Influence of Various Passivators for Nickel Immobilization in Contaminated Soil of China

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Abstract

In agricultural field, nickel (Ni) contamination has become a serious concern/threat all over the world due to its hazardous effects on ecosystem and food chain. An incubation study was conducted to investigate the simultaneous efficiency of rice straw (RS) and its derived biochar (BI), calcium carbonate (calcite), zeolite (ZE), and triple superphosphate (TSP) on the stabilization of Ni in contaminated soil. Various chemical extraction techniques, including the sequential extraction (BCR), leaching toxicity (TCLP) test, and single CaCl_2 extraction, were performed. The results revealed that greater reduction in acid-soluble fractions of Ni was observed by 45%, 65.1%, 42.1%, 55.7%, and 33.9% with RS, BI, ZE, calcite at 2%, and TSP 0.5% application rate, respectively. Similarly, TCLP and CaCl_2 -extractable Ni were significantly decreased by 49.8% and 97.5% with 2% BI application rate, respectively. The soil pH, EC, and organic matter were significantly improved with the incorporation of RS, BI, ZE, TSP, and calcite amendments. Overall, among all the amendments, the incorporation of BI and calcite was considered to be the best option for Ni immobilization and thereby reducing its mobility in Ni contaminated soil. These findings suggest that RS biochar and calcite can be used as Ni stabilizers in contaminated agricultural soils.

Keywords: Biochar; Calcite; Ni immobilization; TSP

Introduction

THE ACCUMULATION OF potential toxic elements (PTEs) in soils has been recognized as one of the major challenges for food security due to their hazardous effects on soil ecosystem (Zhuang *et al.*, 2009; Salam *et al.*, 2018). The PTEs have become more hazardous due to anthropogenic activities such as metallurgy manufacturing, solid waste disposal, mine exploration, paint pigments, and irrigation of untreated water for agricultural production especially in developing countries (Zhao *et al.*, 2014; Shen *et al.*, 2016a). Approximately, 20 million hectares of the total agriculture fields in China have been polluted with PTEs, such as cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), and zinc (Zn) (Ding *et al.*, 2008; Bashir *et al.*, 2018a). Particularly, Ni contamination in soil has become a global concern due to its high environmental and human health risk (El-Naggar *et al.*, 2018; Li *et al.*, 2018). The accumulation of nickel (Ni) has been reported

in the soil due to the weathering of rocks (El-Naggar *et al.*, 2018), municipal and industrial wastes, cadmium batteries, and nickel steel and iron alloys (Khan *et al.*, 2017).

Although Ni is an essential trace element for the proper functioning of plants, its high concentration in soil causes toxic effects on plant growth in polluted soils (Sreekanth *et al.*, 2013; Ramzani *et al.*, 2016). Unfortunately, Ni contamination especially in acidic soil is even more serious because of more susceptibility to Ni leaching into the ground water relative to alkaline soil (Zhang *et al.*, 2015; El-Naggar *et al.*, 2018). Therefore, the immobilization of Ni contaminated soil has become an important task to reduce its mobility within the soil. For this purpose, various remediation techniques have been performed, including physiochemical approaches and phytoextraction (Shaheen *et al.*, 2015; Bashir *et al.*, 2018a). Recently, the use of several organic and inorganic passivators has attained a considerable attention for the remediation of Ni contaminated soils (Shaheen *et al.*, 2015; Radziemska and Mazur, 2016; Khan *et al.*, 2017).

In China, about 25% of crop straw has been incorporated into the soil (Shaaban *et al.*, 2018b). Moreover, Rizwan *et al.* (2016) revealed that the incorporation of rice straw (RS) in contaminated soil not only augmented the immobilized PTEs but also

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improved the soil's health. In the recent decades, Biochar (BI) has attained considerable attention by the researchers due to its availability and ability to detoxify the PTEs. It is prepared from organic biomass through pyrolysis under the limited supply of oxygen (Khan *et al.*, 2017; Shaaban *et al.*, 2018a). BI has exclusive physical and chemical attributes such as high alkalinity, large specific surface area, high cation exchange, porosity, and more functional groups (Shen *et al.*, 2017; Salam *et al.*, 2018), which can play a vital role to immobilize the Ni in contaminated soils (Shaheen *et al.*, 2015; Shen *et al.*, 2017). In addition to this, BI showed significant potential to improve soil physiochemical properties, immobilize PTEs, and reduce their toxicity to plants when incorporated in contaminated soils (Ramzani *et al.*, 2016; El-Naggar *et al.*, 2018).

