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Effects of chelators on chromium and nickel uptake by *Brassica juncea* on serpentine-mine tailings for phytoextraction

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Abstract

This study compares the effect of synthetic aminopolycarboxylic acids ethylenediamine tetraacetate (EDTA) and diethylenetriamine pentaacetate (DTPA) with natural low-molecular-weight organic acids (LMWOAs) oxalic acid and citric acid as chelators for enhancing phytoextraction of Cr and Ni by *Brassica juncea* on serpentine-mine tailings. Chelator treatments were applied at doses of 0.05 and 0.10 mmol kg^{-1} dry soils after seedlings were grown in pots for 56 days. Experimental results indicate that EDTA and DTPA were the most efficient chelators of increasing the levels of Cr and Ni in the soil solutions over time. Additionally, the reduction of plant shoot biomass caused by the two synthetic chelators exceeds that caused by the LMWOAs. The total uptake (mass removal from soil) of metals by plants was enhanced via the chelators. Experimental results supported the use of *B. juncea* for Cr and Ni phytoremediation: *B. juncea* improved the removal of Cr and Ni from serpentine-mine tailings. However, low plant biomass did not assist phytoextraction by using EDTA and DTPA, both of which carry environmental risk. Therefore, adding LMWOAs during phytoremediation can provide an environmentally compatible alternative, which may decrease the use of synthetic chelators.

Keywords: Chelator; *Brassica juncea*; Heavy metals; Phytoextraction; Serpentine-mine

1. Introduction

Phytoremediation of heavy metals typically persisting in the environment is a low-cost and environmentally compatible alternative to chemical techniques and, therefore, has attracted increased interest since last decade [1–3]. Furthermore, phytoremediation has significant benefits in that it causes minimal environmental disturbance, and does not adversely affect soil matrices. Thus, after successful phytoremediation, soil can be used directly in agriculture. However, phytoremediation generally removes only a very small percentage of heavy metals from contaminated soil, and can only be applied in situation with low-level contamination. For extremely contaminated sites, other approaches must be applied [3]. All plants can extract metals from soil; however, some plants have demonstrated ability to extract, accumulate and tolerate high levels of heavy metals that are toxic to other organisms. These plants are so-called hyperaccumulators that, as vegetation, control soil erosion at contaminated sites [4–6]. Successful phytoremediation requires plants with high metal uptake capacity and high biomass production. Since most known hyperaccumulators have a low annual biomass production, considerable research is currently investigating methods that enhance the availability of heavy metals in soils and increase phytoextraction efficiency of potential accumulators [2]. Another shortcoming of hyperaccumulators during phytoextraction is not able to accumulate some metals in multi-metal contaminated soils [7,8].

To overcome these limitations, using plant with high biomass yields, such as Indian mustard (*Brassica juncea*), with a chemically enhanced method of phytoextraction has been proposed as a viable strategy for removing heavy metals from soils over a reasonable time frame [1,7,9,10]. To reach such a goal of enhanced phytoextraction, amendments must increase root uptake of metals via metal solubilization and substantially increase the speed of transfer of metals to shoots. Chelating agents, such as LMWOAs and synthetic chelators, are the most common amendments utilized in chemically assisted phytoextraction of metals from soils [8,11–14]. Chelating agents have been used in agriculture as additives in micronutrient fertilizers since the 1950s [15]. Such substances are capable of forming complexes with metal

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ions, thereby increasing the bioavailability of heavy metals in soils.

Ethylenediamine tetraacetate (EDTA) is probably the chelating agent that is most efficient at increasing the solubility of heavy metals in soil solutions from the soil solid phase, thus increasing the concentration of heavy metals in plant shoot tissues [1,9,16,17]. However, most synthetic chelators form chemically and microbiologically stable complexes with heavy metals that can contaminate groundwater [18,19]. Synthetic chelators such as EDTA and diethylenetriamine pentaacetate (DTPA), typically form metal complexes with high stability constants that are degraded slowly and have been demonstrated as relatively biologically stable, even under conditions favorable to biodegradation [20,21]. In metal contaminated soils treated with EDTA, metal–EDTA complexes leached into soil pore water and persisted for several weeks [7]. As an alternative to these synthetic chelators, widespread natural sources, such as LMWOAs, can be utilized. These LMWOAs are easily biodegraded and more environmentally compatible than synthetic chelators application to the public acceptance of phytoextraction technology [12,14,22–24]. Exudation of LMWOAs by plant roots can affect the solubility of essential and toxic ions directly and indirectly: directly, through acidification, chelation, precipitation and oxidation–reduction reactions in the rhizosphere, and indirectly through the effects of LMWOAs on microbial activity, rhizosphere physical properties and root growth dynamics [11,25–27].

