Removal of Silver and Lead Ions from Water Wastes Using *Azolla filiculoides*, an Aquatic Plant, Which Adsorbs and Reduces the Ions into the Corresponding Metallic Nanoparticles Under Microwave Radiation in 5 min

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Abstract Pollution of water bodies with heavy metal ions is a major worldwide environmental problem. The objective of this study was to elucidate the mechanism in which metallic ions are adsorbed and reduced to metallic nanoparticles onto plant materials using microwave radiation. In this research, we have fabricated metallic silver and lead nanoparticles from their corresponding ions using the aquatic plants *Azolla filiculoides* and *Pistia stratiotes* (since identical results are obtained for both plants, the emphasis will be on the *Azolla*) under microwave radiation. Our data show that metallic silver and metallic lead nanoparticles were completely removed from the polluted solution and were embedded in the *A. filiculoides* surface after 5 min of microwave reaction. It was also found that, for both metals, reduction of the metallic ions was accomplished by the plant matrix without the need of an external reducing agent. Most of the particles had a spherical shape within the 10–50 nm size range. Mass balance data clearly indicate that most of the silver particles were found on the surface of the plant and not in the clean water. Pectin and α-glucuronic acid did not reduce the silver or lead ions under microwave radiation. We therefore hypothesize that perhaps the proteins or sugar alcohols in the plant matrix were serving as the reducing agents. We believe that this technique in which adsorption and reduction are combined using microwave radiation can be applied for removing and recycling metallic ions from contaminated water and industrial wastewater.

Keywords Water pollution · Aquatic plants · Heavy metal ions · Metallic nanoparticles · Microwave radiation

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1 Introduction

Aquatic plant materials have shown a remarkably high sorption capacity for heavy metals from wastewater (Ajmal et al. 2000; Axtell et al. 2003; Chefetz et al. 2005; Marciano et al. 2008; DeWet et al. 1990). These plant materials are available in large quantities and therefore have the potential to be used as alternatively low-cost ($1 per 1 kg of aquatic plants) and environmentally friendly sorbents. However, a major drawback to their application as industrial materials for the removal of heavy metal ions from wastewater is the *slow adsorption* process of the metal ions. It might take several days to complete the adsorption of the ions on the surface of the plant biomass. For example, it took 10 days to remove 90% of Ni ions using an aquatic plant called *Lemna minor* (Delgado et al. 1993).

The use of domestic multimode microwave (Gabriel et al. 1998; Grisaru et al. 2003; Harpeness and Gedanken 2004) or single-mode microwave ovens (Kadirvelu et al. 2000; Katsuki and Komarneni 2003) for the fabrication of inorganic nanomaterials is becoming a common technique. The main advantage of this method when compared to other synthetic nanoparticle techniques is the short reaction time. The reduction of metal ions into the corresponding metal was conducted under microwave radiation using a polyol (Kleiman and Cogliatti 1998) as a reducing agent, and nanosized metallic particles were obtained as the product. The polyol reaction was developed by Fievet et al. (1988) in the late 1980s. They have boiled metallic ions in liquid polyols such as ethylene glycol and obtained submicron metal powders. The process was named the polyol process.

In our previous report (Chefetz et al. 2005), we demonstrated that adsorbed silver ions onto dried *Azolla filiculoides* plant biomass were successfully reduced and converted to metallic nanoparticles by a polyol under microwave heating. It is important to note that, in the previous report (Chefetz et al. 2005), the short (a few minutes) microwave radiation process (polyol reaction) was compared with the 7 days it took to adsorb each of the following ions: Ag^+, Pb^{+2}, and Ru^{+3} onto the aquatic plants without microwave. Moreover, the fabrication was obtained under microwave radiation in ethylene glycol solution, which served as the reducing agent. In another study (Marciano et al. 2008), we demonstrated a different

behavior of cuticular materials with metallic ions under microwave radiation. In this report (Marciano et al. 2008), adsorption of the ions was negligible. However, under microwave radiation in ethylene glycol solution, nanoparticles were observed on the surface of the plant biomass. It was suggested that, when cuticle biomass is used, only the solution-formed nanometallic compounds interact with the biomass surface. The interaction between the silver nanoparticles and the cuticle biomass is accelerated by microwave radiation and carried out in hot spots, which are formed by the strong absorption of the microwave radiation by the metallic nanoparticles. The dipole moment of aliphatic hydroxy acids, which are present in the cuticle, can also absorb microwave radiation, thereby facilitating the adsorptive interactions with the metallic nanoparticles.

