

New Approach for the Removal of Metal Ions from Water: Adsorption onto Aquatic Plants and Microwave Reaction for the Fabrication of Nanometals

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We adsorb heavy metal ions such as Ag^+ , Pb^{2+} , and Ru^{3+} onto an aquatic plant and convert the adsorbed ions to the corresponding nanometallic particles by the polyol reaction carried out in a microwave oven.

Introduction

Heavy metals are toxic contaminants that must be removed from wastewaters before being discharged to the environment. A wide range of physical and chemical processes are available for the removal of heavy metal ions during wastewater treatment. These include ion exchange, electro-chemical precipitation, filtration, and adsorption to commercial activated carbon. A major drawback with precipitation is contamination of the produced sludge, which limits its application in agricultural fields. Ion exchange and adsorption to activated carbon are efficient treatments, but they are not largely used due to the high operational cost. Alternatively, aquatic plant materials have shown a remarkably high sorption capacity for heavy metals from wastewater.^{4–7} Therefore, plant materials that are available in large quantities may have the potential to be used as alternatively low-cost (\$1 per 1 kg of aquatic plant) and environmentally friendly sorbents.

The use of domestic multimode microwave (MW)^{11,13,14} or single-mode MW ovens^{9,12} for the fabrication of inorganic nanomaterials is becoming a common technique. The main advantage of this method when compared to other synthetic techniques of nanoparticles is the short reaction time.

In the current paper, we describe a combined procedure composed of two known technologies, namely, adsorption of metallic ions on aquatic plants and conversion of the adsorbed heavy ions into metallic nanoparticles. The combined process offers a promising approach for the removal of heavy metals from wastewater and the recycling of adsorbed metals into marketable products of metallic nanoparticles. In this study, the aquatic plant *Azolla* was used as the sorbent for Ag^+ , Pb^{2+} , and Ru^{3+} ions in an aqueous solution. These heavy metal ions

are present in industrial (e.g., Ag^+ in photoprocessing) and municipal effluents. They also present a variety of reduction potentials, thus demonstrating the generality of the method. Therefore, it is of great scientific and practical interest to reveal the possible removal and recycling of these metal ions from wastewater using low-cost treatments.

Experimental Section

Silver nitrate and ethylene glycol were purchased from Sigma-Aldrich Co. and used without further purification. *Azolla filiculoides* was grown in IRR1 medium⁸ in the phytotron of the Faculty of Agriculture, Hebrew University. X-ray diffraction (XRD) analysis was performed with a Bruker AXS instrument (model D8), using $\text{Cu K}\alpha$ radiation. Transmission electron micrographs (TEM) were obtained by employing a JEOL-TEM 100SX microscope. The samples for TEM were prepared as follows. Ag^+ -adsorbed dry plants were pounded (dispersed) in an agate mortar, and the powder was suspended in 2-propanol (ethanol) by sonication in an ultrasonic bath for 20 min. Then the suspension was layered on a copper grid (piece of 400 mesh coated with carbon film) and dried in air. The quantity of Ag^+ ions adsorbed by the plant was calculated by differences between the Ag^+ concentration in the solution and the original amount. The concentration of Ag^+ ions in the solution was determined using a well-known titration method. The Ag^+ ions are titrated with a 0.01 M solution of KSCN in the presence FeCl_3 as an indicator.¹⁶

The starting materials for the reduction of Pb^{2+} and Ru^{3+} ions were $\text{Pb}(\text{NO}_3)_2$ and RuCl_3 , respectively. The concentration was 0.02 M in ethylene glycol and ethanol for Pb^{2+} and Ru^{3+} , respectively. The irradiation times were 3 min for Pb^{2+} and 1 min for Ru^{3+} .

