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Research article

Feasibility of Pb phytoextraction using nano-materials assisted ryegrass: Results of a one-year field-scale experiment

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ABSTRACT

The effect of the combined application of nano-hydroxyapatite (NHAP) or nano-carbon black (NCB) on the phytoextraction of Pb by ryegrass was investigated as an enhanced remediation technique for soils by field-scale experiment. After the addition of 0.2% NHAP or NCB to the soil, temporal variation of the uptake of Pb in aboveground parts and roots were observed. Ryegrass shoot concentrations of Pb were lower with nano-materials application than without nano-materials for the first month. However, the shoot concentrations of Pb were significantly increased with nano-materials application, in particular NHAP groups. The ryegrass root concentrations of Pb were lower with nano-materials application for the first month. These results indicated that nano-materials had significant effects on stabilization of lead, especially at the beginning of the experiment. Along with the experimental proceeding, phytotoxicity was alleviated after the incorporation of nano-materials. The ryegrass biomass was significantly higher with nano-materials application. Consequently, the Pb phytoextraction potential of ryegrass significantly increased with nano-materials application compared to the gounps without nano-materials application. The total removal rates of soil Pb were higher after combined application of NHAP than NCB. NHAP is more suitable than NCB for in-situ remediation of Pb-contaminated soils. The ryegrass translocation factor exhibited a marked increase with time. It was thought that the major role of NHP and NBA might be to alleviate the Pb phytotoxicity and increase biomass of plants.

1. Introduction

Heavy metal (HM) contamination in soil has become a serious environmental problem in China, particularly following the rapid industrialization of the nation. Anthropogenic industrial operations are a major source of pollution, including HM contamination. HMs have accumulated in soils through emissions from rapidly expanding industrial areas. These accumulations take the form of mine tailings, high industrial metal wastes, sewage sludge, wastewater irrigation, coal combustion residues, petrochemical spills, and atmospheric emissions (Wuana and Okieimen, 2011). The presence of HMs in a given ecosystem can lead to their accumulation in the food chain with negative effects on human health. HMs, such as lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg), are known to be toxic with the potential to cause dangerous diseases, including chronic poisoning (Ang et al., 2010). Compared with organic pollutants, HMs cannot be decomposed through microbial action, and therefore their presence does not decrease with time, but instead, they can only be translocated within an environment. HMs will result in contamination even at relatively low level emissions because of their accumulation. HM contamination of farmland soil has become a serious concern in China because of their profound effect on food production, specifically on food quality and food safety of agricultural products. A number of remediation techniques have been investigated to remove HMs from soils. The overall objective of any soil remediation technology is to create a final solution resulting in the protection of human health and the environment. The remediation of HMs contaminated soils is still recognized nowadays to be one of the most difficult problems to be solved. Although many remediation technologies are still controversial in terms of their effectiveness and their impact on the deterioration of soil properties, a number of remediation methods have been developed in an attempt to control soil contamination. These technologies can be classified within five categories of general approaches to remediation: isolation, immobilization, toxicity reduction, physical separation and extraction

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(GWRTAC, 1997; Bolan et al., 2014). Several technologies exist for the remediation of HM-contaminated farmland soil. One or more of these approaches are often combined for more cost-effective treatment. Phytoremediation is an innovative use of green plants to extract, adsorb, or detoxify pollutants. It has been intensively studied due to its effectiveness, non-intrusiveness and low cost as an environmentally harmonious and widely accepted remediation technique for polluted soils (Singh et al., 2010; Garbisu et al., 2002; Nunez-Lopez et al., 2008). Nevertheless, phytoremediation has the disadvantage that it takes longer to implement compared with other treatments. For this reason the development of economically feasible remediation techniques represent a very interesting technological and scientific issue.

Lead is one of the most toxic HMs to organisms in the environment. It accumulates in the organs of the body (i.e., brain, kidneys), which may cause to serious injury to them, including the kidneys, where it results in a condition known as plumbism. Lead can also affect the nervous system and red blood cells, and can even cause death. Children exposed to lead are at a substantially greater risk for impaired development, a shortened attention span, hyperactivity, and mental disorders. With the rapid development in industrialization and urbanization, lead contaminated soil has become an increasingly serious problem, which can be directly attributed to atmospheric deposition, precipitation and other sources (Perry et al., 2012). Studies have shown that plants do not take up large quantities of lead found in the soil. Thus, it has been generally considered safe to use garden produce grown in soils with total lead levels of less than 300 mg/kg (Wuana and Okieimen, 2011). These findings indicate that lead does not readily accumulate in plants. In order to reduce the adverse impact of widespread Pb pollution, a growing number of studies have researched plants subject to different types of stabilization or extraction, in which the phytoextraction method has been demonstrated to be the most effective. Certain plant species can take up Pb and concentrate it in their harvestable plant parts. Indian mustard (*Brassica juncea*), alfalfa (*Medicago sativa*), cabbage (*Brassicaoleraceavar.capitata*), tall fescue (*Festuca arundinacea*), sargent juniper (Selaginella pulvinat), and poplar trees (*Populus alba*) have been used at various contaminated sites to extract lead from the soil in order to reduce lead contamination (Lambert et al., 1997; Wu et al., 2004). Ryegrass was used as a model plant due to its rapid growth, tolerance to various environments and soil types, and its common use in phytoremediation studies (Arienzo et al., 2004; Duo et al., 2005).