In the current paper, we present a different approach in which a one-step process takes place in order to obtain the metallic nanoparticles. In other words, during the 5 min of microwave reaction, adsorption and reduction take place when the aquatic plant *Pistia stratiotes* or *A. filiculoides* biomass is present. Moreover, we report that the reactions (adsorption and reduction) are performed in similar efficiencies in aqueous and ethylene glycol solutions. The reaction was performed with two metals having very different reduction potential, silver (E_0 of +0.76 V) and lead having a negative reduction potential (E_0 of −0.13 V).

2 Experimental

Ethylene glycol (spectroscopic grade), tri(ethylene glycol) (99%), silver nitrate (ReagentPlus™ 99.995%), and lead nitrate (99.999%) were all purchased from Sigma-Aldrich and used without further purification. Solutions of Ag^+ and Pb^{2+} were prepared in water. The solutions were prepared by dissolving the corresponding amounts of the salts in the water. The concentration of the Ag^+ and Pb^{2+} ions was always 0.02 M.

An ordinary household microwave oven (Spectra 900 W, 2.45 GHz), modified with a refluxing system, was used for the microwave-assisted reduction. The irradiation time was 5 min for both ions. Prior to their introduction to the microwave oven, both aquatic plants, *Azolla* or *Pistia*, were dried at 60°C. The

plants were not grinded before the chemical process. Dried biomass (0.75 g) was placed in round-bottom flask containing 60 mL of the above-mentioned solutions. At the end of the reaction (microwave radiation), the biomass was separated by centrifugation. The concentration of Ag^+ and Pb^{+2} ions was determined by titration with a 0.01-M aqueous solution of KSCN in the presence $FeCl_3$ as an indicator (Kolthoff and Sandell 1958) and by titration using EDTA and xylenol orange for silver and lead, respectively. All the above-mentioned experiments (reactions and titrations) were conducted in triplicates. Solutions containing silver or lead ions without plant materials were analyzed as controls.

The X-ray diffraction patterns of the products were measured with a Bruker AXS D* Advance Powder X-ray diffractometer (using Cu Kα=1.5418 radiation). The morphology of metallic nanoparticles was determined by transmission electron microscopy (TEM) (JEM-1200EX) working at acceleration voltages of 80 kV.

3 Results and Discussion

We have measured the product of the MW reaction of the aqueous silver solution with the 0.75 g *A. filiculoides* using the XRD technique. This measurement was taken to probe the nature of the product embedded in the plant. Pieces of the solid plant were introduced in the machine for examination. The diffraction pattern of the *A. filiculoides* embedded with silver was identical to our data presented in Chefetz et al. (2005). The diffraction peaks fit those reported in the literature for cubic Ag (PDF 4-783).
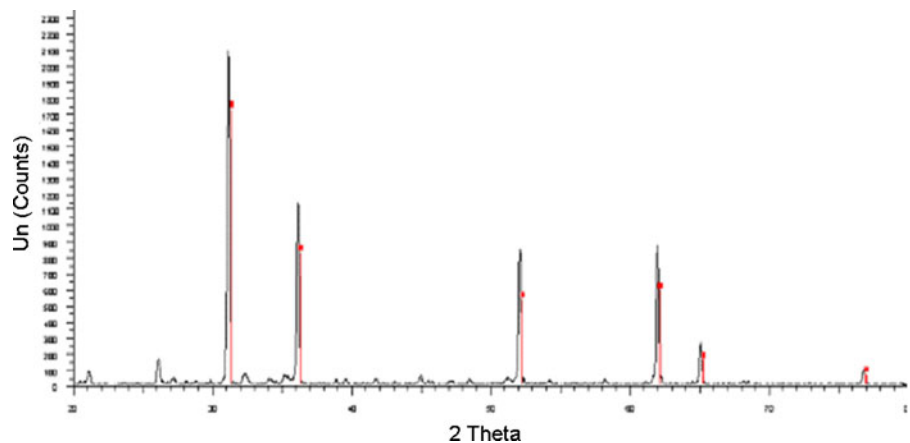
No evidence for the existence of silver oxide is seen in the diffraction peaks.

