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Research Article

Influence of *Gliricidia sepium* Biochar on Attenuate Perchlorate-Induced Heavy Metal Release in Serpentine Soil

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Perchlorate (ClO_4^-) is a strong oxidizer, capable of accelerating heavy metal release into regolith/soil. Here, we assessed interactions between ClO_4^- and serpentine soil to simulate and understand the fate of Ni and Mn and their immobilization with the presence of biochar (BC). A soil incubation study (6 months) was performed using serpentine soil in combination with different ClO_4^- concentrations (0.25, 0.5, 0.75, and 1 wt.%) and three different amendment rates (1, 2.5, and 5 wt.%) of *Gliricidia sepium* BC. Bioavailable fraction of Ni and Mn was analyzed using $CaCl_2$ extraction method. An increase of ClO_4^- concentrations enhanced bioavailability fraction of Ni and Mn. However, BC amendments reduced the bioavailability of Ni and Mn. In comparison, 5% BC amendment significantly immobilized the bioavailability of Ni (68–92%) and Mn (76–93%) compared to other BC amendment rates. Electrostatic attractions and surface diffusion could be postulated for Ni and Mn immobilization by BC. In addition, ClO_4^- may have adsorbed to BC via hydrogen bonding which may reduce the influence of ClO_4^- on Ni and Mn mobility. Overall, it is obvious that BC could be utilized as an effective amendment to immobilize Ni and Mn in heavy metal and ClO_4^- contaminated soil.

1. Introduction

Perchlorate is an inorganic anion and strong oxidizer and can contaminate water and soil due to the dissolution of solid salts of ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+) perchlorate and perchloric acid ($HClO_4$) in water [1, 2]. A wide variety of anthropogenic activities (i.e., fireworks, explosives, stick matches, highway safety flares, and military operations) lead to contamination of ClO_4^- in soil system [3]. In this sense, the presence of ClO_4^- in soil may aid in accelerated mineral dissolution, therefore, increasing heavy metal release potential into the soil and groundwater. It has been experimentally observed that the rate of dissolution of minerals increases with the addition of perchloric acid in ulexite which is considered as one of the most common boron-containing minerals [4]. In addition, Senanayake et al. [5] examined the dissolution of Ni and Co in the presence of perchloric acid in laterite. Moreover, Majima et al. [6] investigated dissolution of Fe in goethite and hematite in the presence of perchloric acid. Therefore, the interaction between ClO_4^- and heavy metal contaminated sites may tend to dissolve heavy metals, and, consequently, it could be a possible pathway for leaching metals to the water bodies and, eventually, accumulate in living organisms through the food chain [7].

Heavy metals continue to pose environmental contamination worldwide (i.e., naturally contaminated soils, industrially contaminated urban soils, shooting ranges, and mining sites) [8–11]. Rajapaksha et al. [8] demonstrated that Ni and Mn have been released from the serpentine soil in Ussangoda in Sri Lanka at rates of 1.55×10^{-13} and 7.89×10^{-14} mol m^{-2} s^{-1}, respectively, with the presence of inorganic (sulfuric, nitric, and hydrochloric) and organic (citric, acetic, and oxalic) acids. In addition, Vithanage et al. [12] examined four serpentinite bodies in Sri Lanka in order to assess the bioavailability fraction and the results revealed that bioavailability fraction of Ni and Mn was ranged between 33 to 323 mg kg^{-1} and 11 to 76 mg kg^{-1}, respectively. Different kinds of techniques (i.e., subsurface barriers, chemical treatment, phytoremediation, and soil washing) have been introduced and proposed to remediate heavy metal contaminated soils and they could change the chemistry of the soil media which may reduce the mobility and bioavailability of heavy metals. In this context, BC is recognized to be an effective adsorbent for heavy metals [13].

