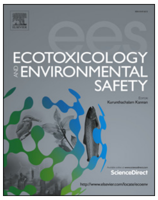
Ecotoxicology and Environmental Safety 161 (2018) 164–172

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Stability of immobilization remediation of several amendments on cadmium contaminated soils as affected by simulated soil acidification

Fuyu Guo[a,c], Changfeng Ding[a], Zhigao Zhou[a], Gaoxiang Huang[a,c], Xingxiang Wang[a,b,*]

[a] *Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, 71 East Beijing Road, Nanjing 210008, China*
[b] *Ecological Experimental Station of Red Soil, Chinese Academy of Sciences, Yingtan 335211, China*
[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Keywords:
Immobilization stability
Hydrated lime
Hydroxyapatite
Biochar
Phytoavailability
Simulated soil acidification

ABSTRACT

Chemical immobilization is a practical approach to remediate heavy metal contamination in agricultural soils. However, the potential remobilization risks of immobilized metals are a major environmental concern, especially in acid rain zones. In the present study, changes in the immobilization efficiency of several amendments as affected by simulated soil acidification were investigated to evaluate the immobilization remediation stability of several amendments on two cadmium (Cd) contaminated soils. Amendments (hydrated lime, hydroxyapatite and biochar) effectively immobilized Cd, except for organic fertilizer, and their immobilizations were strongly decreased by the simulated soil acidification. The ratio of changes in $CaCl_2$-extractable Cd: pH ($\triangle CaCl_2$-Cd/$\triangle$pH) can represent the Cd remobilization risk of different amended soils. Hydroxyapatite and biochar had a stronger durable immobilizing effect than did hydrated lime, particularly in soil with a lower pH buffering capacity, which was further confirmed by the Cd concentration and accumulation in lettuce. These results can be attributed to that hydroxyapatite and biochar transformed greater proportions of exchangeable Cd to other more stable fractions than lime. After 48 weeks of incubation, in soil with a lower pH buffering capacity, the immobilization efficiencies of lime, hydroxyapatite, biochar and organic fertilizer in the deionized water group (pH 6.5) were 71.7%, 52.7%, 38.6% and 23.9%, respectively, and changed to 19.1%, 33.6%, 26.5% and 5.0%, respectively, in the simulated acid rain group (pH 2.5). The present study provides a simple method to preliminarily estimate the immobilization efficiency of amendments and predict their stability in acid rain regions before large-scale field application. In addition, hydrated lime is recommended to be combined with other acid-stable amendments (such as hydroxyapatite or biochar) to remediate heavy metal-contaminated agricultural soils in acid precipitation zones.

1. Introduction

Cadmium (Cd) is considered a critical toxic heavy metal because of its relative mobility and toxicity to human beings through the food chain, even at very low concentrations (Chaney, 2015; Rizwan et al., 2017). As reported, approximately 19.4% of agricultural soils in China are contaminated, and Cd ranks top in the list of major contaminants (Ministry of Environmental Protection, P. R. C., Ministry of Land and Resources, P. R. C, 2014). For most people, dietary food intake accounts for approximately 90% of total Cd exposure, and vegetables and cereals are the greatest contributors. China produces and consumes more vegetables and rice than any other country in the world. Long-term consumption of Cd-contaminated vegetables and rice has been shown to be responsible for pulmonary emphysema and bone demineralization, and it can have adverse health effects on the kidney, cardiovascular system, and musculoskeletal system (Aoshima, 2016; Jarup, 2003). Therefore, feasible technologies to remediate soil Cd contamination are urgently needed to ensure food safety and protect public health in China.

