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Use of Water-Compatible Polystyrene–Polyglycidol Resins for the Separation and Recovery of Dissolved Precious Metal Salts

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The use of polystyrene–polyglycidol (PS/PG) water-compatible resins for the extraction of the precious metal salts gold(I) cyanide and silver(I) cyanide from aqueous phase was studied. The resins studied include polyglycidol grafted onto a polystyrene core, a thiol version of this base PS/PG resin in which the terminal hydroxyl groups are replaced with thiol groups, and a magnetic PS/PG resin. More than 99% of the gold and silver ions of the original solutions could be extracted using the resins, and reverse extraction of the loaded metal ions from the resins was performed. Thus, recycling of the resins was possible and no deterioration in extraction performance of the reused materials was observed. The attractiveness of these resins in water purification is augmented by the fact that the PS/PG resins examined can be easily synthesized from inexpensive commodity chemical starting materials.

Introduction

In recent years there has been increasing environmental concern regarding metal salt pollution in wastewater. The conventional technologies used for metal extraction for water purification include ion-exchange resins, polymer ultrafiltration, and microemulsion techniques. Such extraction processes are generally composed of four separate operations: (1) binding of dissolved metal salts to an extracting material, (2) separation of the metal loaded extracting material from the aqueous phase, (3) elution of loaded metal ions, and (4) recycling of extracting material. Each of the above-mentioned conventional technologies suffers from drawbacks in various steps of the extraction process, such as slow extraction rates, long separation times, difficult reverse extraction, and no recycling of extracting material.

In order to overcome some of these deficiencies, metal salt extraction using an aqueous biphasic extraction system (ABES) has recently been reported.1 In this strategy, water-soluble polymer poly(ethylene glycol) (PEG) is used as the extracting material. The use of PEG in an ABES has the advantage that it is virtually nontoxic, nonflammable, and relatively inexpensive.2 However, such an ABES suffers from the fact that a large quantity of a salt, such as sodium sulfate, is required to achieve phase separation of the aqueous and PEG phases once the extraction is complete. Though most of the salts used for such applications are inexpensive, they do potentially introduce corrosion issues. This method is particularly uneconomical for treating effluents with parts per million concentrations of dissolved metals.

With respect to the problems mentioned above, a solid phase polymer of PEG with a polystyrene (PS) core was first used for metal extraction in this work. A PS core provides a hydrophobic backbone while PEG has hydrophilic properties. This solid phase polymer is commonly applied in biological research for biomolecules such as proteins.

Polyglycidol (PG), a polymer with a structure similar to that of PEG, was synthesized and immobilized on polystyrene (PS) surface. This resin is called PS/PG resin, and it is water compatible and partially soluble in aqueous solution. As opposed to common ion-exchange resins in which binding sites (charges) are hidden inside a hydrophobic substrate (polystyrene or divinylbenzene), the PS/PG structure has exposed swellable external hydrophilic groups. Because of the PS core, the resin can be readily separated by sedimentation or centrifugation without the need of salt addition.

The synthesized PS/PG resin was tested for precious metal extraction such as gold(I) and silver(I) ions. Reverse extraction of metal ions from the resin was also investigated. Furthermore, since thiols have strong affinity to gold, the extraction capability of PS/PG resin was strengthened and possibly made more selective by coupling to thiol groups,4 and the resin became thiol-terminated PG (PS/PG-SH). A magnetic aqueous biphasic system was reported for biomolecules, and an increased rate of separation was achieved. Using methodologies well-known in the art, a magnetite core coated with the PS/PG resin was also synthesized for extraction in order to promote separation efficiency, easy separation, and repeated extractions.

Methods

Preparation of Materials for Extraction. I. PS/PEG Resins. PS/PEG resin was purchased directly from Rapp Polymer GmbH. The resin was used for extraction without any modification. The resin is called TentaGel S 30 900, with a diameter of 90 µm.

II. Synthesis of Polystyrene/Polyglycidol (PS/PG) Resins. In a 100 mL three-necked flask, hydroxymethylated PS beads (1 g, 7.1 mmol of OH groups/g of polymer) were suspended in dry diglyme (25 mL). After swelling for 1 h, KO2Bu (0.8 g, 7.1 mmol) in THF solution was added to deprotonate the hydroxyl groups at 40 °C over 12 h. The mixture was heated to 120 °C, and 50 mL of dry DMF was added. A solution of freshly distilled glycidol (24 mL, 26.4 g, 356 mmol) in dry DMF (40 mL) was added dropwise to the reaction mixture. The mixture was stirred for 12 h at 120 °C and then terminated with 1 N HCl. The mixture was filtered and washed with water and MeOH and finally dried in a vacuum to give the product, with a yield of 21.6 g. The final white resins are composed of core polystyrene, c.a. 5% by weight, covered with polyglycidol, c.a. 95% by weight. The resins swelled in water upon stirring. The resins can be filtered or settled as a bottom layer by gravity. This synthesis is a modification of that of Haag et al.5 A

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scanning electron microscopic (SEM) image of a PS/PG/ magnetite particle is shown in Figure 1.