The XRD pattern of the solid precipitate embedded in the plant obtained after the 5 min of MW irradiation of the 0.02 M aqueous solution of Pb^{+2} in the presence of 0.75 g of *A. filiculoides* is presented in Fig. 1. All the diffraction peaks match the diffraction peaks of metallic Pb as reported in the literature (PDF=4-686). This clearly indicates that the *A. filiculoides* biomass served as both adsorption matrix and more impotently as reducing agent. A control reaction of the MW irradiation of the 0.02 M of silver or lead ions in the absence of the plant for even 10 min did not yield any product. It is important to note that the width of the diffraction lines points out that the obtained metallic particles are of nanometer size and the application of the Debye-Scherrer formula to the diffraction peaks of silver and lead yielded grain sizes of 13 and 20 nm for the lead and silver particles, respectively. The small diffraction peaks at 21.3°, 26.3°, 24.2°, and 25.4° are assigned to the (002), (220), (222), and (040) planes of orthorhombic Pb_5O_8 (PDF file 052-0772). These small peaks indicate that, unlike silver, a noble metal, lead is partially oxidized under ambient conditions.

The TEM image of the lead particles embedded in the *A. filiculoides* biomass is presented in Fig. 2a. To get a good statistics of the size of the silver and lead nanoparticles, about 100 particles were counted and the histogram is built using the *Scion* computer program. For silver, a bimodal distribution of particles is detected. The major part (95%) consists of particles whose size ranges in the 10–50 nm range, and the average particle size is 31 nm. The other 5% have an average particle size of 170 nm, indicating their

Fig. 1 XRD pattern of metallic lead detected in an *Azolla* plant after microwave irradiation

Fig. 2 a Histogram of the sizes of the lead particles embedded in the *A. filiculoides* plant. b TEM image of the *A. filiculoides* plant embedded with the lead nanoparticles
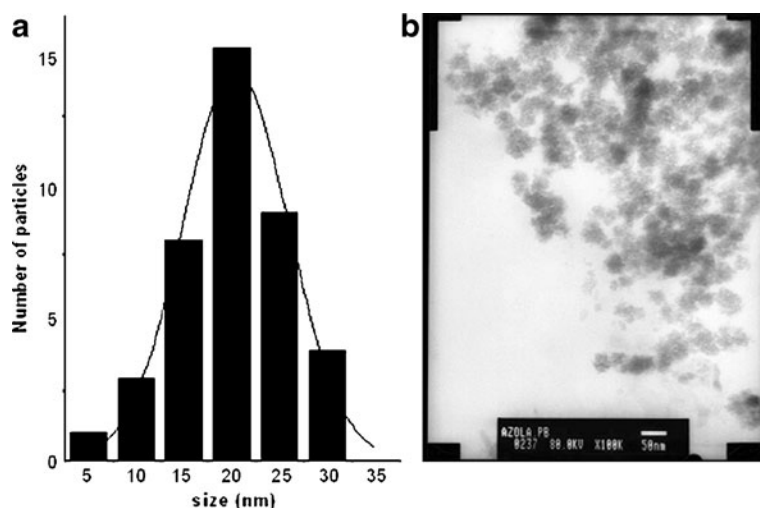
aggregated nature. For the lead nanoparticles, the histogram reveals particles with sizes in the range of 5–30 nm. The average size was calculated as 24 nm. Unlike the silver particles, which are mostly spherical, the morphology of the lead particles was less regular. The pH of the solution was measured after the microwave irradiation and was found to be 3.

