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Silver Modified Hydrophytes for Heavy Metal Removal from Different Water Resources

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Abstract: Phytoremediation of three different aquatic plants powders *Lemna minor* L., *Azolla filiculoides* Lam. and *Pistia stratiotes* L. studied against different heavy metals (HM) and after modifications with interfacial layer synthesized silver nanoparticles. Prepared samples tested for the selective absorbance of chromium, cadmium, lead, and zinc. *L. minor* and *P. stratiotes* show selective absorption against lead, while *Azolla filiculoides* show higher absorption against chromium. Absorption of all heavy metal concentrations was found to be enhanced after interfacial modification with green synthesized silver nanoparticles.

Keywords: aquatic plants; silver nanoparticles, heavy metal; phytoremediation.

1. Introduction

Water is the essential substance after the air, with the importance of water being the second place as an essential requirement. Life as we know it could not have evolved without water; that is, water is also used by all living organisms [1, 2]. During the last decades, removing heavy metal ions from contaminated water may be considered an important issue for different uses, including agriculture [3, 4] and industrial uses [5, 6]. Various materials that were reported to be used, including organic [5], inorganic [7], agro-waste materials [8], and many others, were reported. Phytoremediation can be considered an effective and green developing route with long-range applicability when suitable plants were chosen. Aquatic plants were recently studied [9]. Several authors have reviewed floating and emergent aquatic plants' applications in phytoremediation processes for water contaminated with heavy metals [3, 10-13].

Plants that may be used in the phytoremediation process must have specific standards. Plants for this issue must be native with a quick growth rate with a high biomass yield. Besides, it must have higher heavy metal uptake and have the ability to transport metals in aboveground parts of the plant [14, 15]. Among the various aquatic plant species, *Azolla*, *Eichhornia*, *Lemna*, *Potamogeton*, *Pistia*, *Typha*, *Phragmites*, and *Wolfia* have been reported phytoremediators, and also they are highly efficient in reducing aquatic contamination through bioaccumulation of contaminants in their body tissues [3, 16, 17].

Azolla filiculoides Lam. (family Azollaceae) is a free-floating annual aquatic fern, fast-growing, and high reproduction rate. *Lemna minor* L. (duckweed, family Lemanaceae) is a small free-floating annual aquatic plant on or beneath the surface water. *Pistia stratiotes* L. (Water lettuce, family Araceae) is a perennial monocotyledon aquatic plant that free-floating. Three genera are cosmopolitan distributed worldwide, in Egypt, two species of Azolla, three species of Lemna, and one Pistia species distributed in the Nile delta in all water bodies and rice fields [18, 19].

They pointed to the metal accumulation character of different aquatic plants, including *Azolla*, *Pistia*, and *Lemna*, along with some other aquatic plants. They also reported that their phytoremediation potential could be further improved. Therefore, the presented work aims to introduce a new novel method for modifying the interfacial surface of plant powder with a silver nanoparticle as an antibacterial agent to enhance some aquatic plants' phytoremediation process to study the selectivity of each plant for a specific element.

2. Materials and Methods

2.1. Collection and preparation of the plants.

The three selected fresh hydrophytes for the experiment are commonly available in Egyptian water bodies, particularly around the River Nile system as following: *Azolla filiculoides* Lam. and *Lemna minor* L. In the laboratory, the three selected plants were washed gently in distilled water several times and have been dried well then, each one of dried plants was put in a blender until it became a soft powder then each plant powder were put in a plastic bag ready for the next steps.

2.2. Modification with silver nanoparticles.

The pre-calculated concentration of green synthesized silver nanoparticles was added to 5 gm powdered plant placed in a 100 ml Teflon lined autoclave adjusted at about 50 °C for about 24 h. the powder was then dried in a vacuum dryer adjusted at the same temperature for another 24h.

