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Phytoremoval of Arsenic from Soil

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ABSTRACT

Arsenic is a semimetallic element that has been notorious for its toxicity and carcinogenicity. Arsenic exists in soils mainly as As (V) and As (III). Arsenate compounds predominate in aerobic soils and arsenite in slightly reduced soil. The objectives of this study were to investigate the effects of pH and the ability of the *Pteris vittata* on the absorption of arsenic anion. The removal of arsenic by *Pteris vittata* L. was observed at varying anion concentration and solubility As in an absorption plant. Preliminary results obtained with young plants on arsenic contaminated soil indicate that the arsenic was concentrated in the fronds and *Pteris vittata* L. absorption occur in alkaline environment.

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INTRODUCTION

Arsenic is a semimetallic element and it also may be present as organometallic forms, such as methylarsinic acid and dimethylarsinic acid, which are active ingredients in many pesticides.[1] Arsenic is a toxic element that can be found in anthropogenic wastes and some geochemical environments. Arsenic can be added to soils through the use of synthetic fertilizers and pesticides.[2] The continued application of these products can result in an accumulation of toxic residues that, even in relatively low concentrations, could compromise or limit the use of the water. The complexation of arsenic by dissolved organic matter in natural environments prevents sorption and co-precipitation with solid-phase organics and inorganics, thus increasing the mobility of arsenic in aquatic systems and in the soil.[1]

Inorganic forms of arsenic can be present as either arsenate [As(V)] or arsenite [As(III)]. Arsenate is tetrahedral oxyanions that can compete for adsorption sites on soil mineral surfaces. Arsenate is the predominant inorganic species of As under oxidizing soil conditions and is retained in soils by adsorption reactions. Although arsenite is more toxic, human metabolism of arsenate involves reduction to arsenite before undergoing detoxification by methylation.[3] Arsenic is present in soil at levels ranging from 0.2 to $40\,\mu g\,g^{-1}$ and urban air at levels around $0.02\,\mu g\,m^{-3}$, but for the general population the main exposure to inorganic arsenic is through ingestion. Long-term exposure to low concentrations of arsenic in drinking water can lead to skin, bladder, lung, and prostate cancer. Non-cancer effects of ingesting arsenic at low levels include cardiovascular disease, diabetes, and anemia, as well as reproductive and developmental, immunological, and neurological effects.[4] Substantial evidence led the International Agency for Research on Cancer[5] to conclude that ingestion of inorganic arsenic can cause skin cancer.

Arsenic is distributed widely among plant species. In plant tissues its normal concentration is 0.01 to $5\,mg\,kg^{-1}$ on a dry-weight basis.[6] The soil-plant system is an open system subject to inputs, such as contaminants, agrochemicals, and to losses, such as the removal of trace elements in harvested plant material, leaching, erosion, and volatilization. The factors affecting the amounts of trace elements absorbed by a plant are those controlling (a) the concentration and speciation of the element in the soil solution; (b) the movement of the element from the bulk soil to the root surface; (c) the transport of element from the root surface into the root and; (d) its translocation from the root to the shoot. Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of this ion in the soil, but in the case of strongly adsorbed ions, absorption is more dependent upon the amount of root produced.[7]

Certain species of plants have been found to accumulate very high concentrations of certain trace elements and these are referred to as "hyperaccumulator" species. Plants can also intercept significant amounts of some elements through foliar absorption. Foliar absorption of solutes depends on the plant species, its nutritional status, the thickness of its cuticle, the age of the leaf, the presence of stomata guard cells, the humidity at the leaf surface, and the nature of the solutes.

In 2001, Ma et al.[8] first described brake fern effects, reported that the *Pteris vittata* is extremely efficient in extracting arsenic from soils.

