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Use of ICP and XAS to determine the enhancement of gold phytoextraction by *Chilopsis linearis* using thiocyanate as a complexing agent

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Abstract Under natural conditions gold has low solubility that reduces its bioavailability, a critical factor for phytoextraction. Researchers have found that phytoextraction can be improved by using synthetic chelating agents. Preliminary studies have shown that desert willow (*Chilopsis linearis*), a common inhabitant of the Chihuahuan Desert, is able to extract gold from a gold-enriched medium. The objective of the present study was to determine the ability of thiocyanate to enhance the gold-uptake capacity of *C. linearis*. Seedlings of this plant were exposed to the following hydroponics treatment: (1) 5 mg Au L⁻¹ (2.5×10⁻⁵ mol L⁻¹), (2) 5 mg Au L⁻¹+10⁻⁵ mol L⁻¹ NH₄SCN, (3) 5 mg Au L⁻¹+5×10⁻⁵ mol L⁻¹ NH₄SCN, and (4) 5 mg Au L⁻¹+10⁻⁴ mol L⁻¹ NH₄SCN. Each treatment had its respective control. After 2 weeks we determined the effect of the treatment on plant growth and gold content by inductively coupled plasma–optical emission spectroscopy (ICP–OES). No signs of shoot-growth inhibition were observed at any NH₄SCN treatment level. The ICP–OES analysis showed that addition of 10⁻⁴ mol L⁻¹ NH₄SCN increased the concentration of gold by about 595, 396, and 467% in roots, stems, and leaves, respectively. X-ray absorption spectroscopy (XAS) studies showed that the oxidation state of gold was Au(0) and that gold nanoparticles were formed inside the plants.

Keywords Gold · Phytoextraction · *Chilopsis linearis* · ICP–OES · XAS · Complexing agents

Introduction

Phytomining is an emerging technology that has attracted interest in the last few years. This technology is based on the ability of the plants to extract and translocate valuable metals from the roots to the above ground plant parts (stems and leaves). This process is affected by physical and biological factors such as metal bioavailability, plant–microbe interactions, root exudates, and plant transpiration [1–3].

Ideal plants for phytoextraction purposes have to be both tolerant to the target metal and metal hyperaccumulators [4]. In addition, high biomass production has been linked with higher rates of metal extraction. Metal uptake from growth media can be improved by using strategies such as choosing the correct plant, modifying the pH of the growth medium, using chelating agents, or genetic manipulation. Genetic manipulation has been used to improve biomass production and metal tolerance [5] and to increase plant transpiration rates, which have been shown to increase metal translocation from root to shoot [2]. Many researchers have focused more on the possibility of increasing metal uptake by treatment of the soil rather than use of genetic manipulation [6–11].

Plants have been used as indicators of metal deposits in many places around the world [12]. For example, mesquite (*Prosopis* spp.) and white thorn acacia (*Acacia constricta* Benth.) have been used as indicators of silver, arsenic, and antimony deposits in Arizona [13], and the *Douglas fir* has been used to determine the presence of gold deposits in Mountain Hemlock, British Columbia, Canada [14]. The use of plants as gold-prospecting tools shows that many different plant species have the ability to extract gold from soils. In addition, Gardea-Torresdey et al. [15] showed that alfalfa plants have the

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ability to extract gold and silver from agar media, producing gold and silver nanoparticles within the plants. According to Lasat [3], certain plants can extract up to 10,000 mg Pb kg⁻¹, 1000 mg Co kg⁻¹, and 100 mg Cd kg⁻¹. However, gold uptake is limited by the low solubility of gold under natural conditions. Thus, the criterion for gold hyperaccumulation is defined at 1 mg Au kg⁻¹ of dry biomass [16, 17], which is 100 times higher than gold concentrations normally found in plants. The treatment of soil or growth media to promote extraction of gold has only recently been investigated [16]. Anderson et al. [18] reported that *Brassicca juncea*, grown in a gold-containing medium treated with ammonium thiocyanate as chelating agent, accumulated up to 57 mg Au kg⁻¹ plant. In addition, Lamb et al. [19] have shown that in *B. juncea* and chicory (*Chichorium* spp.) with cyanide treatment increased gold uptake to higher levels than uptake using thiocyanate. Msuya et al. [20] studied the use of ammonium thiosulfate and ammonium thiocyanate as chemical complexing agents for five different crops (carrot, red beet, onion, and two cultivars of radish). They concluded that carrot might be a good crop for recovery of gold; the estimated net value was \$840 ha⁻¹, twice the return value of a crop of wheat.