Besides this, calcium carbonate (calcite) is an oldest and common chemical passivator that could increase PTE immobilization through adsorption and ion exchange mechanism (Zhai *et al.*, 2018). Consequently, BI (Shaaban *et al.*, 2018a; Zhai *et al.*, 2018) and calcite (Lombi *et al.*, 2003; Mallampati *et al.*, 2012; Huang *et al.*, 2016) are considered as the efficient and common immobilizing agents for acid soil restoration. It has been reported that the incorporation of BI and calcite to Ni contaminated soil improves soil health, minimizes the PTE accumulation in plants, and thereby improves their dry biomass (Lee *et al.*, 2009; Cui *et al.*, 2016b; Shahbaz *et al.*, 2018). Furthermore, Huang *et al.* (2016) reported that calcite can be used to remediate PTEs' polluted soils as it has large surface area porous structure, which may contribute to increase Ni immobilization in the soil through adsorption and surface complexation (Hung *et al.*, 2016; Lahori *et al.*, 2017).

Similarly, zeolite (ZE) is crystalline inorganic mineral belonging to the aluminosilicate family that exhibits high adsorptive ability for anion and other molecules due to larger specific area (SSA), porous structure, and high cation exchange capacity (CEC) (Bashir *et al.*, 2018c). Up to now, phosphate, especially triple superphosphate (TSP), has been widely applied for the remediation of heavy metals in polluted soils, as well as in water (Huang *et al.*, 2016; Rizwan *et al.*, 2016a). Li *et al.* (2015) concluded that application of TSP in contaminated soils increased phosphorus and carbon content, which could contribute to heavy metal mobility within soil profile. During the last decade, adequate research has been done for the better understanding of heavy metal immobilization using various types of inorganic and organic passivators in contaminated soils. However, a limited knowledge is available regarding the comparative efficacy of various types of organic and inorganic alkaline materials, that is, RS, RS biochar (BI), TSP, ZE, and calcite for Ni stabilization in acidic contaminated soils. Thus, we hypothesized that the selected organic and inorganic materials will alter soil properties or enhance the sorption/adsorption mechanisms for Ni in soil and, thus, reduce Ni availability. Therefore, the aim of this study was: (1) to test the relative efficiency of organic and inorganic amendments on Ni immobilization in contaminated soil and (2) to evaluate the influence of amendments on Ni transformation, leachability, and soil physiochemical properties.

Materials and Methods

Sampling of soils

Soil samples, characterized as brown red soil, were collected from surface layer (0–20 cm) from Jiangxia District,

Wuhan, Hubei, China (30°17.804'N, 114°19.246'E). These were transferred to the laboratory in polyethylene bags. Soil samples were mixed and dried at room temperature. Samples were crushed manually and passed through 2 mm sieve.

Soil characterization and amendments

RSs were obtained from a cropland area of Huazhong Agricultural University, Wuhan, Hubei, China. These were washed with tap water, rinsed with distilled water, and air-dried. The air-dried straws were chopped (1 mm), and chopped samples were placed in ceramic crucibles covered with a close-fitting lid in the absence of oxygen. RS biochar was produced at 500°C pyrolysis temperature in controlled muffle furnace (TDW-2001 1300) for 2 h (Lu *et al.*, 2014; Bashir *et al.*, 2018b). TSP, ZE, and calcite were of pro-analytical grade. Total concentration of Ni was determined in all amendments by standard Aqua Regia (HCl–HNO₃–HClO₄) digestion method and analyzed using atomic absorption spectrophotometer (AAS) model: Agilent AA-240FS. The pH and EC of all amendments were also tested.

Experimental design and treatments. In incubation study 200 g of air-dried sieved (<2 mm) soil was placed in each plastic cup. Soil was spiked with Ni (SO₄·6H₂O) salt to obtain 100 mg Ni/kg concentration in soil. Soil was incubated at 70% water-filled porespace (WFPS) at 25°C ± 1°C for 60 days. The contaminated soil was thoroughly mixed with RS, BI, calcite, and ZE at the application rate of 1% and 2%, while TSP was added to soil at the rate of 0.2% and 0.5% (w/w) based on previous studies (Huang *et al.*, 2016; Rizwan *et al.*, 2016a; Bashir *et al.*, 2018) and no amendment in the controlled soil. Each treatment had three replicates. The moisture of soil was adjusted to 70% WFPS after mixing with these passivators in the soil. All plastic cups were covered with a thin plastic lid (containing 80 pin holes) to allow gas exchange and to reduce the moisture loss. Finally, all plastic cups were again incubated at 25°C for 65 days. During this incubation period, the moisture content in all cups was maintained at 70% WFPS using distilled water.

