Article
Vol. 21, No. 3, p. 385–396, June 2017
http://dx.doi.org/10.1007/s12303-016-0059-0
pISSN 1226-4806 eISSN 1598-7477
Geosciences Journal GJ

Reclamation of arsenic contaminated soils around mining site using solidification/stabilization combined with revegetation

Zahra Derakhshan Nejad, Jeong Wook Kim, and Myung Chae Jung*

Department of Energy and Mineral Resources Engineering, Sejong University, Seoul 05006, Republic of Korea

ABSTRACT: Arsenic (As) is a known carcinogen and is one of the most commonly reported contaminants in farmland soils around mining sites. This study aimed to investigate four different soil amendments (rice husk biochar (RHB), maple leaf biochar (MLB), red mud (R.M), and steel slag (S.S)) with respect to the stabilization of arsenic in soil combined with revegetation of two hyperaccumulators (Asteraceae (lettuce) and Brassicaceae (mustard green)). Soil amendments at different application rates (0.5%, 1%, and 2% w/w) and small particle sizes (<74 μm) were added to the soil. A different pattern was observed for stabilization of As in treated soils. A meaningful decline in As stabilization was observed with increasing application dosage of MLB, R.M, and S.S, while in case of RHB efficiency was increased. Generally, maximum stabilization efficiency of As was observed following the adding of RHB (2%), MLB (0.5%), R.M (0.5%), and S.S (0.5%), by 90%, 94%, 94%, and 89%, respectively, which was primarily attributed to amendments-induced specific surface area within the structure. For lettuce, As was strongly accumulated by leaves, while As, for mustard green, was extracted much more by its roots. Sequential extraction analysis confirmed high proportions of Fe and Mn oxides and organic fractions of As, before and after planting. Altogether, the establishment of a suitable plant cover on treated soil with amendments showed encouraging results for preventing the dispersion of As through runoff and percolation. Besides, this combined technique, which is aesthetically pleasant, increases biodiversity.

Key words: arsenic, solidification/stabilization, phytoremediation, lettuce, mustard green

Manuscript received February 24, 2016; Manuscript accepted October 21, 2016

1. INTRODUCTION

Arsenic is a common inorganic element found throughout the environment. It is in many industrial products, wastes, and wastewaters, and is a contaminant of concern at many remediation sites. Arsenic contaminated soil, waste, and water must be treated by removing the arsenic or immobilizing it. Arsenic mobilization depends on pH, so that a relatively small change in pH can result in a drastic increase/decrease in As concentrations (Woo and Choi, 2001).

Chemical fixation represents a promising and potentially cost-effective treatment alternative for trace metal-contaminated soils. Alternative potential remediation strategies for metal (loid)s contaminated soils include biological remediation, (for example, phytoextraction and phytostabilization), physical and chemical stabilization, and finally the application of inorganic amendments (elemental immobilization) to reduce mobile species and bioavailability. Stabilization of As in soil can be achieved by soil amendments that absorb, bind or co-precipitate the contaminating elements (Kumpiene et al., 2006). Nonetheless, finding amendments which are not only effective and easily accessible but also free of negative effect on environment is one of the concerns.

Numerous organic/inorganic amendments have been incorporated into As contaminated soils (Mench et al., 1998). Biochar, a carbonaceous product, has shown great potential for stabilization use. Biochar surfaces are known to be involved in As adsorption in soils (Beesly and Marmiroli, 2011; Bundschuh et al., 2015). Regardless of the type of feedstock and pyrolysis conditions, biochar with relatively high cation exchange capacity consistently shows an adsorption capacity towards metal cations and less binding ability for As species vigorously depend on environment pH and component of biochar (Mohan et al.,

---

***Corresponding author:**
Myung Chae Jung
Department of Energy and Mineral Resources Engineering, Sejong University, 209, Neungdong-ro, Gwangjin-gu, Seoul 05006, Republic of Korea
Tel: +82-2-3408-3827, Fax: +82-2-466-4795, E-mail: jmc65@sejong.ac.kr

2007). The Fe and Al sources rich amendments such as red mud and steel slag are essential to mitigate As toxicity and hence facilitate plant survival. Arsenic can be adsorbed and oxidized along the surfaces of some Fe-oxyhydroxides, such as hematite and goethite (Lin and Puls 2000). However, adsorption of As on Fe-oxides is reduced when pH is raised (Manning and Goldberg, 1997; Gimenez et al., 2007).

The immobilization of metal(loid)s by amendments is frequently combined with the revegetation of the contaminated soil, the so-called phytoremediation technique. Plant species with desired abilities to accumulate As is one of the most effective methods for soil treatment (Shipley et al., 2008; Bergqvist, 2011). The establishment of suitable plant cover on the soil is helpful in preventing the dispersion of contaminants through erosion, runoff and percolation. The selection of plant species for As phytostabilization should ensure that the plant species do not increase the As mobility from the area that it is suitable for As phytostabilization in terms of As accumulation (Bundschuh et al., 2015). Lettuce and mustard green are both considered to be plant species capable of accumulating As in their tissues (Huang et al., 2006).

Despite the fact of phytoavailability of As in contaminated soils, evaluation of the simultaneous effects of plant species (revegetation) combined with soil amendments (immobilization) on As treatment has considerably been the subject of only limited studies (Akhtar et al., 2013; EPA, 2002). Hence, considering As exposure problem, this study aimed to investigate the application of chemical stabilization of As in soil through semi-organic (biochar) and inorganic amendments. The efficiency of our amendments including: rice husk biochar (RHB), maple leaf biochar (MLB), red mud (R.M), and steel slag (S.S) on the immobilization of As was assessed. The effect of two hyperaccumulator species on phytoremediation through As extraction and accumulation by plant tissues was evaluated, as well. In order to investigate the effect of plant species and different amendments on As fractionations, the sequential extraction of As was carried out before and after planting.

2. MATERIAL AND METHODS

2.1. Soil Sampling

An abandoned mine site in Okcheon County, South Korea was selected. The study area lies between longitudes 127°44'14" and latitudes 36°19'49" North (the abandoned Goepung Mine) in South Korea (Fig. 1). The mine was active from 1990 to 1998, while the main excavated ore resources were Au, Ag, and Cu (Cheong et al., 2008; Yim et al., 2009). The two tailing impoundments that remained on the abandoned mine site after the closure, affected farmlands around the area. Approximately 150 kg of surface soil samples (0–15 cm) from farmland around the mining site were collected with shovels. Then, the samples were dried at ambient temperature for 3 days (<35 °C). Samples were disaggregated and sieved to <2 mm. Soil samples were ground to a fine powder in a mill. This finely milled soil (–100 mesh or <150 μm) was used for chemical analysis and the <2 mm fraction was used for planting, measuring soil pH, organic matter content, and cation exchange capacity (CEC).

