



Monosilicic acid potential in phytoremediation of the contaminated areas



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HIGHLIGHTS

- Monosilicic acid concentration controls heavy metals mobility in soil matrix.
- Monosilicic acid at low concentration increases heavy metals adsorption by barley.
- The negative influence of heavy metals on barley is alleviated by monosilicic acid.
- Monosilicic acid at high concentration reduces heavy metals adsorption by barley.

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ABSTRACT

The contamination of agricultural areas by heavy metals has a negative influence on food quality and human health. Various remediation techniques have been developed for the removal and/or immobilization of heavy metals (HM) in contaminated soils. Phytoremediation is innovative technology, which has advantages (low cost, easy monitoring, high selectivity) and limitations, including long time for procedure and negative impact of contaminants on used plants. Greenhouse investigations have shown that monosilicic acid can be used for regulation of the HM (Cd, Cr, Pb and Zn) mobility in the soil-plant system. If the concentration of monosilicic acid in soil was increased from 0 to 20 mg L⁻¹ of Si in soil solution, the HM bioavailability was increased by 30–150%. However, the negative influence on the barley by HM was reduced under monosilicic acid application. If the concentration of monosilicic acid was increased more than 20 mg L⁻¹, the HM mobility in the soil was decreased by 40–300% and heavy metal uptake by plants was reduced 2–3 times. The using of the monosilicic acid may increase the phytoremediation efficiency. However the technique adaptation will be necessary for phytoremediation on certain areas.

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1. Introduction

Human activities such as industrial production, mining, agriculture and transportation are the major sources of soil contamination with heavy metals (HM), and an increased its uptake by food crops grow on polluted soils is often detected (Azevedo et al., 2012; Keller et al., 2005; Wuana and Okieimen, 2011). Toxic metals can enter the human body by consumption of contaminated food crops, water or inhalation of dust (Cambra et al., 1999). For example more

than 70% of dietary intake of cadmium is contributed via food chain (Wagner, 1993). HM are non-biodegradable and can remain almost indefinitely in the soil environment. The decontamination of the polluted soil ecosystem is actual problem in many regions.

The following soil remediation techniques are available: (i) ex-situ (excavation) or in-situ (on-site) soil washing/leaching/flushing with chemical agents, (ii) chemical immobilization/stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (iii) electrokinetics (electromigration), (iv) covering the original polluted soil surface with clean soils, (v) dilution method (mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals), (vi) phytoremediation by plants (G.O.C., 2003; Fawzy, 2008; Kord et al., 2010; Nouri et al., 2009; Stupin, 2009).

Abbreviations: HM, heavy metals.

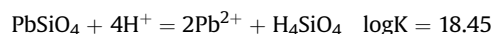
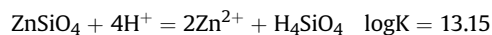
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Phytoremediation is one of the prospective technique, where various types of plants are used for removing, transferring, stabilization, and/or destroy contaminants in the soil (Liang et al., 2012). This procedure has both advantages and limitation. Phytoremediation has been suggested as environment friendly and cost-effective alternative for purification of the HM contaminated lands (Evangelou et al., 2015). Two main problems are related with phytoremediation. First, the total solubility of the HM in the soil is low, but this process is continuous (Tan, 2011). As a result, phytoremediation requires long term operation. Second, HM in contaminated soil negatively affect plant growth and consequently the phytoremediation efficiency (Manara, 2012). Among fields, current research in advanced phytoremediation on, are increasing plant tolerance to the HM toxicity and enhancing HM mobility to increase the availability to a plant.

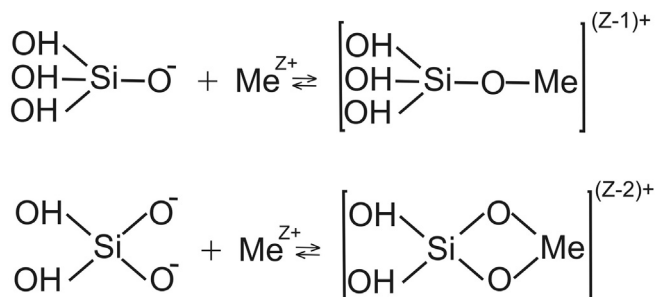
The important role of silicon (Si) in mitigating abiotic stresses in higher plants has attracted the attention of many researchers. The optimization of plant Si nutrition increased the plant tolerance to HM toxicity (Cunha and Nascimento, 2009; Liang et al., 2005; Matichenkov et al., 2013). The mechanism of this process is not clear, but probably related with chemical property of the monosilicic acid. As any acid monosilicic acid can react with metals and forms slightly soluble silicates (Iler, 1979). Secondly, Si-rich substances can adsorb HM in soil matrix and reduce their mobility (Matichenkov et al., 2013). Thirdly, soluble Si can react with HM in the plant roots (Liang et al., 2005).

