Hindawi
Applied and Environmental Soil Science
Volume 2023, Article ID 3417525, 16 pages
https://doi.org/10.1155/2023/3417525

Research Article

Phytoremediation of Engineered Nanoparticles Using *Typha latifolia* and *Carex rostrata*

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Received 7 December 2022; Revised 14 January 2023; Accepted 21 January 2023; Published 8 February 2023

Academic Editor: Rafael Clemente

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Engineered nanoparticles (ENPs) are in demand for numerous industrial, commercial, and domestic applications. Concern has arisen, however, regarding potential adverse environmental impacts from the inadvertent release of ENPs into water bodies. Certain plants have been identified with the capability to absorb metallic ENPs via roots, thus indicating possible application for phytoremediation. The reported study evaluates the potential for two aquatic plant species, viz. cattail (*Typha latifolia*) and sedge (*Carex rostrata*) for uptake of Ag, ZnO, TiO_2, Pd/$BiVO_4$/BiOBr, and Pd/Cu_2O ENPs, each of which were added weekly for 15 weeks. The research was conducted by comparing media doped with metals as nanoparticles and in ionic form. Sedge accumulated greater quantities of Ag, TiO_2, and ZnO ENPs in shoots compared with roots. In contrast, cattail roots accumulated proportionally greater concentrations of all ENPs (in particular ZnO, $BiVO_4$, and Cu_2O) and ionic metals compared to shoots. Such differences may be attributed, in part, to the root architectures of the two plant species. The translocation factor of ENPs in some treatments (Cu_2O, sedge; TiO_2, cattail) was >1.0, indicating a potential for phytoextraction. However, the bioconcentration factor for all ENPs was <1.0. Both species hold promise for the phytoextraction of certain ENPs.

1. Introduction

Engineered nanoparticles (ENPs) are used in numerous industrial, commercial, and household products. ENPs are applied in medicine, biomedical products, pharmaceuticals, paints, textiles, electronics, engineering materials, energy industries, agriculture, personal care products, kitchenware, food packaging, and in many other products and processes [1–4]. New nanomaterials and nanofunctionalized products continue to be developed, and their applications are expected to proliferate.

Many surface waterways have become sinks of pollutants which receive a range of anthropogenic inputs from upstream drainage basins as well as adjacent land. Engineered nanoparticles enter aquatic environments from both point and nonpoint sources during manufacture (e.g., release in industry wastewater; fugitive emissions), use (weathering; wastewater discharges), and disposal [5, 6]. Nanomaterials are used directly in agriculture, for example, in fertilizer and pesticide formulations; in addition, biosolids are applied to the land surface, and ENPs are ultimately lost via leaching and runoff [7]. Nanoparticles also enter the water from irrigation with wastewater and via aerial deposition [8, 9].

Aquatic ecosystems are rich in biodiversity and provide habitat for a range of organisms including microorganisms, invertebrates, insects, plants, fish, and mammals. They perform important ecological roles such as nutrient recycling, soil formation, and climate regulation [10].

Aquatic plants are responsible for the major portion of primary productivity in their environment and represent the base of aquatic trophic webs. Many are capable of production of substantial biomass. Several aquatic plant species are known to tolerate significant water pollution. Certain species have furthermore demonstrated the ability to take up

and accumulate metals and other toxins [11–13]. Many aquatic plants develop extensive root systems which allow for greater surface area for the absorption of contaminant metals into root tissue [14, 15]. This capability can be measured via the bioconcentration factor (BCF), which indicates root accumulation potential [16]. Some have the added capability to translocate contaminant metals from roots to shoots, measurable by translocation factor (TF). A number of aquatic plants can also immobilize metals on root surfaces and in nearby sediment by altering the chemical milieu, including pH and oxidation-reduction status [17]. All these capabilities can be exploited in phytoremediation, which is defined as the engineered use of plants to remediate soil and water. Several applications of phytoremediation are feasible; for example, in phytoextraction, a contaminant (typically a metal) is taken up by the plant root and translocated to above-ground tissue; such plants, termed 'accumulators," have BCF > 1 and TF > 1. The contaminant metal may be removed via plant harvest. In phytostabilization (rhizofiltration), the contaminant is immobilized via uptake and storage in roots, adsorption to root surfaces, and/or precipitation within the plant rhizosphere [18]. These so-called "excluder" species tend to have BCF > 1 and TF < 1 [19].

Phytoremediation with aquatic plants is considered an efficient and cost-effective technique for the cleanup of surface water. Engineered systems employing aquatic plants have been successfully applied for the treatment of wastewater worldwide [20, 21]. *Typha* spp., *Carex*, *Spirodela polyrhiza*, and other freshwater species have demonstrated the potential for phytoremediation to treat metal-contaminated water and sediment [18, 22]. For phytoremediation of ENP contamination of waterways to be effective, however, it must be demonstrated that metal-accumulating plants also possess the ability to take up metals in ENP form. Uptake, translocation, and accumulation of ENPs depend on both plant species and ENP type. Plant factors include transpiration rate, root architecture (fibrous versus taproot), rhizosphere chemistry (pH, EC), and many others. Relevant ENP properties include size, charge, chemical configuration, concentration, stability, and presence of coatings [23, 24].

Knowledge regarding the uptake of engineered nanoparticles by plants is limited, and less is known regarding the capabilities of aquatic species. It is important to determine whether aquatic plants exhibiting potential for metal phytoremediation can also be applied for the recovery of metallic ENPs. With the proper choice of plant host, ENPs may be taken up and sequestered as part of a phytoremediation program.

Bottle sedge (*Carex rostrata*) is a perennial grasslike plant that grows in tufts between 20 and 50 cm tall and has a fibrous root system. Sedge belongs to the Cyperaceae family. It occurs over a wide range of soil types and fertility levels but tends to be found in wetlands such as marshes, peatlands, and riparian zones [25]. Cattail (*Typha latifolia*), also known as bulrush, is a member of the family Typhaceae. Cattail is an obligate wetland species (emergent hydrophyte) and is generally found in flooded locations where it grows rapidly. Its wide leaves can reach to almost 2 meters in height. Roots (rhizomes) are thick with small fibrous roots. This species is widely distributed throughout the Northern Hemisphere [25]. These two aquatic species were chosen for study as they are widespread in aquatic ecosystems, exhibit robust growth, are highly competitive, and are readily adaptable to different environmental conditions.

1.1. Objectives. Given the swift development and wide application of nanostructures and the concurrent risk of ecosystem contamination [9, 26, 27], it is important to understand the interactions between ENPs and aquatic plants and evaluate the potential for uptake and phytoremediation. To date, the response of terrestrial plants to relatively common ENPs such as Ag, TiO_2, and ZnO has received considerable study. Little information is available, however, on effects to aquatic species. Furthermore, data on plant response to many innovative ENPs is virtually nonexistent. For example, both $BiVO_4$ and Cu_2O ENPs have gained popularity in commercial usage as photocatalysts [28], but their behavior in the biosphere is essentially unknown. The purpose of the current study was to evaluate the capability of cattail (*Typha latifolia*) and sedge (*Carex rostrata*) for the uptake of five nanoparticle types including Ag, TiO_2, ZnO, $BiVO_4$, and Cu_2O. The test plants have demonstrated the ability to tolerate heavy metal pollution; some varieties are also known to take up metals and translocate them to above-ground biomass.

A number of studies involving interaction of ENPs with plants have been conducted under unrealistic conditions, such as short-term incubations with exposure to high doses. Such experimental setups may not reflect real-world conditions. The current study involves the addition of ENPs to plant cultures over an extended period, i.e., 15 weeks, which may more accurately reflect conditions in a polluted aquatic environment.

2. Materials and Methods

2.1. Plant Collection and Experimental Setup. Cattail (*Typha latifolia*) plants were collected from a wetland in central Indiana (40.32801, −85.22075), and sedge (*Carex rostrata*) plants were purchased from Spence Restoration Nursery, Muncie, IN. Green specimens without senescent appearance and of similar size were collected. In the growth chamber, plants were rinsed with deionized (DI) water to remove soil adhering to roots. Plants were placed into individual plastic containers with 500 mL of water obtained from a local reservoir. Fifty mL nutrient solution (General hydroponics FloraGro™, containing nitrogen, phosphate, potash, and magnesium) was added once every two weeks and insecticide (Sevin™) was sprayed as needed. Plants were allowed to acclimate to the new conditions for two weeks. All plants were incubated in the growth chamber at $22 \pm 2^{\circ}$C with illumination of about 5,000 lux (16 h light/8 h dark photoperiod) and $80 \pm 5\%$ relative humidity for 15 weeks.