In this manuscript we report on the use of the ammonium thiocyanate as complexing agent for treatment of growth medium to enhance gold phytoextraction by *Chilopsis linearis* (desert willow) a common inhabitant of the Chihuahua Desert. Different concentrations of NH₄SCN were used to determine desert willow tolerance to SCN⁻. Inductively coupled plasma–optical emission spectroscopy (ICP–OES) was used to determine the gold content of tissues of *C. linearis*. X-ray absorption spectroscopy (XAS) was used to investigate the oxidation state and coordination of gold within the plant.

Materials and methods

Experimental set up

Seeds of the desert willow were collected from the El Paso, Texas, and the surrounding area. The sampling areas did not have any prior history of metal contamination. Before each of the studies, the seeds were disinfected for 10 min with 4% sodium hypochlorite solution, with constant stirring, and washed three times with sterile deionized (DI) water. The seeds were germinated in damp paper towels as described by Carrillo-Castañeda et al. [21]. After 10 days, 12 seedlings were transferred to a micro-hydroponics system consisting of 50 mL centrifuge tubes containing modified Hoagland nutrient solution [22] with constant air bubbling. After 10 days of growth, the nutrient solution was replaced by several gold–ammonium thiocyanate (Au–NH₄SCN) solutions. The influence of ammonium thiocyanate on gold uptake was determined by using four different concentrations of NH₄SCN and five replicates per treatment. The treatment was:

5 mg Au L⁻¹, which is equivalent to 2.5×10⁻⁵ mol L⁻¹,
 5 mg Au L⁻¹+1.0×10⁻⁵ mol L⁻¹ NH₄SCN,
 5 mg Au L⁻¹+5.0×10⁻⁵ mol L⁻¹ NH₄SCN, and
 5 mg Au L⁻¹+1.0×10⁻⁴ mol L⁻¹ NH₄SCN.

The source of the gold for each treatment was KAuCl₄. Each treatment had a control consisting of the nutrient solution and the corresponding concentration of NH₄SCN; in addition, a universal control containing only the nutrient solution was used. For each treatment the pH was adjusted to 6.0 using solutions of 0.1 mol L⁻¹ HCl or NaOH, as required, and 0.01 mol L⁻¹ 3-(*N*-morpholino)propane sulfonic acid (MOPS) buffer. This experiment was conducted at 25°C and 14/10 h of light/dark cycle. Light for the experiment was provided through four 34 W Phillips lamps with an illumination of 39 mmol m⁻² s⁻¹. To compensate for water lost due to evapotranspiration, DI water was added to each centrifuge tube to maintain a constant volume.

Treatment evaluation

After 2 weeks of growth the seedlings were harvested and plant elongation was determined by measuring the root and shoot lengths of 30 plants per treatment, selected at random. For determination of gold uptake within the plants, five samples per treatment (10 plants per sample) were collected. The plants were washed with 0.2% HNO₃ for 30 s, to eliminate gold adsorbed on the plant surface, then with DI water. The plants were separated into roots, stems, and leaves, oven dried at 70°C for 72 h, weighed, and acid digested. The digestion was carried out using microwave-assisted digestion (CEM Mars X, CEM Corporation, Mathews, NC, USA) at 105°C for 15 min with 3 mL conc. HNO₃ (trace pure). The volume of the samples was then adjusted to 10 mL using DI water. The gold content was determined using a Perkin Elmer Optima 4300 DV ICP–OES (Perkin Elmer Corporation, Shelton, CT, USA). The ICP–OES was calibrated from 0.01 to 2 mg L⁻¹ gold using a wavelength of 242.795 nm. The calibration curves obtained for all the studies had correlation coefficients of 0.99 or greater. A control sample (external standard) was run every 10 samples to verify the accuracy of the instrument. The gold content was quantified in triplicate for each sample, both the mean concentration and standard deviations were determined.