In recent years, many techniques have been proposed to remediate Cd-contaminated soils, including physical, chemical, biological, and combined methods. For extensive areas of contaminated agricultural soils, in situ chemical remediation by applying amendments to immobilize metals presents a more realistic solution than cleaning up metals from the contaminated soils, particularly for the remediation of mild-to-moderate metal contamination (Hu et al., 2016; Lothenbach et al., 1999; Sun et al., 2016b). Chemical immobilization manipulates the mobility and phytoavailability of metals by changing soil pH or enhancing adsorption, ion exchange, complexation or precipitation

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[*] Corresponding author at: Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, 71 East Beijing Road, Nanjing 210008, China.

E-mail address: xxwang@issas.ac.cn (X. Wang).

https://doi.org/10.1016/j.ecoenv.2018.05.088
Received 24 January 2018; Received in revised form 27 May 2018; Accepted 29 May 2018

Table 1
The pH and heavy metal concentrations of the selected soils and amendments.

	pH	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg;kg^{-1})
DY soil	5.35 ± 0.04e	0.732 ± 0.02b	55.8 ± 4.7a	116 ± 1.9a	78.2 ± 2.1a
YX soil	6.05 ± 0.04d	1.47 ± 0.12a	24.8 ± 1.3b	73.5 ± 4.4b	41.1 ± 1.9b
Hydrated lime	12.5 ± 0.08a	0.462 ± 0.03d	2.74 ± 0.36d	6.47 ± 0.73c	–
Hydroxyapatite	7.37 ± 0.07c	0.430 ± 0.04d	–	–	–
Biochar	9.29 ± 0.05b	0.393 ± 0.03d	9.31 ± 0.47c	64.5 ± 2.2b	13.7 ± 1.0c
Organic fertilizer	6.75 ± 0.04d	0.601 ± 0.02c	62.8 ± 3.6a	119 ± 5.3a	11.0 ± 0.54c

Values are the mean ± standard deviation, and different letters in the same column represent that significant difference at $p < 0.05$ level ($n = 3$, LSD test). "-" denotes not detected. DY and YX refer to soils collected from Dayu and Yixing Counties, respectively.

reactions (Kumpiene et al., 2008; Sun et al., 2016b).

Previous studies have demonstrated that several inorganic amendments (e.g., lime, hydroxyapatite, sepiolite) (Guo et al., 2018; Sun et al., 2016b) and organic amendments (e.g., biochar, manure compost, biosolids) (Bian et al., 2014; Pardo et al., 2014) can effectively reduce the availability of Cd in soils and its uptake by plants. However, it is worth noting that in contrast to the removal and extraction options, immobilized metals may become available to plants again over time (Bolan et al., 2014; Ruttens et al., 2010). Immobilizing ability mostly depends on the amendment properties and soil environmental factors, especially the pH and redox potential, which also control the potential release of the immobilized metals (He et al., 2017a; Zhou et al., 2014). It is widely accepted that the long-term stability of immobilized metals is critically important. However, there are relatively few studies on the stability of immobilized metals, mainly because these investigations require long-term experiments.

As previously reported, heavy metal-contaminated agricultural soils in China are usually acidic in nature (Zhao et al., 2015); therefore, alkaline substances such as lime have been preferentially selected as stabilizers (He et al., 2017b; Hussain Lahori et al., 2017). However, liming is typically temporary, and soil pH will revert to the starting point over time, providing a limited guarantee for long-term safe crop production. More problematically, areas of heavy metal contamination overlap with acid rain zones in most regions of southern China, thus aggravating the risk of remobilization of immobilized metals (Guo et al., 2010; Hu et al., 2016). Therefore, it is crucial to determine whether immobilized metals are reactivated and sufficiently stable under natural conditions, particularly in acid rain zones, when using alkaline amendments. However, how acid rain affects the immobilization remediation stability of heavy metal-contaminated soils has been poorly studied, and additional research is needed to bridge our knowledge gaps on this topic.

In a previous study, we reported that several amendments exhibited different Cd immobilization strengths, and the combination of different amendments could overcome the disadvantages of each amendment (Guo et al., 2018). However, little is known about the stability behavior of these amendments. Therefore, studying the stability of the immobilization will provide a better understanding of the suitability of these amendments for field application.