Four treatments were prepared, i.e., sedge grown with ENPs, sedge grown with an ionic form of metals, cattail grown with ENPs, and cattail grown with ionic form of metals. The nanoparticles used in this study were Ag, TiO_2, ZnO, Pd/$BiVO_4$, and Pd/Cu_2O. The Ag, TiO_2, and ZnO nanoparticles were purchased from US Research Nanomaterials (Houston, TX). The Pd/$BiVO_4$ and Pd/Cu_2O nanoparticles were synthesized.

2.2. Synthesis of Nanoparticles. $BiVO_4$/BiOBr was synthesized by a modified surfactant-assisted aqueous method according to [29]. Briefly, 117 mg NH_4VO_3 was dissolved in 10 mL DI H_2O at 90°C, stirred vigorously for 10 min, and then cooled to room temperature. The NH_4VO_3 solution was added dropwise into a two-neck flask containing 20 mL of 0.05 M CTAB (cetyl trimethyl ammonium bromide) solution under vigorous stirring (500 rpm) at 60°C. Next, 970 mg $Bi(NO_3)_3{\cdot}xH_2O$ was dissolved in 10 mL DI H_2O and stirred for 10 min at room temperature. The newly-formed suspension was added dropwise into the two-neck flask, the temperature was set to 80°C, and the mixture was stirred for 16 h. The m-$BiVO_4$/BiOBr yellow product was filtered and washed with DI water and ethanol several times and air-dried at 60°C. To deposit palladium (Pd) nanoparticles on the surface of the material, 219.3 mg of m-$BiVO_4$/BiOBr composite was dispersed in 300 mL of ethanol; then, 21.9 mg of $Pd(CH_3COO)_2$ was added and stirred overnight in the dark. The product was filtered, washed with ethanol several times, and dried at 60°C [29].

In order to prepare Cu_2O nanostructures, a total of 85 mL DI water, 5 mL $CuSO_4$ (0.68 M), and 1.5 g polyvinyl pyrrolidone (PVP) were added to a 250-mL round-bottom flask. The mixture was stirred for 20 min, then a mixture of 5 mL of 0.74 M sodium citrate and 5 mL of 1.2 M sodium carbonate was added dropwise. The color of the solution changed to a clear deep blue. After 15 min stirring, 10 mL of 1.4 M glucose solution was added dropwise. The round-bottom flask was placed in an oil bath at 80°C for 2 h and the solution was filtered and dried overnight at 60°C [28]. To prepare the Pd-decorated nanomaterial, 100 mg of Cu_2O composite was dispersed in 300 mL of 200-proof ethanol; then, 8 mg of $Pd(CH_3COO)_2$ was added and mechanically stirred overnight in the dark. The material was collected via vacuum filtration and dried at 60°C.

The two synthesized multicomponent nanomaterials will be denoted as "$BiVO_4$" and "Cu_2O" throughout this paper for Pd/$BiVO_4$/BiOBr and Pd/Cu_2O, respectively.

The size of ENPs was determined via transmission electron microscopy using a JEOL model JEM-1400 transmission electron microscope operating at 120 kV.

For the metal treatments, soluble salts were used, i.e., silver (Ag) as $AgNO_3$, bismuth (Bi) as $Bi_2(SO_4)_3$, vanadium (V) as $VOSO_4{\cdot}xH_2O$, zinc (Zn) as $ZnSO_4{\cdot}7H_2O$, copper (Cu) as $Cu(NO_3)_2{\cdot}3H_2O$ and titanium (Ti) as TiO_2. In the case of Ti, bulk TiO_2 was dissolved in DI water and then sonicated.

Each week, ENPs or metals were added to each container at a rate of 1.5 mg L^{-1}. Plants were grown in the ENP- or metal-enriched media for a total of 15 weeks.

2.3. Analysis of Reservoir Water. Reservoir water pH was measured using a standardized AB15 Accumet pH meter, and electrical conductivity with a YSI conductivity meter (Yellow Springs, OH).

The dissolved oxygen (DO) level was determined with a DO meter (HI 9147, Hanna Instruments, USA). Total organic carbon (TOC) and total nitrogen (N) were analyzed on a Perkin Elmer Series II CHNS/O Analyzer 2400 (Shelton, CT). Acetanilide was the standard used. Ammonium concentrations were determined according to the method described by Sims et al. [30] which uses a modified indophenol blue technique. The method was adapted for the BioTeK PowerWave system. Phosphorous was measured using Bray-1 extractant combined with a microplate method (PowerWave XS2 Microplate Spectrophotometer) [31]. For measurement of metal (Cu, Zn) concentrations, the reservoir water was filtered through Whatman no. 2 filter paper and analyzed via inductively coupled plasma-optical emission spectrophotometry (ICP-OES, Varian® 720-ES). To measure the anions fluoride, chloride, nitrate, phosphate, and sulfate, the water was first filtered through Whatman no. 2 filter paper and next through a 0.45 μm membrane filter. The filtrate was injected into a Thermo Scientific™ Dionex™ Integrion™ ion chromatograph (W. Palm Beach, FL) with Chromelion 7 software.

2.4. Metal Analysis of Plant Tissue. After 15 weeks of growth, entire plants were removed from containers. Plants were rinsed with DI water and then separated into shoots and roots using a clean X-acto knife. Plant shoot and root tissue were oven-dried at 95°C for 24 h. One hundred mg (0.1 g) of dried tissue was weighed into Teflon™ reaction vessels and placed in a MARS™ microwave digestion system (Ethos, Milestone; CEM Corporation). Ten mL of 70% HNO_3 was added to each vessel, and the samples were digested for 30 min. Cooled samples were filtered through Whatman no. 5 filter paper and diluted to the appropriate final volume for ICP analysis. Samples were analyzed for concentrations of all metals that were originally present in ENPs (i.e., Ag, Bi, Cu, Pd, Ti, V, and Zn) via ICP. A reagent blank (Merck®; trace metal grade) was used to check the quality of the samples and to validate analytical methods. All glassware in these experiments was washed with Alconox™ detergent and rinsed with DI water prior to use.

2.5. Plant Uptake and Translocation of Metals. The bioconcentration factor indicates the capability of the plant root to accumulate metal from contaminated water. This value was calculated using the following equation:

$$\mathrm{BCF} = C_{\mathrm{root}}/C_{\mathrm{water}}, \quad (1)$$

where C is the metal concentration in root or water.

The translocation factor (TF) measures the transfer of metal from root to shoot. This value is used to interpret the phytoextraction potential of a plant species:

$$\mathrm{TF} = C_{\mathrm{shoot}}/C_{\mathrm{root}}, \quad (2)$$

where C is the metal concentration in the shoot or root [19].

2.6. Identification of Metals/ENPs in Plant Tissue Using SEM. After harvesting plant samples at week 15, a total of 3–5 cm of the root was cut from ENP-treated plants. Plant tissue was prepared using critical point drying (CPD) and sputter-coated with gold, then viewed under a scanning electron microscope (SEM) using a FESEM Magellan 400 SEM (Thermo Fisher Scientific). Energy-dispersive X-ray analysis (EDX) was used for the elemental analysis of each sample.

2.7. Statistical Analysis. Statistical analysis of experimental data was carried out using analysis of variance (ANOVA) on a Windows-based PC. As needed, posthoc least significant difference tests were conducted on means found to be significantly different at $p < 0.05$. SPSS® ver. 23 was employed (SPSS Inc., Chicago, IL) for statistical analysis.

3. Results and Discussion

3.1. Nanoparticle Properties. The commercially purchased ENPs (Ag, TiO_2, and ZnO) ranged in size from 30 nm (TiO_2) to 100 nm (Ag) (Table 1). All tended to have a rounded shape (Figure 1). The synthesized Cu_2O and $BiVO_4$ ENPs measured approximately 700 and 1000 nm, respectively. $BiVO_4$ particles had an irregular shape, and Pd decorations were apparent on surfaces. The Cu_2O ENPs had a cubic shape and were decorated with Pd nanoparticles (~10 nm). Engineered nanoparticles are often defined as those that exhibit the characteristic dimension of 1–100 nm; however, it has been suggested that the size-dependent novel properties of nanoparticles, rather than particle size, must be considered when they are defined and/or studied for their behavior in the environment [32].