X-ray absorption spectroscopic studies

XAS studies were performed on three plant parts of desert willow grown on gold–NH₄SCN-containing medium. For this analysis the plants were washed as previously described and then cut and separated into roots, stems, and leaves. The biomass samples were frozen in liquid nitrogen for 45 min and lyophilized using a Labconco Freeze-dry System (Freezone 4.5, Labconco Corporation, Kansas City, MO, USA). Sub-

sequent to lyophilization the samples were ground to a fine powder and mounted on to 1.0 mm sample plates with Mylar tape windows for XAS analysis at Stanford Synchrotron Radiation Laboratories (SSRL).

The samples and model compounds were run on beamline 2–3 using a Canberra 13 element Ge fluorescence detector. In addition, all the samples and model compounds were run using an internal Au(0) foil (with an energy of 11.918 keV) for calibration purposes. The operating conditions of the beam line were: a Si (111 ϕ 90) double crystal monochromator, an energy of 2.3 GeV, a current of 60 mA, and a 1.0 mm entrance slit, and the beam was detuned by 50% to reduce higher-order harmonics. The samples were collected in fluorescence mode using the 13-element Ge detector, whereas the model compounds were collected in transmission mode. The model compounds Au(0), KAuCl₄, and AuOH were diluted using boron nitride to give a one absorption unit change across the absorption edge. The dilution was performed using a predetermined mass of the model compounds. After addition of boron nitride a homogenous mixture was obtained by use of a mortar and pestle.

X-ray data analyses

The samples were analyzed using the WinXAS software and standard data analysis techniques [23, 24]. The samples were first energy-calibrated on the basis of the second-degree derivative of the absorption edge of the internal gold foil at 11.918 keV. After calibration, the samples were background-corrected using polynomial fittings of the pre-edge and post-edge regions. The pre-edge region was fitted using a one-degree polynomial and the post edge region was fitted using a five-degree polynomial. The X-ray absorption near edge structures (XANES) were extracted from the calibrated and background-corrected sample spectra from 11.87 to 12.05 keV. The same procedure was used to extract the XANES spectra of the model compounds. Subsequent to XANES extraction a linear combination-XANES (LC-XANES) fitting of the sample spectra was performed.

The extended X-ray absorption fine structures (EXAFS) of samples and model compounds were extracted from the calibrated and background-corrected XAS spectra. First, the XAS spectra was converted into k space (\AA^{-1}) based on the energy of the photoelectron ejected from the samples and model compounds. The energy of the ejected photoelectron was determined by the energy of the second-degree derivative of the sample and model compound absorption edges. The EXAFS were extracted using a spline of seven knots and subsequently k weighed to three. The k weighed EXAFS were then Fourier transformed from 2.0 to 13.2 \AA^{-1} and then back transformed to extract the first shell EXAFS interactions only. The backtransformed EXAFS were then k weighed to three and fitted using FEFF 8.00 [25].

The fittings were performed based on the EXAFS of the model compound that best matched the EXAFS of the sample. The FEFF input files were created using the ATOMS software from crystallographic data of the model compounds [26]. The number of nearest neighboring atoms, the Debye–Waller factors, the energy shifts, and the nearest neighboring atom was determined using FEFF 8.00.

Statistical analysis

The data were analyzed using one-way analysis of variance (ANOVA), with SPSS software Version 11.0 (SPSS, 233 S. Wacker Drive, Chicago, IL, USA). Both the gold uptake and growth studies had a statistical significance of $P \leq 0.05$. A Turkey-HSD (honestly significant difference) test was used to determine significant differences between the means.

