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Natural zeolites: prospects for heavy metal polluted soil remediation

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Abstract The environmental concerns related to oil extraction, transportation and refining include the pollution with heavy metals (HMs). Currently, there is a growing interest in the study of an influence of silicon-rich materials, including such natural minerals as diatomite, zeolite, and others, on the HM behavior in the environment with regard to their exploitation in soil remediation strategy. In greenhouse pot experiment, the effects of natural zeolite on the biomass of barley plants grown in artificially cadmium (Cd)-contaminated soil and Cd uptake and translocation were studied. Zeolite applied to soil at a low rate (0.15%) mitigated the Cd phytotoxicity and provided the same plant biomass production as in uncontaminated soil without zeolite. Zeolite stimulated development of root system. The application of zeolite at a low rate enhanced the phytoextraction process–cleaning up the soil from HM at the early (booting) stage of plant development.

1.Introduction

Oil extraction and spillage result in the environment pollution by organic compounds and heavy metals [1]. The pollution by cadmium (Cd) is of severe concern due to its extreme persistence in the environment and high toxicity to plants, animals, and people. Most methods of purifying chemically polluted areas are expensive and don't make the soil suitable for plant growth [2]. At present, phytoremediation attracts high attention as a cost-effective technology for cleaning up polluted territories [3; 4]. The phytoremediation technology is based on using plants that are able to accumulate contaminants with subsequent removal of plant biomass from the ecosystem. One of the main problems that reduce the efficiency of this technology is long duration of a remediation process and toxic effect of pollutants on the plants used in phytoremediation resulting in small production of biomass [5].

Over the last decades, there has been a growing interest in the study of the effect of silicon (Si)-rich compounds, including natural zeolites, on HM-affected plants in regard to their use in soil remediation technologies [6; 7]. Silicon-rich compounds may adsorb HMs, thus reducing their mobility in the soil [8]. Silicon minerals dissolve, releasing silicic acid that can directly react with HM, thus impacting the HM bioavailability [9].

Zeolites are one of the most promising natural Si-rich minerals for use in the soil remediation technologies due to their abundance and low cost. Zeolites are crystalline porous aluminosilicates with a framework structure. Absorption properties of zeolites are identified by a unique crystal lattice, characterized by a developed inner surface with minimum pore diameters of 0.3 to 1.0 nm that provide the selective absorption of molecules depending on their size [10]. Today zeolites are widely studied for remediation of HM-contaminated soils. However, the results of these studies are quite contradictory. Many authors indicate a significant zeolite-induced reduction in the exchangeable forms of HMs in soil and in their translocation into plants [11; 12; 13]. Some data shows that for efficient HM immobilization application rates of zeolite should be about 40-50 t ha^{-1} in the case of low fertile soil. If soil has high clay content and high fertility level, the rates of zeolite should be even higher [14]. Study of the Iranian natural zeolite impact on the Cd leaching from soil showed that an optimal rate for reducing the HM mobility ranged between 9 to 15% depending on the soil texture [15].

Besides the remediation technologies, zeolites are used as soil amendment for increasing yield quality and quantity and for improving soil fertility [16; 17]. However, the recommended high application rates of zeolites often are not cost-effective. Balakhnina et al. [18] showed that low doses of zeolite have a positive impact on the plants under Cd toxicity. However, the effect of low zeolite rates on the migration and bioavailability of Cd in the soil–plant system has not been studied.

The aim of the research was to study the effect of natural zeolite on the growth and the uptake and translocation of Cd in barley plants grown in artificially Cd-contaminated Gray Forest soil.

2.Materials and Methods

Greenhouse pot experiment was conducted with barley (*H. vulgare L.*, *cv. Suzdaletz*) grown in Gray Forest loamy soil (Phaeozems in FAO classification). Soil was collected from an abandoned field (from a depth of 0–20 cm) in the southern Moscow region, Russia. The soil had the following characteristics: pH (1 M KCl), 5.73; Corg, 0.87%; total N, 0.12%; Ca and Mg (1 M KCl), 5.2 and 1.0 cmol kg^{-1}, respectively; P_2O_5 and K_2O (0.2 M HCl) 129 and 136 mg kg^{-1}, respectively. Wet soil was thoroughly mixed and passed through a 1-cm sieve.