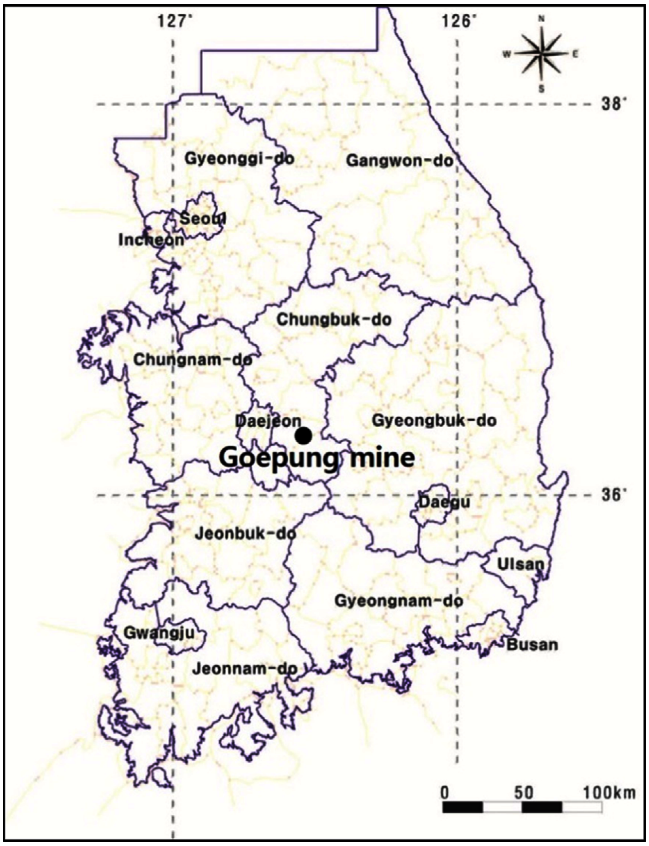

Fig. 1. Map of the Goepung Mine in Korea.

2.2. Preparing Soil Amendments

2.2.1. Biochar

First step for producing qualified biochar as carbonaceous product is the choosing appropriate biomass resources. Hence, rice husk and maple leaves were chosen to produce biochar which are part of the most widely available agricultural wastes and residual organic matter produce annually by maple trees, respectively. A bulk rice husk sample was purchased from a commercial rice mill that processes “white rice” (the most popular rice in Korea). Maple leaves were collected from the fallen leaves around the study area. Samples were washed several times with tap water and finally with distilled water. As pyrolysis temperature has significant effect on the chemical properties of the produced biochar, a specific dry-pyrolysis condition was made at 550 °C temperatures through a residence time of 45 minutes inside an anaerobic furnace (WiseTherm(R) FT Programmable Tube Furnaces) under an N_2 (Hossain et al., 2011). Thereafter, rice husk biochar (RHB) and maple leaf biochar were ground and sieved through a 74 μm-mesh to use as soil amendments.

Concentration of As in biochars following the USA EPA method No. 1311 was measured. The pH values of the biochars were measured by the ratio of 1:5 of samples with deionized water. The solution was then shaken for 1 h and allowed to stand for 5 min and then, pH was measured with a portable pH-EC meter. The specific surface-area (SSA) distribution was obtained from the adsorption isotherms, using the Brunauer-Emmett-Teller (BET) method (Zhang et al., 2011). Cation exchange capacity (CEC) of each amendment and initial soil were measured using 1M sodium acetate, ethanol 95%, and 1M ammonium acetate, respectively (Hesse, 1971). X-ray fluorescence (XRF) used to determine the elemental composition of amendments. In this regard, 4 g of each amendment (DW) were mixed with 1.5 g of X-ray pellet mix powder and 1 g boric acid for 2 min in a puck grinder, and then pressed into a pellet. Then mineral contents were measured by S2 RANGER Energy Dispersive X-ray Fluorescence (EDXRF) Analyzer.

2.2.2. Inorganic amendments

Red mud (R.M) and steel slag which are by-products of alumina smelters and steal companies, respectively, were obtained from commercial suppliers. The samples were dried at ambient temperature for 2 days (<35 °C). Afterward, samples were ground to obtain size of the particles less than 74 μm, to increase specific surface area (MicrotracBEL, 2015).

2.3. Greenhouse Setup

A leaching pot experiment was carried out to investigate the effect of amendments on As leaching and uptake by plants. Each pot was filled with a mixture consisting of 1,000 g of contaminated soil, 300 g of washed sand to prevent soil compaction, and 0.5%, 1%, and 2% dry mass of amendments. A control treatment was also prepared following the same procedure but without adding amendment. All treatments were performed in 2 replicates. Before sowing, the pots were placed in a greenhouse and the mixtures were equilibrated for 60 days at 18 °C, relative humidity of 70%, and 15 h photoperiod. For assessment of phytoremediation two hyperaccumulator plants were chosen. Three premature lettuce and mustard green were separately transplanted in each pot. Pots were irrigated 3 times a week using deionized water (DI), and each pot received 100 ml each time. Every 20 days, soils, plant leaves, and leachate samples were taken to analysis As concentration.

For measuring total concentration of As, soil samples and inorganic amendments were digested in a 3:1 ratio of concentrated nitric acid (A.R. 70% w/w) and perchloric acid (A.R. 60% w/w). The tubes were heated at 70 °C for 1 h in a hot block. After cooling, solutions made with volumes up to 50 ml with deionized water. The solutions then were filtered using Whatman paper and transferred to plastic analysis bottles to analyze As using Atomic absorption spectroscopy (AAS) (AA240, Varian, Australia) (Ure, 1990). For plant analysis, 1 g samples of dried, finely milled plants were weighed in large test falcon tubes, and 5 ml of concentrated nitric acid (70% w/w) were added to wet the samples. The tubes were heated at 120 °C for 1 h in a hot block. After cooling, 1 ml H_2O_2 was added to each tube and finally the filtered samples were analyzed for measuring As concentration using AAS.

Sequential extraction that was based on the method suggested by Jung (1995) was also conducted for the characterizing As fractions. Hence, five steps (Operationally defined) of sequential extraction were used in this study, before and after planting.

3. RESULTS AND DISCUSSION

3.1. Soil and Amendments Characteristics

Mean concentration of As and some of physiochemical properties of surface soil and amendments are shown in Table 1. Soil pH was almost neutral (6.69) and contaminated with As (3.77 mgkg^{-1}). The organic matter (0.59%) and clay content

Table 1. Physical properties of soil and amendments

Samples	pH	As (mgkg^{-1})	T-P (mgkg^{-1})	T-N (%)	OM (%)	K (mgkg^{-1})	CEC (meq100g^{-1})	SSA (m^{2}g^{-1})	Texture
Original soil	6.69	3.77	607	0.04	0.59	ND	7.60	ND	Loamy sand
RHB	7.86	0.38	48,700	3.30	48.76	2,710	20.00	7.36	ND
MLB	8.89	0.45	1,380	0.54	21.00	2,520	22.00	12.20	ND
R.M	10.73	6.00	280	0.01	0.50	48	45.24	44.13	ND
S.S	11.83	1.40	4,980	0.01	0.89	169	25.22	17.86	ND

RHB: rice husk biochar, MLB: maple leaf biochar, R.M: red mud, S.S: steel slag, SSA: specific surface area, OM: organic matter, T-P: total phosphorous, T-N: total nitrogen.

http://dx.doi.org/10.1007/s12303-016-0059-0

Table 2. Chemical compositions of RHB, MLB, R.M, and S.S with X-ray fluorescence analysis

Amendments	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	CaO	P_2O	MnO	TiO_2	SO_3	Cl	Matrix
RHB	61.1	23.6	5.69	4.69	1.33	1.18	0.93	0.25	0.10	0.811	0.05	ND	ND
MLB	2.49	0.05	0.04	2.85	ND	0.98	6.15	0.53	0.08	ND	0.17	0.38	86.3
R.M	20.86	29.79	23.54	0.05	6.73	0.10	15.22	0.14	0.03	2.63	0.29	ND	1.01
S.S	15.06	7.03	31.57	0.41	1.68	3.50	34.83	2.53	0.53	0.857	0.05	ND	ND

ND: not detected, RHB: rice husk biochar, MLB: maple leaf biochar, R.M: red mud, S.S: steel slag.