III. Synthesis of Polystyrene/Thiolated-Polyglycidol (PS/PG-SH) Resins. Mesyl chloride (1.0 g, 9 mmol) was added dropwise to a mixture of PS/PG (0.5 g, 6.0 mmol of OH groups/g of polymer) and pyridine (1.4 g, 18 mmol) in anhydrous CH2Cl2. The reaction mixture was stirred for 12 h at room temperature under N2 atmosphere. The resulting resin can be fully extracted from the aqueous phase to the polymer phase. The determination of gold in aqueous phase after reverse extraction, another set of experiments were performed with high inlet Au or Ag concentration of 100 mg/L and larger quantities of solution and resin. The extraction procedure was similar with but with 50 mL of solution and 10 g of resin.

In our experiment, magnetite core coated with the PS/PG resin was synthesized, and Figure 2 is a SEM image of it. With a magnetite core, the resin can be controlled by a magnetic field to increase the separation efficiency.

Figure 1. Scanning electron microscopic image of polystyrene/polyglycidol (PS/PG).

Figure 2. Scanning electron microscope image of magnetite/polystyrene/polyglycidol (MAG/PS/PG).

dried in a vacuum to give 3.5 g of the product with a weight increase of 250%.

In our experiment, magnetite core coated with the PS/PG resin was synthesized, and Figure 2 is a SEM image of it. With a magnetite core, the resin can be controlled by a magnetic field to increase the separation efficiency.

Extraction Experiments. To investigate the extraction at low gold concentration, a stock solution of 15 mg/L Au was prepared from a corresponding quantity of potassium gold(I) cyanide (obtained from Kenlap PCG Manufacturer Company Limited). A 21.96 mg sample of potassium gold(I) cyanide was dissolved and diluted to 1 L of deionized water. Another stock solution of 15 mg/L Ag was prepared from a corresponding quantity of potassium silver(I) cyanide (obtained from Kenlap PCG Manufacturer Company Limited). A 27.68 mg sample of potassium silver(I) cyanide was dissolved and diluted to 1 L of deionized water. The solutions were then used for metal extraction without modification unless otherwise stated. For each metal extraction, 10 mL of solution was mixed with 0.5 g of polymer. After stirring, the polymer was settled by sedimentation or magnetic separation and the aqueous phase was decanted for metal concentration determination.

To evaluate the uptake capacity of resin and also investigate reverse extraction, another set of experiments were performed with high inlet Au or Ag concentration of 100 mg/L and larger quantities of solution and resin. The extraction procedure was similar with but with 50 mL of solution and 10 g of resin. Repeated extractions were performed on metal loaded resin with 100 mg/L metal concentration.

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Extraction of Gold and Silver by Different Resins. Results of the gold and silver extraction experiments using different resins are summarized in Table 1. The results indicate that gold can be fully extracted from the aqueous phase to the polymer phase. The determination of gold in aqueous phase after extraction showed that the percentage of gold extracted to the
adding HCl to shift equilibrium toward \[\text{Ag(CN)}_2\]

precipitates AgCl formed could be removed by filtration. The

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Type of solid phase & Aqueous phase & Metal concn before extraction (mg/L) & Metal concn after extraction (mg/L) \\
\hline
polystyrene/polystyrene (ethylene glycol) & potassium gold cyanide solution & 15 & <0.1 \\
polystyrene/polystyrene (ethylene glycol) & potassium silver cyanide solution & 15 & 0.1 \\
polystyrene/polyglycidol & potassium gold cyanide solution & 15 & <0.1 \\
polystyrene/polyglycidol & potassium silver cyanide solution & 15 & <0.1 \\
polystyrene/thiolated polyglycidol & potassium gold cyanide solution & 15 & <0.1 \\
polystyrene/thiolated polyglycidol & potassium silver cyanide solution & 15 & <0.1 \\
magnetite/polystyrene/poly(ethylene glycol) & potassium gold cyanide solution & 15 & <0.1 \\
magnetite/polystyrene/poly(ethylene glycol) & potassium silver cyanide solution & 15 & <0.1 \\
\hline
\end{tabular}
\caption{Extraction Results of Gold and Silver by Different Resins}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Partial charges on polymer chain, which can attract gold cyanide complex.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Schematic illustration of gold recovery in electrodeposition. Gold-bearing phase is indicated in yellow.}
\end{figure}

The silver solution had to be treated with diluted hydrochloric acid to remove excess cyanide anions. While \([\text{Au(CN)}_2]^-\) is the only stable complex between gold and cyanide, \([\text{Ag(CN)}_2]^-\), \([\text{Ag(CN)}_3]^2^-\), and \([\text{Ag(CN)}_3]^3^-\) can coexist.\(^{10}\) The additional ligands in \([\text{Ag(CN)}_3]^2^-\) and \([\text{Ag(CN)}_3]^3^-\) affect the binding of the complexes with the polymer. Therefore, the percentage extraction of silver with excess cyanide ions was lower than that of gold. \([\text{Ag(CN)}_3]^2^-\) and \([\text{Ag(CN)}_3]^3^-\) can be removed by adding HCl to shift equilibrium toward \([\text{Ag(CN)}_3]^3^-\) and remove free cyanide (KCN). Free cyanide, if present, reacts with HCl to form HCN, which can escape from the solution. If excess HCl was added, it reacted with \([\text{Ag(CN)}_3]^2^-\) and the white precipitates AgCl formed could be removed by filtration. The pH was 7 as excess protons formed HCN and volatile HCN was easily removed. The percentage extraction of silver using such control pH treated silver solution was higher than 99%.

