

Investigating the synergistic potential Si and biochar to immobilize Ni in a Ni-contaminated calcareous soil after *Zea mays* L. cultivation

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Abstract. In Iran, a significant percentage of agricultural soils are contaminated with a range of potentially toxic elements (PTEs), including Ni, which need to be remediated to prevent their entry into the food chain. Silicon (Si) is a beneficial plant element that has been shown to mitigate the effects of PTEs on crops. Biochar is a soil amendment that sequesters soil carbon, and that can immobilize PTEs and enhance crop growth in soils. No previous studies have examined the potentially synergistic effect of Si and biochar on Ni concentration in soil chemical fractions and immobilization thereof. Therefore, the aim of this study was to examine the interactive effects of Si and biochar, to reduce Ni bioavailability and its corresponding uptake in corn (*Zea Mays*) in a calcareous soil. A 90-day factorial greenhouse study with corn was conducted. Si application levels were applied at 0 (S_0), 250 (S_1) and 500 (S_2) mg Si kg⁻¹ soil and biochar treatments (3% wt.) including rice husk (RH) and sheep manure (SM) biochars produced at 300°C and 500°C (SM300, SM500, RH300 and RH500). At harvest, Ni concentration in corn shoots, Ni content in soil chemical fractions and release kinetic of DPTA-extractable Ni were determined. Simultaneous utilization of Si and SM biochars led to a synergistic reduction (15-36%) of Ni content in the soluble and exchangeable fractions compared to application of Si (5-9%) and SM (5-7%) biochars separately. The application of the Si and biochars also decreased DPTA-extractable Ni and Ni content in corn shoots (by up to 57%), with the combined application of SM500+ S_2 being the most effective. These effects were attributed to the transfer of Ni in soil from more bioavailable fractions to more stable iron oxide bound fractions, related to soil pH increase. The SM500 was likely the most effective biochar due to its higher alkalinity and lower acidic functional group content which enhanced Ni sorption reactions with Si. The study demonstrates the synergistic potential of Si and sheep manure biochar at immobilizing Ni in contaminated calcareous soils.

1 Introduction

One of the most important ways for potentially toxic elements (PTEs) to enter the human food chain is through the consumption of plants grown in soils contaminated with PTEs. Potentially toxic elements pollute soil environments as a result of mining, metal smelting, use of sewage sludge and domestic and industrial effluents in agriculture especially in developing countries (Liu et al., 2018). Potentially toxic elements in soils cannot undergo biodegradation by

43 living organisms, so they possess great stability and longevity in the soil (Poznanović Spahić et
44 al., 2019). Unlike other PTEs found in soils, such as mercury (Hg), cadmium (Cd) and lead (Pb),
45 nickel (Ni) is essential for plant growth at very low concentrations. Nevertheless, at elevated
46 contents ($>35 \text{ mg Ni kg}^{-1}$ soil), Ni causes many physiological and morphological malfunctions in
47 plants and severely stunts their growth (Shahzad et al., 2018; Antoniadis et al., 2017). In a study
48 conducted by Shahbazi et al. (2022), the Ni weighted average concentration of the cultivated lands
49 of Iran in the vicinity of the industrial areas was reported 350 mg kg^{-1} soil. In these soils, the
50 pollution index (the ratio of the element concentration to the standard concentration) calculated
51 for the Ni is greater than 5, which indicates a severe degree of pollution from the point of view of
52 environmental protection. Shahbazi et al. (2020) collected 711 agricultural soil samples located at
53 different climate zones (extra arid, arid, semi-arid, Mediterranean, semi humid, humid and per-
54 humid based on the de Martonne classification system) of Iran and reported that the Ni content in
55 the soils was between 2.79 mg kg^{-1} and 770 mg kg^{-1} with an average of 68 mg kg^{-1} soil. The results
56 showed that the concentration of Ni in 11.3% of these soils was higher than the threshold value.
57 Removing PTEs from contaminated sites via traditional methods such as pump and treat
58 technologies, soil washing and excavation is very expensive and time-consuming, therefore, for
59 plant cultivation in these areas, low-cost and effective methods should be sought to stabilize PTEs
60 in soils and prevent them from being transferred to the plant (Gao et al., 2023).