3.2. Properties of Water. Reservoir water was slightly alkaline (pH 7.6) (Table 2). Total N and P were 0.66 and 0.04 $mg{\cdot}L^{-1}$, respectively. Concentrations of metals and soluble anions were low.

3.3. Plant Uptake of Nanoparticles

3.3.1. Silver. Sedge treated with Ag ENPs had mean root and shoot Ag contents of 27.8 and 71.9 $\mu g{\cdot}g^{-1}$, respectively, ($p < 0.05$) (Table 3). It was not determined whether Ag in tissue occurred as ENPs or dissolved Ag^+; however, uptake as ENPs is likely. Studies using TEM [33] and single-particle inductively coupled plasma mass spectrometry [34] have revealed Ag ENP translocation from root to shoot. Dissolution of Ag ENPs in bulk suspension and at the root/water interface was ruled out by Dang et al. [34], which supports the direct uptake of particles.

Several terrestrial and aquatic species have been found to take up and translocate Ag ENPs to upper plant parts, for example, rice (*Oryza sativa* L.) (size range 70–120 nm, up to 1000 $mg{\cdot}L^{-1}$) [35]; wheat (*Triticum aestivum* L.) (10 nm, 2.5 $mg{\cdot}kg^{-1}$) [33]; and zucchini (*Cucurbita pepo*) (<100 nm, 1000 $mg{\cdot}l^{-1}$) [36]. BCF and TF values in sedge were low in the Ag ENP treatment (0.09 and 0.3, respectively) (Table 3).

Table 1: Size of ENPs used in this study.

NP	Size (nm)
Ag	80–100
TiO_2	30
ZnO	60
$BiVO_4$	1,000
Cu_2O	700

At the end of 15 weeks, the accumulated Ag concentration in roots of Ag^+-treated sedge was approximately twice that for Ag ENP-treated plants (51.8 versus 27.8 $\mu g{\cdot}g^{-1}$, respectively) ($p < 0.05$) (Table 3). This trend is consistent with that of several researchers [37, 38] who measured greater Ag content in tissue upon exposure to Ag^+ compared to ENP forms. Others, however, have measured markedly greater Ag accumulation in plants from exposure to Ag ENPs than from corresponding Ag ion dosages [39]. Uptake and translocation of Ag and other ENPs in plants is complex and variable, and not clearly understood; both processes are known to vary with particle size and charge, plant species, cultivar, growth stage of the plant, and growth conditions [40–43]. When cattail was treated with Ag ENPs, Ag content in roots and shoots was 6.5 and 0.9 $\mu g{\cdot}g^{-1}$, respectively, (Table 3), which are 4.3 and 79.9 times, respectively, lower than that of sedge. Greater root Ag content is consistent with previous studies which determined that ENPs delivered to plants were distributed mainly in roots [1, 34, 44–46]. Stegemeier et al. [47] determined that Ag ENPs accumulated in alfalfa (*Medicago sativa*) plants primarily in the *columella* border cells and elongation zone, whereas Ag^+ accumulated more uniformly throughout the root. Plants that tended to translocate fewer ENPs were those with low transpiration rates, drought–tolerance, tough cell wall architecture, and tall growth [41]. The current data is consistent with these findings, as cattail has a large rhizome with tough cell wall architecture, while sedge has fine fibrous roots.

It is not known if the applied Ag, whether in ionic or ENP form, was compartmentalized within roots or adsorbed to root surfaces. Stegemeier et al. [47] found that the majority (~99%) of silver taken up by alfalfa was sequestered on/in the roots, irrespective of form introduced, i.e., Ag ENPs, Ag_2S ENPs, or as $AgNO_3$. Analysis of plant tissue using SEM/EDX provides insights into possible ENP coating and/or internalization [48]. An SEM/EDX image (Figure 2) shows Ag evenly distributed across cattail root surfaces, thus suggesting that a substantial proportion of Ag had coated the outer root.

In cattail treated with ionic Ag, uptake was markedly greater in both below-ground ($p > 0.05$) and above-ground ($p < 0.05$) plant parts: Ag content in roots was 82.6 $\mu g{\cdot}g^{-1}$ while that in shoots was 17.7 $\mu g{\cdot}g^{-1}$ (Table 3). These values are 12.7 and 19.7 times, respectively, greater than Ag concentrations when plants were fed with Ag ENPs.

BCF and TF of Ag ENPs in cattail were 0.002 and 0.46, respectively, (Table 3). Bioconcentration factor (BCF) and

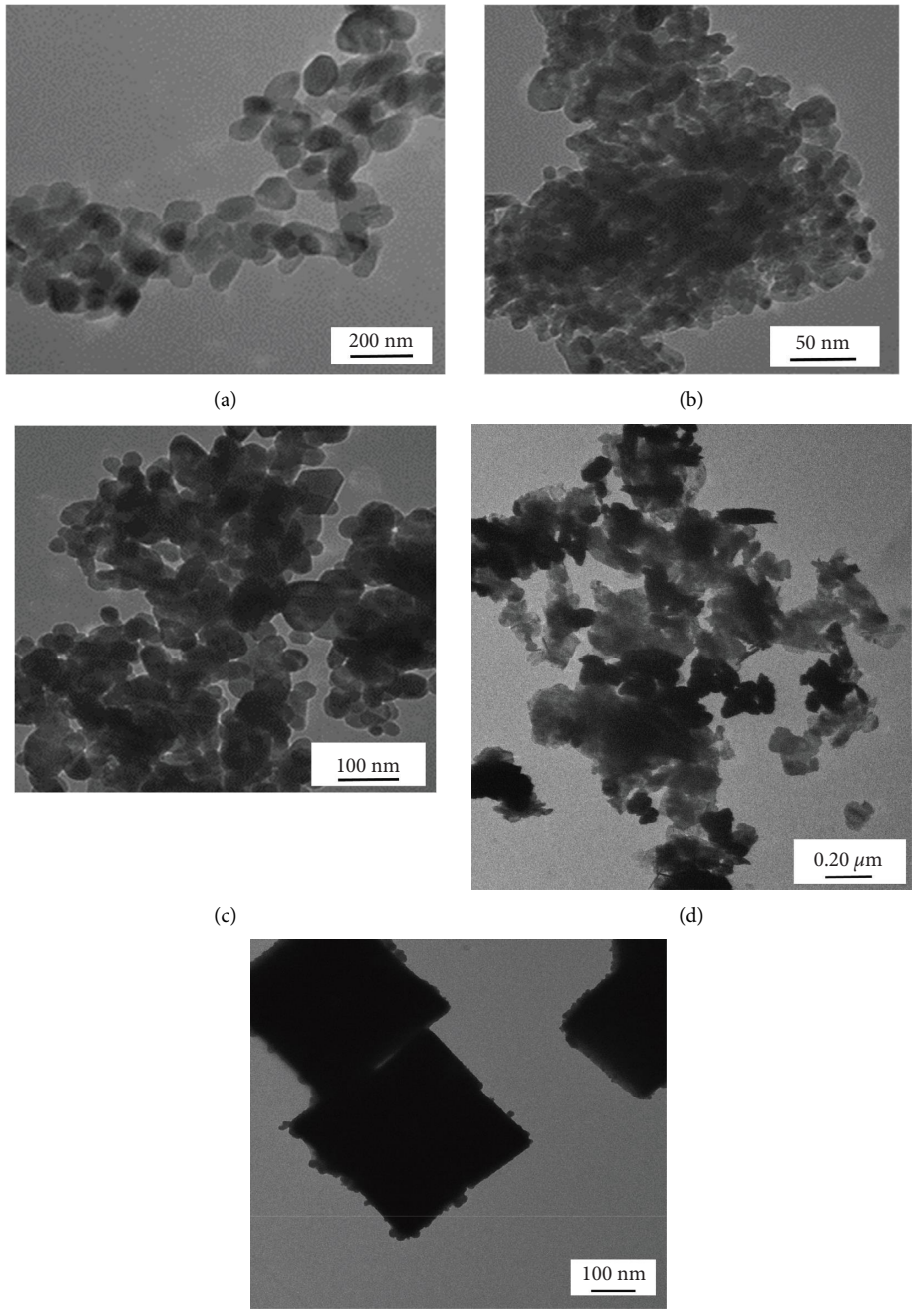


Figure 1: TEM images of ENPs used in this study: (a) Ag, (b) TiO_2, (c) ZnO, (d) $Pd/BiVO_4$, and (e) Pd/Cu_2O.

translocation factor (TF) reflect the heavy metal uptake and accumulation potential of a plant and can also indicate the potential for phytoremediation. When BCF is > 1 and TF < 1, plants can be defined as excluder species for that element. Based on the low BCF data in Table 3, both sedge and cattail are excluders for Ag; due to low TF values, they are not accumulator species. Numerous studies have demonstrated very low TF values of Ag ENPs by plants [39, 49–54].