(11.36%) were relatively low according to average values reported for Korean cultivated soils (Rim et al., 1997; Jo and Koh, 2004). Nutrient status, as reported total N (0.04%), indicated that soil was nutrient poor and additional nutrient supplement was required for optimal plant growth. In addition, CEC of this soil indicated relatively low value (7.6 meq/100 g).

Total concentration of As in all amendments was very low. Hence, the amount of As added to the soil through amendments was negligible. Amendments showed almost neutral to high alkaline pH from 7.86 to 11.83 in RHB and S.S, respectively. Soil amendments showed CEC values much more than control soil. Hence, soil CEC was expected to increase subsequent of each amendment application. The maximum CEC and SSA values were observed in R.M, while consisting of less phosphorous. High concentration of phosphorous (P) and potassium (K) were observed in RHB, S.S, and MLB respectively.

Chemical composition of sorbents obtained from the XRF analysis is given in Table 2. As it is shown, SiO_2 was the main ingredient of RHB. According to previous studies, silica as a major constituent of RHB, is concentrated in outer epidermis cells including protuberances and hairs (trichomes) and also present in the inner epidermis (Prakongkep et al., 2013). XRF results indicated a high content of Ca^{2+} in MLB that can induce ion-exchange reaction. The main chemical compositions of R.M were Al_2O_3, Fe_2O_3, SiO_2, and Na_2O. The main components of the S.S were CaO followed by Fe_2O_3. Other oxides commonly found in slag materials included SiO_2 and Al_2O_3 (Kanel et al., 2006; Liu et al., 2010).

3.2. Influence of Different Treatments on Soil pH

Application of various amendments to contaminated soil at a mixing ratio of 0.5%, 1%, and 2% demonstrated change in soils pH (Fig. 2). As was expected, soil pH increased significantly following treating soils. Soil pH increased from 6.69 to approximately 7.37, 7.55, 8.47, and 8.58 after 60 days in 2% application rates of RHB, MLB, R.M, and S.S amended soils, respectively. In soils at which lettuce was sown, among all amendments with 0.5% application rate, R.M showed the highest soil pH followed by S.S > RHB > MLB. Nevertheless, increasing in amendment application dosage indicated the highest soil pH in S.S followed by

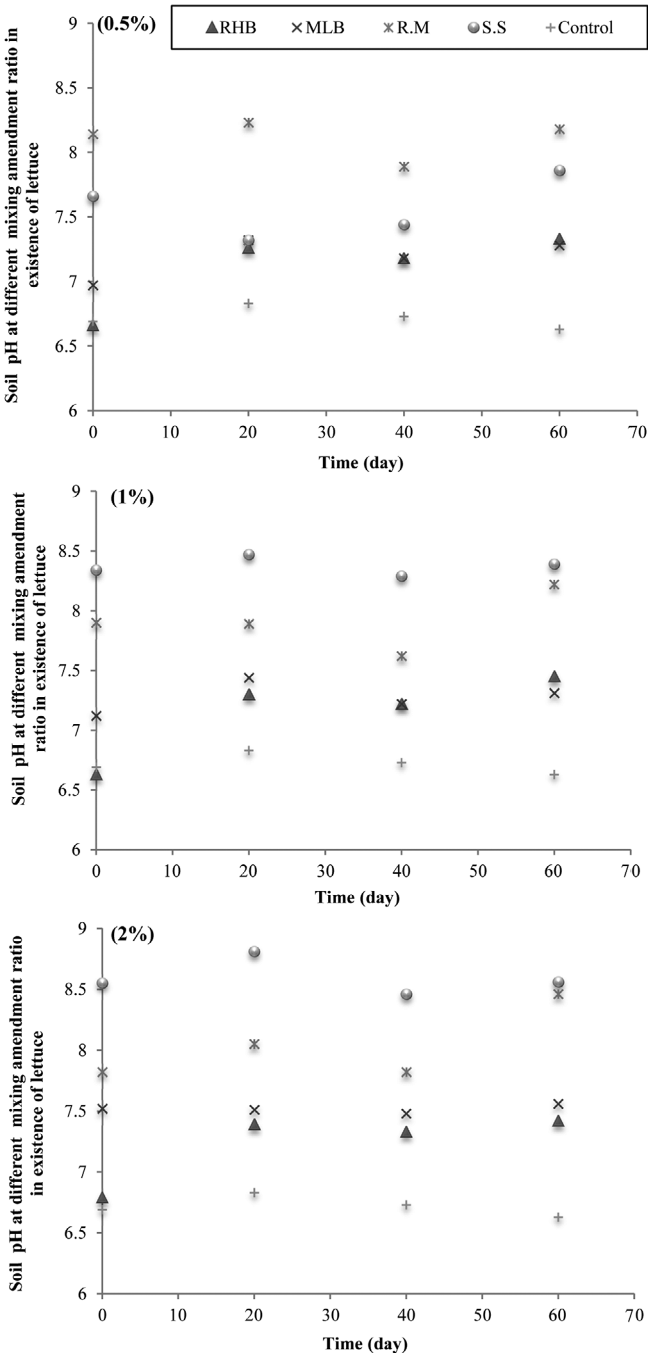

Fig. 2. Variation in soil pH with incubation time at three amendment application rates (0.5%, 1%, and 2% (w/w)) in existence of lettuce. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag.

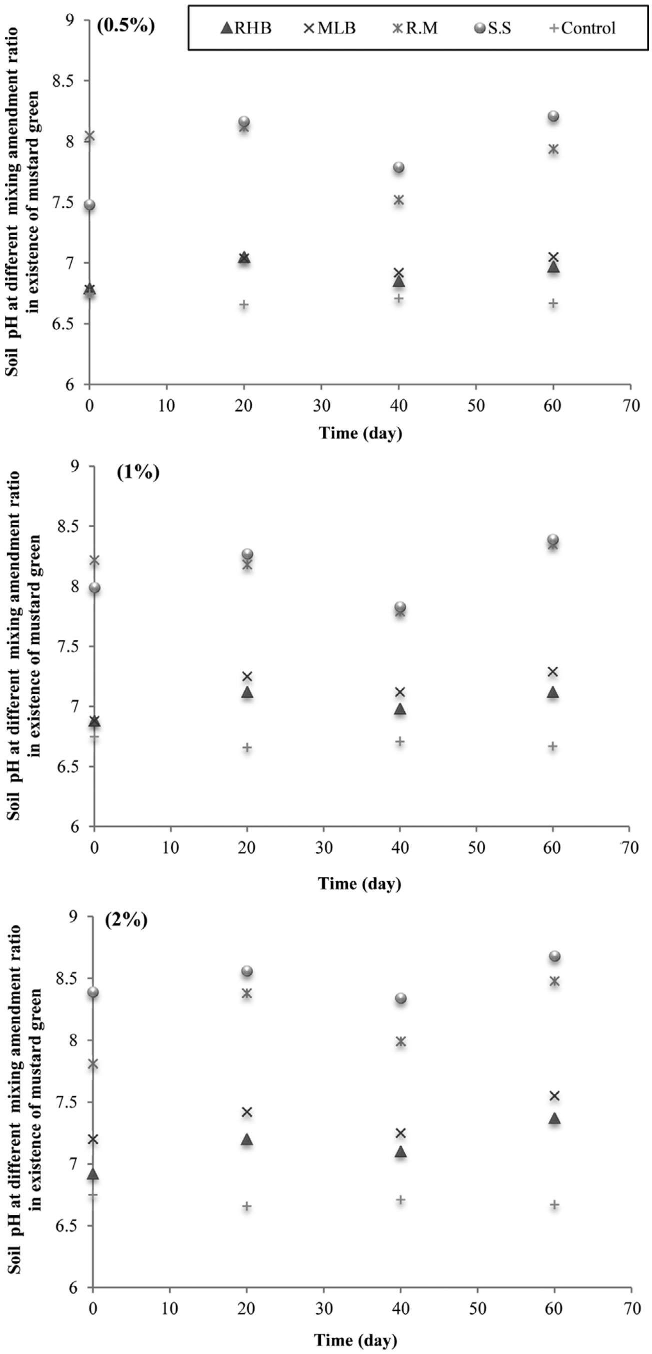

Fig. 3. Variation in soil pH with incubation time at three amendment application rates (0.5%, 1%, and 2% (w/w)) in existence of mustard green. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag.