Biochar is produced through the thermochemical process of biomass under oxygen limited conditions [14, 15]. Different types of biomass such as forestry and agricultural crop residues, invasive plant species, wood waste, animal manures, and organic portion of municipal solid waste have been used as feedstock for producing BC [16–19]. However, pyrolysis conditions, together with feedstock characteristics, mainly govern the physical and chemical properties of the resulting BC [13]. Furthermore, application of BC to soil system has shown a significant importance possibly due to its ability to improve soil nutrient content and water holding capacity as well as carbon sequestration, therefore minimizing greenhouse gas emissions [20–22].

Biochar amendments onto contaminated soils would greatly reduce the total metal concentration and bioavailability fraction [23–26]. For instance, Ahmad et al. [27] found that soybean stover-derived BC more efficiently immobilized Pb (88%) and Cu (87%) in shooting range soil in Cheorwon-gun in Gangwon-do, Korea. In another study, the sequential extraction results in a long-term (three years) field experiment reported that BC amendment (0.5–2%) increased the residue fractions of Ni(II) (from 51% to 61–66%) and Zn(II) (from 7% to 27–35%) [28]. Possibly due to the high porous microstructure, pH, active functional groups, surface area, and cation exchange capacity, BC may immobilize heavy metals through different processes (i.e., adsorption, ion exchange, precipitation, and surface complexation) [29, 30]. Hence, we hypothesized that BC may be a possible material to be used in the attenuation of heavy metals in ClO_4^- contaminated soil. In this study, the serpentine soil was used as a model soil due to the high heavy metal concentrations and bioavailability [12, 31]. Although it has been observed that the ClO_4^- addition may increase the heavy metal release and enhance leaching, no studies have focused their attention on immobilizing the metals released due to ClO_4^-. Therefore, this study assessed the effectiveness of BCs derived from *Gliricidia sepium* biomass on the Ni and Mn immobilization in a serpentine soil with the presence of ClO_4^-.

2. Experimental Section

2.1. Soil Collection and Characterization. Serpentine soil, obtained from Yudhaganawa (latitude 7° 71′ 67″ N and longitude 80° 93′ 33″ E), Sri Lanka, was used for this study. The soil was collected from 0 to 15 cm below the surface, air-dried, and mechanically sieved to <2 mm fraction.

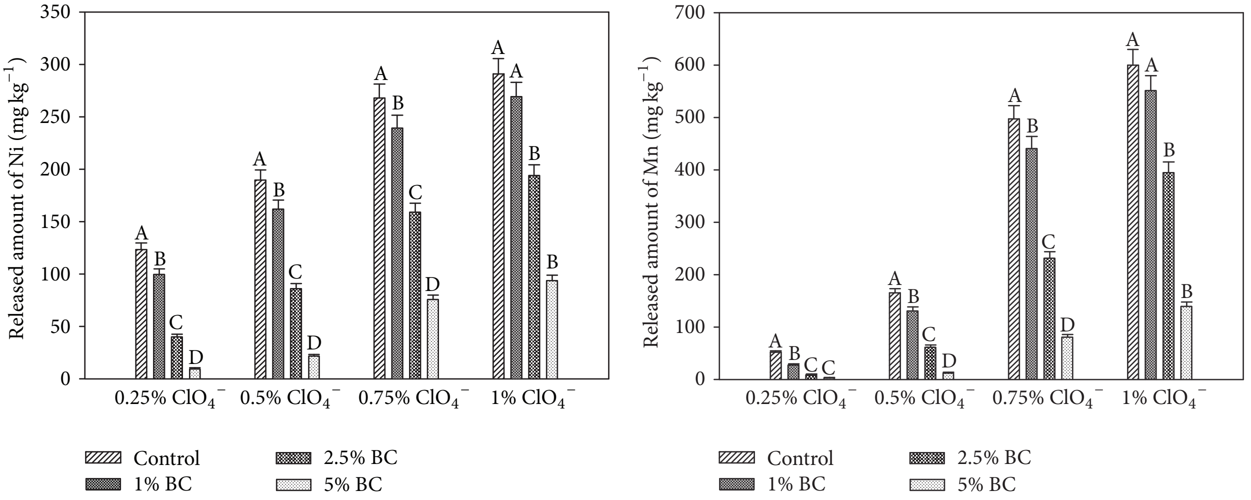
The total heavy metal concentrations in serpentine soil was analyzed by completely dissolving the sample in a closed vessel device using temperature controlled microwave heating system (Mars 6, CEM Corporation) with a mixture of hot, concentrated HNO_3 and HCl.