Chemical analyses. Soil pH and electrical conductivity (EC) were measured with the ratio of soil:water (1:5, 1:2.5 v/w) using Mettler Toledo Delta 320 pH meter and DDS-307 EC meter, respectively, according to the method of Bashir *et al.* (2018d). The organic matter and total nitrogen content of soil were analyzed using H₂SO₄–K₂Cr₂O₇ wet oxidation and Kjeldahl method (Lu, 1999). Available phosphorus (P) was extracted using 0.5 mol l^{−1} sodium bicarbonate (NaHCO₃) and then measured by spectrophotometer, while available potassium (K) was extracted with ammonium acetate according to Lu (1999). The particle size of sand, silt, and clay was measured using pipette method (Gee *et al.*, 1986). The CEC was evaluated at pH 7.0 using ammonium acetate method (Hendershot *et al.*, 1993). The elemental composition of all amendments was measured by Micro series Analyzer (EA3000, Italy), and SSA was evaluated with the BET–N₂ method using a surface area analyzer (AUTOSORB-IMP-CR). Total concentration of Ni in soil was determined by AAS (model: Agilent AA-240FS) followed by standard Aqua Regia (HCl–HNO₃–HClO₄) digestion method (Lu, 1999).

Ni fractionation and mobility. The sequential extraction technique European Community Bureau of Reference (BCR)

was adopted to measure the Ni partitioning among different fractions (Rauret *et al.*, 1999), which was described in detail by Bashir *et al.* (2018a). Briefly, in the first step (acid soluble fraction), the test soil 500 mg was extracted with 20 mL of 0.11 M $C_2H_4O_2$; after that, the extractants were shaken in a thermostatic reciprocating shaker with 200 rpm at 25°C. After that the extractants were separated by centrifugation at 4000 rpm for 20 min, and then aliquot was filtered, stored at 4°C, and concentration of Ni was determined by AAS. In the second step (easily reducible fraction), remaining soil residues from first step were again extracted with 20 mL of 0.1 M NH_2OH in a similar way as described briefly in step 1. In the oxidizable fraction (step 3) remaining soil residues from second step were digested twice in a water bath at 85°C with 10 mL 8.8 M H_2O_2 , acidified to pH 2–3, and then again extracted with 25 mL 1.0 M $NH_4CH_3CO_2$ in a similar way as described briefly in step 1. In the fourth step (residual fraction), the residual soil from third step was air-dried, grinded, and digested with standard Aqua Regia ($HCl-HNO_3-HClO_4$). After digestion, the samples were diluted to 25 mL with deionized water, stored at 4°C, and the concentration of Ni was determined by AAS. Each treatment was performed in triplicate to obtain the mean value.

The leaching toxicity (TCLP) of Ni was analyzed by acetic acid solution (pH 2.88) following the procedure of Bashir *et al.* (2018a). Briefly, TCLP extractable Ni was performed by acetic acid in centrifuge tube by mixing 1.0 g of air-dried soil with 0.1 M acetic acid extracting solution (1:20 w/v), shaken for 18 h, centrifuged, filtered, and measured the Ni concentration by AAS. Similarly, 2.0 g air-dried soil sample from each treatment was extracted with 0.001 M $CaCl_2$ (1:10 w/v) followed by Houben *et al.* (2013b). The available Ni concentration in soil was determined by AAS model: Agilent AA-240FS. Blanks and the certified reference material (GBW07405) Geophysical Geochemical Exploration, Geological Sciences Institute, Chinese Academy of Sciences, IGGE, Hubei, China were used in all analyses for quality control.

Statistical analysis

Since the data were normally distributed (Shapiro–Wilk test, $p < 0.05$), the significance of differences between treatments was checked by one-way ANOVA, using Tukey's test ($p < 0.05$) for *post hoc* comparisons. Results are expressed as mean $\pm$ standard error.