3.3.2. Titanium. When sedge was treated with TiO_2 ENPs, Ti content in roots and shoots was 81.6 and 140.5 $\mu g \cdot g^{-1}$, respectively (Table 3); however, these differences are not significant ($p > 0.05$). In contrast to many other ENPs, nano-TiO_2 is very stable, persists in water and soil due to low solubility and can be taken up by roots in the nanoparticulate form [55]. The TiO_2 ENPs used in this study measured 30 nm (Table 1), which is sufficiently small for entry through pores in plant cell walls. Pore sizes of cell walls

Table 2: Selected chemical and physical properties of the reservoir water used in this study.

Parameter	Value
pH	7.63 ± 0.53
Specific conductivity (μs/cm)	324.4 ± 132.6
DO (mg·L^{-1})	5.69 ± 3.66
Turbidity (NTU)	21.73 ± 12.67
TOC* (mg·L^{-1})	3.48
Total N (mg·L^{-1})	0.66 ± 0.84
NH_4^+ (mg·L^{-1})	0.05 ± 0.07
Total P (mg·L^{-1})	0.04 ± 0.06
Metals (mg·L^{-1})	
Cu	0.09 ± 0.03
Zn	0.03 ± 0.02
Soluble anions (mg·L^{-1})	
F^-	1.77 ± 0.02
Cl^-	31.82 ± 2.76
NO_3^-	0.67 ± 0.06
PO_4^{3-}	0.57 ± 0.07
SO_4^{2-}	6.49 ± 1.04

*TOC = total organic carbon.

Table 3: Metal uptake from exogenously applied ENPs and ionic metal by sedge and cattail.

Element	Plant species		Treatment	Total in roots (μg·g^{-1})	Total in shoots (μg·g^{-1})	$LSD_{0.05}$	BCF	TF
Silver	Sedge		ENP	27.8 ± 10.7	71.9 ± 2.1	23.0	0.09	0.30
			Ionic	51.8 ± 11.5	21.0 ± 3.7	21.2	0.18	0.03
		$LSD_{0.05}$		25.2	6.9		—	—
	Cattail		ENP	6.5 ± 7.7	0.9 ± 0.8	18.1	0.002	0.46
			Ionic	82.6 ± 91.3	17.7 ± 5.7	237.2	0.02	0.82
		$LSD_{0.05}$		146.9	9.2		—	—
Titanium	Sedge		ENP	81.6 ± 68.5	140.5 ± 21.4	196.7	0.5	0.07
			Ionic	686.9 ± 97.8	304.7 ± 36.0	321.7	0.74	0.11
		$LSD_{0.05}$		191.4	67.1		—	—
	Cattail		ENP	35.9 ± 24.6	21.0 ± 17.0	32.3	0.02	9.06
			Ionic	398.1 ± 221.2	63.5 ± 37.4	502.2	0.18	2.65
		$LSD_{0.05}$		356.7	65.8		—	—
Zinc	Sedge		ENP	513.0 ± 191.8	1096.7 ± 168.9	471.0	0.4	0.49
			Ionic	64.9 ± 20.4	196.9 ± 194.2	43.8	0.14	0.30
		$LSD_{0.05}$		309.1	272.4		—	—
	Cattail		ENP	1193.3 ± 223.7	98.5 ± 56.7	627.5	0.51	0.55
			Ionic	777.9 ± 153.5	53.2 ± 18.5	427.3	0.33	0.04
		$LSD_{0.05}$		434.7	95.5		—	—
Bismuth	Sedge		ENP	84.1 ± 18.5	79.8 ± 30.3	63.8	0.07	0.829
			Ionic	174.1 ± 32.4	22.4 ± 0.00	80.4	0.68	0.015
		$LSD_{0.05}$		59.8	48.6		—	—
	Cattail		ENP	293.5 ± 16.2	4.7 ± 3.5	34.8	0.11	0.150
			Ionic	254.3 ± 109.3	22.9 ± 0.8	273.0	0.12	0.984
		$LSD_{0.05}$		177.1	5.8		—	—
Vanadium	Sedge		ENP	BDL	BDL*	—	0.09	<0.01
			Ionic	147.0 ± 15.6	49.0 ± 69.1	136.1	0.83	0.089
		$LSD_{0.05}$		25.0	110.8		—	—
	Cattail		ENP	27.5 ± 0.8	BDL	2.0	0.006	<0.01
			Ionic	176.9 ± 84.9	68.6 ± 84.0	367.3	0.33	1.821
		$LSD_{0.05}$		143.2	134.6		—	—
Copper	Sedge		ENP	509.4 ± 80.5	482.1 ± 224.6	452.8	0.25	2.359
			Ionic	709.8 ± 457.8	452.2 ± 361.5	1,300.6	0.88	0.255
		$LSD_{0.05}$		745.0	682.1		—	—
	Cattail		ENP	917.5 ± 340.1	68.6 ± 2.4	840.8	0.65	0.374
			Ionic	403.7 ± 65.6	15.4 ± 0.00	163.0	0.39	0.426
		$LSD_{0.05}$		555.2	3.9		—	—

*BDL = below detectable limits.

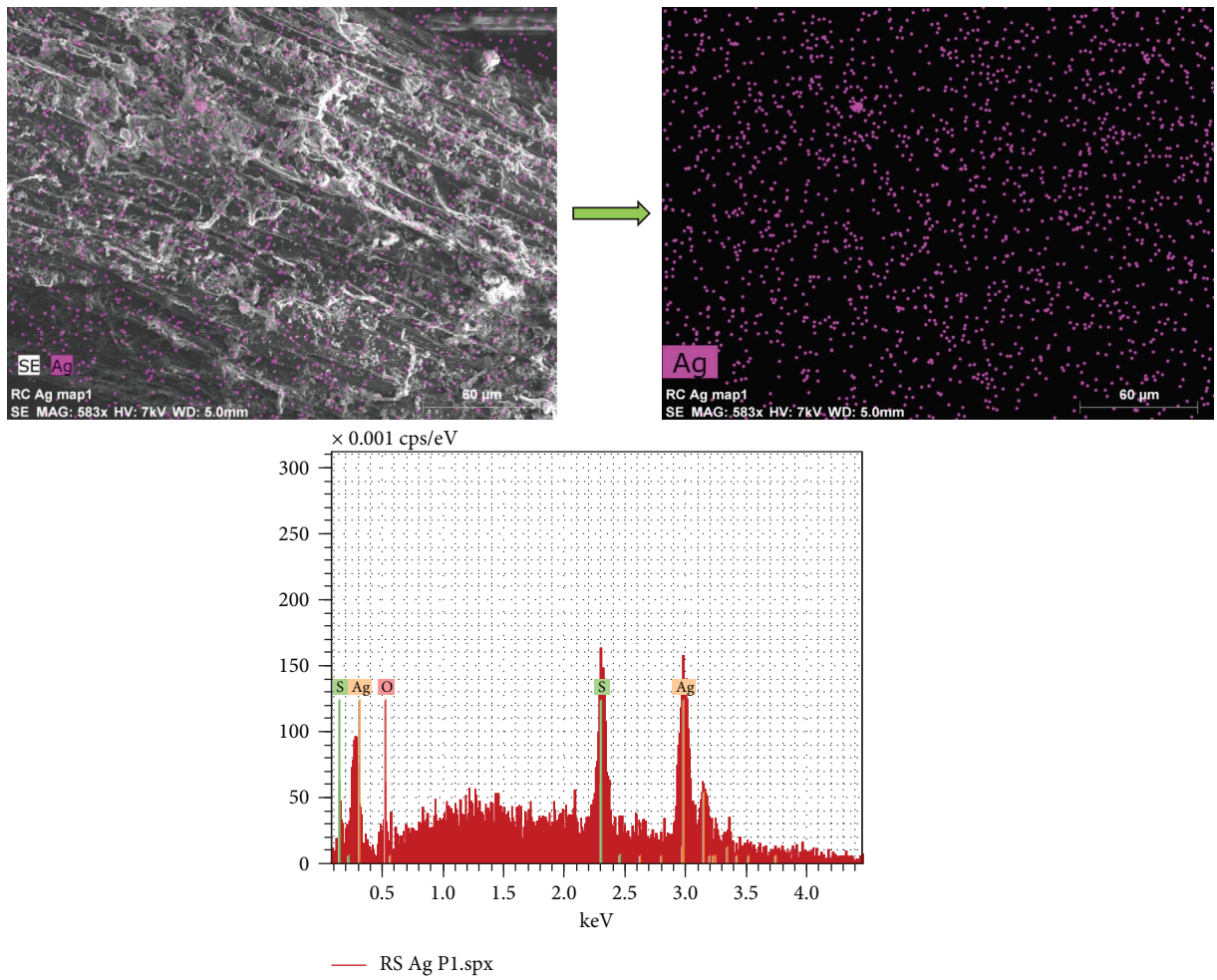


Figure 2: SEM/EDX image of cattail root showing distribution of Ag.

