An Innovative Approach on the Separation of Metal

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Introduction

There has been increasing environmental concerns on the metallic pollution in recent decades. The conventional technologies used for metal extraction are ion-exchange resins, polymer ultrafiltration and microemulsion. The whole extraction mechanism can be divided into 4 steps: 1) The binding of dissolved metal to active sites, 2) Separation of the metal load extractant from the lean phase, 3) Reverse extraction of loaded metal for recovery 4) Recycling of extractant for repeated extraction. Each of the conventional methods suffers different drawbacks in different steps of the extraction mechanism.

In addition to the above technologies, metal extraction using aqueous biphasic system (ABS) has been reported and investigated. Water-soluble polymers such as polyethylene glycol (PEG) were commonly used in ABS separation. ABS could be applied in separation of various solutes such as biomolecules and particulates. ABS has all advantages of liquid-liquid extraction due to their aqueous properties. Furthermore, polyethylene glycol-based aqueous biphasic systems (PEG-ABS) are virtually nontoxic, nonflammable and inexpensive. However, in ABS, usually a large quantity of salt such as sodium sulfate is required to achieve phase separation. Though most of the salts are inexpensive, the significant amount required salts inevitably introduce additional costs, further post-treatment and corrosion problems.

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

In addition, polyglycidol (PG), a polymer with similar structure with 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. 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. Reversely extraction of metal ions from the resin was also investigated. Furthermore, since thiol have strong affinity to gold, the extraction capability of PS-PG resin was strengthened by coupling to thiol groups and the resin become thiol-terminated PG (PS-PG-SH). Magnetic aqueous biphasic system was reported for biomolecules and increase in the rate of separation was achieved. Using methodologies well known in the art, magnetite core coated with the PS/PG resin was also synthesized for extraction in order to promote higher separation efficiency.

Results and Discussion

The obtained results indicated that gold can be extracted from the aqueous phase to the polymer phase. The determination of gold in aqueous phase after extraction showed the percentage of gold extracted to the polymer phase was higher than 99%. For silver extraction, the percentage of silver extracted to the polymer phase was 99%.

In fact, the silver solution had to be treated with diluted hydrochloric acid to remove free cyanide anions. Since $[Au(CN)_2]^-$ is the only complex between gold and cyanide anions while $[Ag(CN)_2]^-$, $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ were all been found. $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ may interfere the complex formation between the polymer and the complexes. Therefore, the percentage extraction of silver was lower than that of gold.

$[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ can be removed by adding HCl. The purpose of adding HCl is to remove free cyanide (KCN). Free cyanide, if present, reacts with HCl to form HCN which can escape from the solution as it formed. If HCl was added, it react with $[Ag(CN)_2]^-$ and white precipitates AgCN is formed and can be removed by filtration.

The percentage extraction of silver using such treated silver solution was higher than 99%.

Recovery of gold and silver

After extraction, gold can be extracted reversely and recovered by means of electro-deposition as illustrated in Figure 1.

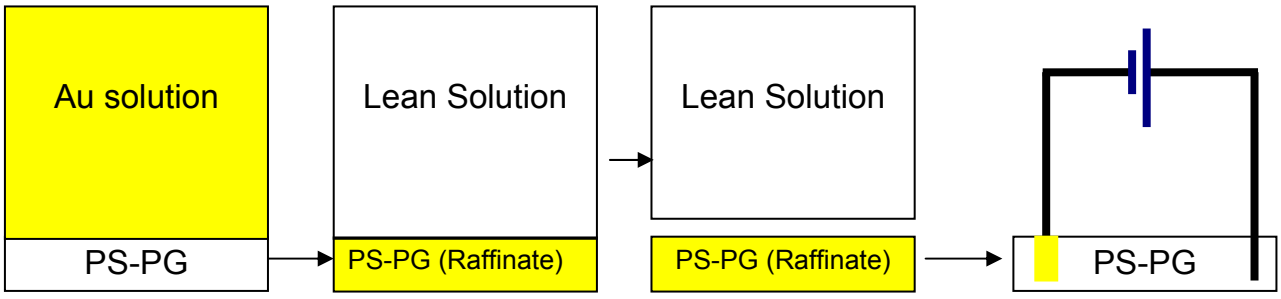

Figure 1. Schematic illustration of gold recovery

First, the gold ions in the water phase were extracted to the polymer phase so that resin saturated with gold was obtained. Secondly, the aqueous phase was discarded and only the resin phase (raffinate) was remained. Finally, a platinum wire as anode, the gold was plated on a clean nickel or copper wire. The

electrical resistance in the polymer was very high and this caused high electrical voltage. The voltage could be reduced by adding small amount of salt such as sodium chloride or sodium sulfate.

The nickel wire was weighted before and after electro-deposition so that the mass of gold plated could be calculated.

Similarly, silver recovery was also performed. From the experiment, though only about 40% to 50% of gold or silver were recovered from the resins, no deterioration of extraction capability on the resins was observed.

Enhancement for 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 thiol group in which some of hydrogen atoms in the polymer are replaced by sulfur atoms. The lone pair electrons in the sulfur atoms have strong affinity towards metal ions as metal ions are generally electron deficiency. Therefore, metal-sulphide bond has been regarded as strong bonding and promote the extraction performance.

