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Micron-size metal-binding hydrogel particles improve germination and radicle elongation of Australian metallophyte grasses in mine waste rock and tailings

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HIGHLIGHTS

- We synthesised micron-size thiol-functional cross-linked acrylamide particles (X3).
- X3 reduced toxic soluble metals in mine wastes to below the phytotoxicity threshold.
- X3 remarkably increased water holding capacity of mine wastes.
- X3 provided moisture to seeds during germination in water restricted conditions.
- X3 enhanced seed germination and radicle elongation in phytotoxic mine wastes.

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ABSTRACT

Metal contamination of landscapes as a result of mining and other industrial activities is a pervasive problem worldwide. Metal contaminated soils often lack effective vegetation cover and are prone to contaminant leaching and dispersion through erosion, leading to contamination of the environment. Metal-binding hydrogel particle amendments could ameliorate mine wastes prior to planting and enhance seedling emergence. In this study, micron-size thiol functional cross-linked acrylamide polymer hydrogel particles (X3) were synthesised and tested in laboratory-scale experiments on phytotoxic mine wastes to determine their capacity to: (i) increase substrate water holding capacity (WHC); (ii) reduce metal availability to plants to below the phytotoxicity threshold; and (iii) enhance germination characteristics and early radicle development of two Australian metallophyte grasses under limiting and non-limiting water conditions.

Addition of X3 to mine wastes significantly increased their WHC and lowered toxic soluble metal concentrations in mine waste leachates. Germination percentages and radicle elongation of both grasses in wastes were significantly increased. Highest germination percentages and greater radicle development recorded in X3 amended wastes under water limited conditions suggests that X3 was able to ameliorate metal toxicity to radicles, and provide moisture, which improved the imbibition and consequent germination of the seeds.

1. Introduction

Heavy metal contaminated soils resulting from mining and other industrial activities are major environmental problems because they create unfavourable conditions for plant growth due to the lack of soil structure, low nutrient content, high salinity, high or low soil pH and elevated concentrations of toxic elements such as aluminium (Al), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn) and arsenic (As) [1]. As a consequence, contaminated soils, tailings and waste rock may lack protective layers of vegetation that prevent dispersion of toxic contaminants to adjacent aquifers and other areas [2–4]. The contaminants may be leached, absorbed by vegetation or retained by the soil [2] so they may enter the food chain and put human and wildlife health at risk.

A vegetative cover on mine wastes reduces dispersion of toxic elements to surrounding ecosystems [1]. Phytoremediation is the use of metal tolerant plants (i.e. metallophytes) to remove or stabilise toxic elements in soils and is a cost-effective and ecologically advantageous approach compared to other remediation techniques such as excavation and disposal to landfill [5–7]. Native plant species are often preferred for phytoremediation as they are likely to be resilient to local stresses such as low soil nutrient and organic matter contents and climate (for instance drought in

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arid and semi arid environments) [4]. Moreover, they are generally not invasive, and thereby maintain and possibly increase local plant biodiversity [4,8]. Grasses can often achieve rapid ground cover and limit short term erosion [9] and shrubs and trees offer a broad canopy cover and establish deep root systems that prevent erosion over the long term [10,11]. However, successful plant establishment of even metallophytes may be limited or impossible when metal contaminations in soils exceed plant toxicity thresholds. So, enhancing the quality of heavily impacted soils prior to revegetation is often a prerequisite for effective phytoremediation.

Nanotechnology offers a further approach to in situ remediation of metal contaminated soils which could complement existing techniques [12]. The use of nanoparticles (surface-functionalized polymer and nanoscale zero-valent iron) to remove metals such as mercury (Hg), Pb, cadmium (Cd) and chromium (Cr) from contaminated water and soils has been reported previously [13,14]. Plant establishment in polluted sites could be enhanced through the targeted design and application of micron- or nano-sized particles that have the capacity to bind toxic soluble metals in soils and improve plant–water relations [15]. For example, application of insoluble hydrophilic polyacrylate polymers in mine soil contaminated with Pb^{2+} has been shown to increase soil water holding capacity [16], reduce bioavailability of toxic trace elements such as Pb^{2+} and Cu^{2+}, and enhanced plant growth [16–18]. Application of hydrophilic polymers from diapers at 0.3% (m/m) to mine soil has also been found to induce faster establishment of plant cover [19]. Nano-sized vivianite was effective in reducing the leachability and bioaccessibility of Cu(II) in calcareous, neutral and acidic soils [20]. Rossato et al. [15] showed that micron-size thiol functional cross-linked acrylamide polymer particles (called X3) were able to reduce the available solution concentrations of Pb^{2+} (9.65 mM), Cu^{2+} (4 mM) and Zn^{2+} (10 mM) by 86.5, 75.5 and 63.84%, respectively. They also reported that X3 was not toxic to seed germination as it allowed normal germination and root elongation of the native metallophyte curly Mitchell grass (*Astrebla lappacea*) at phytotoxic available concentrations of Pb^{2+} (9.65 mM) and Zn^{2+} (10 mM).