61 Silicon (Si) is a valuable nutrient for plant growth, and it is only considered essential for
62 some plant species such as rice. Applying Si to the soil can enhance plant resistance against
63 biological and non-biological tensions, including physiological stress caused by PTEs in soil (Bhat
64 et al., 2019; Yan et al., 2018). The use of Si to promote plant growth and mitigate the toxicity of
65 PTEs is becoming increasingly popular in agriculture (Li, 2019; Adrees et al., 2015). The
66 application of Si in soils contaminated with PTEs may reduce the bioavailability of PTEs by
67 increasing soil pH, increasing the secretion of organic ligands by the roots and the formation of
68 insoluble compounds with PTEs, and ultimately enhancing plant growth (Bhat et al., 2019; Xiao
69 et al., 2021). The soil pH increase associated with Si application is attributed to the hydrolysis
70 reaction of the silicate anion in soil solution which generates hydroxyl ions (Ma et al. 2021).

71 Biochar can be used for a number of applications including as a soil amendment that
72 sequesters soil carbon (C) and for stabilization of PTEs in polluted sites (El-Naggar et al., 2018).
73 Biochar is a carbon-rich, porous organic material which is prepared in a limited or no oxygen
74 conditions by pyrolysis of organic wastes, including crop and animal residues, urban waste, wood
75 byproduct (Vickers, 2017; Ankita Rao et al., 2023). The organic surface functional groups of
76 biochar such as carboxylic and phenolic groups provide cation exchange capacity in soils
77 (Tomczyk et al., 2020). Addition of biochar to the soil not only improves the soil chemical and
78 physical properties, but also reduces the bioavailability of PTEs in contaminated soils through
79 some physicochemical processes such as sedimentation, complexation, and electrostatic
80 adsorption (Bandara et al., 2020; Deng et al., 2019; Derakhshan Nejad et al., 2018). The
81 complexation of Ni with oxygen-containing functional groups on biochar surfaces including
82 carboxyl, ether, carbonyl, and hydroxyl, has been identified as a key mechanism for Ni
83 immobilization in soil (Alam et al., 2018; El-Naggar et al., 2018). Electrostatic attraction of Ni by
84 negatively charged functional groups on the surfaces of biochar is another potential mechanism
85 for Ni stabilization in soil (Ahmad et al., 2014). Increased soil pH following the application of
86 biochar also promotes Ni adsorption reactions (Uchimiya et al., 2010). However, the efficiency of

87 biochar prepared from different feedstocks and under different production conditions in stabilizing
88 PTEs in soils can vary significantly (Dey et al., 2023).