An ordinary household microwave oven (Spectra 900 W, 2.45 GHz), modified with a refluxing system, was used for the microwave-assisted reduction. Dried *Azolla* biomass (0.7 g) was placed in 60 mL of an aqueous solution (or ethylene glycol) of 0.02 M AgNO_3 . The reason for choosing this high concentration

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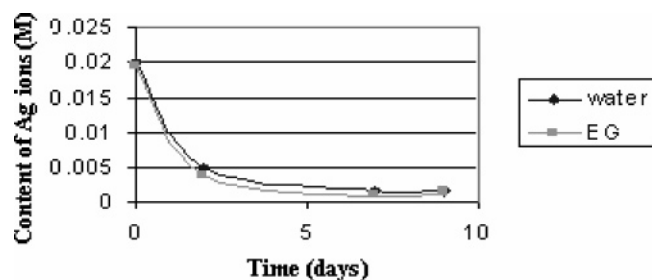


Figure 1. Adsorption kinetic of silver ions by *Azolla* biomass in EG and water solutions.

of Ag^+ ions is that in this paper we intend to present a new idea and are not concerned with treating real metallic wastes. However, it is worth mentioning that according to Internet sources¹⁷ “depending on the stage from which the wastes originate and the type of film processed, the silver concentration can range between 5 mg/L and 12,000 mg/L”. This means that the concentrations used in the current experiments are not far from reality.

The mixture was allowed to equilibrate at room temperature for a few days to reach maximal Ag^+ ion adsorption. Then, the Ag^+ -adsorbed plant biomass was dispersed in an ethylene glycol solution and placed in the microwave reflux system⁹ for 3 min for the reduction of adsorbed silver ions. Before the reaction, argon was purged for 30 min through the solution, and then the microwave oven was switched on under a continued flow of argon. The power level of the oven was 50%. The resulting product was centrifuged, washed with double-distilled water, ethanol, and dried in a vacuum. The portion of the plant with silver nanoparticles was heated under argon at 500 °C for 5 h for residue analysis.

Results and Discussions

The adsorption kinetics of silver ions onto *Azolla* biomass are presented in Figure 1. The adsorption kinetics of the ions by the biomass were similar in either ethylene glycol or water. In both solvents, 90% of the Ag^+ ions (as determined by the SCN^- titration¹⁶) were adsorbed by the *Azolla* biomass within

3 days. The calculated adsorption capacity of the plants was 190 mg Ag^+ /g biomass.

A new concept that is currently under study has shortened the adsorption time from 7 days to 5 min.

The microwave irradiation of the adsorbed Ag^+ biomass was aimed at reducing the silver ions into the corresponding metallic silver.¹⁰ Coupling microwave dielectric heating and the polyol reaction has recently led to the fabrication of a long list of metallic nanoparticles^{9–12} as well as binary¹³ and ternary chalcogenide nanoparticles.¹⁴ The polyol process, described by Fievet,¹⁵ is completed in a much shorter time when conducted under microwave power than under reflux conditions. The identification of the product of the polyol reaction was done by XRD analysis (Figure 2). The particle size calculated by the Debye–Scherrer formula was 30 nm, and the major diffraction peaks are assigned to pure metallic cubic silver. The intensities and positions of the peaks are in a good agreement with literature values of cubic silver (PDF: 4-783). The presence of impurities such as silver oxide peaks was not detected. However, a very small diffraction peak at $2\theta = 29.6^\circ$ is measured and assigned to the mineral residues left after the burning of the aquatic plant.

A TEM image of the *Azolla* biomass containing silver nanoparticles after the microwave-assisted reduction (from aqueous solution) is presented in Figure 3. Nanoparticles (20–30 nm in size) are clearly observed on the surface of the plant materials. The shapes of these particles are almost spherical, and the identification of the nanoparticles as silver was aided by XRD measurements. The TEM images obtained for the reduced metallic silver from water or ethylene glycol (EG)-adsorbed ions are almost identical. TEM images (Supporting Information) of the material obtained after the burning of the aquatic plants in argon show 20–30 nm silver particles similar to their sizes in the *Azolla*. However, part of the silver is aggregated in 300–500 nm particles as expected from annealing nanoparticles at 500 °C.