Nano-materials with large surface areas and excellent optical properties have been widely used to improve the environment. Nano-carbon black (NCB) is the product of biomass pyrolysis under minimal oxygen supply. Its high biocarbon content and its chemical stability in soil have encouraged experimentation on its potential use for long-term carbon sequestration (David et al., 2013). It has also been shown that the application of biochar to soils rapidly increases the soil fertility and, in turn, plant growth by supplying and retaining nutrients while improving soil physical and biological properties (Uzoma et al., 2011). Nano-hydroxyapatite (NHAP) can be used for HM contaminated soil in natural settings because it is a natural mineralized calcium apatite and is biocompatible; furthermore, it is readily available and inexpensive. Nano-materials can adsorb and fix lead in soils, which acts to reduce lead and its compounds in the environment by reducing their mobility. Over the years, many researchers have explored using new synthetic methods for the preparation and modification of nano-materials to promote their widespread use in pollution treatment (He et al., 2013; Ramesh et al., 2013).

The aim of this study is to investigate the effect of NHAP and NCB soil application for enhancing the phytoextraction of Pb from contaminated soils when using ryegrass (*Lolium perenne L.*). The effect of NHAP and NCB with ryegrass on the potential to remediate Pb-contaminated soils was determined by the Pb concentrations in different plant parts, the bioaccumulation and translocation factors of the plants, and the changes in the Pb content of rhizosphere soils. To carry out the study of the effect of the nano-materials on Pb remediation using ryegrass, the ryegrass treatments were established in pots indoors and then transferred to the field for the experiment.

Table 1
The physical and chemical properties of the soil after fertilization.

pH (1:5)	Organic carbon (mg/kg)	Total nitrogen (g/kg)	Total phosphorus (mg/kg)	Cation exchange capacity (cmol/kg)	Total Pb (mg/kg)
8.5	27.18	4.74	9.76	156.04	1150.28

2. Materials and methods

2.1. Site description and soil characteristics

An experimental phytoextraction plot (16 m × 4 m) was established on an artificial soil simulating Pb-contaminated soil of northern China. The soil was treated with 0.15 g/kg nitrogen (N), 0.075 g/kg phosphorus (P), and 0.15 g/kg potassium (K) once it was water permeable soft after half a month. Next, the physico-chemical properties of the soil were analyzed at six randomly selected points using standard methods. The basic physico-chemical properties of the soil are listed in Table 1. For the treatments where Pb was applied, lead nitrate ($Pb(NO_3)_2$) salt was used at a concentration of 1200 mg/kg of soil. The soil treatments were thoroughly mixed and later stabilized under natural conditions for a month to yield a homogeneous composite soil for use as the growth medium.

2.2. Experimental design

The experimental design comprised 15 randomly selected field plots corresponding with five treatments and three replicates for each treatment. Each plot area was 1.8 × 1.8 m^2 and protection line for each plot was 20 cm wide. NHAP and NCB were added to 0.2% soil weight (Soil thickness was 20 cm). The distribution of experimental plots is shown in Fig. 1.

Ryegrass seeds each weighing 70 g were sprayed over the plots and germinated 5 days later. Surface soil samples were collected after 1, 1.5, 2, 3 and 12 months. Three randomly selected samples were collected for treatment in which one was collected from each replicate.

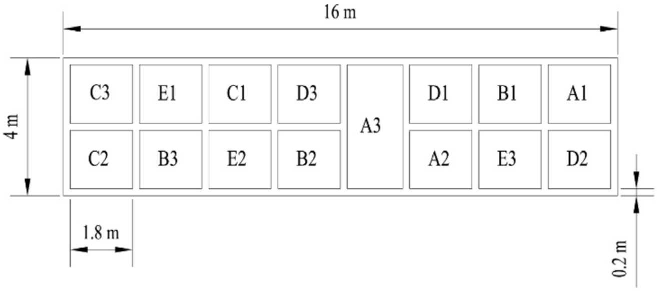

Fig. 1. The distribution of phytoextraction plots.
A-ryegrass; B-ryegrass + NCB; C-ryegrass + NHAP; D-NCB; E-NHAP.