

The Extraction Of Gold From Plants And Its Applications To Phytomining

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Abstract:

Phytomining is the use of hyperaccumulating plants to extract a metal from soil with recovery of the metal from the biomass to return an economic profit. This work looks at the possible methods for recovering gold from plant material, including chemical reduction with and without solvent extraction, thermal reduction and copper electrodeposition. Some progress was made with ascorbic acid as the chemical reductant. A solid phase was produced at the liquid-liquid interface after solvent extraction. The deposition reaction reduced the gold concentration in methyl isobutyl ketone (MIBK) to less than 2 ppm, equating to 85% recovery, in 3.5 hours. Copper electrodeposition also gave some promising results. However, both, require much more work before they are viable for scale-up.

Keywords: Phytomining, gold extraction, biomass.

Introduction

It has been recognised for some years that some plants can accumulate metals from the soil in which they are grown. It is also known that a smaller number of plants can accumulate a given metal to a concentration very much higher than the substrate concentration.

Plants that can accumulate a metal to 1000 times the highest concentration found in 'normal' accumulator plants are termed 'hyperaccumulators', and can be used to extract metals from soils [1]. This has found application in two main areas.

The first of these is *phytoremediation*, where hyperaccumulators are used to 'clean up' soils of metal pollutants such as lead or cadmium *in situ* [2]. The second is phytomining, the extraction of metals from soils or ores for recovery and sale, for example nickel or gold.

The phytomining of gold has several hurdles in its path to commercial viability. The first is a lack of plants that would naturally hyperaccumulate gold. This is because gold is insoluble in soil solutions and therefore unavailable for uptake by plants. The addition of chelating agents such as thiocyanate to the soil to complex and solubilise gold has overcome this problem [3]. The approach used was based on the concept of 'induced hyperaccumulation' for lead [4].

The second hurdle is taking hyperaccumulation results obtained in the laboratory and extending them to the field, something that has proven not to be easy [5]. The final problem is extracting the gold economically from the plant material.

So far work carried out in this laboratory to extract gold has used the following extraction method. The plant material is ashed and dissolved in 2 M HCl, followed by solvent extraction of the gold into methyl isobutyl ketone (MIBK). Addition of the reducing agent sodium borohydride to the organic layer causes a black precipitate to form at the boundary between the layers. Heating the precipitate at 800 °C causes metallic gold to form.

This method presents several problems for scale-up. The highly reactive reducing agent produces gas upon reaction and quite possibly degrades the solvent. Solvent use gives high cost and environmental restrictions. Separation of the precipitate from the boundary layer is difficult. The use of both a reducing agent and thermal reduction requires two process steps.

The project described in this paper seeks to address these problems and make some inroads into providing a cost-effective method of extracting the gold on an industrial scale. Solvent extraction, copper electrodeposition and thermal reduction methods were investigated.

Materials and Methods

Standards

A 1000 mg/kg gold standard was prepared by dissolving a known amount of 22 carat gold in aqua regia and making the solution up to volume with 2 M HCl. Once the solution cooled the silver precipitated and the supernatant was decanted, removing the silver.

Ascorbic acid and sodium borohydride solutions were made up to approximately 2 wt % through dissolution in distilled water.

Ashing

All ashing was done at 550 °C in borosilicate test tubes for between 15 and 20 hours.

Solvent Extraction

The distribution ratio of gold between MIBK and water is such (~10⁶) that shaking the two phases for 5 minutes in a separating funnel was used for quantitative extraction. A ratio of 1 mL MIBK per 10 mL aqueous phase was employed.

Ascorbic Acid Reduction of Gold

A gold loaded MIBK layer was contacted with an equal volume of ascorbic acid solution. This was carried out in a

plastic sample container to avoid the precipitate plating onto the side of the vessel as it did with glass. A reflux condenser was fitted and the container held in a water bath at 50 °C.

Thermal Reduction of Gold

Spectroscopy grade graphite was used where a carbothermal reduction was carried out. All thermal reductions were done in crucibles at 800 °C.

Copper Electrodeposition

Five strips of copper were obtained and cleaned with 2 M HCl and weighed. These were placed in the solutions described below.

- 1 25 mL 2 M HCl
- 2 25 mL of a 2 M HCl solution containing 80 mg Au/L.
- 3 25 mL of a 2 M HCl solution containing 80 mg Au/L and 80 mg ferrous ions per litre (added as ferrous chloride).

After 5 hours the first three solutions were inspected. The copper strip from each was dried and reweighed and in the case of the HCl replaced in the solution. 1 mL aliquots of the solution from solutions 2 and 3 were taken and made up to 50 mL with distilled water in a volumetric flask for analysis by atomic absorption (AA) spectroscopy. The remaining solution was filtered through Whatman 42 filter paper and ashed.

Plant Preparation

Plant material was prepared for extraction by ashing and dissolving in hot 2 M HCl.

Analysis

After dilution (if necessary) the solutions were analysed using a graphite furnace AAS and the concentration of the gold in the original sample determined.

Results and Discussion

Solvent Extraction and Chemical Reduction

A chemical reductant that did not have the difficulties associated with borohydride, as discussed above, was required. Ascorbic acid was decided upon as an alternative reducing agent.

The high distribution ratio of MIBK for gold was confirmed in the literature [6, 7], and no other candidate was found with sufficient distribution ratio, availability and relative non-toxicity [8], therefore MIBK was retained as the solvent.