Pteris vittata is characterized by having 1-pinnate-imparipinnate fronds, pinnae linear, not articulate to the rachis and with truncate base, free venation with simple or furcate veins and trilete spores. The pinnae display wide variation in size, angle of divergence from the rhachis (acute or right angle), and shapes (straight to shortly falcate). Plants terrestrial or rupestral. Generally found in sunny, open places, such as banks along highways and on city walls (like weeds), above sea level to approximately 2000 m. The typical plant's habit and characteristics morphological of *Pteris vittata* respectively can be observed in Figs. 1 and 2; Linnaeus classified ferns into genera based on the shape of the spores. It is native to the Old World (China) and was introduced in California, Mexico, Cuba, Bahamas, Dominica, Martinique, Barbados, Trinidad, Guiana, Peru, Brazil, and Argentina. It can be found in Brazil from the northern to the southern region.[9] This study investigates the concentration of arsenic in a brake fern, shows that the removal of arsenic in soil is a combination of the effects of *Pteris vittata* Linnaeus and arsenic solubility. The interaction of soil-plant system is fundamental for controlling the migration of arsenic to groundwater and its impact on drinking water.

MATERIALS AND METHODS

The method is based on use of brake fern as a soil-cleaning agent. The soil sample used was a Latossol with clay texture, having acid pH (5.7) and a high cation exchange capacity (CEC) with 2.3% organic matter and mineralogy (quartz, kaolinite, and goethite). In this study,

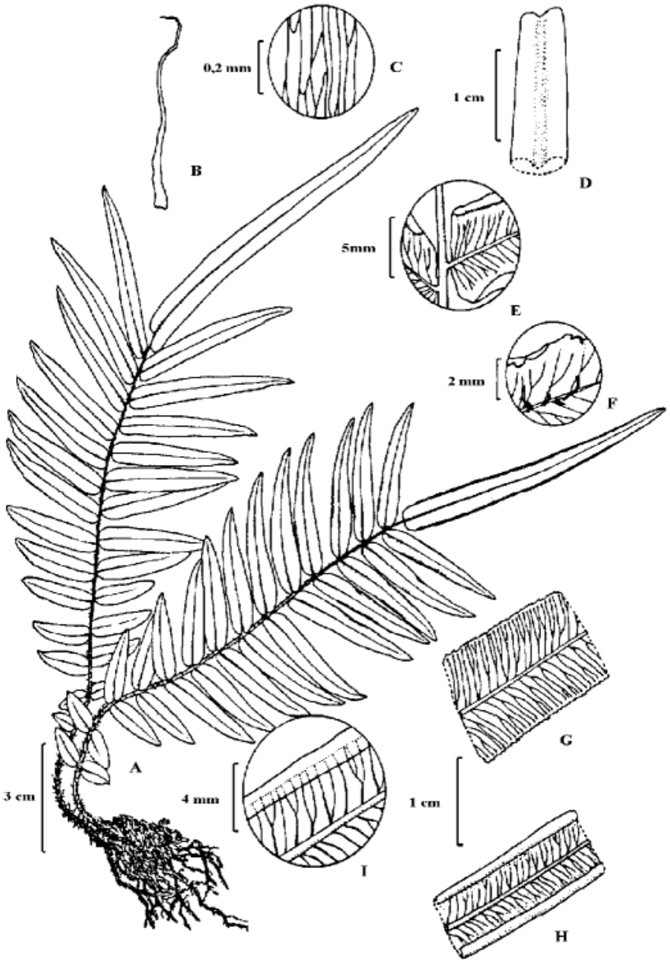

Figure 1. *Pteris vittata* general characteristics[9]: A. habit; B. rhizome scales; C. detail of the cells of a rhizome scale; D. stipe; E. detail of nonarticulated pinnae; F. abaxial view of a lamina; G. venation of the sterile lamina; H. venation and pseudoindusium of fertile lamina; I. detail of the venation and pseudoindusium.

plant samples were cultivated from a greenhouse. Attempts to elucidate the mechanisms of anion absorption on ferns have included studies with young plants.