Results and discussion

Effect of Au–NH₄SCN concentration on plant growth

Figure 1 shows the elongation of roots and stems of the plants exposed to the different treatment. As seen in Fig. 1, NH₄SCN, either used alone or with Au, did not affect the shoot elongation of *C. linearis* plants at any concentration. However, NH₄SCN at 1×10^{-4} mol L⁻¹ concentration significantly reduced ($P < 0.05$) root elongation. Compared with the control, the root elongation of the plants exposed to the highest concentration of NH₄SCN containing gold was reduced by approximately 40%. To the best knowledge of the authors there are no reports related to the effect Au–NH₄SCN on plant growth, although Yih-Fen et al. [27] reported that

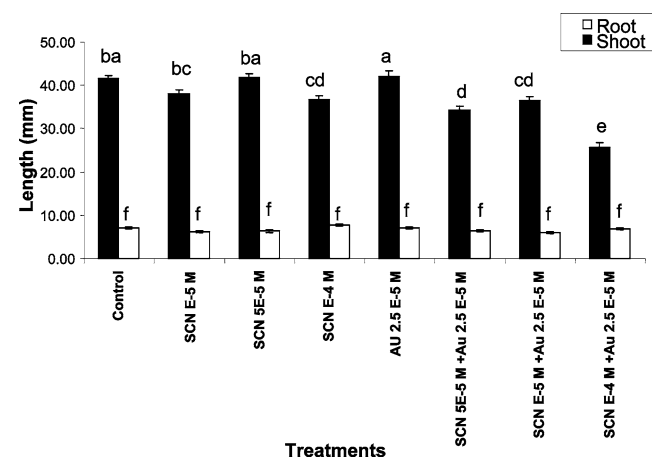
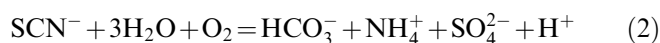


Fig. 1 Root and shoot length of *C. linearis* seedlings after 15 days of growth in hydroponics containing 5 mg Au L⁻¹ and different concentration of NH₄SCN. Letters represent different statistical groups. Each datum represents an average of 30 plants

ammonium thiocyanate at a concentration of 2000 mg L^{-1} (0.026 mol L^{-1}) inhibited the conversion of glycine to sugars without effect on the conversion of glycine to organic acids in leaf tissue. Other researchers have reported the use of NH_4SCN as a plant-growth stimulator [28, 29]. Furthermore, Msuya et al. [20] reported an uptake of $48.3 \text{ mg Au kg}^{-1}$ dry weight mass (DWM) when carrot was grown in an artificial substrate containing gold dispersed in sand. Therefore, the adverse effects of NH_4SCN at $1 \times 10^{-4} \text{ mol L}^{-1}$ (7.6 mg L^{-1}) could be attributed more to the toxic effects of NH_4^+ [30]. The NH_4^+ ion is produced by dissociation (Eq. 1) or oxidation (Eq. 2) of NH_4SCN , as shown below [31].



The effect of NH_4SCN on Au uptake

Figure 2 shows Au concentrations in roots, stems, and leaves of desert willow plants exposed for 2 weeks to 5 mg Au L^{-1} and different concentrations of NH_4SCN . For treatment with 5 mg Au L^{-1} , gold concentrations in roots, stems, and leaves were $63, 18, \text{ and } 4.5 \text{ mg Au kg}^{-1}$ DWM, respectively. Compared with Au treatment alone, addition of NH_4SCN at $1 \times 10^{-5} \text{ mol L}^{-1}$ significantly ($P < 0.05$) increased the gold concentration in the leaves (18 mg Au kg^{-1} DWM) but not in the roots and stems. However, treatment with 5×10^{-5} and $1 \times 10^{-4} \text{ mol L}^{-1}$ NH_4SCN increased gold uptake (mg