2.2. Biochar Production and Characterization. Biochar was collected as a waste byproduct from a bioenergy industry at Thirappane, north central province, Sri Lanka, where biomass of *Gliricidia sepium* was gasified to produce electricity. The reactor temperature of this process is maintained at 900°C and the limited air is used for the gasification. The obtained BC was air-dried and ground to less than 1 mm before use. The characteristics such as pH and electrical conductivity (EC) were measured in 1 : 5 suspensions of BC-to-water using a digital pH meter (702SM Titrino, Metrohm) and electrical conductivity meter (Orion 5-Star Meter, Thermo Scientific), respectively. Proximate analysis was conducted based on the experimental procedure given in Ahmad et al. [32]. Elemental compositions, BET surface area, pore volume, and pore size of *Gliricidia sepium* BC were obtained from our previous study [23].

Spectral characteristics of bare *Gliricidia sepium* BC and ClO_4^- adsorbed BC, which was obtained reacting 1% ClO_4^- solution and *Gliricidia sepium* BC (2.5 w/v) for 3 h at room temperature (~30°C), were analyzed by Fourier Transform Infrared (FTIR) Spectroscopy (Nicolet 6700, USA). A wavelength range of 500–4000 cm^{-1} was used to obtain FTIR spectra with 128 scans at a resolution of 6 cm^{-1}. Sample pellets were prepared for FTIR by mixing 4 mg of samples with fused 100 mg of KBr. Spectral analyses were performed using OMNIC (version 8.0) software tools (Nicolet 6700, USA).

2.3. Soil Amendments and Incubation Experiment. An incubation experiment was performed for serpentine soil with adding different ClO_4^- concentrations (1, 0.75, and 0.5 w/w) by using $HClO_4$ acid (AR, BDH, 70%) and different BC amendment rates (1, 2.5, and 5 w/w). In addition, controls (without BC) were used for purposes of comparison. To ensure homogeneous distribution of ClO_4^-, soil samples were mixed thoroughly after the addition of ClO_4^-. Serpentine soil (100 g) was placed in polypropylene bottles, and perchloric acid was added with three different concentrations mentioned above. In addition, water was added to ~70% of water holding a capacity of the soil and then allowed for the incubation in airtight condition at room temperature (~30°C) for 6 months. Each treatment was performed in triplicate. After 6-month incubation period, single extraction ($CaCl_2$ extraction) was performed to evaluate the bioavailability of Ni and Mn. Serpentine sediment (1 g) was extracted with 10 mL of 0.01 M $CaCl_2$. The solid solution was stirred for 2 h. The soil solution was centrifuged, filtered through membrane filtration (0.45 μm), and analyzed for Ni and Mn using Atomic Absorption Spectrometry (AAS-Model GBC 933 AA).

2.4. Statistical Analysis. Statistical analysis was performed to compare how different BC amendment rates influence the immobility of Ni and Mn in serpentine soil. All results were expressed as the mean values. Data were analyzed by using one-way analysis of variance (ANOVA). The mean separation was done using Duncan's Multiple Range Test (DMRT) (at $P = 0.05$). The Pearson correlation coefficient is used to measure the strength of linear associations. All statistical analyses were carried out using SAS statistical software package (SAS 9.1).



(a)

(b)

Figure 1: Effect of different rates of BC amendments on bioavailability of heavy metals, (a) Ni and (b) Mn. Letters (A, B, C, and D) within a single graph indicate whether the means significantly differ from each other. Means topped with the different letter differ significantly ($p = 0.05$) and vise versa.