The physical and chemical properties of this soil were measured by standard methods—organic matter by the method of Walkley and Black,

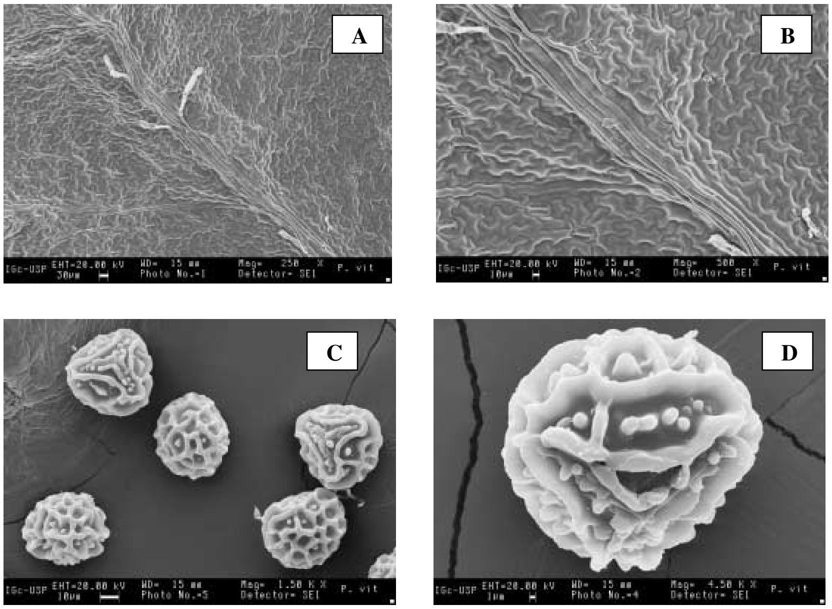

Figure 2. A. abaxial surface of a pinna showing hairs, stomata, costa, secondary veins, and free venation pattern (250x); B. detail of abaxial surface of a pinna showing hairs, stomata, costa secondary veins, and epidermal cells (500x); C. general view of the spores (500x); D. detail of a trilete spore and its surface (4500x).

soil pH in a 1:2 soil/water suspension, CEC by summation of exchangeable bases by method of Black, and mineralogy by X-ray Diffraction analysis.

The initial experiment was conducted using arsenic solution containing different concentrations. The solute solutions were made with an arsenic pentoxide, As_2O_5, dissolved in NaOH. Arsenate solution was added to the soil to obtain treatments with 1, 10, 20, 30, and 40 mg L^{-1}. Five grams soil and 10 mL of each of these solutions were equilibrated for 1 day at 25°C in a constant temperature. The rhizome and frond were analyzed for total inorganic arsenic.

In the second experiment, 40 mg of treatment As_2O_5 were added directly to 5.00 g of soil in the vase. The arsenic pentoxide salt was moderately soluble in the acid conditions, however, it dissolved quickly in an alkaline environment and formed arsenate species. Each treatment was replicated five times (1, 7, 14, 21, and 28 days).

Total arsenic contents in soil and plant were determined by instrumental neutron activation analyses—INAA, Nuclear Reactor IEA-R1m. The sample irradiation was carried out at nuclear reactor for eight hours and under thermal neutron flux of $2.7 \times 10^{12}\,\mathrm{ncm^{-2}\,s^{-1}}$; subsequently, a decay time of 3-day and 3 h counting time were employed. The radionuclide activities were measured using a gamma-ray spectrometer comprising a hyperpure GE detector and associated electronic system. The spectra of the samples were measured under the same experimental conditions of the standard photopeak of 657 KeV of ^{76}As.

Scanning electron microscope (SEM) studies are directed toward the delineation of systematic relationships of the genera. The morphological properties of the *Pteris vittata* L. may be recognized by microscopic observation, especially by SEM that reveals important aspects of tissue, size, and morphology.

Arsenic sorbed by the plant was calculated as the difference between the initial and final concentrations in solution.

RESULTS AND DISCUSSION

In this study, the amount of arsenic absorbed and relative distribution in plant tops are given in Fig. 3. The amount of anion absorbed was calculated as the difference between the anion concentration before and after reaction with the soil-plant systems. Redox potential exceeded 480 mV in all suspensions, suggesting that the primary form of dissolved arsenic was [As(V)].

The ability of *Pteris vittata* to absorb arsenic by roots can be by passive processes. Passive (nonmetabolic) uptake involves diffusion of ions in the soil solution into the rhizome due to free venation pattern (Fig. 2). Scanning electron microscopy reveals information on the venation pattern which contribute to the amount arsenic in fronds. The rhizome is a vital link between the roots and the frond, the results explain enhanced As phytoavailability observed in soluble solution; arsenic solubility was controlled by the dissolution of NaOH.

