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Short communication

Remediation of alkaline soil with heavy metal contamination using tourmaline as a novel amendment

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ABSTRACT

Tourmaline, a novel mineral material, was utilized to remediate agricultural alkaline soil that had been subjected to heavy metals contamination. The results showed that tourmaline increased the maximum dry matter and total chlorophyll content of lettuce by 109.11% and 31.76%, respectively, and decreased the Cd and Cu content in lettuce shoots by up to 49.01% and 30.90%, respectively. DTPA-extractable metals and BCR results indicated that tourmaline could decrease the available heavy metal content and transform heavy metals into less toxic forms. Meanwhile, PCR–DGGE results showed that tourmaline could increase indigenous microbial populations and increase Ca, Mg and K ion content. The increase in ion content of water-soluble nutrient elements, such as Ca and Mg, in soils where tourmaline was added indicates that an ion exchange mechanism is involved, providing nutrients for plant growth. Therefore, tourmaline could be used to remediate alkaline soils with historic heavy metal contamination.

Introduction

Urban and agricultural soils become contaminated by the accumulation of heavy metals and metalloids due to mining and manufacturing; the land application of fertilizers, animal manures, sewage sludge, pesticides, and wastewater irrigation; and the accidental accumulation of coal combustion residues, petrochemical spills, and other atmospheric depositions [1–3]. Excess heavy metal accumulation in soils cannot be [4], resulting in long-term residuals that are toxic to humans, animals and ecosystems [5,6]. Hence, it is important to develop an efficient remediation method for agricultural soil polluted by heavy metals.

Accordingly, a number of methods have been developed to remediate soils contaminated by heavy metals. These common methods are grouped into physical, biological and chemical remediation techniques. Compared with other remediation techniques, *in situ* chemical amendment of soil is a cost-effective remediation approach that stabilizes heavy metals in contaminated soil [7]. This technique uses inorganic amendments to reduce heavy metal mobility and bioavailability through adsorption, precipitation, ion exchange, and complexation [8]. Inorganic amendments include natural alkaline- and phosphate-based minerals, such as lime [9–11], apatite [12], fly ash [13] and calcium carbonate [14], as well as additional minerals, such as goethite [15], zeolite [16–18] and bentonite [14], that have been successfully used as soil amendments to stabilize soil polluted by heavy metals. Although these inorganic amendments have been used to remediate soil, additional problems arise from their application. For instance, lime, apatite and fly ash can decrease metal mobility in contaminated soil by changing soil pH [9–12,14–16,18]. However, using too much of an amendment can make the soil alkaline and compacted, further decreasing agricultural productivity. In some cases, an amendment may be effective at immobilizing one pollutant but may increase the mobility of another [15]. This is especially true of the Tianjin alkaline soil, where the traditional inorganic amendments mentioned above are not appropriate for amending alkaline soil. Therefore, it is imperative to develop a new material for chemically remediating alkali soils with heavy metal contamination, an area of major concern in the field of environmental science.

Tourmaline is a borosilicate mineral with a very complex chemical composition, generally expressed as $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$, where the X site is commonly occupied by Na^+, K^+, Ca^{2+} or Mg^{2+}; the Y site is occupied by Li^+, Fe^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+} or Ti^{4+}; and the Z site is occupied by Fe^{3+}, Cr^{3+}, Al^{3+}, Mg^{2+} or Fe^{2+} [19]. The variety of atom and ion species at the three sites, X, Y and Z, allows a wide range of compositions and colors. Tourmaline's chemical structure gives it many unique physical–chemical properties, such as the ability to radiate far infrared energy, permanently release negative ions, produce an electrostatic field, release rare microelements [20], and stimulate the growth and metabolism of microorganisms [21,22]. Previous research has found that tourmaline can adsorb metals from the aquatic environment [20,21]. The mineral, black tourmaline, is low cost and has been widely distributed in China, yet no research exists on applying tourmaline to remediate heavy metals from polluted soils despite

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its many unique properties.

Until now, many studies have focused on the effectiveness of immobilization techniques under environmental conditions by measuring the solubility and bioavailability of heavy metals in the soil [23]. However, the impact of chemical amendment processes on soil properties, such as biodiversity of the active microorganism community, has not been well assessed. Microbial diversity in soils is considered important in maintaining the sustainability of agricultural production systems [24]. Hence, the impact of tourmaline on soil microbial diversity should be investigated to facilitate the understanding of the mechanisms of heavy metal exchange in rhizospheric soil.

The aims of this study were: (1) to evaluate the feasibility of tourmaline as a novel amendment for the remediation of soil contaminated by heavy metals by analyzing lettuce growth and total chlorophyll content alongside the uptake and distribution of heavy metals in the plant roots and shoots under greenhouse conditions before and after soil amendment with tourmaline; and (2) to evaluate the mechanisms of tourmaline remediation, determine the effects of tourmaline on soil properties by elucidating soil bacterial diversity using the polymerase chain reaction (PCR) and denaturing gradient gel electrophoresis (DGGE) and measure the levels of soil nutrient elements after tourmaline addition.