Results and Discussion

Physicochemical properties of soil and amendments

The basic physicochemical properties of soil, organic, and inorganic passivators are given in Tables 1 and 2. The results revealed that soil texture was classified as silty clay loam with acidic nature (pH 5.3 ± 0.02) and low organic matter (14.79 ± 0.43 g/kg). Moreover, all the passivators were alkaline except TSP, which was highly acidic (pH 2.5 ± 0.003). In addition, BI had highest C content (47.07%) followed by RS 36.40% and calcite 12.12% (Tables 1 and 2).

Influence of amendments on chemical characteristics of soil

The results of soil pH and EC are presented in Figures 1 and 2. The incubation study confirmed that the applications of organic and inorganic passivators, such as BI, calcite, RS,

TABLE 1. SELECTED CHARACTERISTICS OF THE SOIL

Parameter	Soil
pH	5.3
EC (mS/cm)	0.2
Texture	Silty clay loam
Sand %	12.46
Silt %	50.72
Clay %	36.82
Organic matter (g/kg)	14.79
CEC (cmole/kg)	12.75
Total Ni (mg/kg)	35
Total Nitrogen (mg/kg)	1.25
Available Phosphorus (mg/kg)	8.74
Available Potassium (mg/kg)	150

ZE, and TSP, significantly ($p < 0.05$) improved the chemical properties of Ni contaminated soils. The application of various passivators in polluted soil showed the significant increase in soil pH and EC as illustrated in Figures 1 and 2. The addition of calcite at 1% and 2% to Ni contaminated soil showed the highest increases in soil pH values (7 ± 0.05 – 7.7 ± 0.004) compared to all amendments and control. Our results were consistent with the observation of Houben *et al.* (2013a) who showed that the addition of liming agent like calcite logically increased the soil pH due to its alkaline nature and contained the sufficient amount of Ca^{2+} , which increased alkaline condition in contaminated soils. Similarly, the addition of BI showed the prominent increment in soil pH compared to control (Fig. 1). The similar trend was also observed by the previous study (Uchimiya *et al.*, 2010). We assumed that an increment in soil pH could attribute to the alkaline nature, more functional groups, more carbonates, and ash content of BI (Yuan *et al.*, 2011). BI could promote heavy metal immobilization through the adsorption and precipitation (Zhang *et al.*, 2013). Generally, in all amendments, values of soil pH after 65 days of incubation period increased in the order of calcite 2% > calcite 1% > BI 2% > BI 1% > RS 2% > RS 1% > TSP 0.2% > TSP 0.5% > ZE 2% > ZE 1% > CK.

Similarly, the EC of soil EC was also influenced when BI, calcite, RS, ZE, and TSP were applied at the rate of 1% and 2% (Fig. 2). Compared to the CK, the incorporation of TSP, BI, and calcite at 0.5 and 2% showed the highest increase in soil EC values (235 ± 3.77 , 230 ± 3.86 , and $194.1 \pm 4.39 \mu S \cdot cm^{-1}$). This trend was similar with the study of Rizwan *et al.* (2016b).

TABLE 2. ORGANIC AND INORGANIC PASSIVATOR PHYSICOCHEMICAL CHARACTERISTICS

Parameter	Rice straw	Biochar	Calcite	Zeolite	TSP
pH	6.8	10.29	8.6	8.2	2.5
EC (mS/cm)	—	1.1	0.1	1.1	0.001
Total Ni (mg/kg)	1.5	10.75	0.75	1.5	N/D
BET-SA (m^2/g)	2.3	14.5	1.77	17.13	3.66
C %	36.4	47.07	12.12	—	—
N %	1.99	2.53	0.102	0.026	0.011
O %	40.19	17.5	32.7	10.08	26.83
H %	5.86	1.96	—	0.295	1.83
Ash %	—	65.3	—	—	—
Yield %	—	33	—	—	—

FIG. 1. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on soil pH. Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

However, 2% of RS and ZE showed slight increase in soil EC values (104 ± 1.64 and $86.6 \pm 0.74 \mu\text{S}/\text{cm}$) compared to CK. Overall, in all amendments, the values of soil EC after 65 days of incubation period increased in the order of TSP 0.5% > BI 2% > calcite 2% > calcite 1% > TSP 0.2% > BI 1% > RS 2% > RS 1% > ZE 2% > ZE 1% > CK.