3. Results and Discussion

3.1. Biochar and Soil Characteristics. Characteristics of the *Gliricidia sepium* BC are summarized in Table 1. The data demonstrate that fixed carbon amount of *Gliricidia sepium* BC is higher than that of mobile matter indicating loss of volatile matter during the thermal decomposition. It is known that mobile and fixed carbon in BCs are prevailing factors in terms of short-term and long-term availabilities of carbon in soil system [27]. The relatively high amount of ash content indicated the accumulation of inorganic minerals as well as organic matter combustion residue [33]. The high BET surface areas in *Gliricidia sepium* BC could be attributed to the developments of mesopores, as indicated by their pore sizes of 4.08 nm. Atomic H/C and O/C ratios are an index of aromaticity and carbonization. Comparatively, a low ratio of H/C and O/C is possibly due to the dehydration, decarboxylation, and decarbonylation of *Gliricidia sepium* biomass [34].

It is obvious that soil pH significantly affects the mobility of metals [35]. Typically, BC is alkaline in nature and, therefore, it would play a major role for immobilization of metals on one hand and mobilization of oxyanions on the other hand. In addition, owing to the liming effect of BC in soil, BC could affect the sorption of metals. According to Table 2, it clearly shows that soil pH has increased gradually with increasing BC amendment rates. However, soil pH dropped slightly when increasing ClO_4^- concentrations in serpentine soils.

Furthermore, it appeared that serpentine soil contains a high concentration of Ni and Mn (Table 3). In addition, bioavailable fractions of Ni and Mn were 0.30 and 0.25% of total Ni and Mn in serpentine soil.

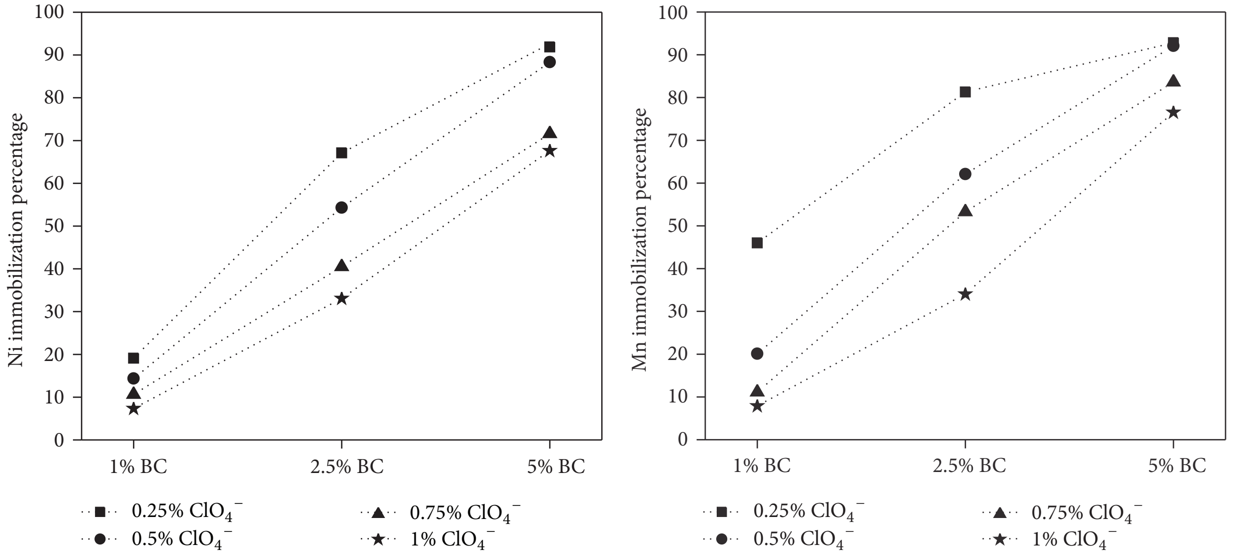
3.2. Release of Heavy Metals at ClO_4^- *Addition.* With the addition of ClO_4^- concentrations, $CaCl_2$ extracted Ni and Mn were readily increased. For instance, 0.25% ClO_4^- addition mobilized 123 and 52 $mg\,kg^{-1}$ of Ni and Mn, respectively, after 6-month incubation period. In comparison, 1% ClO_4^- addition mobilized 291 and 600 $mg\,kg^{-1}$ of Ni and Mn, respectively, and this figure corresponded to 4.43 and 22.99% of total Ni and Mn concentrations, respectively. In addition, when increasing ClO_4^- concentrations from 0.25 to 1%, $CaCl_2$ extracted Ni and Mn increased by 57.73 and 91.33%, respectively.