may measure as large as 50 nm [56]. Other mechanisms (e.g., endocytosis, entry through wounds in roots) may be involved in Ti uptake and translocation as well.

BCF and TF values for TiO_2 ENPs in sedge were 0.5 and 0.07, respectively.

Various researchers have reported that small TiO_2 ENPs (<25 nm) could be translocated from roots to leaves [57]. Nano-TiO_2 has been determined in edible plant tissue [57]. Servin et al. [58] detected translocation of TiO_2 ENPs in cucumber (*Cucumis sativus*). It was reported that Ti was transported from the root to trichomes of leaves, which apparently act as a sink for Ti. Following exposure of wheat (*Avena sativa*) roots to TiO_2 ENPs, Ti was detected in shoots using SEM/EDX [59]. *Oenanthe javanica* and *Isoetes japonica* were exposed to 1.8 mg·L^{-1} TiO_2 ENPs [60]. After 17 days, the total accumulated Ti in *O. javanica* (root + stem) was 489.1 μg·kg^{-1}; for *I. japonica*, whole-body Ti was 54.5 μg·kg^{-1}. When tomato plants were treated with TiO_2 ENPs [61], the concentration of Ti in plant tissue followed the sequence stem > roots > leaves > fruits.

It is suggested that natural organic matter (NOM) in the reservoir water caused TiO_2 to mobilize to some degree, allowing greater translocation to above-ground parts. NOM can affect the transport of nano-TiO_2 by altering the surface properties of particles [62]. Possible interactions include adsorption to uncoated ENPs, displacement of the original coating of nano-TiO_2, and bridging of ENPs [63]. The NOM concentration in the reservoir water was 3.48 mg·L^{-1} (Table 2).

When sedge was treated with dissolved TiO_2, the Ti root content was more than double that in shoots (686.9 versus 304.7 μg·g^{-1}, respectively) ($p < 0.05$).

In cattail treated with TiO_2 ENPs, Ti content in roots and shoots were 35.9 and 21.0 μg·g^{-1}, respectively. A similar trend was noted in cattail grown with dissolved TiO_2: the Ti content in roots was 398.1 μg·g^{-1} as compared with 63.5 μg·g^{-1} in shoots. The TF for TiO_2 was highest in the cattail treatment, attaining a value of 9.1 (Table 3). This value, combined with its high biomass production, reflects the potential of cattail for phytoextraction of TiO_2 ENPs. Several studies have determined higher concentrations of Ti in roots compared to shoots after treatment with TiO_2 ENPs [60, 64]. Larue et al. [65] found that TiO_2 ENPs in ultrapure H_2O were taken up by roots and localized in the parenchymal region and vascular cylinder. Protein peroxidation by TiO_2 ENPs is possible, which may result in

increased cell membrane permeability, thus allowing greater entry of ENPs into cells. In other cases, Ti ENPs may agglomerate and/or sorb to root tissue, thereby restricting uptake. TiO_2 ENPs have the tendency to aggregate and coalesce into large particles [66]. Li et al. [64] found sorption to cell surface exudates of *Lemna minor* to be the main mechanism for TiO_2 ENP removal from solution. The formation of large TiO_2 ENP agglomerates was also suggested as a mechanism for limited TiO_2 ENP internalization [64]; after several days, the diameter of nano-TiO_2 particles ranged from 266 nm to 1614 nm. No TiO_2 ENPs were detected inside the plant using TEM and field emission SEM analysis. In the current study, TiO_2 agglomerations were detected via SEM/EDX in both sedge and cattail roots (Figure 3).

3.3.3. Zinc Oxide. When sedge plants were grown with exogenously-added ZnO ENPs, Zn content in shoots was approximately twice that in roots (1096.7 $\mu g \cdot g^{-1}$ versus 513.0 $\mu g \cdot g^{-1}$, respectively) ($p < 0.05$) (Table 3). These data are similar to that of Hu et al. [67], where leaf Zn content of *Salvinia natans* treated with ZnO ENPs measured up to 3650 $\mu g \cdot g^{-1}$ Zn as compared to a maximum of 2970 $\mu g \cdot g^{-1}$ Zn for roots. Likewise, [68] measured 2.8 times greater Zn content in leaves of ZnO ENP-treated soybeans versus in roots (344 and 123 $mg \cdot kg^{-1}$, respectively).

At the external final concentration of 22.5 $mg \cdot L^{-1}$, the accumulated Zn concentration in roots of ZnO ENP-treated sedge was 7.9 times higher than in the roots of Zn^{2+}-treated plants (Table 3). This trend is consistent with others who reported substantially greater root Zn concentrations under ZnO ENP treatment compared to Zn^{2+} treatment, including softstem bulrush (*Schoenoplectus tabernaemontani*) [69]; alfalfa [70]; and cucumber [71]. The BCF for the ZnO ENP treatment was higher than that for the Zn^{2+} treatment (0.40 and 0.14, respectively), suggesting that sedge had greater potential to take up Zn from ZnO ENPs than from the Zn^{2+} treatment. Some researchers propose that the high mobility of ZnO ENPs in certain plants is due to the solubilization of the Zn^{2+} ion within the plant; this process is considered by Thwala et al. [48] as being dominant for Zn translocation. Nano-ZnO is rather soluble and dissolves readily [72]. Not all studies agree, however, regarding the relatively greater uptake of ZnO ENPs compared to ionic zinc. Lin and Xing [73] reported very low Zn uptake in ZnO ENP-treated ryegrass (*Lolium perenne*) compared to Zn^{2+} treatment.

In cattail treated with ZnO ENPs, Zn content was 12-fold higher in roots compared to shoots, i.e., 1193.3 $\mu g \cdot g^{-1}$ versus 98.5 $\mu g \cdot g^{-1}$, respectively ($p > 0.05$) (Table 3). This relationship is opposite that observed for sedge. Uptake, translocation, and accumulation of ZnO ENPs by plants depend, in part, upon the structure and physiology of the host plant [74]. Cattail is an emergent hydrophyte having thick rhizomes with small fibrous roots; in contrast, sedge has a fine fibrous root system. Root surface area and number of lateral roots strongly influence response and sensitivity of plants to nanoparticles [42, 75, 76].

The accumulated Zn concentration in roots of ZnO ENP-treated cattail was 1.5 times higher than that for Zn^{2+}-treated plants. This trend agrees with that for sedge. Lin and Xing [73] also determined minimal translocation of ZnO ENPs in ryegrass (*Lolium perenne*). In a study by [77] bioaccumulation varied among soybean tissue in the order: root > seed > leaf > stem. When maize was treated with ZnO ENPs, the majority of Zn taken up was derived from Zn^{2+} released from the ENPs [78]. No ZnO nanoparticles were observed to translocate to shoots, possibly due to the dissolution of ZnO ENPs within the plant.

In the current study, it is possible that some ZnO ENPs had precipitated and/or sorbed to cattail roots. Kopittke et al. [79] have suggested the possibility of Zn precipitation on roots of cowpea (*Vigna unguiculata*). Hu et al. [67], working with *Salvinia natans*, found that the removal of ZnO ENPs from suspension occurred via both root uptake and precipitation to roots. To date, the different plant physiological mechanisms of mobility (and potential toxicity) of Zn^{2+} and nano-ZnO in plants have not been fully documented. SEM/EDX images of cattail root reveal the presence of ZnO ENPs, primarily as agglomerations (Figure 4). This further supports the suggestion of ZnO immobilization on root surfaces.