2.3. Preparation of the standard heavy metal solution.

Four different heavy metals, Chromium, Zinc, Cadmium, and lead, were selected to test the test plant's selectivity for absorption. A stock solution (1000 mg/L) was prepared in distilled water with analytical grade $K_2Cr_2O_7$, $ZnSO_4.7H_2O$, $CdCl_2$, and $Pb(C_2H_3O_2).3H_2O$, which was later diluted as required. The plants were maintained in tap water supplemented with 2, 3, 4 mg/L of Cr, 5, 10, 20 mg/L of Zn, 0.5, 1, 2 mg/L of Cd, and 10, 20, 30 mg/L of Pb.

2.4. Simple multi-stage purification system.

A multi-stage system was adopted to treat contaminated water samples containing different heavy metals. The system consists of five to seven layers. The first layer represents a thick layer of cotton or charcoal in the burette's bottom to prevent the second layer of plant powder from being lost or plugging the burette. The third and fifth layers are represented by small gravel that prevents solid contaminated materials from being passed. In case of heavily contaminated water, two additional layers of powder plant and gravel were added. The thickness of layers was adjusted to a range between 2-2.5 cm. Figure 1 represents a simple multi-stage purification system.

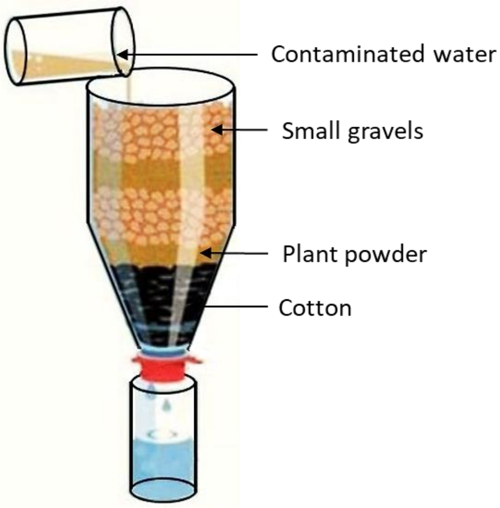

Figure 1. Simple multi-stage purification system.

The flow rate can be adjusted through the burette tape. For fair comparison and to eliminate the factor of time or flow rate, the flow rate was adjusted in all measurements to be 250 ml/h. 25 ml of contaminated water was poured into the burette's upper opening, and purified water samples were collected from the tape. The process was repeated for the same water sample contaminated with a specific element three times, and an average value of triplicate measured parameters was recorded. The system compartment was changed both with changing concentration and/or heavy metal. The processes were repeated for three different plant powders, namely (*A. filiculoides, L. minor,* and *P. stratiotes*) and 4 different contaminants (Pb, Cd, Zn, and Cr).

2.5. Determination of the absorbance and concentration of heavy metals in water samples.

The absorbance of synthetic wastewater was carried out by Atomic Absorption Spectrophotometer (Metertech SP-8001 UV/Visible Spectrophotometer). Determination of heavy metal (Cd, Cr, Pb, and Zn) contents in synthetic wastewater were carried out by Atomic Absorption Spectrometer (Buck Scientific Accusys 211 Atomic Absorption Spectrophotometer, USA) with air-acetylene flame at the wavelength of 228.8, 357.87, 283.31 and 213.9, respectively [20-22]. The concentration of metals in the samples was determined in mg/L [23].

2.6. Calculation methods.

The percentage removal was calculated from the initial and final concentration of metal according to Tanhan *et al*. [24].

$$\%\,Removal = \frac{(C_0 - C_f}{C_0}$$

Where C_0 and C_f are initial and remaining concentrations respectively in the medium (mg/L).

2.7. Statistical analysis.

The experiment was set up in replicates, and all the data was mean of triplicate (n=3). Data of both absorbance and the calculated values for removal efficiency were subjected to one-way ANOVA followed by Duncan's post hoc test at probability level 0.05 using CoStat software program (CoHort Software, Monterey, CA, USA).

3. Results and Discussion

The application of nanoparticles provides an effective alternative method for mitigating various environmental stresses, including heavy metal stress [25]. In the present study, Table 1 reveals the value of absorbance and removal percent of a pre-prepared solution containing heavy metals (Cr, Cd, Pb, and Zn) before and after being modifying the *Lemna minor* powder with silver nanoparticles. It was clear from the experimental data that the removal percentage generally higher in the case of plant powder modified with silver nanoparticles by about 22% of the original value for chromium ions and 15% for cadmium ions, 4 % for lead, and 91% for zinc respectively at lower concentrations (2, 0.5, 5 and 10 ppm) which decrease with increases of some heavy metal concentration (Cr, Pb, and Cd) and increase in 10 ppm then decrease in 20 ppm of Zn.