Monosilicic acid or ortho-silicic acid (H_4SiO_4), $\text{pK} = -9.85$ and its anion (H_3SiO_4^-) are the most widely distributed varieties of silicic acid in natural waters, including soil solution. Monosilicic acid can differently impact the HM mobility related with its chemical properties (Matichenkov et al., 2013). Monosilicic acid reacts with HM and forms sparingly soluble silicates:



The constants of these reactions are available in handbooks (Lindsay, 1979). Our investigations have shown that such reactions are possible only when the concentration of monosilicic acid in soil solution is high (Bocharnikova et al., 1995). However monosilicic acid at low concentrations can form soluble complexes with HM (Schindler et al., 1976). This reaction results in increasing the mobility of HM (Bocharnikova et al., 1995; Schindler et al., 1976) (Fig. 1).

By this means, original monosilicic acid or silicic acid from dissolving of Si-rich minerals has the potential to regulate the



Where Me is any heavy metal

Fig. 1. Formation of the metal complexes with monosilicic acid (Schindler et al., 1976).

mobility of HM in the soil-plant system. The using of this process can reinforce the phytoremediation technique. However the mechanisms of monosilicic acid HM interactions in both soil solution and plant sap are investigated very poor.

The aim of this study was investigation of the heavy metals (Cd, Cr, Pb and Zn) mobility in the soil-barley system under different monosilicic acid concentrations in soil solution.

2. Materials and methods

The upper horizon of soil (0–10 cm), classified as Soddy Podzolic Soil (Moscow region, Russia) was used in this investigation as soil matrix. This soil had the following properties: 45% sand, $\text{pH}_{\text{H}_2\text{O}} = 5.8\text{--}5.9$, organic matter ($\text{C}_{\text{org}} = 1.21\text{--}1.23\%$; cation exchange capacity (CEC) = $8.3\text{--}8.5 \text{ cmol}^+/\text{kg}$. The total contents of the HM were determined as $\text{Cd} = 1.141\text{--}1.147 \text{ mg kg}^{-1}$, $\text{Cr} = 0.84\text{--}0.86 \text{ mg kg}^{-1}$, $\text{Pb} = 2.21\text{--}2.27 \text{ mg kg}^{-1}$ and $\text{Zn} = 0.95\text{--}0.97 \text{ mg kg}^{-1}$.

The interaction between soil and HM is a complex time-consuming process where the equilibrium between soluble, potentially soluble and insoluble forms of metals will be established (Tan, 2011). Therefore the simulation of the soil contamination was realized before greenhouse test. Dry soil was placed in a barrel and polluted with 500 mg kg^{-1} of Cd as CdCl_2 ; 500 mg kg^{-1} of Cr as $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$; 500 mg kg^{-1} of Pb as $\text{Pb}(\text{NO}_3)_2$ and 500 mg kg^{-1} of Zn as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. All HM-contained salts were separately dissolved in the distilled water, which then was mixed with soil in the barrel. During 4 weeks soil was agitated every week, moisture level was kept around 25% and temperature regime was $+20 \text{ }^\circ\text{C} - +24 \text{ }^\circ\text{C}$. Every week the soil was shuffled.

One kg of dried at $65 \text{ }^\circ\text{C}$, ground and sieved through 3 mm contaminated and original soils were placed into 1 L plastic pots. Then 10 seeds of barley (*Hordeum vulgare L.*) were planted in each pot. Barley is one of the most common plant species, which used for phytoremediation and for study of HM mobility in the soil plant system (Qi et al., 2015; Rathod et al., 2015; Rezvani et al., 2015). All pots were irrigated daily by 50 mL of distilled water or water solution with monosilicic acid at the following concentrations: 5, 10, 20, 50, and 100 mg L^{-1} . The solutions of MS were prepared from metasilicic acid (Fisher Scientific, CAS-No 7699-41-4) by dilution with deionized water. The air temperature in the greenhouse was kept at $24 \pm 2 \text{ }^\circ\text{C}$ during the day and $20 \pm 2 \text{ }^\circ\text{C}$ during the night. The light period was 12 h; at intensity of $950 \text{ mmol photons m}^{-2} \text{ s}^{-1}$. The relative air humidity was $45 \pm 5\%$ during the day and $70 \pm 5\%$ during the night.

One-month-old barley plants were harvested. The biomass of roots and above-ground organs of barley was dried at $65 \text{ }^\circ\text{C}$ and weighted. The total Si, Cd, Cr, Zn, and Pb were analyzed in roots and shoots of barley. The Elliot (1991) method was used for Si testing in solution after $\text{NaOH-H}_2\text{O}_2$ digestion technique in autoclave. The total HM content in plant tissue was determined by using microwave digestion in $\text{HNO}_3\text{-H}_2\text{O}_2$ media (Liu et al., 2013). The contents of Si, Cd, Cr, Zn, and Pb were measured by ICP-OES Perkin Elmer Optima 5300 DV.

The content of monosilicic acid in soil was determined by using water extraction from fresh soil, which gives possibility to test monosilicic acid directly (Matichenkov and Snyder, 1996). Monosilicic acid in the purified water extraction was determined by using molybdenum blue technique (Mullin and Riley, 1955). The mobile forms of HM were tested by using MgCl_2 -extracts (Jena et al., 2013). The potentially mobile forms of Cd, Cr, Pb and Zn were tested by using 0.1 n HCl extracts (McLaughlin et al., 2000; Sabiené et al., 2004). ICP-OES Perkin Elmer Optima 5300 DV was used for HM in extracts.

Each treatment and each analysis had 5 replications. All

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