The objectives of this study were (i) to assess the potential of X3 to bind toxic soluble metals in extremely saline and metal contaminated mine waste rock and tailings, and to increase substrate water holding capacity (WHC), and (ii) to investigate X3 effect on the germination characteristics and early radicle development of two Australian metallophyte grasses, *Astrebla lappacea* and *Austrostipa scabra*, under water limiting and non-limiting conditions.

2. Materials and methods

2.1. Substrate collection and characterisation

Substrates were collected from two mine sites where revegetation attempts had been unsuccessful for over 30 years. Waste rock (top 10 cm only) was collected from an abandoned gold mine in Queensland. Tailings (representative sample from the top 7 m) were collected from an active base metal mine in Queensland, Australia. River sand with no metal contamination was used as a control and was collected from Mt. Tamborine (Australia) and acid washed and thoroughly rinsed with deionised water (DIW) prior to experiments.

All substrates were air dried, crushed, mixed and sieved (<2 mm) to produce a fine, homogenous medium. Substrates were then analysed for pH and EC in a soil water suspension (4 g of soil to 20 mL distilled water) after shaking for 1 h by inversion at ∼40 rpm in a Heidolph ReAx shaker and standing for 1 h [21]. Plant available metals were extracted using 0.01 M $CaCl_2$ (4 g of soil to 40 mL 0.01 M $CaCl_2$) [22]. Determination of total metals was achieved by reducing the substrate to fine particles using a ball mill (Planetary Ball Mills PM 200, RETSCH, Germany). Acids (5 mL nitric acid 70% from Labscan Asia Co., Ltd., Bangkok, 2 mL hydrochloric acid 32% and 2.5 mL hydrofluoric acid 50% from Ajax Finechem, Australia) were added to 150–200 mg of sample which was then heated in a microwave digester (MDS-200, CEM Corporation) at 120 atm (12.16 MPa) and 185 °C for 30 min. Samples were then analysed for a range of metals using inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). A National Institute Standard and Technology (NIST) Standard Reference Material (SRM) (2709 San Joaquin soil) which has certified values for most of the metals was used to verify the measurements.

2.2. Determination of metal-binding and water holding capacities of X3 in mine substrates under various pH conditions

Micron-size thiol-functional cross-linked acrylamide particles (X3) were synthesised as described in Rossato et al. [15]. Mixing experiments were carried out to test the efficiency of X3 in reducing available concentrations of metals and increasing the WHC of the waste rock and tailings over a large pH range (6.3–2) in DIW and 0.01 M $CaCl_2$. Two different percentages of X3 were added to each substrate based on their plant available metal contents so as to bind all or half of the soluble metals as described by Rossato et al. [15]. For DIW treatments (pH 6.3), percentages of X3 added to substrates were 18.4 and 9.2% DW for waste rock and 3.2 and 1.6% DW for tailings. For 0.01 M $CaCl_2$ treatments (pH 6.3–2), 9.2% DW and 1.6% DW of X3 were added to waste rock and tailings, respectively. Required amounts of X3 were thoroughly mixed with substrates for 12 h using a shaker (Gerhardt Rotoshake RS12 Elution Shaker) at 5 rpm.

Ten milliliters of DIW (pH 6.3) or 0.01 M $CaCl_2$ at various pH were added to one gram of waste rock or tailings unamended or amended with X3 in 50 mL polypropylene conical tubes. Samples were shaken overnight (12 h) at 5 rpm and then centrifuged (3000 rpm for 30 min at 22 °C). The supernatant (mine substrate leachate), which contained the fraction of free soluble metals not bound to the particles, was pipetted into 10 mL PPTR tubes and 25 μL of nitric acid (70%) was added per 1 mL of supernatant with stirring to digest the samples prior to metal analysis via ICP-OES/MS. Three replicates per treatment were used.

The metal-binding efficiencies of the particles in mine substrates were calculated using the formula by Rossato et al. [15]:

$$\%\,\text{metal adsorption} = \frac{[\text{Metal concentration in supernatant of unamended mine substrate}] - [\text{Metal concentration in supernatant of X3 amended mine substrate}]}{\text{Metal concentration in supematant of unamended substrate}} \times 100 \qquad (1)$$

The water holding capacities (WHC) of waste rock and tailings under saturated conditions were calculated using the formula below [15]:

$$\text{WHC}\,(\%\text{DW}) = \frac{w_h - w_d}{w_d} \times 100 \qquad (2)$$