Similarly, the soil organic matter (SOM) of the brown red soil was increased from 37–68.5%, 16–50% to 10–14%, when soil was amended with BI, RS, and calcite at 1% and 2%, respectively, relative to the CK (Fig. 3). Our findings are

FIG. 2. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on soil electrical conductivity (EC). Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

FIG. 3. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on soil organic matter (SOM). Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

in accordance with the study of Shaaban *et al.* (2018b) who investigated that the increase in SOM was due to the greater level of C content in the applied organic and inorganic passivators such as BI, RS, and calcite. Similarly, Bashir *et al.* (2018b) also concluded that the addition of BI into acidic contaminated soil increased SOM content, which prominently increased the habitat for soil organisms.

Fractionation of Ni

The concentrations of Ni in different soil fractions are illustrated in Fig. 4. The acid soluble proportion of Ni was decreased with the increasing rates of various soil amendments. The addition of calcite at 1% and 2% showed the significant reduction in acid soluble portion of Ni by 51.2–55.7%, respectively, relative to CK. Similarly, the greater reduction (54.3–65.1%) was observed in acid soluble portion of Ni when 1% and 2% BI was added, respectively, relative to CK (Fig. 4). These findings suggested that the incorporation of BI and calcite in Ni contaminated soil was considered as more effective for Ni immobilization/stabilization during an incubation period. Thus, it can be demonstrated that addition of alkaline materials to acidic soil could ameliorate soil acidity and increase the soil pH, which might contribute to enhance Ni immobilization through adsorption and precipitation. The results suggested that the maximum immobilization of Ni was occurred due to its transformation from soluble to residual portion. These results are in line with the study of El-Naggar *et al.* (2018) who suggested that BI was proved to be a suitable candidate to stabilize Ni and to remediate contaminated soil. The decreases in acid soluble phase of Ni could be due to the larger surface area and higher sorption ability of BI (Shen *et al.*, 2017; Bashir *et al.*, 2018c).

The concentration of Ni in reducible portion was also increased under the same condition as shown in Fig. 4, particularly, 1% and 2% of BI showed the higher content of Ni in

FIG. 4. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on Ni fractionation. Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

reducible portion by 26–31.7%, respectively, relative to CK (Fig. 4). These obtained findings also indicated that the application of calcite, RS, TSP, and ZE increased the reducible portion of Ni. It could be demonstrated that the incorporation of BI showed the formation of Fe-Mn oxides and bonds with the mineral phase of BI, which ultimately resulted in the formation of an insoluble stable complex form of metals (Shaheen *et al.*, 2015).

The oxidizable proportion of Ni was also significantly increased with the addition of 1% and 2% BI and recorded as 11.5% and 17%, respectively. The oxidizable portion of Ni enhanced with the increasing calcite and RS application. Furthermore, the incorporation of other amendments also increased residual portion of Ni. The residual phase of PTEs was strongly bounded with inner sphere in contaminated soil. These results showed that BI had greater impact and more longevity as a passivator in terms of Ni reduction bioavailability. The BI, calcite, RS, ZE, and TSP at 2% and 0.5% application rate increased the residual proportion of Ni by 129%, 95.6%, 66.1%, 48%, and 41%, respectively, compared to the unamended (CK). In our study, BI was considered more potential amendment for Ni immobilization in soil compared to other passivators in the contaminated soil. According to the results, the acid-soluble phase of Ni was decreased, while the reducible portion was increased with the increasing rate of BI, calcite, and RS. Obviously, BI has greater surface area, higher CEC, and pH values, and the functional groups on the surface have the ability to reduce Ni toxicity in contaminated soil, as well as increase the Ni immobilization. These findings are similar with the previous reports (Shen *et al.*, 2016b; Bogusz and Oleszczuk, 2018). It can be demonstrated that Ni ion can make complexes with functional groups present on BI surface such as carboxylic, phenolic, and hydroxylase compared to the other passivators, which might contribute to enhance the oxidizable and residual portion of Ni metal in contaminated soil (Rees *et al.*, 2014; Bashir *et al.*, 2018a). The greater immobilization of Ni by BI transformed the easily available fraction to geochemically more stable residual portion, thus the availability and activity of Ni decreased (Jalali and Hemati, 2012; Wu *et al.*, 2013).