Once the arsenic ions have been absorbed through the rhizome and have been transported to the xylem vessels, there is the possibility of movement throughout the whole plant. The rate and extent of movement within plants depends on the time, concentration, and the age of the plant. In the fronds, arsenic ions may be incorporated into proteins or translocated around the plant in the phloem with photosynthates.

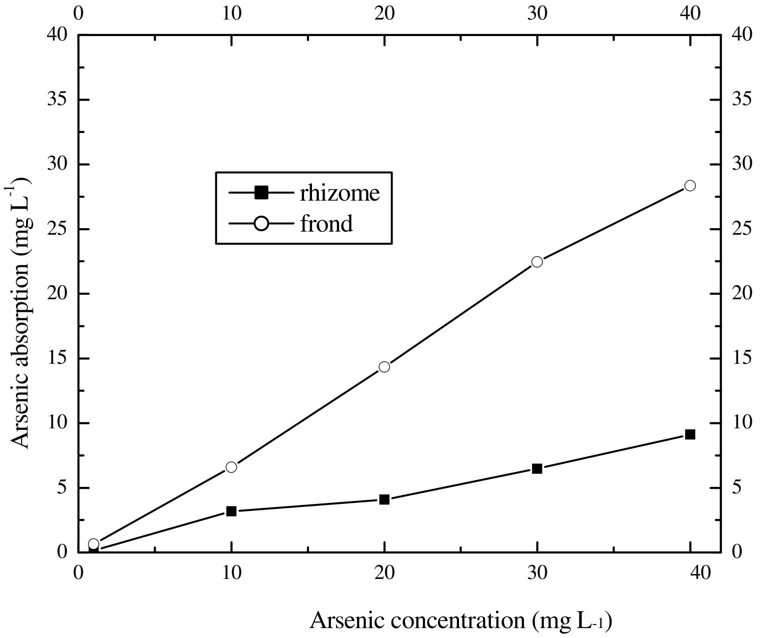

Figure 3. The amount of arsenic absorbed by *Pteris vittata* (rhizome and frond) containing different concentrations of arsenic (mg L^{-1}).

In addition to rhizome absorption, *P. vittata* can accumulate significant amounts of arsenic through frond. It is important to note the rapid removal of arsenic was observed in 24 h at pH value above 6.5. The values in Figs. 3 and 4 show that arsenic has a gradual removal, but the amount sorbed on the first experiment shows that the increased pH accompanied an increase in absorption of arsenic.

Plant growth was significantly affected by the arsenic treatments in first experimental and arsenic concentration in *P. vittata* rhizome were less than fronds. The vascular specie, therefore, has potential for being used for the in situ cleaning-up of arsenic-contaminated soils.

The results indicate that in the first experiment, As removal was influenced by the addition of soluble solution, but was decreased by the presence of insoluble substances. Dissolved As was sorbed by all five concentrations. This result parallels the pH data and may reflect enhanced anion absorption at enhanced pH.

The pH range in the second experiment was too narrow to clearly exhibit an effect of pH on As absorption (Fig. 5). The pH of the second

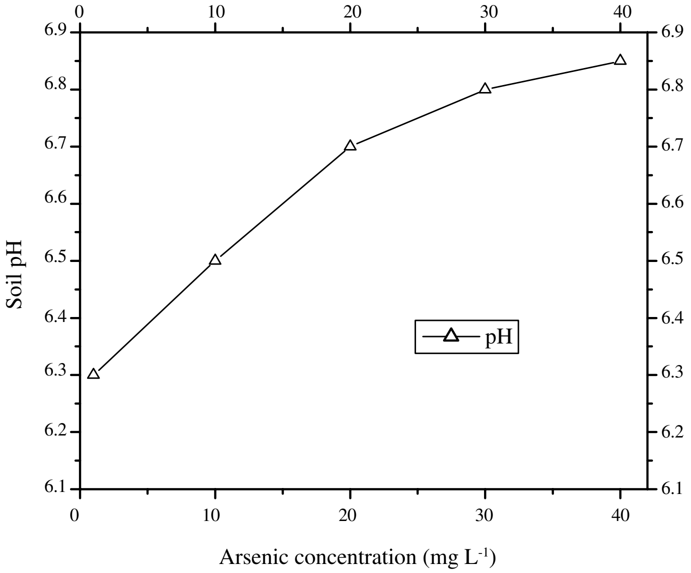

Figure 4. Changes in the soil pH in response to soluble arsenic concentrations.

