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Short communication

Pb detoxification in *Equisetum diffusum*

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ABSTRACT

Current research highlights the use of aquatic macrophyte *Equisetum diffusum* (Himalayan horsetail) for lead detoxification. This plant species can grow in waste cathode ray tube (CRT) powder and absorbs its Pb. X-ray fluorescence spectroscopy (XRF) analysis of plant ash shows that 68 mg/kg lead concentration in the untreated plant was improved to 7600 mg/kg in CRT powder after 90 days. The role of monosilicic and/or monoplumbic acid as reaction intermediates for Pb detoxification and associated bioaccumulation is proposed. Pb detoxification in *E. diffusum* is mainly rendering around the iso-electronic nature of Pb and Si and forms similar phytochelatin (PC) complexes with available family of peptide ligands. The study focuses on the underlying functions of silicon containing plants in metal detoxification.

1. Introduction

Cathode ray tubes (CRTs) from computer monitors and TV sets have been replaced continuously by thinner and lightweight versions like Liquid Crystal Display (LCD) or plasma screen monitors. Continuous discarding of CRTs has now become a global environmental problem [13] for its management. This waste consists of large quantities of lead [12,15] as potentially hazardous material and therefore poses a severe danger to the environment and human health if not properly managed [14]. Other techniques such as incineration, land filling or recycling are not suitable as they could lead to the release of contaminants into the air and water [11,1].

Phytoremediation is an environment friendly technique that uses plants to remove hazardous pollutants from contaminated sites [3,2]. Aquatic macrophytes are known to concentrate trace elements in their tissues [18] and it depends upon the metal concentration, pH and nutrient status of substrata in which they are grown [7]. Silicon in plants can affect the metal mineralization by solution or solid state interactions and silicon metal interactions are an important part of its biology [16].

The purpose of this study is to highlight the role of silicon containing plants in phytoremediation and metal detoxification. Silicon imparts structural, defensive and photosynthetic advantages to plant system and silicon–metal interaction is an important part of their biochemistry. *Equisetum* Spp. has large amount of silicon (25% of dry wt.) and can form complexes with its isoelectronic Pb for its detoxification.

2. Material and methods

Mechanically pulverized waste CRT powder of particle size 40–70 microns was taken for the study. Plant samples of *E. diffusum* with complete roots and shoots (12–15 cm) were collected from a seasonal river bank near Manduwala, Dehradun (India). Five such plants were planted in 1 kg of crushed CRT powder mixed with 100 g biofertilizer (from cow dung) in a container for a period of 90 days (S_e) and

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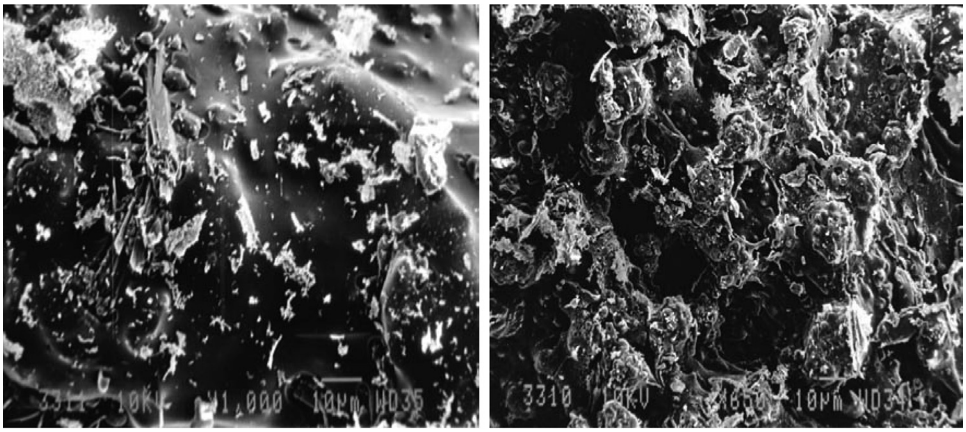
Table 1
% Atomic composition of CRT powder.

Element	OK	NaK	MgK	AlK	SiK	KK	CaK	BK	FeL	SrL	BaL	PbM
Atomic %	58.9	3.57	0.6	0.98	22.55	3.67	0.83	2.83	2.33	1.53	0.91	1.3

Table 2
Comparison of CRT and biofertilizer with soil.