CaCl₂ and TCLP extractable Ni

The changes in extractable Ni by CaCl₂ in Ni contaminated soil amended with various organic and inorganic passivators are illustrated in Fig. 5. All the treatments showed a decreasing trend for soil CaCl₂ extractable Ni after 65 days of incubation period. The CaCl₂ extractable Ni was significantly decreased by 95–97.5% when treated with 1% and 2% of BI, respectively. In contrast, the application of RS and calcite at the rate of 1% and 2% significantly decreased the extractable concentration of Ni from 85.5–87.9% to 95–95.9% compared to CK (Fig. 5). According to Zeng *et al.* (2011), soil pH is a key factor to examine the heavy metal fractions and their soluble pools in polluted soils. Our results also showed that the incorporation of BI could decrease the leachability and mobility of Ni due to the large surface area, high adsorption

FIG. 5. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on CaCl₂ extractable Ni. Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

FIG. 6. Effects of amendments (rice straw, biochar, zeolite, triple superphosphate, and calcite) on TCLP extractable Ni. Treatments: control (CK), rice straw (RS), biochar (BI), zeolite (ZE), triple superphosphate (TSP), and calcite.

capacity, and precipitation of soluble ions due to the effective increase in soil pH after these amendments (Shen *et al.*, 2017). The obtained results are similar with the investigation of previous studies (Cui *et al.*, 2016a; El-Naggar *et al.*, 2019). Consequently, BI and calcite had volatile, porous, carbonaceous, and larger pore size and greater surface area, which provided the maximum adsorption capacity. Calcite is an effective option for heavy metal stabilization in polluted soils as Lahori *et al.*, (2017) suggested that calcite have immense tendency to react with heavy metals it can be exhibited by Ca^{2+} in various frictions in calcite. Similarly, Tahervand and Jalali, (2017) investigated that the mobility of heavy metals was decreased by calcite because of its high pH and crushed brick and gravel nature. They investigated that calcite decreased >90% of PTEs. Similarly, Rizwan *et al.* (2016a) reported that the application of RS showed the noticeable reduction in the metal concentrations in CaCl_2 extract. BI, calcite, and RS had a positive effect on Ni stabilization in contaminated soil. It can be described that high pH and calcareous nature of BI and calcite have ability to minimize Ni mobility in acidic contaminated soils. Overall, in all amendments, the values of CaCl_2 extractable Ni after 65 days of incubation period reduction were in the order of BI > calcite > RS > TSP > ZE > CK.

Similarly, according to the obtained findings, the concentration of TCLP extractable Ni was significantly ($p < 0.05$) decreased in organic and inorganic amendments, specifically with the addition of BI and calcite (Fig. 6). The influence of BI and calcite was considered as more effective for Ni reduction in TCLP extractable Ni. The main mechanism for TCLP Ni reduction in contaminated soil might be due to the greater increase in soil pH, which could promote the metal precipitation in the forms of hydroxides, phosphates, and carbonates, after the incorporation of BI and calcite (Houben *et al.*, 2013a). The BI, calcite, and RS applied at 1% and 2% application rate decreased the leachability of Ni by 46.5–

49.8%, 34–45.7%, and 7–34%, respectively, compared to CK. These trends are almost similar with the results reported by Lu *et al.* (2017) that revealed that the application of organic material such as BI decreased the PTEs due to its liming properties, volatile and aromatic substance, and large surface area with high porosity and high CEC. Moreover, the obtained findings also confirmed that the addition of RS exhibited less reduction in TCLP extractable Ni. Furthermore, the application of calcite also showed the reduction in TCLP extractable Ni, at the rate of 2% by 45.7%. Overall, in all amendments, the values of TCLP extractable Ni after 65 days of incubation period reduction were in the order of BI > calcite > RS > TSP > ZE > CK.

Conclusions

The incorporation of RS, BI, and calcite could be proficient to alleviate Ni toxicity through reducing the bio-available Ni concentration (CaCl_2 extractable) and leaching (TCLP) in soil. Overall, BI applied at the rate of 2% recognized the most effective organic passivators as a soil amendment for Ni stabilization in contaminated soil. The immobilization of Ni in soil could be due to the large surface area, alkalinity, and greater CEC of RS derived biochar, while calcite was observed to be effective due to its high pH, which ameliorates soil acidity and Ni mobility in polluted soil. In addition, the stabilization/immobilization of potential toxic heavy metal especially Ni contaminated soil by these passivators need to be assessed on field conditions. It is suggested that further studies should be conducted to elucidate the effect of various passivators on Ni immobilization under field conditions.

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