R.M > MLB > RHB.

In present of mustard green, different pattern for changing soil pH compared with lettuce was observed. After adding amendments, soil pH increased almost more than 2 units from that of the control, with increasing amendment dosages. In all amendment application rates the highest increase in soil pH was observed in S.S treated soils followed by R.M > MLB > RHB, respectively (Fig. 3). The main reason of such difference may attribute to the different ratio of degradation capability of each amendment and exudation products of plant roots. A rise in pH often results in mobilization of As in the soil. In general, a rise in soil pH causes a release of anions from within their exchange positions, such that arsenate and arsenite are released. However, several experiments have shown that high pH values, in the presence of sulfate and carbonates, can produce either a co-precipitation of As in the subsequently formed oxyhydroxides and sulfates (Moreno-Jiménez et al., 2012). In present study, biochars contained high content of organic and inorganic carbon fractions which can form of several carbon content compounds.

3.3. Influence of Different Treatments on Concentration of As in Soil

The evaluation of As concentration as a function of time indicated the positive or the negative effects of amendments on As stabilization that was already weak at the very beginning of the experiment (Fig. 4). One probable explanation was that the soil containing amendments progressively moved toward equilibrium continuously during the experiment. Before planting average concentration of As in untreated soil was 3.77 mgkg^{-1}. At the end of the experiments concentration of remained As in treated soils was more than control, especially in RHB and MLB (0.5%), while lettuce planted in soil (Fig. 4a). Due to the chemical similarity of P and arsenate, the presence of P is a main factor influencing the uptake and further fate of As in soil and plants. A low level of P displaces As from soil particles to increase uptake and phytotoxicity, while larger amounts of P competes with As at root surface to decrease uptake. In present study, among all amendments, RHB showed the maximum content of P. In addition, Hartley et al. (2009) reported that the extractable arsenic in soil increased in the biochar treated soil compared to the control. A reduction in leached arsenic upon the application of Ca rich amendment was observed, resulting from the binding of As with Ca^{2+} and resulting in reduced As mobility (Hartley et al., 2009). Results of present study indicated Ca as the main component of MLB.

Present of mustard green in treated soils showed different results. When R.M and S.S were added in ratio of 0.5%, stabilization of As in soil was observed. Although, with increasing application dosage of each one As extraction from soil was decreased. However, adding RHB in 1% and 2% showed an ability to stabilize As through soil (Fig. 4b). Indeed, the oxyhydroxide species of As forming on the surface of Fe, Al, and Ca functions in amendments are effective adsorption sites for As at neutral and basic pH (Jung et al., 2011).

Gimenez et al. (2007) found that hematite had the largest

http://dx.doi.org/10.1007/s12303-016-0059-0

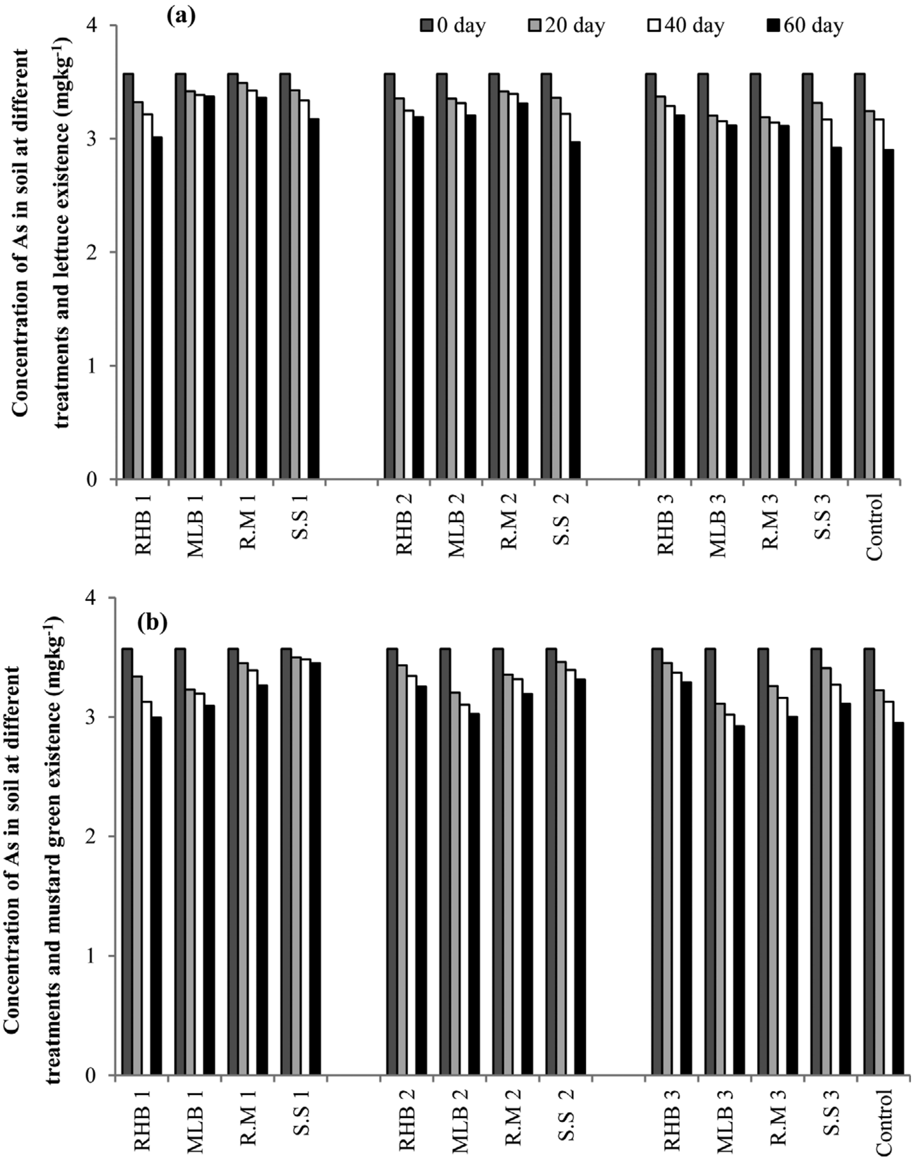

Fig. 4. Effects of different treatments on As concentration in soil. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag. 1= 0.5%, 2 = 1%, 3 = 2% mixing ratio.

sorption capacity, followed by goethite and then magnetite. The addition of Fe and Al to the soil in several forms immobilizes As. For example, additions of Fe oxides, Fe-rich materials such as R.M and S.S, inorganic Fe salts or industrial by-products, rich in Fe and Al together with $CaCO_3$, have all been used to raise the quantity of soil oxides, which, in turn, immobilizes As (Hartley et al., 2004; Vithanage et al., 2007; Hartley and Lepp, 2008). As already was mentioned, adsorption of As on Fe-oxides is reduced when pH is raised. In agreement with previous researches, the same process in present study was obviously observed in treated soils with R.M and S.S. In addition, using small particle size of the amendments, due to an increase in specific surface area, showed promising results in As immobilization even in low application ratio of soil amendments. Hence, using such small particles not only increased efficiency in soil remediation but also reduced application ratio and costs.