S. No.	Parameters	Soil	CRT powder with biofertilizer
1.	pH value	8.35	9.8
2.	Electrical conductivity (millimhos/cm)	0.07	0.89
3.	Organic carbon (%)	0.61	0.52
4.	Available phosphorus (Kg/acre)	3.02	2.50
5.	Available potash (Kg/acre)	115	101



(a) (b)

Fig. 1. SEM micrograph of the ash from R_e (a) and S_e (b).

another five were treated as reference samples (R_e). For the determination of metal concentration S_e and R_e were initially dried at 150 °C and finally 800 °C for a period of 30–30 min respectively. Metal content from the ash thus obtained was analyzed using Bruker WD-XRF. For this purpose 35 mm of pellet was prepared with the aid of hydraulic 43 press using 6 g of ash with 2 g boric acid as a binder. MicronsPerPixY SMT EVO scanning electron microscope (SEM) was used to obtain the SEM-EDAX of the plant ash, 10–15 Å thickness films were prepared by pasting the material on carbon tape and gold coated to improve its conductivity. Soil was analyzed in NFL, Nangal (HP) India. All experiments were replicated thrice to ensure reproducibility.

3. Results and discussion

3.1. Pb bioaccumulation and its mechanistic explanation

EDAX elemental analysis of CRT powder shows the presence of (Table 1) silicon as major elements along with calcium, magnesium, potassium, sodium, which can manageably provide a soil like composition with biofertilizer (Table 2). XRF analysis of plant ash shows that 68 mg/kg lead concentration in untreated plant was improved to 7600 mg/kg after 90 days in CRT waste powder. SEM micrograph (Fig. 1) provides the structural pattern of the ash and shows a modified morphology (changed lattice) by Pb accumulation.

Both external (soil-associated) and internal (plant-associated) factors are responsible for the plants grown in metal-enriched substrata (Fig. 2). External factors as soil pH and the internal factors as the organic environment of the plant like proteins, carbohydrates, lipids, metal ion and phenolic compounds, plays a fundamental role in the metal uptake by a plant [17,8]. Lead uptake in *E. diffusum* can involve the following mechanistic paths:

3.1.1. Via monosilicic acid

Lead absorption in *E. diffusum* can (Eqs. (1)–(2)) be initiated by the formation of monosilicic acid [$Si(OH)_4$] or its anion [$Si(OH)_3O^-$] [6]. In absorption step monosilicic ions react with lead to form $Si(OH)_3OPb^{3+}$ and/or $Si(OH)_3OPb^+$ ions. Higher pH of the soil (>9) accelerates the formation of monosilicic acid [6,21].

Soluble lead is then transported from the roots to the shoots by means of the conducting tissue (xylem), similar to other macrophytes [19] and associates with the carbohydrate and proteinaceous components of the cell-wall [5]. Lead with silica is then deposited as discrete knobs and