3.3. Immobilization of Heavy Metals through Biochar. Figures 1(a) and 1(b) show the bioavailability of Ni and Mn with the presence of different ClO_4^- and BC amendments. The statistical analysis explains that immobilization of Ni and Mn is significantly different with BC amendment rates. However, at higher ClO_4^- concentrations (i.e., 1% ClO_4^-), a significant difference could not be identified between the control and 1% BC addition in terms of Ni and Mn immobility. Compared to other BC amendment rates, 5% BC amendment reduced the bioavailability of Ni and Mn greatly. In addition, BC performed well in the presence of low ClO_4^- concentrations (i.e., 0.25% ClO_4^-) (Figures 2(a) and 2(b)). For instance, 5% BC-0.25% ClO_4^- combination reduced 91.9 and 92.9% of $CaCl_2$ extractable of Ni and Mn, respectively, compared to the control. The final concentration of the $CaCl_2$ extractable Ni and Mn in 5% BC-0.25% ClO_4^- combination corresponded to the 0.15 and 0.14% of the total metal concentrations of Ni and Mn in serpentine soil, respectively. However, 5% BC-1% ClO_4^- combination reduced only 67.6 and 76.5% of the bioavailability of Ni and Mn, respectively, compared to the control. In that combination, $CaCl_2$ extractable Ni and Mn corresponded to the 1.43 and 5.3% of the total metal concentrations of Ni and Mn, respectively. Therefore, it clearly indicates that pH variations in serpentine soils due to BC and ClO_4^- addition (Table 2) show close correlation

Table 1: Proximate composition,elemental compositions, and surface area of the *Gliricidia sepium* BC.

pH	EC (μS cm^{-1})	Proximate analysis (wt.%)				Ultimate analysis (wt%)[a]					Atomic ratio[a]		BET surface area (m^2 g^{-1})[a]	Pore diameter (nm)[a]	Pore volume (cm^3 g^{-1})[a]
		Moisture	Mobile matter	Ash content	Fixed carbon	C	H	N	O	S	H/C	O/C			
9.72	174.9	7.1	11.0	20.6	61.3	50	1	0.5	44	0.1	0.24	0.66	714	4.08	0.89

[a] [23].



(a) (b)

Figure 2: Influence of BC addition on Ni (a) and Mn (b) immobilization percentage in serpentine soil with each of the ClO_4^- concentrations.

Table 2: Variation of pH in serpentine soil with different ClO_4^- and BC amendment combinations.

ClO_4^- concentration (w/w)	BC amendment rate (w/w)	pH
0.25	0	5.73
	1	5.72
	2.5	5.89
	5	6.09
0.5	0	5.38
	1	5.44
	2.5	5.59
	5	6.02
0.75	0	4.90
	1	5.11
	2.5	5.10
	5	5.43
1	0	4.49
	1	4.63
	2.5	4.85
	5	5.02

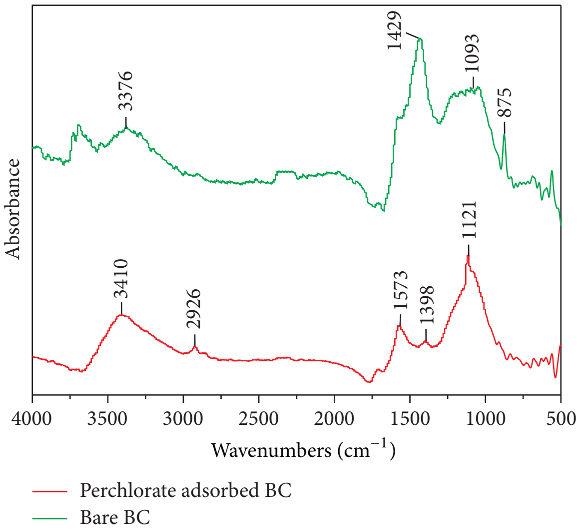


Figure 3: FTIR spectrums for bare *Gliricidia sepium* BC and ClO_4^- adsorbed *Gliricidia sepium* BC.