3.4. Phytoremediation of As using Lettuce and Mustard Green

3.4.1. Accumulation of As in aerial parts of plants

Average concentration of As in leaves of lettuce after 60 days of growth in control soil was 0.36 $mgkg^{-1}$ DW (Fig. 5). Overall, the decline of As concentration in plant leaves induced by all amendments, was more pronounced at the end of the experiment. Compared with the control condition, concentrations of As in leaves of plants grown in soil treated with RHB and MLB were less than half after 60 days of growth mainly due to stabilizing effect of soil amendments (Fig. 5a). The addition of R.M and S.S decreased the amount of As that was taken up by plants, as well. However, increasing application dosage of R.M remarkably increased accumulation of As in lettuce. This was due to an increase in the phytoavailable form of As

http://dx.doi.org/10.1007/s12303-016-0059-0

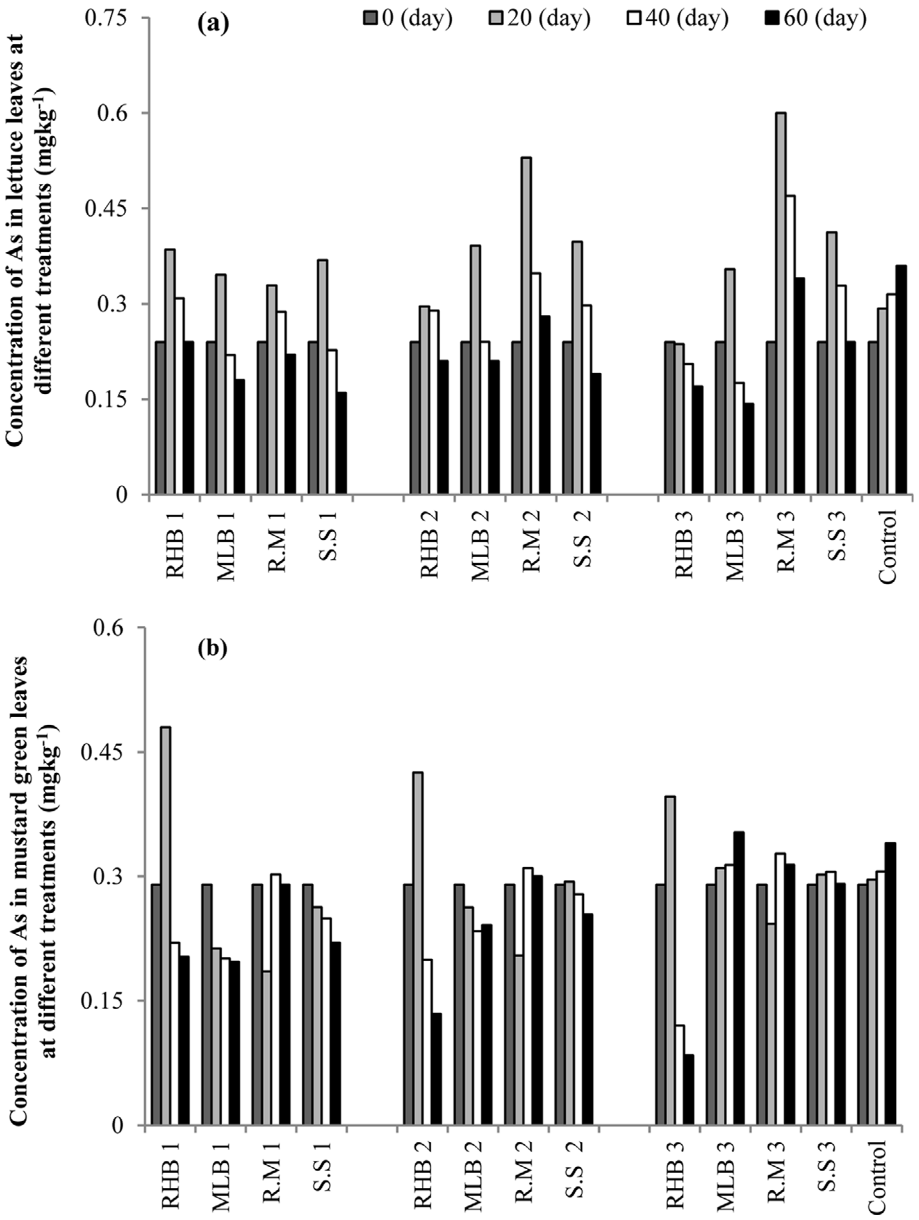

Fig. 5. Effects of different treatments on As accumulation in lettuce and mustard green leaves. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag. 1 = 0.5%, 2 = 1%, 3 = 2% mixing ratio.

fractions in R.M treated soils subsequent of an increase in soil pH (Violante et al., 2010).

The average concentration of As in leaves of mustard green grown in control soil after harvesting was 0.34 mgkg^{-1} DW (Fig. 5b). During plant growth, As was accumulated in mustard green when no treatment was put on the soil. Compared with the control, low concentration of As was observed in leaves of plants grown in treated soil with RHB. On the contrary, there was no meaningful difference among other treatments and control. Overall, different plant species showed different ability for adsorbing and accumulating As.

Huang et al. (2006) described the following pattern of As concentrations in the edible parts of the following edible crops: celery > mustard > spinach > lettuce > taro > bokchoy, whereas Warren et al. (2003) found concentrations of As to be greater in lettuce and broccoli than spinach. In agreement with these previous studies, accumulation of As in edible parts of the lettuce was averagely more than mustard green.

3.4.2. Accumulation of As in plant roots

Different pattern of As accumulation in plant roots than plant leaves was observed. Concentration of As at the beginning of transplanting of both plant was nearly the same, but a meaningful difference at the end of the experiment was observed. As shown in Figure 6, accumulation of As was much more in mustard green roots than lettuce. This rise was more pronounced since RHB and MLB added to the soil mainly due to form plant available form of As. Although, accumulation of As in lettuce

