method after mineralization of the sample of resin (about 200 mg) in the concentrated sulfuric acid containing copper sulfate and potassium sulfate.

The chlorine content was measured by burning about 20 mg of dry polymer sample in oxygen in a flask containing 25 mL of 3% hydrogen peroxide solution. The content of Cl was determined using Volhard's method.

The sulfur content was measured by burning about 20 mg of dry polymer sample in an oxygen-filled flask. The products of burning were adsorbed in 15 mL of 3% hydrogen peroxide solution. After 1 h the flask was heated in a water bath for 30 min in order to evaporate carbon dioxide. Then the content of the flask was titrated with 0.01 M NaOH in the presence of bromothymol blue.

Quaternary ammonium group content was determined using Leikin method. Resin sample in chloride form was placed in chromatographic column. The resin bed was washed with 200 mL of 4% sodium sulfate solution and the effluent was collected in a 250 mL volumetric flask. Then, 15 mL of effluent was taken and titrated by using 0.01 mol/L silver nitrate solution. In this manner, chlorides from the strongly alkaline group were determined.

The sorption capacity of resins towards gold, silver and copper from ammonium buffer solutions was determined by contacting the resin samples with 10 mL of metal ion solution. Metal ion solutions containing Au(I) (19.90 or 21.57 mg/L), Ag(I) (11.44 or 12.20 mg/L) and Cu(II) (6.76 or 22.44 mg/L) were used in the sorption experiments. The ratio of ligands in the resin to metal ions in the solution was set to 10:1. After 24 h the polymers were separated by filtration and the concentration of Au was measured using atomic absorption method on a Perkin-Elmer Analyst 100.

For the kinetics of sorption, the identical samples of resin were shaken with 10 mL of solution containing 19.90 or 21.57 mg/L of Au(I) in an ammonium buffer (100 g/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, 5.00 g/L $(\text{NH}_4)_2\text{SO}_4$). Samples were taken at different intervals of time, resin and solution separated and the concentration of gold was determined by AAS.

The distribution coefficient (K_d) was calculated as the ratio of the amount of metal taken by 1 g of resin and the amount of metal remaining in 1 mL of solution after sorption.

The selectivity coefficient (α_{se1}) was calculated as the quotient of distribution coefficients for each metal.

FTIR spectra of resins in KBr pellets were recorded on a Perkin-Elmer System 2000 spectrophotometer.

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