3.1. Removal capacity of Lemna minor.

It was also observed that *L. minor* best removal percentage combined with Zn ions. Similar results were obtained by Neidoni *et al*. [26] observed that it had been an increased affinity for zinc accumulation (72% removal at the initial concentration of 15 mg/L Zn) than copper and nickel. Kinraide *et al*. [27] reported that Zn excess and Zn deficiency cause Zn to become prooxidant. As a result, various sets of proteins responsible for sensing, carrying, buffering, holding, and releasing Zn closely regulate the cellular concentration and compartmentation of mobile Zn in all organisms [28]. Figure 1 shows the relative change in absorbance for different metal concentrations (Cr, Cd, Pb, and Zn) before and after modifying the *L. minor* powders with silver nanoparticles.

Table 1. Absorbance and removal percent of the pre-prepared solution containing heavy metals (Cr, Cd, Pb, and Zn) before and after modifying the *Lemna minor* powders with silver nanoparticles.

Element	Conc. (ppm)	Without nanoparticles		With nanoparticles	
		Absorbance	% removal	Absorbance	% removal
Cr	2	0.458	77.12	0.116	94.22
	3	0.618	79.40	0.314	89.54
	4	0.757	81.07	0.426	89.36
Cd	0.5	0.112	77.68	0.652	89.6
	1	0.219	78.13	0.130	86.99
	2	0.199	90.04	0.341	82.97
Pb	10	0.563	94.37	0.191	98.19
	20	0.431	97.84	0.410	97.95
	30	0.368	98.77	0.571	98.10
Zn	5	0.334	93.31	0.745	85.09
	10	0.537	94.63	0.566	94.34
	20	3.013	84.93	2.407	87.97
	$LSD_{0.05}$	0.016***	0.807***	0.004***	0.298 ***

3.2. Removal capacity of Azolla filiculoids.

Table 2 discloses the value of absorbance and removal percent of the pre-prepared solution containing heavy metals before and after modifying the *Azolla filiculoids* powders with silver nanoparticles. It was clear that the removal percentage generally higher in the case of plant powder modified with silver nanoparticles by about 10% of the original value for chromium ions and 30% for cadmium ions, 22 % for lead, and 14% for zinc, respectively, at lower concentrations (2, 0.5, 10 and 5) which decrease with increases of heavy metal concentration (Cr, Pb, and Zn) except in Cd removal percentage there is an increase in removal percentage in high Cd concentration (2ppm).

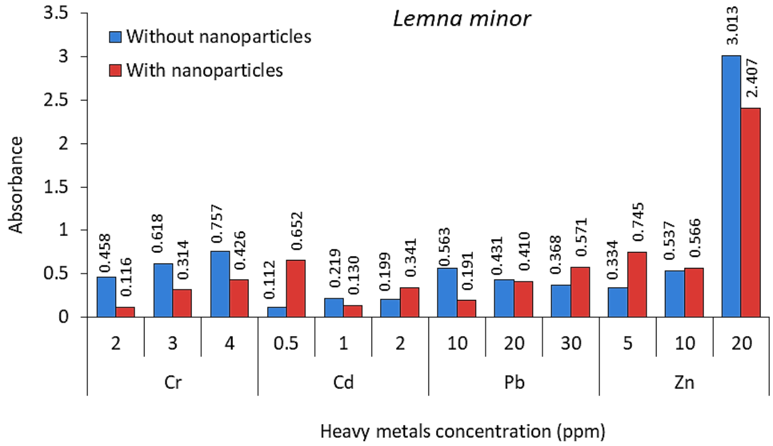

Figure 1. Relative change in absorbance for different metal concentrations before and after modifying the *Lemna minor* powders with silver nanoparticles.