Initially excess ascorbic acid solution was added to an artificial gold-bearing aqueous phase. Although the gold did precipitate, it was soon apparent that this approach was not feasible as the actual solution that would be obtained from the plant material was too dilute in gold, and ascorbic acid would also reduce iron and copper that would be present in solution.

Instead, in qualitative experiments, artificial aqueous solutions containing 2 mg Au were extracted into MIBK and the organic phase contacted with ascorbic acid solution and heated to 50 °C for three hours. A black precipitate could be seen to form at the interface. When heated to 550 °C metallic gold formed. Circumstantially, the evidence points to the black precipitate as being finely divided gold – there are no other metal species present and ascorbic acid solution contacted with pure MIBK for the same length of time did not form a precipitate. However there is no direct proof to support this as of yet.

The following method was used to produce gold from the plant material that was available. Dried plant material (30 g), with a gold content of 30 mg/kg dry plant material, was ashed and dissolved in 300 mL HCl. The aqueous phase was extracted into 50 mL MIBK and contacted with an equal volume of ascorbic acid solution. The concentration of gold in the organic phase was monitored over time in order to get an indication of the reaction rate (Figure 1).

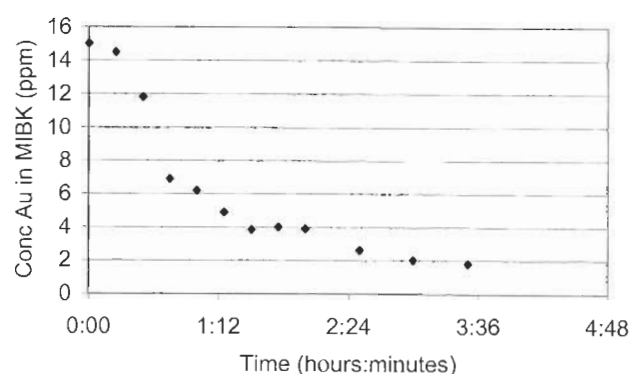


Figure 1: Concentration of gold in MIBK during chemical reduction.

The concentration of gold decreased most rapidly within the first 1½ hr and then leveled off. The advantage of leaving the solution longer than four hours is marginal, especially if it is considered that in the industrial process the solvent will be recycled.

After 3½ hours the solution was filtered and the paper and precipitate ashed. Metallic gold residue resulted. No attempt was made to measure quantitatively the amount of gold precipitate.

Further work needs to be carried out in this area, firstly to determine that the precipitate is gold, and secondly to improve the quality of the precipitate. It has been reported that the same type of reduction using oxalic acid in an agitated vessel produces a sand like precipitate which settles and is easily recovered by filtration [9]. This is much more desirable than the very fine precipitate that accumulates at the interface which was obtained in these experiments.

Although this reaction is a slow one, the nature of the mining method means that any processing step be a batch one.

Two types of reductions were carried out, in the absence and presence of carbon from the MIBK layer. Both of these reductions gave a metallic gold residue but they also indicated that some gold was being lost in the process (Table 1).

Table 1. Gold recovery for thermal reduction.

Reactants	Au Added (mg)	Au Recovered (mg)
MIBK + C	2.00	1.59
MIBK	2.00	1.34
Water	2.00	1.63

More trials need to be carried out to determine the optimum temperature to reduce the gold in order to minimise losses.

Copper Electrodeposition

Copper will cement gold from solution as it is higher in the electrochemical series, but will not cement iron or any other metal species likely to be present in the plant ash. An experiment was carried out to determine whether copper electrodeposition was feasible from the acid solution (Table 2).

Table 2. Results of copper electrodeposition.

Reactants	Cu Weight Loss (mmol)	Au Deposited (mmol)	Au in Solution (mmol)
HCl	0.019	-	-
HCl/Au	0.031	0.007	0.003
HCl/Au/Fe	0.031	0.005	0.003

This shows that after five hours the electrodeposition reaction was not complete and the copper was dissolving in the 2 M HCl. A possible solution to this is to neutralise the acid prior to electrodeposition, provided this does not affect the gold in solution.

Applications to Phytomining

The aim of this work was to go some of the way towards establishing a cost-effective method for gold extraction to be used in the phytomining process.

A solvent extraction and chemical reduction method using MIBK and ascorbic acid has emerged as a possibility, as has electrodeposition by copper. Both of these require much more testing to be done before they could even be considered for scale up.

A rough costing was done on a projected solvent extraction plant which indicated that the raw plant material would have to contain 70 mg/kg gold to break even, something which has not yet been achieved in field trials.

Thermal reduction from MIBK is less likely to be economic as a large effort would have to be made to recover the solvent, as well as the possibility of losing gold at the high temperatures used.

CONCLUSIONS

Ascorbic acid will precipitate a fine black solid at the interface of the gold bearing MIBK layer and an aqueous ascorbic acid layer. The precipitate yields metallic gold upon heating to 550 °C. Use of a solvent extraction process with ascorbic acid as the reducing agent may be a possibility for recovering the gold in phytomining process but further work needs to be carried out on several points. Copper electrodeposition of the gold from a 2 M HCl solution is impractical due to the copper dissolving in the acid. Further work could determine if prior neutralisation of the acid would render the process feasible.

Thermal reduction of the gold loaded MIBK layer in both the presence and absence of carbon did decompose the gold complex to metallic gold but some gold was lost at the temperature used (800 °C).

Overall, some progress has been made in determining a method for the extraction of gold from the plant material. Ascorbic acid is a much more benign reducing agent than borohydride for a solvent extraction process, and an electrodeposition process would require very little in the way of chemicals or running costs.

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