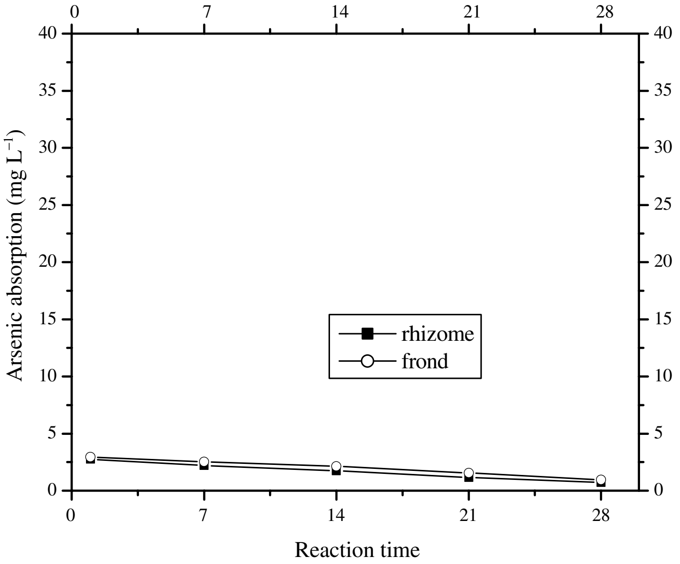

Figure 5. The amount of arsenic absorbed by *Pteris vittata* (rhizome and frond) containing insoluble arsenic ($40\,\mathrm{mg\,L^{-1}}$).

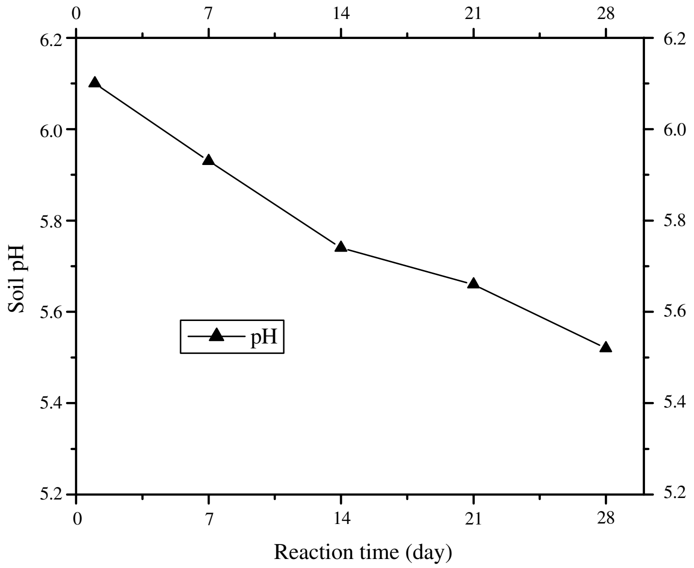

Figure 6. Soil pH after 28 days of contact (arsenic concentration 40 mg kg^{-1}).

experiment decreased and stabilized with time (Fig. 6), the gradual acidification, from 6.1 to 5.52, observed during the entire period affected the absorption reaction by plant.

CONCLUSIONS

The addition of insoluble substances influences not only absorption, but also their mobility. Arsenic adsorption maxima at pH 5.0 in kaolinite, adsorption of $H_2SO_4^-$ declined steeply at $pH > 6.5$ in all clays, however, these results explain observations of enhanced arsenic phytoavailability. However, the effects may vary according to the in situ soil conditions and quality of the organic matter in the soil. Complexes with humic substances are particularly common.

Finally, the removal of arsenic to fern proved to be a suitable means of assessing the success of remediation. Removal and decontamination were more pronounced when the arsenic soluble was added. The mechanism of absorption can occur under high and low concentrations, but in alkaline conditions.

The *Pteris vittata* has a good absorption capacity for arsenic soluble. The ability of brake fern to absorb arsenic is directly related to its conductor tissue (vascular plant).

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