Soil was contaminated with Cd as chemically pure $Cd(NO_3)_2{\cdot}4H_2O$ at a rate of 10 mg kg^{-1} Cd. Ground (0.2-0.3 mm size) natural zeolite (clinoptilolite, $(Na,K,Ca)_2\text{-}3Al_3(Al,Si)_2Si_{13}O_{36}{\cdot}12(H_2O)$, Khotynetz deposit, Orel region, Russia) was applied at a rate of 1.5 g kg^{-1} soil (0.15%). Zeolite had the following chemical composition: SiO_2, 69.0–74.0%; TiO, 0.08–0.16%; Al_2O_3, 11.4–14.0%; Fe_2O_3, 0.60–1.8%; MnO, 0.02–0.05%; CaO, 1.7–3.3%; MgO, 0.4–1.7%; K_2O, 0.5–5.0%; Na_2O, 0.4–0.9%; P_2O_5, 0.4%; and pH 6.5. The following treatments were conducted: control, Cd, Cd+zeolite; each in 4 replicates.

All treatments included application of N, P and K at a rate of 100 mg kg^{-1} of each element as NH_4NO_3, KH_2PO_4 and K_2SO_4. The treatments with $Cd(NO_3)_2$ were adjusted to the same level of N as that in the corresponding control variants of uncontaminated and N-fertilized soil by adding NH_4NO_3. Cadmium salt, zeolite and mineral fertilizers were thoroughly mixed with the soil 10 days before seeding. Twelve (12) germinated seeds were planted in a pot containing 800 g of soil and grown for 28 days until the booting stage. The air temperature in the growth area was kept at 20 ± 2° C during the day and 12 ± 2° C during the night. The light period was 12 h; the light intensity was 950 µmol photons m^{-2} s^{-1}. The relative air humidity was 45 ± 5% during the day and 70 ± 5% during the night. Distilled water was added to each pot daily to maintain soil moisture at 21%.

Plants were harvested and separated into leaves, stems and roots. Roots were separated from soil with tap water and washed with distilled water. Plant material was dried at 70° C, weighed and ground. A 0.4–0.5-g plant sample was digested with a 20-mL mixture of concentrated HNO_3 and $HClO_4$ (2:1 v/v) and analyzed for Cd with the Optima 5300 DV ICP optical emission spectrometer (Perkin Elmer, USA).

Values are means ± standard error of 4 replicates. Significant differences were calculated using Student’s t test ($\alpha = 0.05$).

3.Results and Discussion

The results obtained evidenced the toxic effect of Cd on plant growth in the booting stage. The biomass of whole plants in Cd-contaminated soil was reduced by 16% and a decrease in the weight of shoots amounted to 18% compared to the control plants (Table 1).

Table 1. Weight of barley plants in the booting stage.

Treatment	Leaves	Stems	Leaves + stems	Roots	Whole plants
			Dry matter, g pot^{-1}		
Control	1.36 ± 0.15	0.63 ± 0.09	1.99 ± 0.30	0.26 ± 0.04	2.25 ± 0.25
Cd	1.18 ± 0.11	0.46 ± 0.07	1.64 ± 0.25	0.24 ± 0.02	1.88 ± 0.10
Cd + zeolite	1.42 ± 0.18	0.65 ± 0.12	2.07 ± 0.31	0.33 ± 0.03	2.40 ± 0.35

The zeolite applied to Cd-polluted soil has benefited the plant growth. The weight of shoots increased by 26% as compared to the Cd-exposed plants without zeolite application. Moreover, the weights of aboveground parts in the unpolluted soil without zeolite and in the Cd-polluted soil with zeolite were approximately the same. The Cd contamination had no adverse impact on the root biomass. Application of zeolite resulted in increases in the root biomass by 27 and 38% compared to the control and Cd-exposed plants, respectively.

Cadmium was not detected in the shoots of plants grown in uncontaminated soil, whereas the Cd content was significant in the Cd-exposed plants (Table 2). The maximum Cd content was observed in the roots. The Cd contents in stems and leaves were almost 4 and 8 times lesser, respectively, than those in roots. Zeolite resulted in an insignificant increase in the leaf Cd, a double increase in the stem Cd and a 6-fold increase in the root Cd compared to the Cd-exposed plants without zeolite.

Table 2. Cadmium content in barley plants in the booting stage.

Treatment	Leaves	Stems	Roots
		mg kg^{-1} of dry weight	
Control	n/d	n/d	n/d
Cd	7 ± 1	12 ± 2	45 ± 8
Cd + zeolite	8 ± 1	26 ± 6	270 ± 32

n/d - non-detectable.