In the present study, lettuce (*Lactuca sativa* L.) was employed as a model plant to certify the immobilization stability of several amendments, since lettuce is a nutritious leafy vegetable at high risk of Cd uptake that has a short duration of planting and is commonly grown in many districts around the world. Our main objective was (1) to investigate changes in the immobilization efficiency of several amendments under simulated soil acidification and (2) to explore changes in the Cd fractions in soil and the accumulation of Cd in lettuce as affected by simulated soil acidification.

2. Materials and methods

2.1. Soil and amendment

The soil samples were collected from the plow layer (0–20 cm) of farmland in Dayu County (DY), Jiangxi Province (25°26′N, 114°22′E), and Yixing County (YX), Jiangsu Province (31°15′N, 119°52′E), China. DY is known for its tungsten ore exploitation, and YX is labeled the famous pottery capital; the soils of both counties are categorized as mildly and moderately Cd-contaminated soils, respectively (Guo et al., 2018). Soils were air dried, homogenized, manually crushed and passed through a 2-mm sieve prior to use. The basic physical-chemical properties of the selected soils were determined as described by Lu (2000). DY soil consisted of 30.6% sand, 50.9% silt and 18.5% clay, while YX soil consisted of 11.2% sand, 67.3% silt and 21.5% clay. The cation exchange capacity (CEC) and organic matter (OM) contents were 9.15 cmol kg^{-1} and 28.5 g kg^{-1} for the DY soil and 18.5 cmol kg^{-1} and 46.6 g kg^{-1} for the YX soil, respectively.

Four common amendments, viz. hydrated lime (L), hydroxyapatite (H), biochar (B) and organic fertilizer (F), were selected in the present study. L was purchased from Nanjing Shangfang Lime Co., Jiangsu, China. H (12 μm) was purchased from Nanjing Emperor Nano Material Co., Ltd., Jiangsu, China. B (< 0.15 mm) was derived from rice straw by pyrolysis at 300 °C by Sanli New Energy Ltd., Shangqiu, China. F, a mixed compost of animal manures and wood sawdust, was purchased from Nanjing Ningliang Biofertilizer Co., Ltd., Jiangsu, China, and its water, OM, N, P_2O_5, and K_2O contents were 11.6%, 48.3%, 4.0%, 0.7%, and 3.1% (w/w), respectively. The pH and heavy metal concentrations of the selected soils and amendments are shown in Table 1.

2.2. Experimental design

2.2.1. Incubation study

An incubation experiment was set up to investigate the immobilization remediation stability of several amendments on two Cd-contaminated soils as affected by simulated soil acidification. The amendments alone and L combined with H, B or F were applied. Based on published scientific papers (Zhou et al., 2014; Zhang et al., 2016) and our previous study (Guo et al., 2018), the application rates were designed as follows: 2.23 t ha^{-1} (0.1%, w/w) L, 4.45 t ha^{-1} (0.2%) H, 11.13 t ha^{-1} (0.5%) B, 11.13 t ha^{-1} (0.5%) F, 0.05% L + 0.1% H (LH), 0.05% L + 0.25% B (LB), and 0.05% L + 0.25% F (LF). No amendment application was used as a control treatment (CK), and a total of eight treatments were involved in the present study.

Nationwide surveys from the 1980s to the 2000s have revealed significant acidification in major Chinese croplands, with average soil pH declines of 0.13–0.80 (Guo et al., 2010). The typical values of acid rain in southern China range from pH 3.5–5.0, while it is expected that the pH of acid rain would turn lower with the development of the economy and technology (Larssen et al., 2006). Moreover, according to our preliminary experiment, an extremely low pH of 2.5 was set to simulate the worst-case scenario of long-term soil acidification in a short period with a gain in the soil pH of 0.8 units. The stock acid solution