BCF and TF in cattail were 0.51 and 0.54, respectively. Hernandez-Viezcas et al. [80] also measured low BCF values in soybean (*Glycine max.*) plants treated with ZnO ENPs. Translocation factors of Zn from root to shoot of ryegrass were very low under ZnO nanoparticle treatment and much lower than that under Zn^{2+} treatment, implying minimal translocation of ZnO ENPs [73].

When treated with ionic Zn, cattail root content was nearly 15-fold higher than in shoots (777.9 versus 53.2 $\mu g \cdot g^{-1}$, respectively). Accumulation of ionic Zn in cattail root was 12-fold greater compared with uptake by sedge. Cattail is well known for the sequestration of heavy metals in root tissue [81].

3.4. Bismuth. In sedge exposed to $BiVO_4$ ENPs, Bi content was 84.1 $\mu g \cdot g^{-1}$ and 79.8 $\mu g \cdot g^{-1}$ in roots and shoots, respectively, (Table 3). BCF and TF were 0.07 and 0.83, respectively.

$BiVO_4$ is slightly soluble in water [82]. The presence of plants tends to promote the dissolution of metallic ENPs, including many relatively stable types. A primary process leading to enhanced dissolution by roots is the release of low-molecular-weight organic acids in root exudates, which lower the pH in the root region and function as electron donors to facilitate the reduction of metals on the nanoparticle surface [43, 83]. Following solubilization, Bi and/or V may be taken up in ionic form. In certain conditions in aqueous solution, the Bi^{3+} ion is solvated to form the bismuth ion complex $Bi(H_2O)_8{}^{3+}$ [84].

At the external final concentration of 22.5 $mg \cdot L^{-1}$, the accumulated Bi concentration in roots of Bi^{3+}-treated sedge was approximately twice that for $BiVO_4$ ENP-treated plants (174.1 versus 84.1 $\mu g \cdot g^{-1}$, respectively ($p < 0.05$) (Table 3).

In cattail exposed to $BiVO_4$ ENPs, Bi content was 293.5 $\mu g \cdot g^{-1}$ and 4.7 $\mu g \cdot g^{-1}$ in roots and shoots, respectively, and BCF and TF were 0.11 and 0.15, respectively. When

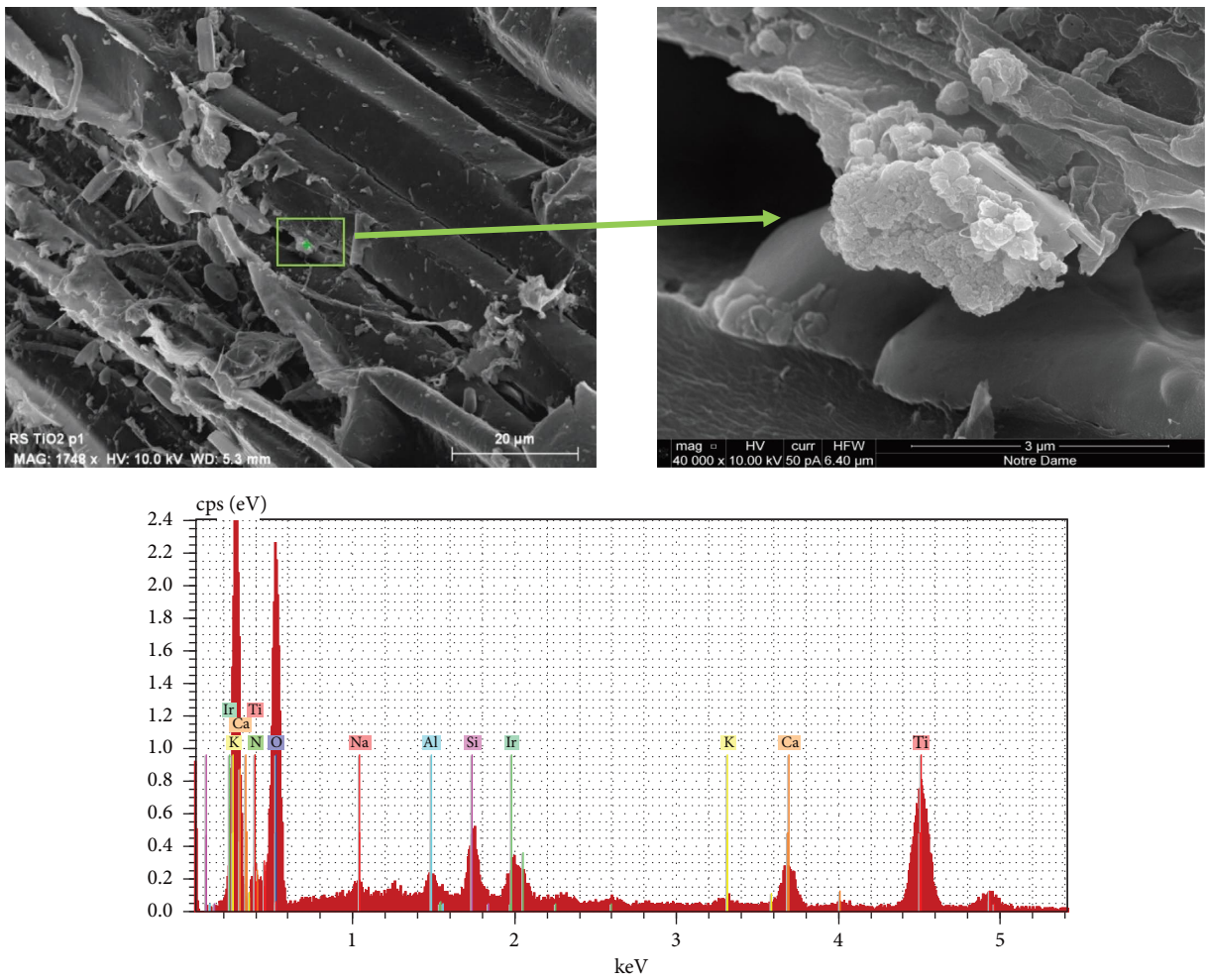


Figure 3: SEM/EDX image of cattail root showing the presence of TiO_2 ENPs.

treated with ionic Bi, the Bi content was 254.3 $\mu g \cdot g^{-1}$ and 22.9 $\mu g \cdot g^{-1}$ in roots and shoots, respectively. TF measured 0.98. These numbers are unusually high, given the relative insolubility of Bi in water [85]. The Bi content of plants has not been studied extensively. Shacklette et al. [86] reported that Bi was found only in about 15% of samples of Rocky Mountain trees and that the Bi range was from 1 to 15 $\mu g \cdot g^{-1}$ [87]. Berg and Steinnes [88] found Bi in Norwegian mosses to range up to 0.9 $\mu g \cdot g^{-1}$ (average 0.03 $\mu g \cdot g^{-1}$) [87]. In a study by Fahey et al. [85], Bi levels in 20 of 24 aboveground tissue samples from the *Carex lacustris–Agrostis scabra* community were below detection levels (0.057 $\mu g \cdot g^{-1}$ DM). The mechanisms of bismuth transport in plants is still unknown [86].

SEM/EDX images of cattail root reveal the presence of $BiVO_4$ ENPs (Figure 5), which tended to appear as large agglomerations.

3.4.1. Vanadium. In sedge plants exposed to $BiVO_4$ ENPs, the V content in shoots and roots was below detectable limits (Table 3). In contrast, when grown with soluble V, uptake was substantial (147 $\mu g \cdot g^{-1}$ and 49 $\mu g \cdot g^{-1}$ in roots and shoots, respectively). BCF was 0.83 and TF was 0.09.

In cattail grown with $BiVO_4$ ENPs, V content in roots was 27.5 $\mu g \cdot g^{-1}$, while that in shoots was below detectable limits. Both TF and BCF were very low (<0.01). Vanadium uptake in ionic form for cattail was approximately 2.5-fold higher in roots than in shoots (177 $\mu g \cdot g^{-1}$ vs. 69 $\mu g \cdot g^{-1}$, respectively). Researchers have reported pronounced differences in V content among plants [87]. Soluble soil V appears to be readily taken up by roots, and some species show a great ability to accumulate this metal. The range of V in the ash of most vegetables is given by Shacklette et al. [86] to be from <5 to 50 $\mu g \cdot g^{-1}$. Petrunina [91] stated that some bryophytes may contain as much as 180 $\mu g \cdot g^{-1}$ DW when grown in mineral media. Other accumulator plant species are also known [92]. Welch [93] studied the uptake of V by barley (*Hordeum vulgare*) from a radiolabeled V solution and concluded that V is passively absorbed by roots. Vanadium occurs primarily as VO_3^- and HVO_4^{2-} species in neutral and alkaline solutions. The pH of the reservoir water was 7.6 (Table 2). Both anionic species could contribute to V uptake by plants from water [87].