HRTEM measurements of the lead nanoparticles embedded in the *A. filiculoides* plant are illustrated in Fig. 3. They provide further support for the identification of the embedded nanoparticles as metallic Pb. The spacing between the fringes observed in Fig. 3 is 0.285 nm. The literature value in the PDF table 4-686 is also 0.285 nm. This

distance corresponds very well to the *d* value of the (111) plane in metallic lead. In addition, small particles of 5–10 nm are clearly observed in this figure. Further support can be obtained from the electron diffraction pattern depicted in Fig. 4. The crystalline nature of the product is clearly observed in the figure, and the diameter of the 0.289 nm circle fits well the *d* value of the (111) plane.

To probe whether all the silver or lead ions are embedded in the plant as metallic particles, we monitored their mass balance. The amount of silver detected in the supernatant after the reaction was less than the detection limit of the titration method. The lead behaved differently. Only 33 wt.% of the applied lead ions were obtained in the *A. filiculoides* biomass,
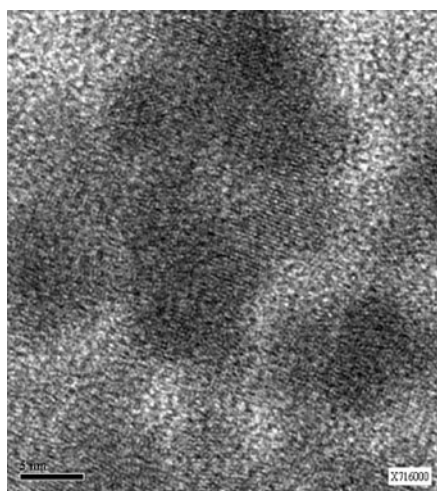

Fig. 3 HRTEM picture of the lead nanoparticles embedded in the *A. filiculoides* plant. The fringes are distanced by 0.285 nm which can be assigned to the (111) planes of fcc lead
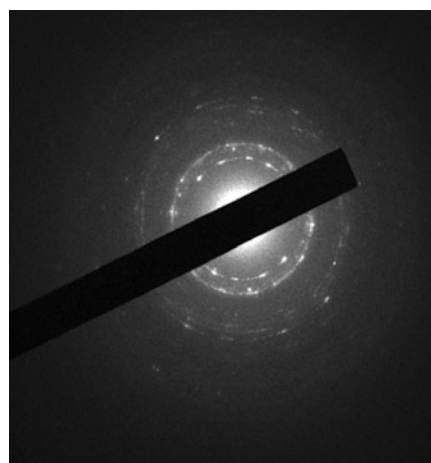

Fig. 4 Electron diffraction pattern of the lead nanoparticles embedded in the *A. filiculoides* plant

whereas a minor amount (<0.5%) of the lead nanoparticles were precipitated to the bottom of the reaction vessel. This suggests that, at the end of the microwave reaction, lead was present either as free ions in the solution or as metallic Pb attached to the plant biomass. Silver was found only in the plant as metallic Ag after the reaction. This can be rationalized by arguing that, since the reduction is carried out by the *A. filiculoides* biomass, naturally the particles have to be found embedded in the plant. The maximum adsorption capacities of the *A. filiculoides* biomass towards silver and lead were 171 and 109 mg/g biomass (1.6 and 0.52 mmol/g), respectively. These values were calculated assuming that the amount of silver and lead ions left in the solution are due to the maximum loading of the metallic nanoparticles by the aquatic plants. In fact, a longer microwave irradiation did not change the concentration of the ions left in the solution. This also indicates that the aquatic plant is saturated in the metallic nanoparticles. The differences in the adsorption capacities of silver and lead are attributed to the standard reduction potentials of the two ions Ag=+0.76 V and Pb=−0.13 V. It is clear that the K_{eq} of the reduction of silver ions by the aquatic plant will be much larger than that of lead ions. It is therefore possible that the lead ions found in the solution at the end of the reaction is due to their equilibrium concentration while the reduction of silver goes to completion.