89 Potentially toxic elements in soil can exist in different chemical fractions such as water
90 soluble and exchangeable (WsEx), bound to carbonates (Car), organic matter (OM), iron and
91 manganese oxides (FeMnOx) and residual (Res) (found in minerals) (Singh et al., 1988). The
92 bioavailability of these forms differs, the WsEx fraction has the highest bioavailability and the Res
93 form is considered unusable by plants. PTEs in other chemical fractions in soils could be
94 potentially accessible for plant roots depending on soil characteristics such as soil texture, soil pH
95 and soil organic matter content (Kamali et al., 2011; Bharti et al., 2018). The diethylene triamine
96 penta-acetic acid (DTPA) extraction is commonly employed for assessing Ni availability in
97 calcareous soils (Lindsay and Norvell, 1978). However, it is important to acknowledge that this
98 methodology solely assesses Ni availability for plants, while the quantity of released Ni may vary
99 across distinct stages of plant development. Consequently, the examination of alterations in
100 extractable Ni levels over time using the DTPA solution can prove valuable in estimating
101 bioavailability of Ni in soil. The PTEs desorption capacities of soils are anticipated to be contingent
102 upon factors such as soil pH, cation exchange capacity, the specific nature of metal ions, and the
103 source of the metals (Kandpal et al., 2005). Furthermore, the release kinetic parameters can provide
104 insight into the bonding mechanisms of PTEs in soils and their potential risk for leaching into
105 groundwater or surface water (El-Naggar et al., 2021). Therefore, sequential extraction methods
106 and release kinetic models have been employed to assess the efficacy of amendment materials in
107 stabilizing PTEs in contaminated soils. Xiao et al. (2021) found that addition of mineral Si fertilizer
108 to a contaminated paddy soil caused a significant decrease in the Cd and Pb fractions bound to
109 carbonates and iron-manganese oxides while the residual and organic matter-bound forms
110 experienced a notable increase. In another study, application of cotton residue biochar (1.5 wt. %)
111 to a calcareous soil with a sandy loam textural class containing different levels of Cd contamination
112 was more efficacious than corn and wheat straw biochars in decreasing Cd content in the WsEx
113 and Car fractions and enhancing Cd concentration in the Res fraction. In addition, application of
114 cotton residue biochar decreased EDTA-extractable Cd by 45–52% compared to the control
115 (Boostani et al., 2023b).

116 As both biochars and Si are economical and effective soil amendments to reduce plant
117 uptake of PTEs and stress in contaminated soils, their potential synergistic effect on the
118 immobilization of PTEs in soils should be further investigated. Currently, no previous studies have
119 examined the combined application effects of Si and biochars on the Ni content in various soil
120 chemical fractions and release kinetic of Ni in calcareous soils. The primary objective of the
121 present study was to elucidate the interaction of biochars and Si levels, to reduce bioavailability of
122 Ni in soil and its corresponding accumulation in corn (*Zea Mays* L. 604) plant. Additionally, the
123 study sought to elucidate the underlying soil chemical mechanisms that are likely to be responsible
124 for such effects.

125 **2 Materials and methods**

126 **2.1 Soil sampling, characterization and Ni treatment**

127 A composite soil sample from the surface layer (0-30 cm) was collected with an auger at
128 the research farm of the College of Agriculture and Natural Resources in Darab, southern Iran (28
129 ° 45' 0.99" N 54° 26' 52.14" E, Elevation 1105 m) (Fig. 1). The climate, mean annual
130 precipitation, soil moisture and thermal regimes of the studied area were semi-arid, 250 mm, ustic

131 and hyperthermic respectively. The composite soil sample was placed in polyethylene bags in the
132 field and then transported to laboratory where it was immediately air-dried, passed through a 2
133 mm sieve and then stored at room temperature until the physicochemical analysis was performed.
134 Soil sand, silt and clay content were determined by the hydrometer method (Gee and Bauder,
135 1986). Soil pH and EC were determined using a saturated paste (Rhoades, 1996), while organic
136 matter was determined using Walkley-Black procedure (Nelson and Sommers, 1996). Calcium
137 carbonate equivalent (CCE) was determined by acid neutralization (Loeppert and Suarez, 1996),
138 while cation exchange capacity was determined using 1M ammonium acetate (Merck, 99%)
139 method (Sumner and Miller, 1996). Available Ni was determined using DPTA (Merck, 99%)
140 extraction (Lindsay and Norvell, 1978). Plastic containers were filled with two kilograms of soil
141 and then 500 ml NiCl₂ (Merck, 99%) solution was mixed into to them to achieve a Ni concentration
142 of 300 mg Ni kg⁻¹ soil. The Ni-treated soil samples were then allowed to dry out at room
143 temperature, and then rewetted to field capacity using deionized water and allowed to dry out
144 again. The rewetting and room temperature drying cycle was repeated three times to allow the Ni
145 to equilibrate with the soil. The repeated wetting and drying cycles were performed to simulate
146 field processes (Boostani et al., 2023c). The incubation period was 60 days and the ambient
147 temperature was 25±2 °C.