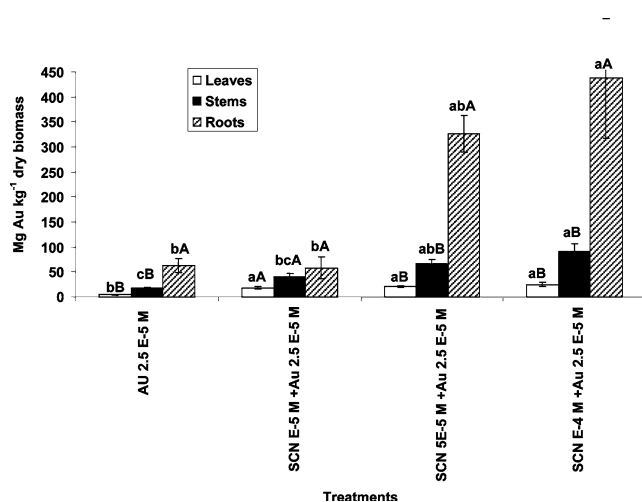


Fig. 2 Au concentrations in the leaves, stems, and roots of *C. linearis* seedlings after 15 days of growth in hydroponics containing 5 mg Au L^{-1} and different concentration of NH_4SCN . Lowercase letters represent statistical differences for the same tissue with different treatment. Uppercase letters represent statistical differences for different tissue with the same treatment. Each datum represents an average from 50 plants

Au kg^{-1} DWM) to 326 and 437 in roots, 66.5 and 91 in stems, and 21 and 25 in leaves, respectively. These values were statistically significant ($P < 0.05$) compared with Au uptake from 5 mg Au L^{-1} . For each treatment the highest gold concentrations were found in roots and the lowest in leaves. Girling and Peterson [32] found that *Zea mays* (maize) plants exposed to gold foil and a cyanogenic extract obtained from *Prunus laurocerasus* (a natural gold-chelating compound) concentrated 1.36 and $31.10 \text{ mg Au kg}^{-1}$ DWM in shoots and roots, respectively. In our study, addition of NH_4SCN at $5 \times 10^{-5} \text{ mol L}^{-1}$ increased gold concentrations in roots, stems, and leaves by about 420, 264, and 376%, respectively, compared with uptake from Au alone. However, when NH_4SCN was added at $1 \times 10^{-4} \text{ mol L}^{-1}$ the gold uptake by roots, stems and leaves increased by about 595, 396, and 467%, respectively, compared with uptake from gold treatment alone. These results showed that Au uptake in roots and stems increased significantly ($P < 0.05$) as the concentration of NH_4SCN was increased; increases in Au concentrations in the leaves were not statistically significant.

XAS studies

Results from the XANES studies are presented in Figs. 3 and 4 and the LC-XANES fittings are shown in Table 1. Figure 3 shows the XANES of the model compounds Au(0), KAuCl_4 , and AuOH over the same energy range as in the samples (Fig. 4). The presence of the edge peak or white line features in the Au(III) (KAuCl_4) and Au(I) (AuOH) samples at 11.919 keV are shown in Fig. 3. This white line feature is characteristic of Au(III) and Au(I) compounds and is not present in Au(0) (Fig. 3). In Fig. 4 the white line is absent from the spectra, indicating that the gold absorbed by the plant roots and shoots was present in the reduced form Au(0).

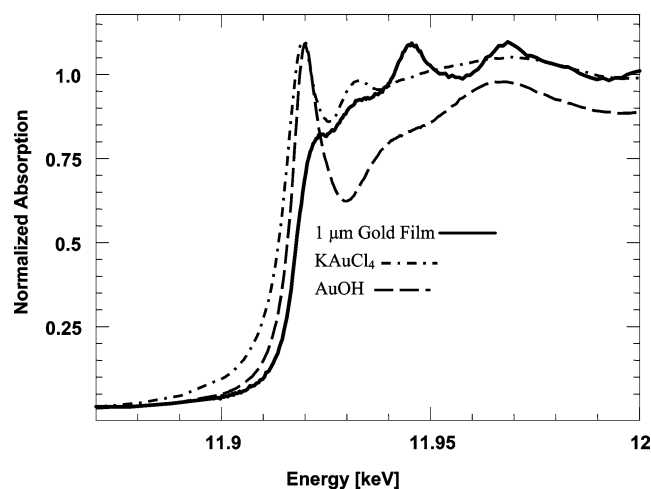


Fig. 3 XANES of gold model compounds used for LC-XANES fitting, spectra were background-corrected and extracted from 11.87 to 12.0 keV