A similar process of adsorption and reduction was conducted with ions of Ru^{3+} and Pb^{2+} and yielded similar results. Ions were adsorbed by the plant biomass and were further reduced by microwave-assisted radiation. Experiments using another

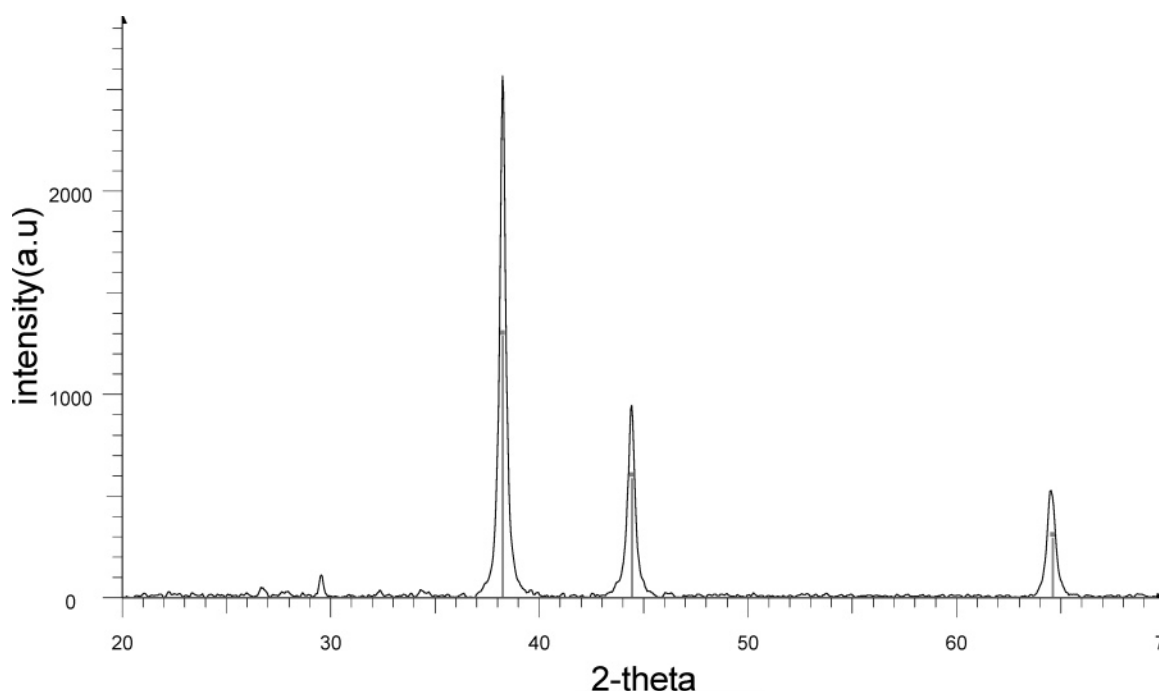


Figure 2. XRD of the product after annealing of the product of the microwave reduction in argon at 500 °C.

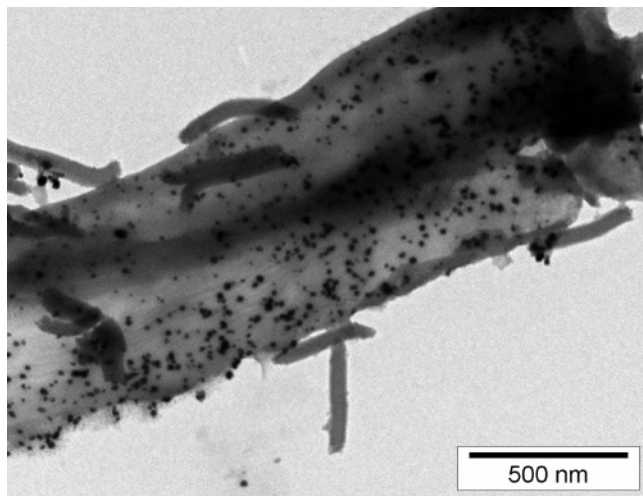


Figure 3. TEM picture of the *Azolla* plant after the reduction of the adsorbed silver ions.

aquatic plant (*Pistia*) were also successful and yielded similar results. Thus, we suggest that the described technology can be used for removal of metal ions from water and transforming them to nanoparticles.

Supporting Information Available: TEM images of the silver nanoparticles after burning in argon at 500 °C. These images demonstrate that the material is only partially aggregated

and a major part of the particles remain monodispersed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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