The thiolated PG-PS was used for silver and gold extraction. It was found that the thiolated resin showed higher extraction capability than the normal one as shown in Figure 3 and 4. With 5 consecutive extractions, the thiolated resin still showed good extraction performance while the normal one was declined in third or fourth extractions.

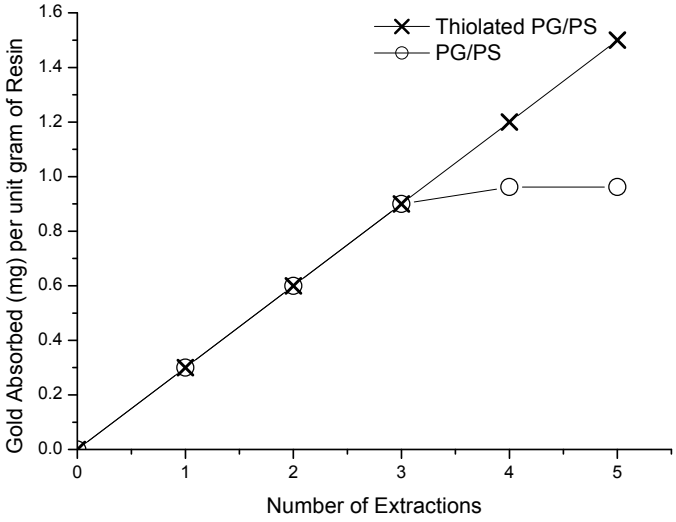

Figure 3. Comparsion between thiolated PS-PG and normal PS-PG on gold extraction capability

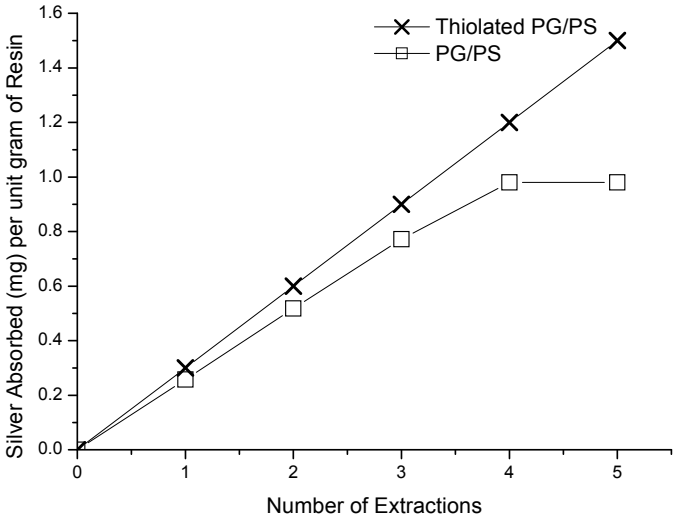

Figure 4. Comparsion between thiolated PS-PG and normal PS-PG on silver extraction capability

Gold could be reversely extracted from the thiolated polymer by means of sodium cyanide. A range of sodium cyanide with different concentrations was used to extract the gold from the thiolated resin saturated with gold reversely.

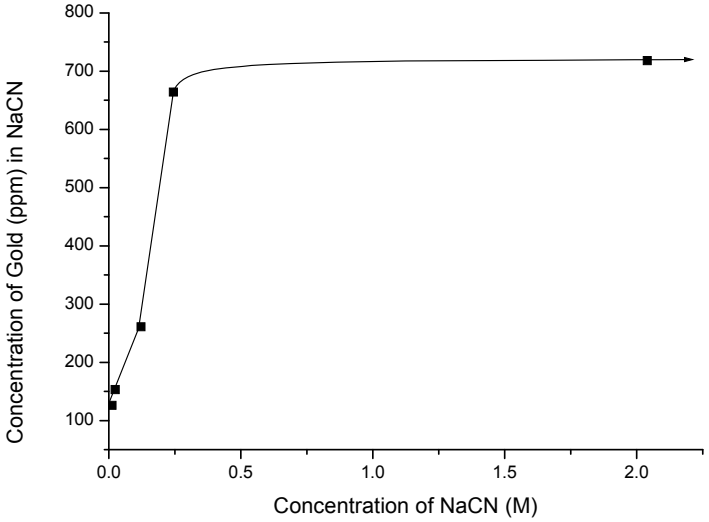

Figure 5. Effect of concentration of sodium cyanide on the gold reversely extracted from the thiolated PS-PG resins.

From the Figure 5, the optimum sodium cyanide concentration for gold reverse extraction is about 0.5M as higher concentration didn't provide further improvement.

Conclusions

In conclusion, a polystyrene-grafted-polyglycidol (PS-PG) resin synthesized and was used for gold and silver extraction. The resin can be recycled without deterioration in extraction capability. In addition, significant increase in loading could be accomplished by introduction of thiol groups to the polymer. The metal re-extraction from the polymer phase is possible and can be made by electro-deposition or sodium cyanide leaching.

PS-PG can be a good candidate or replacement for polyethylene glycol in polyethylene glycol-based aqueous biphasic systems (PEG-ABS) as no addition of salt is required. Therefore, the system becomes less complicated and more convenient and easier for investigation and study.

Acknowledgement

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