Release of gold nanoparticles from phytomined biomass by enzymatic digestion

A. T. Marshall[1], R. G. Haverkamp[1], C. E. Davies[1], J.G. Parsons[2], J.L. Gardea-Torresdey[2] and D. van Agterveld[3]

[1]Institute of Technology and Engineering, Massey University, Private Bag 11222, Palmerston North, New Zealand
[2]Environmental Science and Engineering Ph.D. Program and Department of Chemistry, The University of Texas at El Paso, 500 West University Avenue, El Paso, TX 79968-0513, USA
[3]Akzo Nobel Research and Technology Chemicals, Department of Chemicals Analytics and Physics, Microstructure Analysis and Atomic Spectrometry, P.O. Box 9300 6800 SB, Arnhem, The Netherlands

ABSTRACT

Gold nanoparticles are produced in some plants when soluble gold is present in the growth medium nutrients. Release and recovery of this gold by pyrolysis can sinter the particles, and enzymatic digestion is proposed as an alternative. *Brassica juncea* grown on soil containing low levels of gold, copper and silver (22–48 mg Au kg^{-1}, 44–45 mg Cu kg^{-1} and 0–31 mg Ag kg^{-1} respectively) contained gold at weight concentrations circa 1000 ppm dry matter. 55-60 wt% of the dried plant matter was solubilised by enzymatic digestion, but 50-60% of the gold initially present was lost to solution during the digestion. XANES analysis shows that gold is present in the plant in approximately equal quantities in the metallic (Au^0) and oxidized (Au^{+1}) states. The gold lost during digestion is thought to be gold present in the plant in a soluble form (Au^{+1}).

INTRODUCTION

The tissues of plants grown on media containing gold and solubilizing agents such as cyanide, bromide, iodide and thiosulphate can contain gold in metallic form, as nanoparticles. The recovery of these particles inevitably involves selective removal or destruction of the plant tissues, with accompanying risk to the target nanoparticles. In trials with removal by pyrolysis for example, there was evidence of sintering. We propose enzymatic digestion as method with potential for removing bio-mass without altering the size or functionality of the particles.

EXPERIMENT

Bio-mass growth and nutrient

The growth medium used was soil prepared by applying gold chloride solution with silver nitrate or silver nitrate and copper chloride solution to sieved agricultural soil. Three test soils were prepared: one with 22 mg Au kg^{-1}, one with 45 mg Cu kg^{-1} and one soil having 48 mg Au kg^{-1} and 44 mg Au kg^{-1} and 31 mg Au kg^{-1}. *Brassica juncea* seed was planted and after 9 weeks each pot was irrigated with potassium cyanide solution. After a further 14 days, the seedlings were harvested, oven dried at 110°C, and then ground and sieved to -180 μm. Samples were analysed and characterised using AA Spectroscopy, XANES, TEM and EDX.

Enzymatic digestion

The biomass was digested using cellulase (Cellulysin, Calbiochem). Controls were also run with no enzyme. Biomass was separated by centrifuging and washing with deionised water. The recovered biomass was dried at 105°C, and the reduction determined by weighing.

Gold analysis

Gold concentrations in the starting biomass, the digested material, and the digestion solution were measured by AA spectroscopy. Gold concentrations were ~1000 ppm.

Gold speciation was determined by XANES.

Transmission Electron Microscopy was used to determine particle size. EDX was also used to obtain information on particle composition.

RESULTS AND DISCUSSION

Maximum digestion was at a concentration of 6.25g L^{-1} cellulase, and extending the digestion time beyond 24 hours did not increase the amount of material digested.

Approximately 50% to 60% of the gold initially present is lost in the digestion process.

Comparison of XANES spectra for materials known to contain gold and control samples with no gold, confirm the presence of gold as Au^{+1} and Au^{0}. The presence of Au^{0} implies that the plants are actively reducing gold cyanide.

Particle diameter was found to be in the range 5-50 nm. EDX indicated the presence of Ag and Cu in the particles.

CONCLUSIONS

Gold nanoparticles were present in biomass grown on media containing gold and a solubilizing agent, at concentrations circa ~1000 ppm.

XANES has shown that gold was present as An^{+1} and Au^{0}.

Enzymatic digestion solubilised 50-60% of the biomass in ~24 hours, but 50%-60% of the gold present in the initial biomass was lost.