Serpentine terrain occupies <1% of the earth's land surface; however, it is locally abundant in ophiolite belts along tectonic plate margins. Moreover, ophiolites are sections of oceanic crust and the subjacent upper mantle that have been uplifted or emplaced and exposed within continental crustal rocks [28]. The ore deposits in serpentine terrain are scarce worldwide. Mining activities frequently generate high amounts of waste. Among these wastes, tailings have the strongest environmental effects due to high concentrations of heavy metals in tailings and increased wind and water erosion. Erosion processes in tailings pose risks by decreasing structural stability of soils and releasing heavy metals via tailing drainage. These pollutant effects can attain local and, in some cases, regional scales and impact urban activities and agricultural production. Consequently, a risk of metal uptake by humans is associated with the tailing disposal [29,30]. Previous studies generated little information regarding amendment effects on enhanced metal phytoextraction by hyperaccumulators at mine-tailing sites, particularly, few studies have explored the unique contributions and significance of LMWOAs and synthetic chelators on Cr and Ni uptake by *B. juncea* in serpentine-mine tailings. Kidd and Monterroso [31] examined the phytoextraction efficiency of a species of *Brassicaceae* (*Alyssum serpyllifolium*) for two acid mine-spoil sites in Spain. They identified that increased uptake of Cr and Ni can be attained by increasing plant biomass via fertilized with lime, nitrogen, phosphorus and potassium. Robinson et al. [32] indicated that uptake of Co and Ni by *Berkheya coddii* (*Brassicaceae*) was enhanced by sulfur fertilizer in a serpentine-spoil in New Zealand.

Studies investigating phytoextraction by *B. juncea* largely focused on issues associated with uptake of toxic metals enhanced by different chelators in contaminated sites where heavy metals were introduced into soils from wastewater discharge, hazardous waste dumping and sewage sludge application. These principal metals of concern at such sites for chelator-enhanced phytoextraction by *B. juncea* are Cd, Cu, Ni, Pb and Zn [2,3,13]. Phytoextraction must remove toxic metals from serpentine-mine tailings, and provide vegetation to control soil erosion [29,30]. Conversely, phytoextraction efficiency is related to both plant metal concentration and dry matter yield, thus the ideal plant species to remediate a contaminated site should be a high-yield crop that tolerates and accumulates target contaminants [2]. Phytomining, a common use for such plants, is fundamentally similar to phytoremediation; however, the aim of phytomining operation is to mine metals from low-grade ore bodies [4,32]. To date most phytoremediation work has focused on the accumulation of moderate-to-high levels of Cd, Cu, Pb and Zn by *B. juncea* grown on spiked or contaminated soils [1,6,14,16]; however, few studies have investigated removal of Cr and Ni for serpentine-mine tailings [32,33]. The present study has the following three objectives: (i) investigate biomass production of *B. juncea* in serpentine-mine tailings under pot experiments; (ii) explore the effects of natural and synthetic chelators on Cr and Ni mobilization in tailings and uptake of metals by *B. juncea*; and (iii) compare the efficiencies of different chelators in technology-enhanced phytoextraction by *B. juncea*.

2. Materials and methods

2.1. Serpentine-mine tailing characterization

Serpentine minerals are locally found in the eastern section of the Central Ridge and Costal Range in eastern Taiwan, adjacent to the convergent boundary of the Eurasia Plate and Philippine Sea Plate [34]. Serpentine minerals are formed by exotic blocks of ophiolite from the Philippine Sea Plate. Study tailings were obtained from a spoiled site with histories of serpentine-mining activities in eastern Taiwan for 20 years (1960–1980). The mine was exploited for serpentine and talc. The mine tailings were spread over approximately 0.4 ha of land at the mine surface that was devoid of plant growth. Five duplicated soil samples (0–5 cm) were obtained from the 0.4 ha land area and mixed well into a composite sample. The soil sample was air-dried, ground, and passed through a 2-mm sieve for pot experiments in a greenhouse and for physiochemical analysis in a laboratory.

The soil pH was measured in a mixture of soil and deionized water (1:1, w/v) with a glass electrode [35]. Total organic carbon (OC) content was determined using the Walkley-Black wet oxidation approach [36]. Total N was determined using the Kjeldhal method [37]. Total P was measured using the sodium carbonate fusion method [38]. Cation exchange capacity (CEC) and amounts of exchangeable Ca and Mg were determined using the ammonium acetate method OR (pH 7.0) [39]. The total amount of heavy metals was digested by a mixture of $HF–HNO_3–HClO_4–H_2SO_4$ [40]. Metal contents in