The zeolite-mediated total Cd removal by shoots per pot was almost twice as high as that in the contaminated soil without zeolite (Fig. 1). Cadmium was mainly accumulated in the roots. The use of zeolite led to an almost 7-fold increase in the root Cd and to a 4-fold increase if calculated for whole plants in the booting stage.

Our results have shown that zeolite applied at a low rate eliminated the Cd toxic effect on barley growth. Zeolite at a rate of 0.15% promoted increased Cd in above-ground organs and its maximum accumulation in the roots at the early (booting) stage of plant development. An increase in the root Cd as influenced by Si-rich compounds was reported in several studies [19; 20].

Zeolite-mediated Cd increase in the roots, stems, and leaves indicates enhanced metal translocation from the soil to the vegetative organs. This finding could relate to the interaction between Cd and monosilicic acid, the product of zeolite dissolving. The effect of soluble Si on the HM plant-availability was found to depend strongly on the monosilicic acid concentration in the soil solution [9]. Monosilicic acid at lesser concentrations forms the water-soluble Si-HM complexes or it precipitates HM via the formation of slightly soluble silicates at higher concentrations, thus increasing or decreasing the HM mobility. A slight increase in monosilicic acid at a low rate of zeolite could result in the formation of soluble Cd-Si complexes.

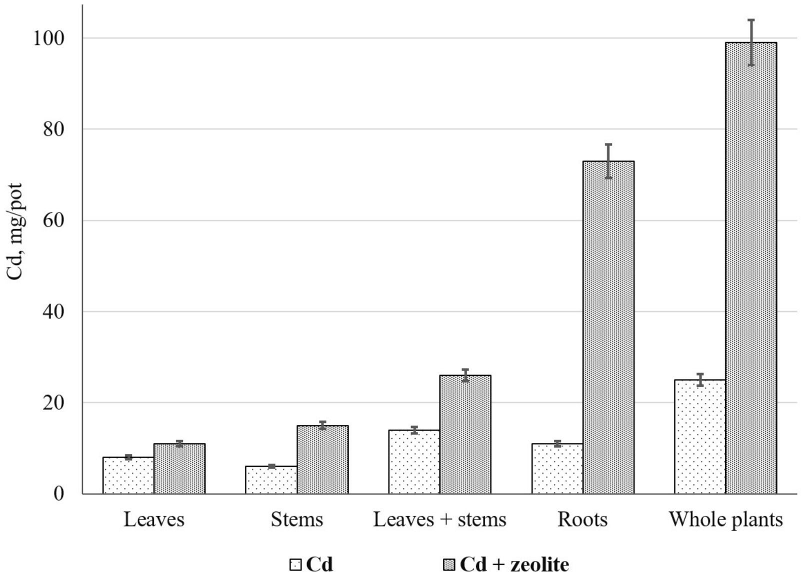

Figure 1. Cadmium uptake by barley plants in booting stage.

Zeolite-induced mitigation of adverse Cd impact on barley growth can be caused by the several processes in soil and plant. In soil, Cd may be adsorbed on the surface and in the pores of zeolite, resulting in a decrease in the metal availability, however, these processes are more pronounced at high application rates. Additional plant Si nutrition was shown to facilitate the root system development due to the fact that Si is a constituent of the root cap [21]. In our experiment, zeolite, despite the low rate, promoted the root growth even in comparison with the Cd free plants.

Some studies reported that the toxic effect of HMs, including Cd, on plants is associated with intensifying the production of reactive oxygen species (ROS) [22; 23]. Improved Si nutrition was found to reduce the ROS generation and stimulate enzymatic and non-enzymatic antioxidants [18]. It was supposed that mono- and polysilicic acids present inside or outside plant cell may precipitate or encapsulate and deactivate Cd [8; 20; 24]. As was determined, the concentrations of mono- and polysilicic acids in the plant sap exceed manifold those in the soil solution, this fact may induce intensifying Si-HM interactions inside plant [25].

4.Conclusions

The Cd-induced inhibition of barley growth was overcome by the soil-applied natural zeolite. The beneficial effect of zeolite on plant tolerance was attributed to increased root biomass. The use of natural zeolite at a low rate could be promising for increasing the efficacy of phytoremediation of Cd-contaminated areas.

5.Acknowledgement

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