http://dx.doi.org/10.1007/s12303-016-0059-0

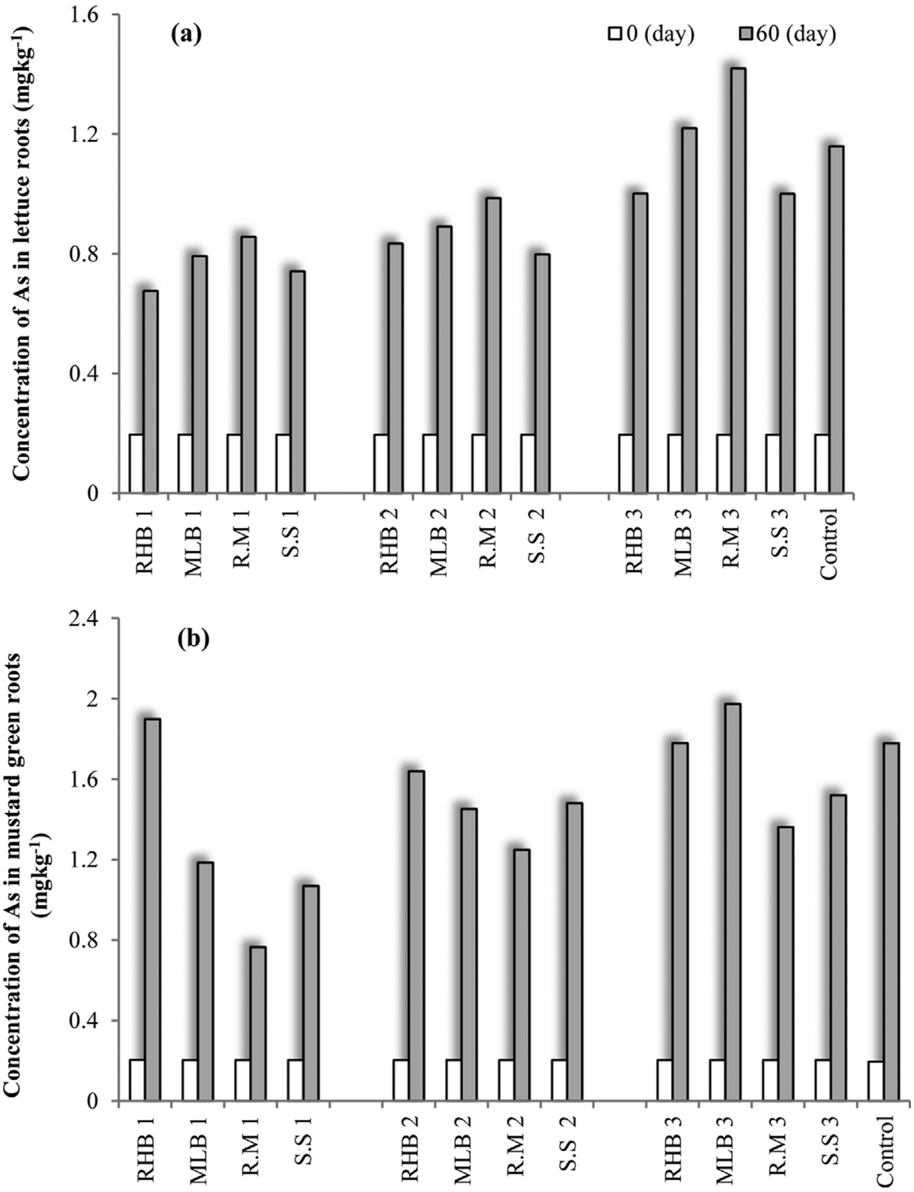

Fig. 6. Effects of different treatments on As accumulation in lettuce and mustard green roots. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag. 1 = 0.5%, 2 = 1%, 3 = 2% mixing ratio.

roots was increased when MLB and R.M (2%) were added to the soil. Generally, results demonstrated a higher ability of mustard green roots in phytoextraction of As through contaminated soil.

3.5. Fractions of As under Different Treatments, before and after Planting

In the soils under study in general, before and after amendments application, the predominant fraction for As was the residual one. Therefore, most As would be in a less extractable or unavailable form, possibly associated to clay minerals and small particles of amendments in treated soils. Results demonstrated exchangeable fractions; especially in treated soils was the least important. There was no substantial difference between As fractions before and after planting for both plants. Without considering the residual fraction, the As before sowing in treated soils was distributed mainly in the reducible (organic matter) and oxidizable fractions (Fe and Mn). Although, As fraction after sowing was mainly bound to organic matter fractions and mainly to Fe and Mn oxides in case of S.S treated soils (Fig. 7). Arsenic present in soils can be associated with several reactive components. Although the total As concentrations may indicate the overall level of As in soils, they provide no information regarding the chemical nature or potential mobility and bioavailability of a particular element (Vijver et al., 2004; Jin et al., 2005; Powell et al., 2005). Particularly in the treated soils with biochar due to high content of P, may have resulted in the section of increased amounts of low-molecular-weight organic acids into the rhizosphere which resulted in high amounts of As organic complex bound species by chelation

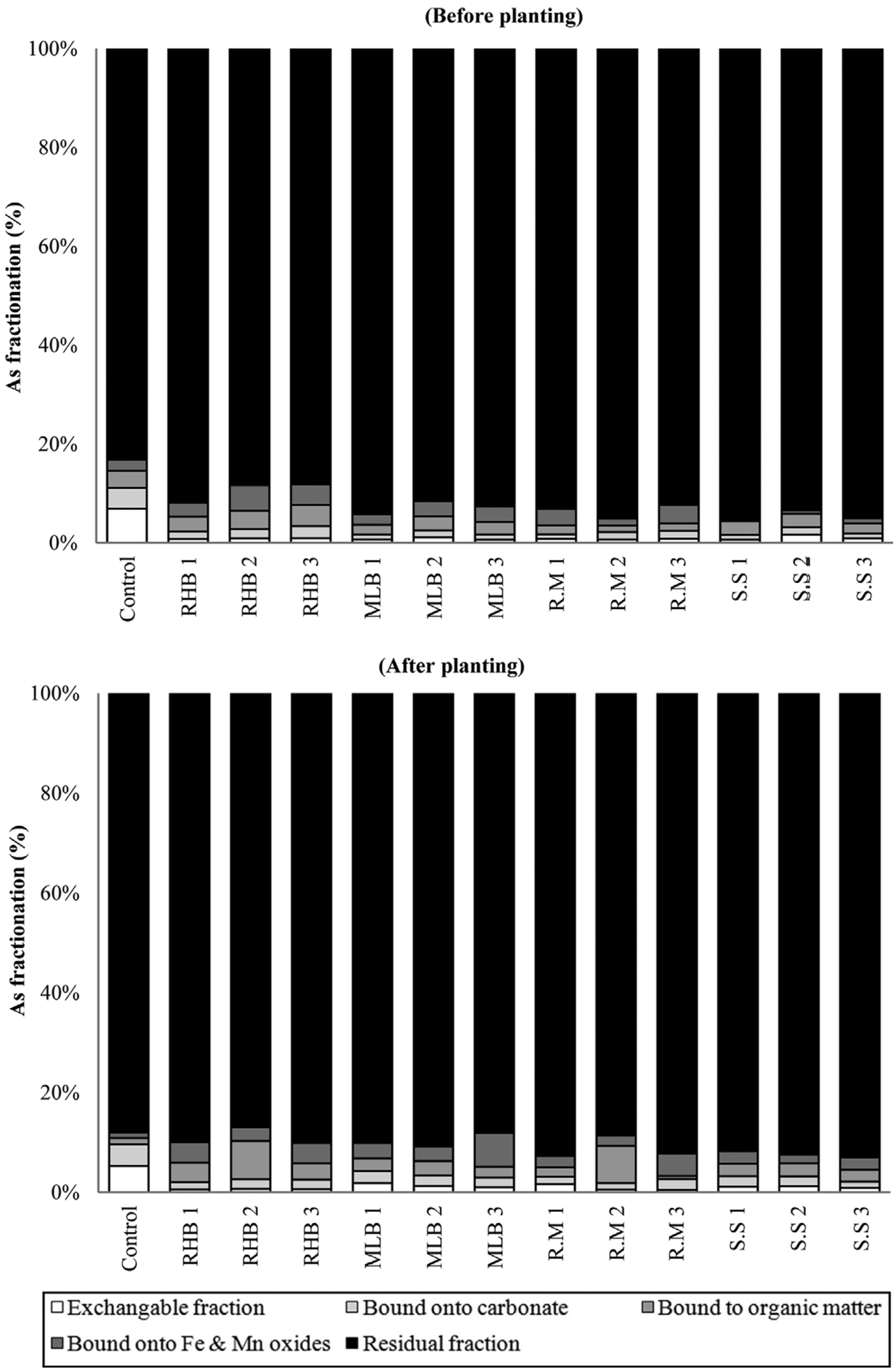

Fig. 7. Distribution of As fractions in different amended soils. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag. 1 = 0.5%, 2 = 1%, 3 = 2% mixing ratio.

and subsequently increased absorption of As through plant roots (Anstoetz et al., 2015; Seshadri et al., 2015).