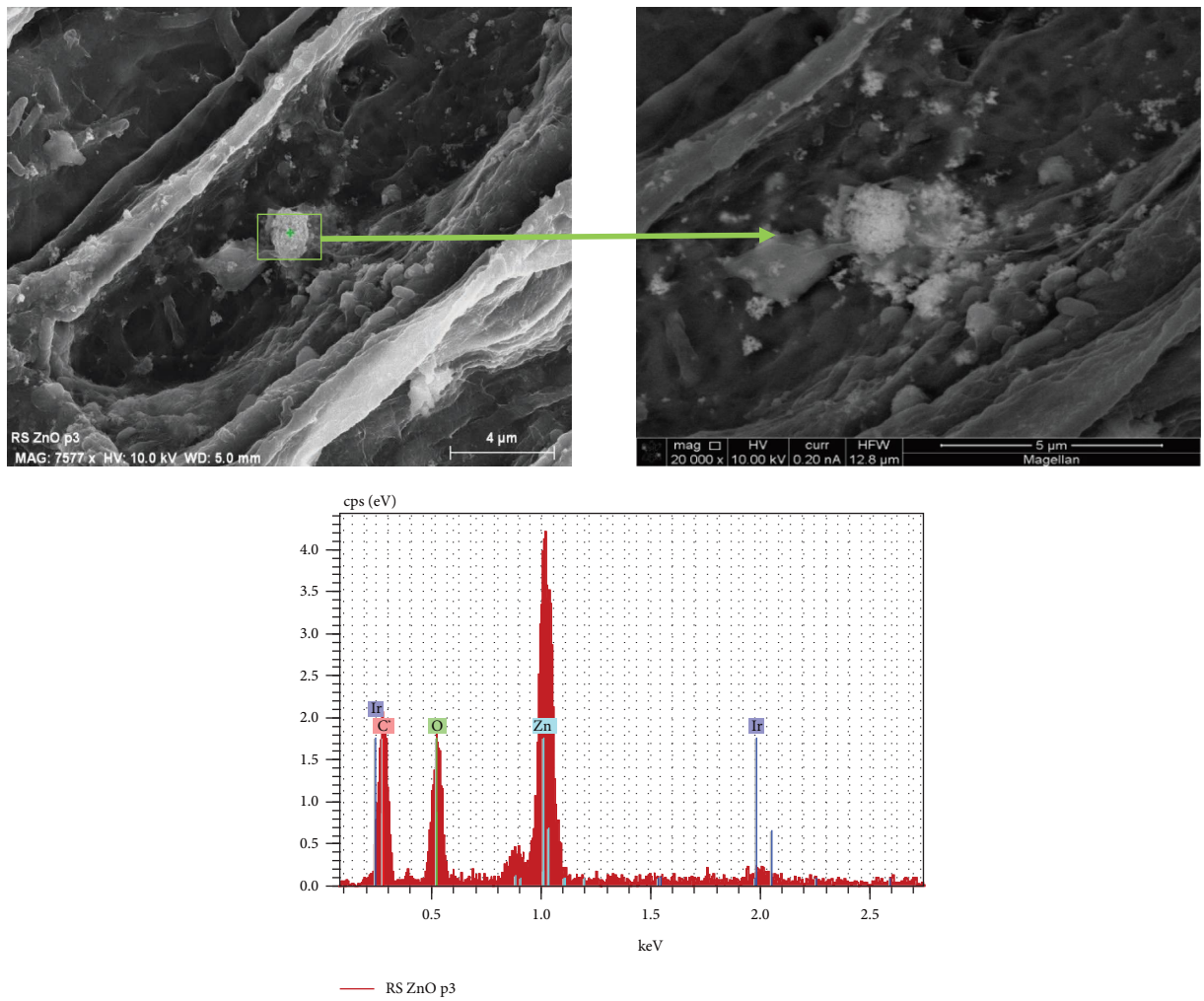


Figure 4: SEM/EDX image of cattail root showing the presence of ZnO ENPs.

3.4.2. Copper. In both sedge and cattail plants treated with Cu_2O ENPs, Cu content was greater in roots than in shoots (Table 3). Differences were significant ($p < 0.05$) in cattail.

In sedge exposed to Cu_2O ENPs, Cu content was 509.4 and 482 $\mu g \cdot g^{-1}$ in roots and shoots, respectively. Copper levels in tissue range between 5 and 20 $\mu g \cdot g^{-1}$ dry matter in most plant species [94, 87]; however, Cu concentration varies as a function of species, stage of growth, and environmental factors. BCF and TF in this treatment were 0.25 and 2.36, respectively. TF values > 1 indicate the potential of a plant species for phytoextraction of an element; however, BCF values should be > 1 for maximum efficiency of extraction.

The uptake of ionic Cu^+ by sedge was similar to the uptake of Cu_2O ENPs (Table 3); this suggests that Cu_2O nanoparticles were dissolved to Cu^+ prior to uptake by plants. When wheat was grown in sand [33], the total Cu level in shoots was similar under both nano- and ionic Cu exposures. Mechanisms of Cu absorption and uptake by roots have been characterized [95, 96]. Perreault et al. [27] hypothesized that Cu accumulation from CuO ENP exposure was mainly via the dissolved form. In soil and water, Cu is extensively bound with organic and mineral matter [87], and dissolved organic matter has been found to result in substantial release of Cu^{2+} from CuO ENPs [97]. It is further plausible that attached organic matter promotes the transport of Cu to upper portions of the sedge plant. The TOC content of reservoir water was 3.48 $mg \cdot L^{-1}$ (Table 2).

In cattail treated with Cu_2O ENPs, Cu uptake was 172% higher in roots compared with shoots–a total of 917 $\mu g \cdot g^{-1}$ was detected as compared with 69 $\mu g \cdot g^{-1}$ in shoots (Table 3). A similar trend in Cu accumulation was noted for cattail grown in the Sudbury, Ontario region [98], which is heavily contaminated from former nickel-copper smelting operations. The Cu uptake trend for cattail, however, is quite different from that in sedge, where Cu was fairly evenly distributed between roots and shoots. Research on plant uptake and accumulation of Cu nanoparticles has generated sometimes conflicting data [99–102]. For example, total Cu uptake observed in radish (*Raphanus sativus*) (400 $mg \cdot kg^{-1}$ shoots) was approximately 17 times greater than in ryegrass (23.2 $mg \cdot kg^{-1}$