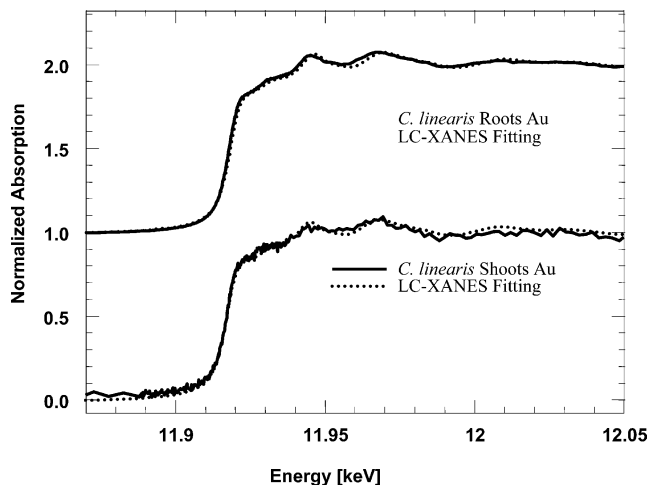


Fig. 4 XANES spectra and LC-XANES fittings of Au in the roots and shoots of *C. linearis* taken from Au-SCN in hydroponics solution

Table 1 LC-XANES fitting for the gold composition found within the roots and shoots of *C. linearis* after uptake from hydroponics solutions in the presence of NH_4SCN

Sample	Au(0) (%)	KAuCl ₄ (%)	AuOH (%)
Au <i>C. linearis</i> roots SCN hydroponics	93.0	4.41	2.56
Au <i>C. linearis</i> shoots SCN hydroponics	93.5	6.54	0.0

The LC-XANES fittings of the samples (Table 1) confirmed that most (93%) of the Au in the *C. linearis* roots and shoots samples was present as Au(0), and a small percentage was a mixture of Au(III) and Au(I). The amount of Au present as Au(III) and Au(I) in the desert willow was residual. By using XANES calculations, researchers have observed the reduction by living plant systems of metals such as Au(III), Cr(VI), and As(V)

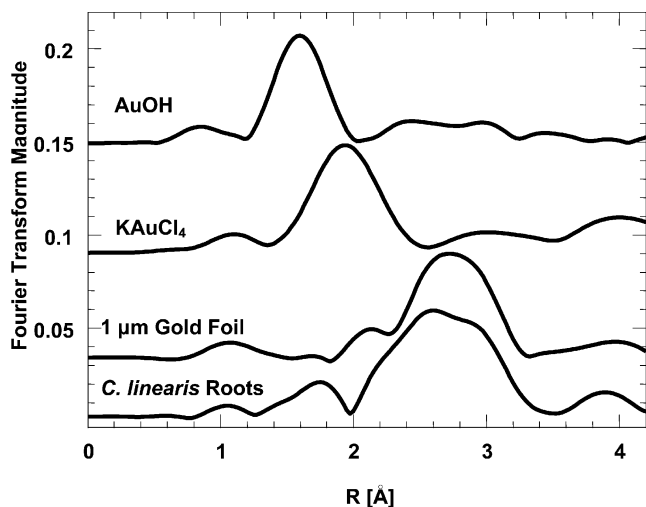


Fig. 5 EXAFS of the gold taken up by *C. linearis* roots from hydroponics solution containing Au and SCN