Materials and methods

Soil and amendments

The soil was collected from the bank of the Dagu Drainage River in Tianjin, Northern China (longitude: 117°12′11.49″, latitude: 38°57′36.20″). The soil was taken from depths between 0 and 20 cm. All the soil used was air-dried, thoroughly mixed and passed through a 2-mm mesh sieve to remove gravel. Several physiochemical properties of the soil were determined according to standard Chinese methods [25]. Several physiochemical properties of the soil and heavy metal content are given in Table 1. The pH was measured with a pH Meter (310P-02, Thermo-Orion, Thermo Fisher Scientific Inc., NY, USA) in a 1:2.5 (w/w) soil–$CaCl_2$ water suspension. The organic matter content was determined using the potassium dichromate-outside heating method. Cation exchange capacity (CEC) was measured using the barium chloride method. Particle size distribution was estimated using the hydrometer method. The soil was typical of alkali soil.

The tourmaline used here (325 mesh powder) was black tourmaline produced in Xinjiang Province, China and was purchased from the Lingshou Minerals processing factory in Hebei province, China. The chemical composition of tourmaline was examined with a Zeiss MD 940 SEM operating at 25 kV equipped with X-ray energy dispersive spectroscopy (EDS).

Incubation and pot experiments

One kilogram of each amended soil and the control soil were packed into respective pots. Soils were amended in the laboratory using tourmaline (T). A control treatment (C) with no amendment added was also prepared. The experimental design included four treatments for each soil (C, T1, T2, T3), in which 1, 2 and 3 represent an amendment application rate of 1%, 2% and 5% (w/w), respectively. After the samples of C, T1, T2 and T3 were incubated for a month, ten lettuce seeds were planted and then reduced to six seedlings in each pot after germination. The pots were laid out using a random complete block design under glasshouse conditions (day/night period 16/8, room temperature), with regular watering and random rotation. After 2 months, all the plants were harvested. The heavy metal content in each plant, its biomass and its chlorophyll levels were analyzed.

Effect of tourmaline on metal ions in soil

To evaluate effect of tourmaline on heavy metal availability and distribution in soil and on soil water-soluble nutrient elements, soil with only tourmaline added (CT) but without plants was prepared. The experimental design included four treatments for each soil (C, CT1, CT2, and CT3), in which 1, 2 and 3 represent an amendment application rate of 1%, 2% and 5% (w/w), respectively. The mixtures were carefully homogenized. One kilogram of each amended and control soil were packed into separate planting pots. Distilled water was added up to 60% of the water-holding capacity of each soil. To maintain water-holding capacity, the pot was weighed every 2 days and water loss was compensated.

After samples of C, CT1, CT2 and CT3 were incubated for 2 months, the soil samples were air-dried, ground and passed through a 0.15-mm mesh sieve to investigate available heavy metals.

The available heavy metals in the soil samples were measured via chemical soil extraction with DTPA, conducted according to a modified procedure offered by Lindsay and Norvell [26]. We used 5 mM DTPA, 10 mM $CaCl_2$ and 100 mM triethanolamine at a pH of 7.3, with a ratio of 2:20 soil to solution, shaken for 2 h, and then processed by centrifugation and filtration through a 0.22 μm membrane before conducting analysis. The filtered supernatant was analyzed using an atomic adsorption spectrophotometer (WFS-210, Rayleigh Analytical Instrument Corp., China).

The distribution of heavy metals in soil before and after tourmaline addition was determined by employing a modified BCR three-step sequential extraction [27]. The method was as follows:

(1) acid exchangeable (EX): 1 g of dry soil shaken 16 h with 40 mL of 0.1 mol/L CH_3COOH in a centrifuge tube; (2) Fe and Mn oxides-bound (OX): residue from the acid exchangeable fraction extracted using 40 mL 0.1 mol/L of $NH_2OH{\cdot}HCl$ for 16 h; (3) organic-bound (OB): 10 mL of 30% H_2O_2 was added to the residue from the Fe and Mn oxides-bound fraction and digested for 1 h at room temperature, followed by 1 h at 85 °C in a water bath with another 10 mL of H_2O_2. The solution was then evaporated to 1–2 mL. Finally, 50 mL of 1 mol/L CH_3COONH_4 was added to the residue and shaken for 16 h at 25 °C; (4) residual forms (RES): residue from the organic matter-bound fraction was removed into beakers, digested with an aqua regia solution of 4 mL of HF, 10 mL of HNO_3 and 4 mL of $HClO_4$. Additionally, soil water-soluble nutrient elements were extracted according to methods described by Jackson et al. [28]. Water-soluble nutrient elements were obtained using an aqueous extraction with a 1:10 soil to deionized water suspension, the suspension was shaken for 2 h, centrifuged and filtered with a 0.22 μm membrane [28]. The filtered supernatant was analyzed.

Chlorophyll and heavy metals in plant samples

At harvest, the shoots and roots were separately and rapidly washed with deionized water. A small fraction of the lettuce leaves (0.1 g) was used to analyze the content of chlorophyll, while the remainders were dried in an oven at 70 °C until a constant weight was reached. Total dry plant biomass was weighed, before being finely grounded to determine the heavy metal content.

Total chlorophyll content was measured using the modified methods of Arnon [29], and the Arnon formula was then applied for calculations from the following equations. Fresh leaves (0.1 g) were cut up and put in a volumetric flask containing 25 mL of a 2:1 mixture of acetone and 95% ethanol before being mixed and allowed to stand until the leaves were totally white, with a measured absorbency between 645 and 663 nm (T6 new century, Beijing Persee General Instrument