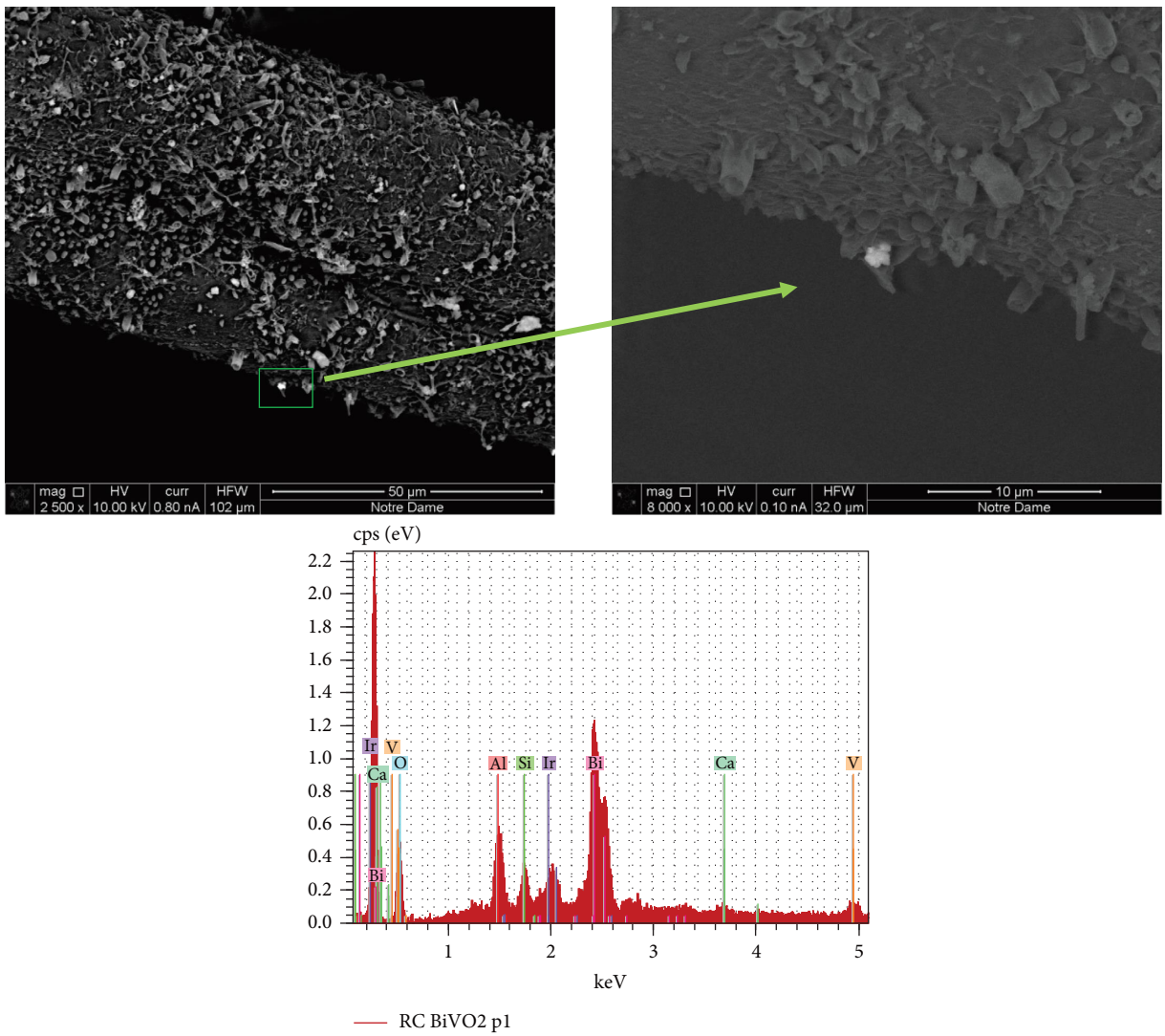


Figure 5: SEM/EDX image of cattail root showing the presence of $BiVO_4$ ENPs.

shoots), possibly due to a Cu-uptake mechanism present in the former species, for example a Cu-stimulated protein transporter [103–105]. SEM/EDX images of cattail root reveal the presence of numerous dispersed Cu particulates (Figure 6).

3.4.3. Palladium. Palladium was not detected in plant tissue in any treatment (data not shown). This finding contradicts the fact that Pd is rather soluble and more chemically reactive than other Pt metals [87, 106, 107].

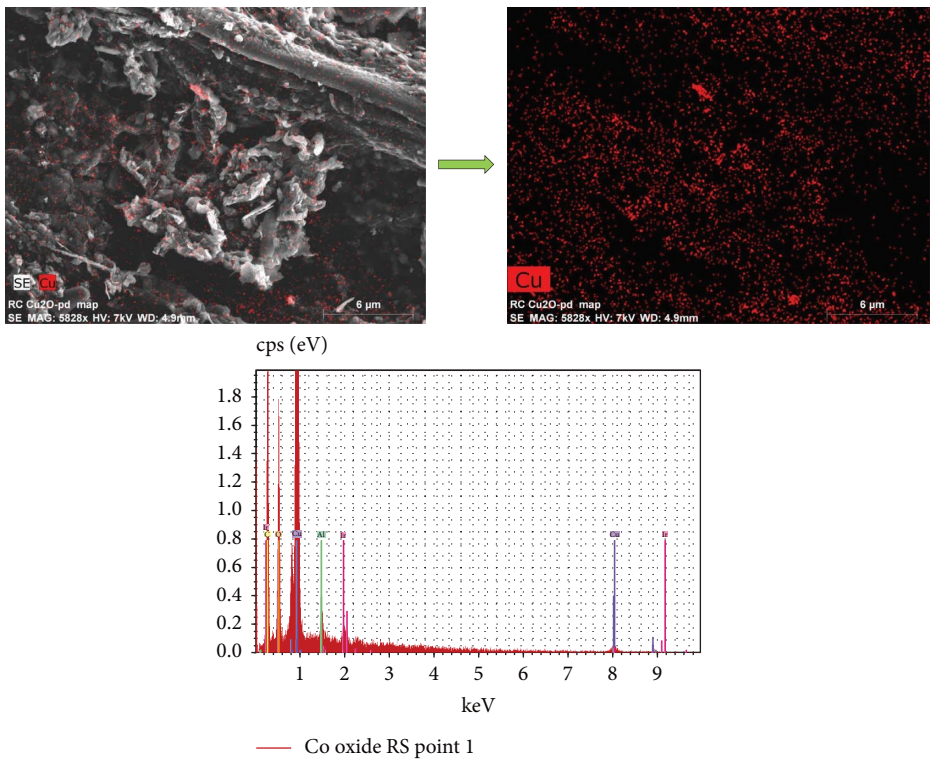


Figure 6: SEM/EDX image of cattail root showing the presence of Cu_2O ENPs.

4. Conclusions

Nanoparticles have diverse and growing uses in many fields; unfortunately, however, these innovative particles have also been recognized as emerging contaminants of water and soil. This study showed that sedge and cattail tolerate modest to high concentrations of metallic ENPs, including light-activated ENPs (TiO_2, $BiVO_4$, and Cu_2O). The potential for phytoextraction is moderate among both species.

Sedge accumulated greater quantities of Ag, TiO_2, and ZnO ENPs in shoots compared with roots. In contrast, cattail roots accumulated proportionally greater concentrations of all ENPs (in particular ZnO, $BiVO_4$, and Cu_2O) and ionic forms of metals compared to shoots. Such differences may be due, in part, to differing root architectures between the two species. Plants that tend to translocate fewer ENPs are those with drought-tolerance, tough cell wall architecture, and tall growth [41]. For several ENPs (ZnO and Cu_2O, sedge; TiO_2, cattail) the TF in certain treatments was >1.0, indicating the potential for phytoextraction.

This study applied ENPs over a prolonged period (15 weeks) rather than as a single dose. Such long-term application more accurately reflects real-world conditions (i.e., gradual inputs of pollutants to an ecosystem) than a single dose. It is possible that such prolonged application may have allowed plants to acclimate to the continued exposure to ENPs.

As regards copper oxide nanoparticle reactions with plants, the preponderance of literature relates to CuO (cupric form), rather than Cu_2O (cuprous). This paper is among the first to address the uptake and translocation of Cu_2O nanoparticles by aquatic plants. Both $BiVO_4$ and Cu_2O ENPs have become popular in commercial usage, and this report is the first to present data on plant uptake of these complex light-activated nanoparticles.

Uptake and accumulation of ENPs by aquatic plants has been confirmed, but there is a need to explore further the behavior, fate, and toxicity of these ENPs. The mechanisms involved in nanoparticle interaction with plants are relatively unknown and require further study.

Data Availability

The data used to support the study are available upon request from Parisa Ebrahimbabaie.

Ethical Approval

Not applicable.

Consent

Not applicable.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Authors' Contributions

PE contributed to conceptualization; writing original draft; preparation of figures and tables; editing of the manuscript. AS performed data collection. JP contributed to

conceptualization; writing the original draft; preparation of figures and tables; editing of the manuscript. EZ contributed to directing the synthesis and characterization of nanoparticles; editing of the manuscript.

Acknowledgments

This paper was derived from a Ph.D. dissertation by Parisa Ebrahimbabaie entitled, Phytoremediation of Engineered Nanoparticles Using Aquatic Plants and Decomposition of Trichloroethylene (TCE), by Cu_2O/Pd Light-Activated Nanostructures (Ball State University, Muncie, IN; https://cardinalscholar.bsu.edu/handle/123456789/203310). Funding from Sigma Xi Scientific Society and Indiana Academy of Science is gratefully acknowledged. The authors thank Dr. Klaus Neumann, Ball State University, for technical support with the inductively coupled plasma instrument.

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