The amount of silver in the plant could not be detected chemically. However, the silver content in the plant was examined by EDAX measurements (penetration of 600–1,000 nm). Pieces of the plant were probed for their silver percentage. It became clear to us that a large amount of silver does exist in the plant and is strongly anchored to it, but we could not receive a good estimate for the total silver weight because the silver is not homogeneously dispersed in the plant. The percentages of silver varied between 7 and 29 wt.%. The reason for the silver concentration varying that much has to do with the specific places in which the silver nanoparticles were accumulated. This is dependent on the reducing agent in the plant which is not homogeneously distributed in the plant. Figure 5 substantiates this claim. The figure, a SEM image of the plant embedded with metallic silver, illustrates the distribution of the nanoparticles in the plant. The figure shows that the silver is located in specific areas
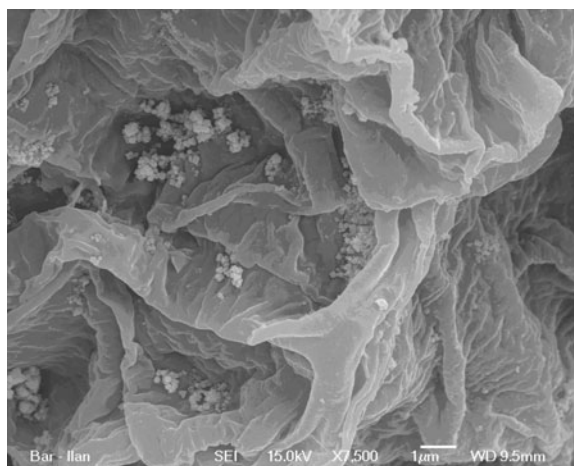

Fig. 5 SEM pictures of the silver particles embedded in the *A. filiculoides* plant

and is not distributed homogeneously over the plant. The silver nanoparticles have a crystalline morphology, and their sizes range from 50 to 200 nm.

To isolate and emphasize the importance of the MW radiation and to point out its major role, we have conducted another control reaction. As pointed above, reduction of silver or lead ions can be accomplished by various polyols. We have eliminated the MW oven and heated the same amounts of starting materials (0.75 g of *A. filiculoides* and 0.02 M of silver or lead in ethylene glycol) to the boiling temperature of ethylene glycol without a microwave oven. Reaching boiling point took about 1 h. The results showed that the same percentage of silver ion reduction is obtained after 2 h of heating at the ethylene glycol boiling point.

Thus, the same results are obtained both with and without microwave heating. The only advantage using this solvent in using the microwave oven is the shortening of the reduction time. This is a well-known phenomenon for the use of microwave radiation related to the superheating of the solvent (Komarneni et al. 2002). It is worth mentioning that repeating this experiment with an aqueous solution of the silver ions did not yield the same reduction rate even after 5 h.

Naturally, we intend to associate the reducing power of the *A. filiculoides* plant to the presence of sugars known for their reducing capacity. Veys et al. (2002) have examined the composition of a few *Azolla* plant species and concluded that "proteins, acidic polysaccharides, and pectin are always detected." Based on this statement, we have carried

out experiments using pectin and an aqueous solution of silver nitrate under microwave radiation for 5 min. No evidence for the appearance of metallic silver was observed. The same experiments were repeated by replacing the pectin with α-glucuronic acid. The experiment yielded negative results.

The reduction of the metallic ions by the plant and not by the water clarifies somewhat the mechanism of the reaction. In our previous paper (Chefetz et al. 2005), the question was asked whether the ions are reduced in the solution and the metallic particles are then adsorb to the plant or are they first adsorb and then reduced. In the current process, this question mark is eliminated because water cannot reduce the ions under MW. It is therefore clear that the ions are first adsorbed on the plant and then reduced by the plant. It is also suggested that the reduction power of the microwave radiation is a result of the superheating phenomenon which was demonstrated recently by Pol et al. (2007).

4 Conclusion

This study demonstrates that the removal of heavy metal ions Ag^+ and Pb^{+2} from solutions can be done in a one-step process, and the long adsorption stage of the ions by the aquatic plant can be shortened drastically, reaching the same level of residues. Moreover, the aquatic plant has shown itself as a strong reducing agent capable of reducing not only silver but also lead ions into the corresponding metallic particles.

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