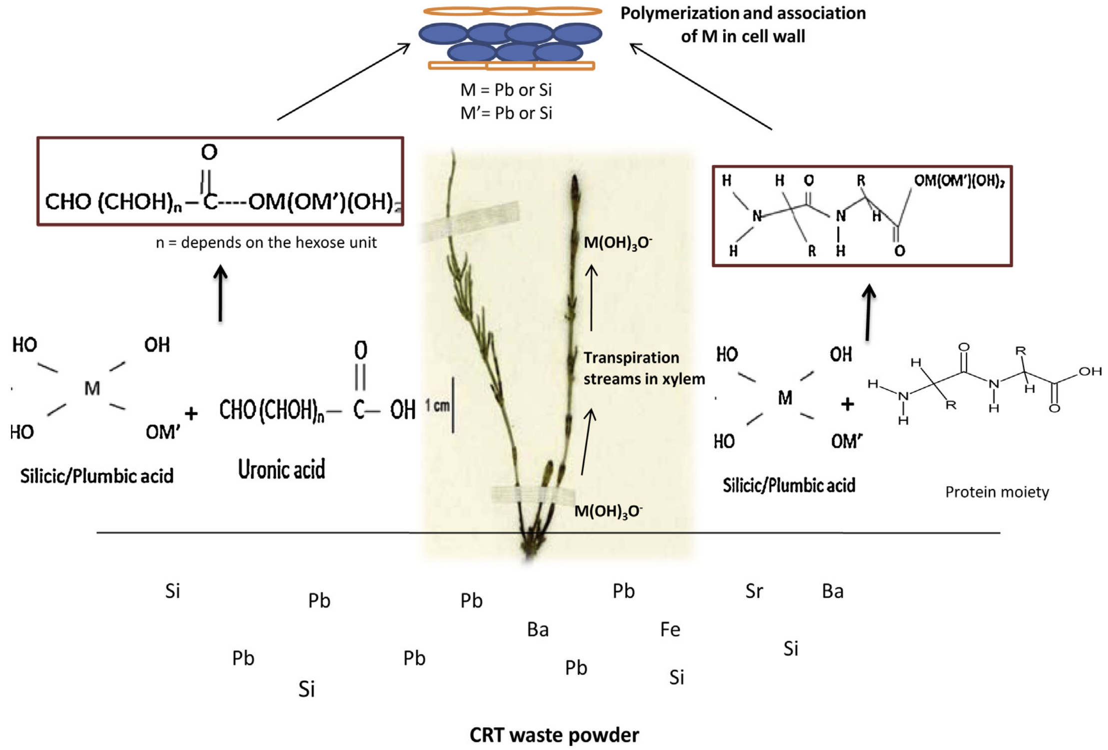


Fig. 2. Mechanism of lead uptake in *Equisetum diffusum*.

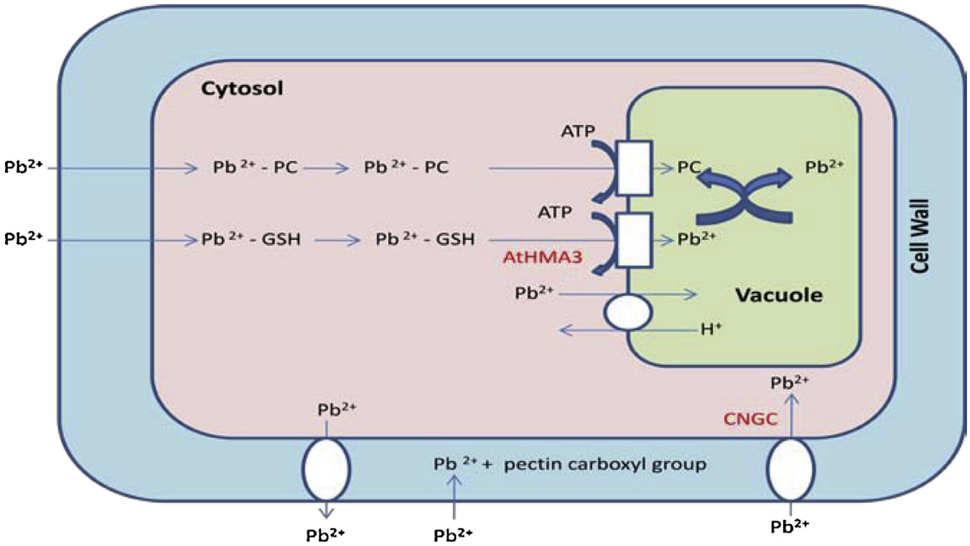
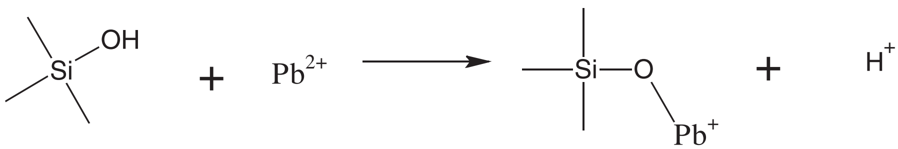


Fig. 3. Pb complexes in cytosol and vacuole.

rosettes in spicules of the epidermal surface of entire cell walls [22].