3.6. Simple Steady-State Mass Balance Model and Related Input Data

To compare the effectiveness of each treatment on the movement of metals through soil, mass balance method in soil, plant, and leachate phases can be performed. A simple mass balance of heavy metals in soil can be expressed as follows (Alloway, 1995):

$$M_{total} = (M_p + M_f + M_a) - (M_{cr} + M_l), \quad (1)$$

where “M” is the heavy metal, “p” is the parent material, “a” is the heavy metal from amendment deposition, “f” is the fertilizer sources, “cr” is crop removal, and “l” is the losses by leaching, volatilization, and so forth. After estimating M_{total}, the percentage of each element in each phase was separately calculated. Results

http://dx.doi.org/10.1007/s12303-016-0059-0

Table 3. Results of mass balance of As in soil, plant and leachate systems according to accumulation percentage (%)

Treatments		Critical load of heavy metals (%)							
		Soil		Aerial part of plant		Root		Leachate	
		LT	MG	LT	MG	LT	MG	LT	MG
RHB	1	77	59	6	4	17	37	0.0	0.1
	2	75	65	5	3	20	33	0.0	0.1
	3	73	67	4	2	23	31	0.0	0.0
MLB	1	78	69	4	4	18	27	0.0	0.0
	2	74	64	5	5	21	31	0.5	0.1
	3	69	56	3	7	27	38	0.2	0.1
R.M	1	76	76	5	7	19	18	0.1	0.1
	2	72	67	6	6	22	26	0.2	0.1
	3	64	64	7	7	29	26	0.5	0.2
S.S	1	78	73	4	5	18	23	0.2	0.1
	2	75	66	5	5	20	29	0.2	0.2
	3	70	63	6	6	24	31	0.4	0.4
Control	0	66	58	8	7	26	35	0.2	0.2

RHB: rice husk biochar, MLB: maple leafbiochar, R.M: red mud, S.S: steel slag.
1: 0.5%, 2: 1%, and 3: 2% DW of amendments.
LT: lettuce, MG: mustard green.

of mass balance of heavy metals in soil, plant and aqueous systems are shown in Table 3. Observations of mass balance indicated high performance of RHB in high application dosage and other amendments in low application dosage for stabilizing As in treated soils. The main reason corresponded to the pH and surface reactions (due to the present of oxyhydroxides on their surfaces) that each one of amendment performed in soil.

3.7. Assessment of Metal Immobilization Efficiency

The effectiveness of different amendments (RHB, MLB, R.M, and S.S) for stabilizing As in contaminated farmland soil was investigated. The results of metal extractions on the unamended and post-amended soils are presented in Figure 8. The stabilization efficiency, E (%) was calculated using equation below (Wuana et al., 2013).

$$E = \left(\frac{M_e}{M_0}\right) \times 100\,, \qquad (2)$$

where, M_0 = concentration of As in unamended soil ($mgkg^{-1}$); M_e = concentration of As in amended soils after plant growth ($mgkg^{-1}$).

A different pattern for As stabilization at different treated soils was observed. Stabilization efficiency of As was steadily increased with increasing in application dosage of RHB agent. On the contrary, a meaning full decline in As stabilization was observed with increasing the application dosage of MLB, R.M, and S.S. The main reason corresponded to the soil pH variation under different treatments. Noteworthy, adding 0.5% of MLB, R.M, and S.S showed a high level of As stabilization as the same as RHB where 2% of that was applied. This is mainly due to presenting oxyhydroxide surfaces which are efficient to absorb As through specific/nonspecific reactions under neutral pH (Bolan et al., 2003).

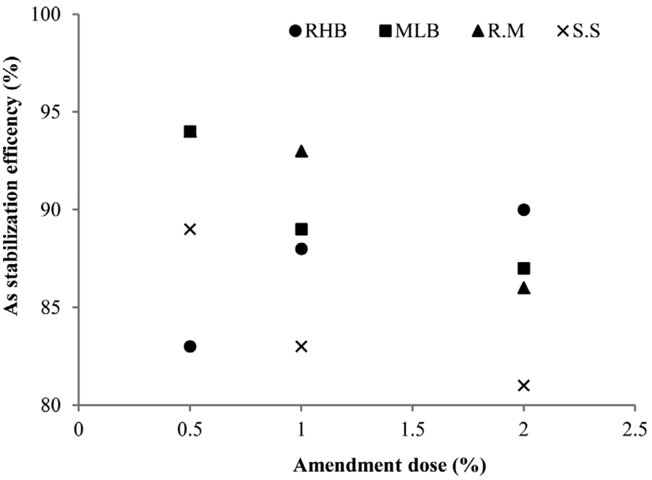

Fig. 8. Efficiency of As stabilization in amended soils with different sorbents. RHB = rice husk biochar, MLB = maple leaf biochar, R.M = red mud, and S.S = steel slag.

4. CONCLUSION

Using soil amendments in small particle sizes in this study caused specific properties for each one. Noteworthy, using such small size of particles reduced the sufficient application dosage of amendments (from high application dosage to only 0.5%). At the end of the experiments, the concentration of remaining As in the treated soils was more than the control, especially in R.M, MLB, and S.S (0.5%) followed by RHB (2%). Therefore, they were distinguished as useful stabilizer amendments for As in soil.

All amendments showed higher CEC value than soil, with relation to the importance to optimum plant growth. The nature of the amendments, high specific surface area (SSA) and porous characteristics of them might be the reason for the higher CEC. Soil pH increased following the adding of amendments.

Compared with the control, all treatments induced a significant increase in As stabilization and a decline in plant metal accumulation, under cultivation of lettuce and mustard green plants. However, plant species was the most effective factor on the amount of As accumulation in plant tissues. Overall, the decline of As in plant leaves was induced by all amendments, and was more pronounced at the end of the experiment. Generally, RHB showed a higher efficiency than MLB in reducing plant uptake due to having high content of phosphorous (P), sulfur (S) and lower pH value.

Sequential extractions generally distinguished only operationally defined fractions. The results of sequential fractionations provided some evidence of the mechanism of fixation following soil amendment applications. The application of the biochars showed an increase in As associated with carbonate and organic matter more than R.M and S.S. Moreover, due to their rich source of Fe and Al, R.M and S.S led to an increase in As shifting into residual fractions. In addition to public health care and prevention, we must develop remediation technologies that are sustainable in the communities affected by As. Specifically, focus must be placed on removal efficiency and the economic impact on the communities.

REFERENCES

Akhtar, M.S., Chali, B., and Azam, T., 2013, Bioremediation of arsenic and lead by plants and microbes from contaminated soil. Research in Plant Sciences, 3, 68–73.

Alloway, B.J., 1995, Heavy metals in soils (2nd edition). Springer, Dordrecht, 368 p.

Anstoetz, M., Rose, T.J., Clark, M.W., Yee, L.H., Raymond, C.A., and Vancov, T., 2015, Novel applications for oxalate-phosphate-amine metal-organic-frameworks (OPA-MOFs): can an iron-based OPA-MOF be used as slow-release fertilizer. PLOS ONE, 10, 1–16.

Beesley, L. and Marmiroli, M., 2011, The immobilization and retention of soluble arsenic, cadmium and zinc by biochar. Environmental pollution, 159, 474–480.

Bergqvist, C., 2011, Arsenic accumulation in various plant types. Licentiate of Philosophy Thesis, Department of Botany, Stockholm University, Stockholm, 30 p.

Bolan, N.S., Adriano, D.C., and Curtin, D., 2003, Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. Advances in Agronomy, 78, 215–272.