[15, 33, 34]. From investigations of the uptake of Au(III) from agar media, Gardea-Torresdey et al. [15] showed that alfalfa plants were able to absorb the Au(III) and reduce it to Au(0). Study of the uptake of Cr(VI) by mesquite showed that all the Cr taken up by the plants was found in the reduced, relatively nontoxic, form of Cr(III) [33]. In another study, uptake of As(V) by mesquite plants showed that the As present in the plants was present as As(III) at levels greater than 90% [34]. Furthermore, XANES spectroscopy has been successfully used to study the reduction of Au(III) and Cr(VI) binding to inactivated alfalfa, oat, and wheat biomasses [35, 36]. The gold studies showed that all the Au bound to the biomasses was present as Au(0) [35] whereas binding of Cr(VI) to different biomasses resulted in complete reduction of Cr(VI) to Cr(III) [36]. Therefore, XANES is a very valuable technique to investigate the reduction of Au(III), Cr(VI), and As(V).

The EXAFS of the Au model compounds, including 1 μm Au(0) foil, KAuCl₄, and Au(OH), and Au absorbed by desert willow roots are shown in Fig. 5. Table 2 shows the FEFF fittings of the Au model compounds and the Au taken up by the roots of the desert willow. From the EXAFS of the Au present in the roots of desert willow, the nearest neighboring atoms were found to be Au atoms with a coordination number of approximately 7.4 atoms (Table 2). This low coordination for gold indicates the presence of Au(0) nanoparticles as the first coordination shell for bulk Au(0) consisting of 12 neighboring Au atoms. It has been shown that the size of gold nanoparticles can be calculated from the interatomic distances and the number of neighboring Au atoms in a sample [35]. The calculation is performed using an equation developed by Borowski for determination of the size of copper nanoparticles using EXAFS [37]. However, it has been shown that this equation can be used to calculate the size of nanoparticles of metals that have a FCC structure [35]. It should be noted that the size of nanoparticles can be calculated using this equation if there is an incomplete first coordination shell [35, 37]. Using the equation developed by Borowski, the average size of gold nanoparticles produced in inactivated cells of alfalfa have been successfully calculated and shown to be approximately 6.5 and 9.0 \AA [35]. As can be seen in Table 2, the average radius of the gold nanoparticles found in desert willow roots

Table 2 EXAFS fitting of Au model compounds KAuCl₄ and 1 μm Au(0) foil and the Au taken up by *C. linearis* roots from hydroponics solutions containing $1 \times 10^{-4} \text{ mol L}^{-1} \text{ NH}_4\text{SCN}$ and $5 \text{ mg L}^{-1} \text{ Au}$

Sample	Bond	<i>N</i>	<i>R</i> (\AA)	σ^2 (\AA^2)	Radius (\AA)
KAuCl ₄	Au-Cl	4.0	2.29	0.0015	N/A
1 μm Au(0) foil	Au-Au	12.0	2.87	0.0048	N/A
Au <i>C. linearis</i> roots hydroponics SCN	Au-Au	7.4	2.86	0.0089	5.5

N coordination number; *R* (\AA) interatomic distance; Radius (\AA) actual particle radius

was 5.5 Å, thus the desert willow plants are producing Au(0) nanoparticles with an average size of 1.1 nm. Because of the low concentrations of Au present in the shoots, no EXAFS could be extracted from these samples.

Conclusions

Desert willow seedlings grew very well in the presence of NH_4SCN concentrations lower than $1 \times 10^{-4} \text{ mol L}^{-1}$. It was found that shoot elongation was not affected by either the Au or NH_4SCN concentrations. In addition, when using NH_4SCN at a concentration of $10^{-4} \text{ mol L}^{-1}$ with 5 mg Au L^{-1} , Au uptake was enhanced by approximately 595, 396, and 467%, in roots, stems, and leaves, respectively, compared with gold uptake by plants grown at 5 mg Au L^{-1} . XAS studies showed that desert willow reduced Au(III) to Au(0) within the roots and shoots of the plants. Calculations from EXAFS studies showed that this plant produced Au(0) nanoparticles with an approximate radius of 0.55 nm. In addition, this study showed that *C. linearis* is a potential plant for gold phytomining.

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