(1)

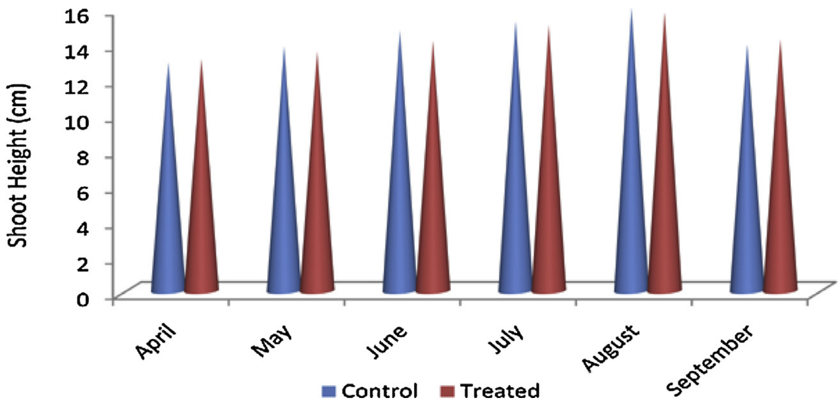
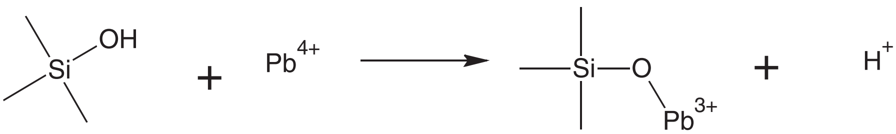


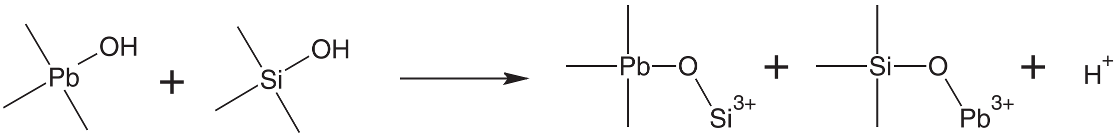
Fig. 4. Average shoot height (cm) in control and treated plants.



(2)

3.1.2. *Via monoplumbic acid*

Lead and silicon belongs to the same group of the periodic table and reasonably some monoplumbic acid is also formed in the roots with monosilicic acid. These two acids react together to form $Pb(OH)_3OSi^{3+}$ and $Si(OH)_3OPb^{3+}$ ions (Eq. (2)). The resultant ions then undergo polycondensation reactions leading to polymerization [16] to form dimer, oligomer and aggregates.

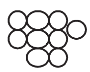


(3)

$$\underset{\text{Monomeric Anions}}{Si(OH)_3O^-} + Pb(OH)_2 \longrightarrow \underset{\text{Dimer anion}}{Si(OH)_3OPb(OH)O^-} \quad (4)$$

$$Si(OH)_3OPb(OH)O^- + Pb(OH)_2 \longrightarrow \underset{\text{Oligomer}}{Si(OH)_3OPb(OH)OPb(OH)O^-} \quad (5)$$

$$Si(OH)_3OPb(OH)OPb(OH)O^- + Pb(OH)_2 \longrightarrow$$



Aggregates

(6)

Pb detoxification in *E. diffusum* is mainly rendering around the isoelectronic nature of Pb and Si and it forms similar phytochelatin (PC) and glutathione (GSH) complexes with available family of peptide ligands in the cystosol and vacuole of the plant (Fig. 3). PC and GSH are well known to be involved in metal detoxification in plants [4]. Lead complex restricts its free movement and detoxification. Plant growth was found to be normal in both control and lead treated plant (Fig. 4; on the basic of average height of 10 plants on monthly basis). These facts justify the use of silicon containing plants like *E. diffusum* in the bioaccumulation and detoxification of lead from waste CRT.

4. Conclusions

E. diffusum is one of the plant species that spontaneously colonizes in tailing dumps with extensive root system and extremophile [9,10,20]. It is found to be useful for the direct removal and safe management of lead from waste CRT. CRT waste contains silicon as major element along with calcium, magnesium, potassium, sodium that can manageably provide a soil like composition. The following are the outcomes of this study:

1. Lead absorption in *E. diffusum* can be initiate by the formation of monosilicic and/or monoplumbic acid with phytochelatin (PC) and glutathione (GSH) complexes;
2. XRF analysis of plant ash shows that 68 mg/kg lead concentration in the control plant was improved to 7600 mg/kg after 90 days in waste CRT powder.

Equisetum is available throughout the world with annual to perennial varieties. It easily colonizes in e- waste tailing dumps in low pH, so can be used for large scale management.

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