It was also observed that *A. filiculoides* best removal percentage combined with Cd ions. It was concluded that the removal percentage increases with modifying plant powder with silver nanoparticles. The bioaccumulation potential of *Azolla* spp. for various heavy metals has been compared with other aquatic macrophytes by many workers [29-31].

Table 2. Absorbance and removal percent of a pre-prepared solution containing heavy metals before and after modification of the *Azolla filiculoids* powders with silver nanoparticles.

Element	Conc. (ppm)	Without nanoparticles		With nanoparticles	
		Absorbance	% removal	Absorbance	% removal
Cr	2	0.135	93.25	0.109	94.57
	3	0.399	86.69	0.177	94.09
	4	0.453	88.67	0.286	92.85
Cd	0.5	0.229	54.18	0.147	70.70
	1	0.340	65.98	0.264	73.61
	2	0.237	88.15	0.423	78.84
Pb	10	3.558	64.42	2.119	78.81
	20	9.929	50.35	8.454	57.73
	30	16.620	44.60	11.745	60.85
Zn	5	1.840	63.20	1.3787	72.43
	10	3.677	63.24	2.7476	72.52
	20	5.015	74.93	5.4087	72.96
	$LSD_{0.05}$	0.007***	0.115***	0.002***	0.117***

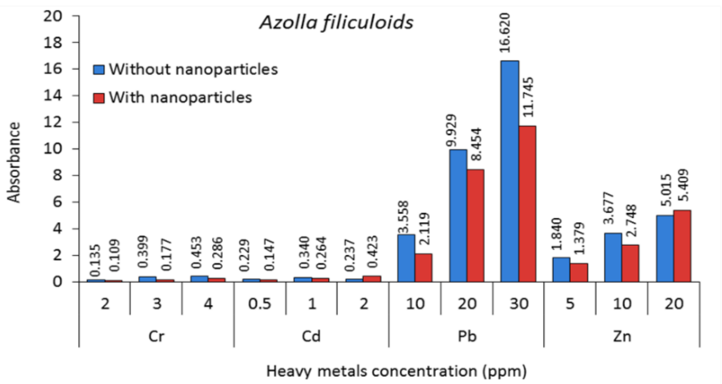

Figure 2. Relative change in absorbance for different metal concentrations before and after modifying the *Azolla filiculoides* powders with silver nanoparticles.

They reported that *A. filiculoides* accumulate heavy metals in tissues such as Cd, Cr, and Zn from wastewater. Similar findings were observed by Khosravi *et al*. [32] showed that the maximum uptake capacities of heavy metals (Cd, Pb, and Zn) after chemical modifying the *A. filiculoids* powders were increased in wastewater. Figure 2 displays the relative change in absorbance for different metal concentrations (Cr, Cd, Pb, and Zn) before and after modifying the *A. filiculoides* plant powders with silver nanoparticles.

3.3. Removal capacity of Pista stratiotes.

Table 3 discloses the value of absorbance and removal percent of a pre-prepared solution containing heavy metals (Cr, Cd, Pb, and Zn) before and after being modifying the *Pista stratiotes* plant powders with silver nanoparticles. It was clear that the removal percentage generally higher in the case of plant powder modified with silver nanoparticles by about 6% of the original value for chromium ions and 19% for cadmium ions, 0% for lead and 1% for zinc, respectively, at lower concentrations (2, 0.5, 10 and 5 ppm) which decrease with increases of heavy metal concentration especially in all (Cd) concentration and (Pb) concentration with concentration and (Zn) concentration with (10 ppm) Then decrease in (30 ppm).

It was observed that *P. stratiotes* best removal percentage combined with Cd ions. It was concluded that the removal percentage increases with modifying plant powder with silver nanoparticles.

Table 3. Absorbance and removal percent of the pre-prepared solution containing heavy metals before and after modification of the *Pistia stratiotes* plant powders with silver nanoparticles.