(0.8751 and 0.9150, resp.) with the bioavailability of Ni and Mn.

3.4. Possible Mechanisms. Several sorption mechanisms such as organometallic interactions and sorption due to π electron donor-acceptor interaction and pore diffusion [13, 36] may act as a strong foundation for immobilization of Ni and Mn in serpentine soil. The Ni and Mn, being transition metals, tend to have good coordination affinity to bond with oxygen functional groups (i.e., COH, C=O and -COOH) of BC surface and FTIR spectroscopic analysis revealed that bare BC contains oxygen functional groups (Figure 3). In a study, Uchimiya et al. [36] concluded that high content of oxygen functional groups is more effective in terms of heavy metals stabilization. The O atoms of these functional groups can donate their lone pair electrons to electron deficient metal centres and, consequently, this may form organometallic interactions [23]. In addition, the BC produced at high temperatures shows high aromaticity from which metals are sorbed via π electron donor-acceptor interactions [23, 37]. More precisely, aromatic carbon consists of double and triple bonds with a pool of π electrons; therefore, it leads to forming π electron donor-acceptor interactions in order to sorb Ni and Mn. Moreover, physical properties (i.e., pore diameter,

Table 3: Chemical properties, total metal digestion, and bioavailable concentration for Ni and Mn in serpentine soil.

pH	EC (dS m^{-1})	Total metal concentration (mg kg^{-1})		Bioavailable metal concentration (mg kg^{-1})	
		Ni	Mn	Ni	Mn
6.26	0.03	6,567	2,609	19.8 (0.30)	6.4 (0.25)

Value in parentheses is the percentage of bioavailable metal concentration compared to the total metal concentrations.

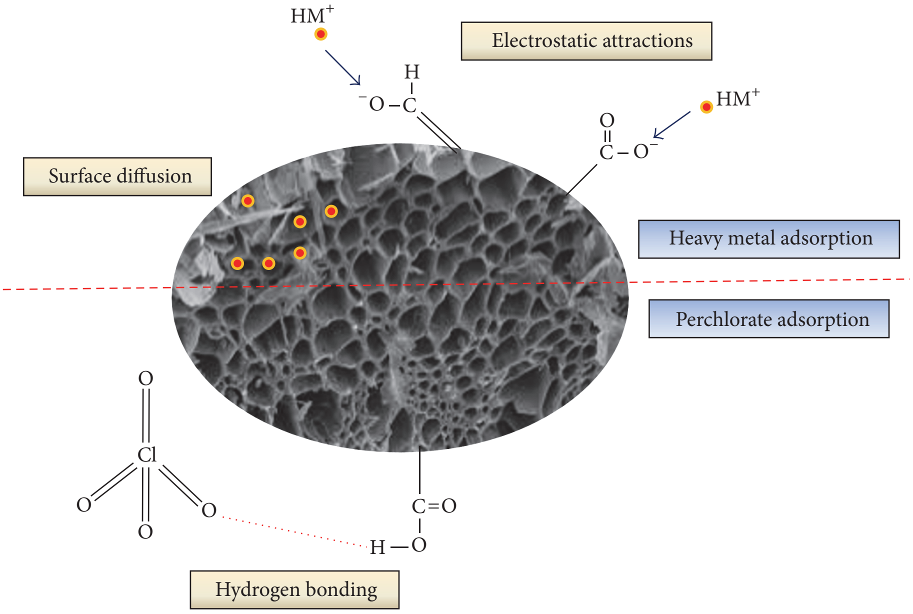


Figure 4: Possible mechanisms for Ni and Mn immobilization (HM$^+$ denoted the respective Ni and Mn cations) and ClO_4^- adsorption onto *Gliricidia sepium* BC.s

pore volume, and surface area) of BC could govern the diffusion of heavy metals into the BC. However, dissolved organic carbon would block the pores of BCs disturbing heavy metal sorption [38]. Nevertheless, at higher temperatures, BCs are deficient in dissolved organic carbon; as a result, BCs enhance heavy metal immobilization in soil.