Bundschuh, J., Hollander, H.M., and QiyingMa, L., 2015, In-situ remediation of arsenic-contaminated sites. Taylor & Francis Group, London, 208 p.

Cheong, Y.W., Yim, G.J., Ji, S.W., Park, H.Y., Min, D.S., and Park, I.W., 2008, Impact of the rain on the geochemical and hydrological characteristics within a mine waste impoundment at the Geopung mine, Korea. Journal of the Korean Society for Geosystem Engineering, 45, 495–504.

EPA, 2002, Arsenic treatment technologies for soil, waste, and water. Solid waste and emergency response (5102G). www.epa.gov/ti, 3-1.

Giménez, J., Martínez, M., de Pablo, J., Rovira, M., and Duro, L., 2007, Arsenic sorption onto natural hematite, magnetite, and goethite. Journal of Hazardous Materials, 141, 575–580.

Hartley, W., Edwards, R., and Lepp, N.W., 2004, Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environmental Pollution, 131, 495–504.

Hartley, W. and Lepp, N.W., 2008, Remediation of arsenic contaminated soils by iron-oxide application, evaluated in terms of plant productivity, arsenic and phytotoxic metal uptake. Science of the Total Environment, 390, 35–44.

Hartley, W., Dickinson, N.M., Riby, P., and Lepp, N.W., 2009, Arsenic mobility in brown field soils amended with green waste compost or biochar and planted with Miscanthus. Environmental Pollution, 157, 2654–2662.

Hesse, P.R., 1971, A textbook of soil chemical analysis. John Murry Ltd., London, 184 p.

Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., and Nelson, P.F., 2011, Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. Journal of Environmental Management, 92, 223–228.

Huang, R., Gao, S., Wang, W., Staunton, S., and Wang, G., 2006, Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China. Science of the Total Environment, 368, 531–541.

Jin, C.W., Zheng, S.J., He, Y.F., Zhou G.D., and Zhou, Z.X., 2005, Lead contamination in tea garden soils and factors affecting its bioavailability. Chemosphere, 59, 1151–1159.

Jo, I.S. and Koh, M.H., 2004, Chemical changes in agricultural soils of Korea: data review and suggested countermeasures. Environmental Geochemistry and Health, 26, 105–117.

Jung, M.C., 1995, Heavy metal contamination of soil, plants, waters, and sediments in the vicinity of metalliferous mines in Korea. Ph.D. Thesis, University of London, London, 455 p.

Jung, H.B., Bostick, B., and Zheng, Y., 2011, Field, experimental, and modeling study of arsenic partitioning across a redox transition in a Bangladesh aquifer. Environmental Science & Technology, 46, 1388–95.

Kanel, S.R., Choi, H., Kim, J.Y., Vigneswaran, S., and Wang, G.S., 2006, Removal of arsenic (III) from groundwater using low-cost industrial by-products-blast furnace slag. The Water Quality Research Journal of Canada, 41, 130–139.

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A., and Maurice, C., 2006, Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environmental Pollution, 144, 62–69.

Lin, Z. and Puls, R.W., 2000, Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging processes. Environmental Geology, 39, 753–759.

Liu, S.Y., Gao, J., Yang, Y.J., Yang, Y.C., and Ye, Z.X., 2010, Adsorption intrinsic kinetics and isotherms of lead ions on steel slag. Journal of Hazardous Materials. 173, 558–562.

Manning, B.A. and Goldberg, S., 1997, Arsenic (III) and arsenic (V) adsorption on three California soils. Soil Science, 162, 886–895.

Mench, M., Vangronsveld, J., Lepp, N.W., and Edwards, R., 1998, Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. In: Vangronsveld, J. and Cunningham, S.D. (eds.), Metal-contaminated soils: in situ in activation and phytorestoration. Springer, Berlin, p. 151–182.

MicrotracBEL, 2017, Specific surface area and particle size. Seminar on adsorption, Total solution in particle characterization. http://www.microtrac-bel.com/en/tech/bel/seminar06.html

Mohan, D., Pittman Jr, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre Franco, M.F., Gáez-Serrano, V., and Gong, H., 2007, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science, 310, 57–73.

Moreno-Jimenez, E., Esteban, E., and Penalosa, J.M., 2012, The fate of arsenic in soil-plant systems. In: Whitacre, D.M. (ed.), Reviews of rnvironmental contamination and toxicology, volume 215. Springer, New York, p. 1–37. DOI: 10.1007/978-1-4614-1463-6_1

Rim, S.K., Hur, B.K., Jung, S.J., and Hyeon, G.S., 1997, Physico-chemical properties on the management groups of upland soils in Korea. Korean Journal of Soil Science and Fertilizer, 30, 67–71.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., and Sjoberg, S., 2005, Chemical speciation of environmentally significant heavy metals with inorganic ligands, Part 1: The Hg^{2+}, Cl^- , OH^- , CO_3^{-2}, SO_4^{-2}, and PO_4^{-3} aqueous systems. Pure and Applied Chemistry, 77, 739–800.

Prakongkep, N., Gilkes, R.J., Wiriyakitnateekul, W., Duangchan, A., and Darunsontaya, T., 2013, The effect of pyrolysis conditions on the chemical and physical properties of rice husk biochar. International Journal of Material Science, 3, 97–103.

Seshadri, B., Bolan, N.S., and Naidu, R., 2015, Rhizosphere-induced heavy metal(loid) transformation in relation to bioavailability and remediation. Journal of Soil Science and Plant Nutrition, 15, 524–548.

Shipley, S., Nordin, A.B., Tang, C.G., and Kim, S.K., 2008, Phytoremediation for arsenic contamination: arsenate reductase. Undergraduate Journal of Baylor University, 6, 1–12.

Ure, A.M., 1990, Methods of analysis for heavy metals in soils. In: Alloway, B.J. (ed.), Heavy metals in soils. Blackie, Glasgow, 339 p.

Vijver, M.G., Van Gestel, C.A.M., Lanno, R.P., Van Straalen, N.M., and Peijnenburg, W.J.G.M., 2004, Internal metal sequestration and its ecolotoxicological relevance: a review. Environmental Science and Technology, 38, 4705–4712.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G., and Pigna, M., 2010, Mobilityand bioavailability of heavy metals and metalloids in soil environments. Journal of Soil Science and Plant Nutrition, 10, 268–292.

Vithanage, M., Senevirathna, W., Chandrajith, R., and Weerasooriya, R., 2007, Arsenic binding mechanisms on natural red earth. A potential substrate for pollution control. Science of the Total Environment, 379, 244–248.

Warren, G.P., Alloway, B.J., Lepp, N.W., Singh, B., Bochereau F.J.M., and Penny, C., 2003, Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Science of the Total Environment, 311, 19–33.

Woo, N.C. and Choi, M.J., 2001, Arsenic and metal contamination of water resources from mining wastes in Korea. Environmental Geology, 40, 305–311.

Wuana, R.A., Yiase, S.G., Lorungwa, P.D., and Lorungwa, M.S., 2013, Evaluation of copper and lead immobilization in contaminated soil by single, sequential and kinetic leaching test. African Journal of Environmental Science and Technology, 7, 249–258.

Yim, G.J., Ahn, J.S., Cheong, Y.W., Min, D.S., and Baek, H.J., 2009, An evaluation of theinfiltration control of a soil covers overlying tailings impoundment, Korea. Journal of the Korean Society for Geosystem Engineering, 46, 351–361.

Zhang, G., Zhang, O., Sun, K., and Liu, X., 2011, Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. Environmental Pollution, 159, 2594–2601.