The mechanism of extraction is based on the special binding between the metal cyanide complex and the polymer resin. The lone pair electrons of oxygen on the PEG or PG group can attract the positively charged gold atoms in gold cyanide complexes, as illustrated in Figure 3.

**Recovery of Gold and Silver.** After extraction, gold can be reverse extracted and recovered via chemical means. An alternative convenient means of electrodeposition is illustrated in Figure 4.

First, gold solution was mixed with PS/PG resin for extraction as shown in step 1 (Figure 4). After extraction, the gold content in the polymer phase increased significantly. In step 3, the aqueous phase could then be discarded and only a wet polymer phase was retained for metal recovery. In step 4, using a platinum wire as the anode, the gold was plated onto a clean nickel or copper wire. The electrical resistance in the polymer required a high plating voltage. In this experiment, the current was 0.1 A and the voltage was 15 V. The voltage could be reduced to about 1 V by adding a small amount of salt such as sodium chloride or sodium sulfate.

During electrodeposition (Figure 5), the gold ions loaded on the resin are reduced by the applied current. The change in oxidation state and charge neutralization disrupt the attractive interaction with the C−O−C group. The desorbed gold atoms are immediately deposited onto the nickel or copper surface. The nickel wire was weighed before and after electrodeposition so that the mass of gold plated could be calculated. See Table 2.

Similarly, silver recovery was also performed (see Table 3). In the experiment, only about 40−50% of gold or silver was

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Mechanism of metal desorption from resin followed by electrodeposition.}
\end{figure}

\begin{table}
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\begin{tabular}{|l|c|c|c|c|}
\hline
Sample description & Gold concn in 100 mL of lean soln (mg/L) & % removal & Au recovery by electrodeposition (mg) & % recovered by electrodeposition \\
\hline
After first extraction & <1 & >99 & 5 & 2.1 & 42 \\
After second extraction & <1 & >99 & (5−2.1)+5=7.9 & 3.8 & 48 \\
\hline
\end{tabular}
\caption{Results of Gold Recovery After Reverse Extraction and Recycling of Resins}
\end{table}

\begin{table}
\centering
\begin{tabular}{|l|c|c|c|c|}
\hline
Sample description & Silver concn in 100 mL of lean soln (mg/L) & % removal & Ag recovery by electrodeposition (mg) & % recovered by electrodeposition \\
\hline
After first extraction & 19.26 & 80.74 & 4.04 & 2.1 & 52 \\
After second extraction & 14.43 & 85.57 & (4.04−2.1)+4.28=6.22 & 2.8 & 45 \\
\hline
\end{tabular}
\caption{Results of Silver Recovery After Extraction and Recycle of Resins}
\end{table}
stripped from the resins. The metal loaded resins could be reused for repeated extraction until saturation.

**Infrared Analysis of Resins.** To investigate the structure and functional groups on the resin, infrared spectra were obtained from the resins.

From the infrared spectrum of PS/PG resin (Figure 6), O–H (3391 cm⁻¹), C–H (2901 cm⁻¹), aromatic C=C (1643, 1450, and 1350 cm⁻¹), and C–O (1077 cm⁻¹) functional groups could be observed. The presence of these groups is consistent with the structure of the resin.

The infrared spectrum obtained for PS/PG resin after extraction is presented in Figure 7 (lower spectrum). Compared with the PS/PG resin before extraction, several additional absorption peaks were observed between 2000 and 2800 cm⁻¹. They correspond to the presence of adsorbed gold cyanide ions. This observation is in agreement with the extraction mechanism proposed previously.

**Enhancement of the Extraction Capability.** In order to enhance the extraction performance of the polymer, a functional group was introduced into the PS/PG copolymer.

The functional group incorporated is a thiol group, and some of oxygen atoms in the polymer are replaced by sulfur atoms. The sulfur content in thiolated PS/PG resin was about 20% (m/m) from X-ray fluorescence (XRF) analysis. The lone pair...
PS/PG can be a good candidate to replace poly(ethylene glycol) in poly(ethylene glycol)-based aqueous biphasic extraction systems (PEG ABES) without needing the addition of salt. The system is simple and convenient and should be considered for larger scale operations.

Acknowledgment

This research is a joint project between the University of Hong Kong and Kenlap PGC Manufacturer Company Limited and has been supported by an award from the Innovation and Technology Fund (UIM/166).

Literature Cited