As previously mentioned, at higher temperatures, BCs gain low polarity and high aromaticity which stimulate the ClO_4^- adsorption onto BC. Thus, a further aspect of Ni and Mn immobilization is that BC could adsorb ClO_4^- as a result; the influence of ClO_4^- on mobilization Ni and Mn may minimize. At higher temperatures, smaller aromatic units in BC condensed into larger sheets. Aromatic surfaces are rich in π electrons which can stimulate the hydrogen bonding or act as acceptors related to most H-bond donors. Therefore, condensed aromatic surface of BC may strengthen hydrogen bond force by facilitating a hydrophobic microenvironment which accommodate weakly hydrated ClO_4^- and favor ClO_4^- binding owing to its π system [40].

The FTIR spectra (Figure 3) showed that some peaks were shifted or disappeared and new peaks were also detected between bare and ClO_4^- adsorbed BC. In bare BC, the peak at 3376 cm^{-1} could be attributed to phenolic -OH stretching [41]. The peaks at 1429 and 1093 cm^{-1} were ascribed to C=C and C-O-C stretching vibrations [23]. Aromatic CH out-of-plane deformation appeared at 875 cm^{-1} [42]. In ClO_4^- adsorbed BC, the new peak at 2926 cm^{-1} may be attributed to the oxidative reaction of ClO_4^- with BC surface to produce aliphatic C-H in addition to producing more oxygenated functional groups in the BC surface. The band that appeared at the 1573 cm^{-1} could be assigned to -COOH and peaks at 1318 and 1121 cm^{-1} were recognized to be -C-O groups [37, 42]. Therefore, it is evident that, apart from electrostatic attractions, H-bond interactions between weakly hydrated ClO_4^- and oxygen-containing functional groups such as -COH, -COOH on the aromatic and hydrophobic surface of BC may play a major role with regard to adsorption of ClO_4^-. It is evident that far wood derived BC produced at 500–700°C successfully adsorbed ClO_4^- and the mechanism behind that was the H-bonding interactions [37]. Furthermore, metal oxide present in the BC may play another adsorptive role in terms of ClO_4^- adsorption due to the fact that BC contains high ash content (20.6%) [43]. Therefore, it could be proposed that BC immobilizes Ni and Mn and adsorbed ClO_4^- simultaneously (Figure 4). Eventually, the effect of ClO_4^- on Ni and Mn immobilization from serpentine soil would be minimized to a greater extent. However, molecular level understanding is required to address the sorption mechanism of the BC in detail.

4. Conclusions

In summary, serpentine soil contained a high concentration of Ni and Mn in which 0.30 and 0.25%, respectively, are retained as a bioavailable fraction. Addition of ClO_4^- leads to increasing $CaCl_2$ extractable Ni and Mn (4.43 and 22.99%, resp.) in serpentine soil. However, application of *Gliricidia sepium* BC acts as a strong foundation for immobilizing Ni and Mn. In addition, it is clear that high rate of BC amendment could reduce high percentage of $CaCl_2$ extractable Ni and Mn and BC is able to decrease more than 90% of $CaCl_2$ extractable Ni and Mn at low ClO_4^- concentrations (i.e., 0.25% w/w). Taking this into account, it could be concluded that not only immobilization of Ni and Mn but also adsorption of ClO_4^- onto BC might act simultaneously in order to minimize $CaCl_2$ extractable Ni and Mn. However, molecular level understanding will be important to explain the sorption mechanism of the *Gliricidia sepium* BC.

Competing Interests

The authors declare that they have no competing interests.

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