Polystyrene-grafted-polyglycidol (PS-PG), a water-compatible resin, is applied for the extraction of precious metal in effluents of electroplating process. The extractions of gold (I) and silver (I) cyanide using this resin are investigated. More than 99% of gold and 99% of silver ions of the originally dissolved could be extracted from the aqueous phase to polymer phase. Recycling of the resins is possible and no deterioration in extraction performance was observed. Thiolation on the chemical structure shows improvement on the extraction capability and separation efficiency. The PS-PG group resin is a good option for metal extraction and separation because it is economical, environmental-friendly, non-toxic, non-flammable and inexpensive.

**Preparation of materials for extraction**

1. **PS/PEG resins**

PS/PEG resin was purchased directly from Rapp Polymere GmbH. The resin was used for extraction without any modification. The resin is called TentaGel S 30 900 with diameter of 90 micron.
II. Synthesis of polystyrene/polyglycidol (PS/PG) resins

This synthesis is a modification of R Haag et al.. In a 100 mL three-necked flask, hydroxymethylated magnetic beads (1 g, 7.1 mmol of OH group/g polymer) were suspended in dry diglyme (25 mL). After swelling for one hour, potassium t-butoxide (KO\textsubscript{t}Bu) (0.8 g, 7.1 mmol) in tetrahydrofuran (THF) was added at 40 °C over 12 h to deprotonate the hydroxyl groups on the PS beads. The mixture was heated to 120 °C and 50 mL dry dimethyformamide (DMF) was added. A solution of freshly distilled glycidol (24 mL, 26.4 g, 356 mmol) in dry DMF (40 mL) was added drop-wise to the reaction mixture. The mixture was stirred for 12 h at 120 °C and then quenched with 1 N hydrochloric acid (HCl). The mixture was filtered and washed with water and methanol (MeOH) and finally dried in vacuum to give the product (21.6 g). The final white resins are composed of core polystyrene (4.64% by weight) covered with polyglycidol (95.36% by weight).

III. Synthesis of polystyrene/thiolated-polyglycidol (PS/PG-SH) resins

Mesyl chloride (1.0 g, 9 mmol) was added drop-wise to the mixture of PS-PG (0.5 g, 6.0 mmol of OH groups/g polymer) and pyridine (1.4 g, 18 mmol) in anhydrous methylene chloride (CH\textsubscript{2}Cl\textsubscript{2}). The reaction mixture was stirred for 12 hours at room temperature under an N\textsubscript{2} atmosphere. The resulting resin was filtered, washed with water and MeOH and then dried in vacuum to give the product 0.73 g of the product PS/PG-OMs.

Thiourea (1.6 g, 21 mmol) was added to the PS-PG-OMs (0.73 g) in ethanol (20 mL). The reaction mixture was refluxed overnight. After work-up, 0.48 g of functionalized polymer (PS-PG-SH) was obtained having a sulfur content of S 5.4 mmol/g.
IV. Synthesis of polystyrene/polyglycidol resins with a magnetite core (Mag/PS/PG)

Synthesis of polymer with magnetic core has been reported by many authors. Oleic acid, Fe(II) and Fe(III) were commonly used. In our experiment, magnetite nanoparticles were prepared by mixing 11.1 g FeCl$_3$.6H$_2$O and 5.6g FeSO$_4$.7H$_2$O in 50 ml deionized (DI) water followed by addition of 20 ml of concentrated ammonia at 70°C. 1.5g oleic acid was added to the mixture and stirred for 30 minutes with sonification. The mixture was heated at 110°C for 30 minutes to remove water and excess ammonia. The synthesized magnetite nanoparticles were about 10 nm.

The oleic acid grafted magnetite nanoparticles were mixed together with 4-vinylbenzyl alcohol, divinyl benzene (DVB), and azobisisobutyronitrile (AIBN) in a three-necked flask with the mass concentrations of 0.48%, 4.26%, 0.54% and 0.09% respectively. The reaction mixture was stirred and degassed at room temperature under nitrogen (N$_2$) over 1 hour. DI water (94.54 wt %) with 0.09% dissolved polyvinyl alcohol (PVA) was also added to the mixture. Polymerization was performed for 16 hours at 70 °C. The PS-coated magnetite was washed with excess DI water and dried under vacuum.

In a 100 mL three-necked flask, hydroxymethylated PS-coated magnetic beads (1 g) were suspended in dry diglyme (25 mL), using methodologies well known in the art. After swelling for one hour, KO'Bu (0.8 g, 7.1 mmol) in THF was added at 40 °C over 12 hours to deprotonate the hydroxyl groups. The mixture was heated to 120 °C and 50 mL dry DMF was added. A solution of freshly distilled glycidol (24 mL, 26.4 g, 356 mmol) in dry DMF (40 mL) was added drop-wise to the reaction mixture. The mixture was stirred for 12 hours at 120 °C and then quenched with the addition of 1 molar HCl. The mixture was filtered and washed with water and methanol and finally dried in vacuum to give the product (3.5 g) with weight increase of 250%.
VI. Extraction Experiments

A stock solution of 15ppm Au was prepared from potassium gold (I) cyanide. Another stock solution of 15ppm Ag was prepared from potassium silver (I) cyanide. They were then used for metal extraction. For each metal extraction, 10 ml solution was mixed with 0.5g polymer. After stirring, the polymer was settled by sedimentation or magnetic separation and the aqueous phase was decanted for metal concentration determination.

One of the methods to determine the metal concentration is by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). ICP-AES consists of a source of plasma. The plasma is generated in a quartz torch. Around the torch is a two or three turn induction coil, to which radio-frequency (RF) energy is applied. Argon is introduced into the torch and the RF-field is switched on. A magnetic field around the coil is developed and induces an electric field in the coil region. When seed electrons and ions are introduced with a Tesla discharge, plasma will be formed. The temperature of the plasma can be as high as 10000k which is sufficient to excite the electron to upper energy level as the sample flow through the plasma. As the lifetime of the excited atom is brief, its return to the ground state is accompanied by the emission of a photon of radiation. Since the emission line is characteristic to different metals, the intensity of the emission line is related to the concentration of the ion dissolved.

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%.
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](image)

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/PD 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.

**Figure 2.** Comparison between thiolated PS-PG and normal PS-PG on gold extraction capability

**Figure 3.** Comparison 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.

![Graph showing the relationship between concentration of NaCN (M) and concentration of Gold (ppm) in NaCN](image)

**Figure 4.** Effect of concentration of sodium cyanide on the gold reversely extracted from the thiolated PS-PG resins.

From the Figure 4, the optimum sodium cyanide concentration for gold reverse extraction is about 0.5M as higher concentration didn’t provide further enhancement.

**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.

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