Element	Conc. (ppm)	Without nanoparticles		With nanoparticles	
		Absorbance	% removal	Absorbance	% removal
Cr	2	0.202	89.91	0.082	95.89
	3	0.254	91.54	0.141	95.29
	4	0.269	93.27	0.119	97.03
Cd	0.5	0.161	67.80	0.337	80.70
	1	0.245	75.50	0.198	80.19
	2	0.367	81.66	0.521	73.95
Pb	10	0.266	97.34	0.260	97.40
	20	0.509	97.46	0.710	96.45
	30	0.387	98.71	0.808	97.31
Zn	5	0.283	94.34	0.235	95.31
	10	0.252	97.48	0.312	96.88
	20	1.860	90.69	0.945	95.27
	$LSD_{0.05}$	0.002***	0.117***	0.002***	0.117***

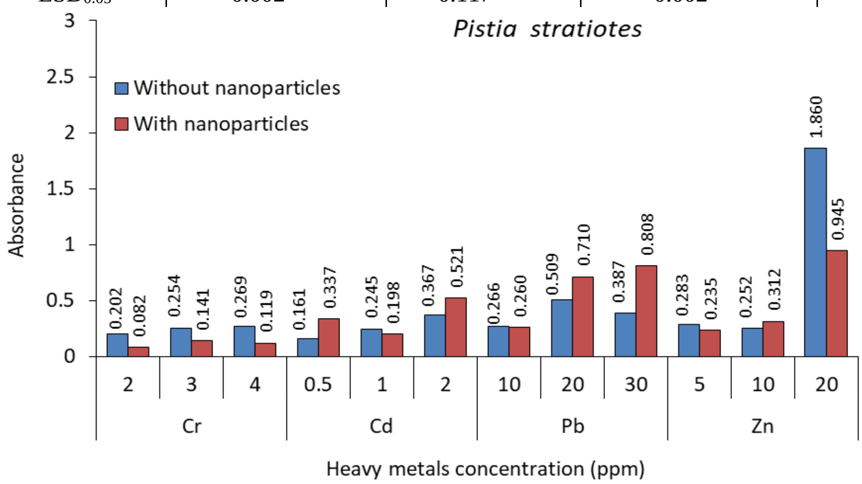

Figure 3. Relative change in absorbance for different metal concentrations before and after modifying the *Pistia stratiotes* plant powders with silver nanoparticles.

Similar results were observed by Miretzky *et al*. [33] and by Rodrigues *et al*. [34] found that *P. stratiotes* biomass can be effectively used for the removal of Cd and Zn from contaminated water bodies, with its efficiency being related to the immersion time and the concentration of these elements in the solution. Figure 3 shows the relative change in absorbance for different metal concentrations (Cr, Cd, Pb, and Zn) before and after modifying the *P. stratiotes* powders with silver nanoparticles.

According to a literature survey, floating aquatic plants have been shown to exhibit a higher accumulation of metals (Cd, Pb, Ni, Zn, and Cu) with higher bio-concentration factors than submerged and emergent plants in water [35, 36]. In the present study, regarding the plant species, percent heavy metals removal was increased in this order: *A. filiculoides* < *L. minor* < *P. stratiotes*. The morphological adaptive capacity determines the ability of the plant to absorb contaminants from water. The removal efficiency of any ion in tissues of macrophytes depends on the concentration of that ion in a water environment, physical-chemical characteristics of that pollutant, temperature, pH of water, and physiological and biochemical properties of the plant [4, 37]. Finally, studied hydrophytes may be used in “Ecotechnology” (environmental technology) in constructed wetlands. Moreover, wetlands help to prevent the spread of heavy metal contamination from land to the aquatic environment.

4. Conclusions

Three different fresh hydrophytes commonly available in Egyptian water bodies, particularly around the River Nile system, namely, *Lemna minor*, *Azolla filiculoides*, and *Pistia stratiotes* were collected, dried, and powdered. Prepared plant powder was modified through an interfacial layer of green synthesized silver nanoparticles. Powdered plants were studied against absorption of three different concentrations of four different heavy metals (HM), namely, chromium, cadmium, lead, and zinc. Obtained data reveals enhancement of HM absorption after modification with nanoparticles in all samples. Besides, studied plants show selective absorption against different metals.

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Conflicts of Interest

The authors declare no conflict of interest.

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