148



149

Fig. 1. The location of soil sampling in Darab region, southern Iran.

150

151

152 2.2 Production of biochar and its properties

153 The sheep manure and rice husk were respectively procured from an active animal
154 husbandry and rice mill factory situated in the Darab region, Fars province, Iran. Subsequently,
155 the raw materials underwent a 1-week period of air-drying, followed by electrical milling and
156 sieving through a 2 mm mesh. A slow pyrolysis procedure (2 h at 300 °C and 500 °C) in an oxygen-
157 limited environment was carried out to generate biochars from feedstocks (Anand et al., 2023).

158 The generated biochars were then cooled at ambient temperature and sieved with a 0.5 mm mesh
159 to ensure consistent particle size. The chemical characteristics of the biochars were assessed using
160 the following standard methods. Biochar pH and EC were determined in a 1:10 deionized water
161 suspension (Sun et al., 2014), while CEC was determined using the method of Abdelhafez et al.
162 (2014). Biochar total C, N and H contents were determined by elemental analyzer
163 (ThermoFinnigan Flash EA 1112 Series, ThermoScientific, USA). Biochar moisture and ash
164 content were determined by heating in an oven, while the O+S content was calculated by
165 subtraction of C, N, H, ash and moisture content from total biochar mass (Keiluweit et al., 2010).
166 Biochar total Ni content was determined by combustion and dissolution of the ash in 2M HCl
167 (Merck, 37%) (Boostani et al., 2018b). The Ni content in the acid solution was determined using
168 atomic absorption spectroscopy (AAS) (PG 990, PG Instruments Ltd., UK). Surface functional
169 groups of the biochars were assessed using Fourier Transform Infrared (FTIR) spectroscopy using
170 a Shimadzu DR-8001 instrument and KBr pellet transmission method. The morphology of surface
171 biochar was assessed using scanning electron microscopy (SEM) (TESCAN-Vega3, Czech
172 Republic).

173 2.3 Greenhouse experiment

174 A completely randomized factorial experiment was conducted in a greenhouse
175 environment with three replications. The first factor consisted of the biochar treatments including
176 rice husk (RH) and sheep manure (SM) generated at 300 °C and 500 °C (Control (C) (with no
177 biochar), SM300, SM500, RH300 and RH500), each at the level of 3%wt. The second factor
178 included Si application levels (0 (S₀), 250 (S₁) and 500 (S₂) mg Si kg⁻¹ soil) supplied as Na₂SiO₃
179 (Sigma Aldrich, 98%) solution. Based on the experimental design, Si levels were added to the 2
180 kg of Ni-treated soil samples and after drying the soil and mixing it, the prepared biochars were
181 added to the required amount. Immediately after that, the treated soil samples were transferred to
182 plastic pots (45 pieces each containing 2 kg soil) and to facilitate the required reactions, the
183 moisture content of the samples was kept at field capacity level for a duration of two weeks.
184 Thereafter, 6 corn seeds (*Zea mays* L. 604) were planted in each pot, and at the 4-leaf stage, 2
185 plants were kept in each pot until the end of cultivation. During the growth of the plant, distilled
186 water was used to maintain the soil moisture content in the pots at field capacity. After 90 days,
187 the plants were harvested at the soil interface, rinsed with distilled water to remove contamination,
188 immediately air-dried and kept for Ni determination of plant shoots. After separating the roots,
189 the soil from the pots was immediately air-dried, and then passed through a 2 mm sieve and stored
190 in labelled polyethylene bags at room temperature, to be subsequently utilized for performing Ni
191 sequential extraction and release kinetics.

192 2.4 Sequential extraction procedure

193 The present study employed a successive extraction technique (Singh et al., 1988) to
194 fractionate Ni in the following soil chemical fractions, namely water-soluble and exchangeable
195 (WsEx), carbonate-bound (Car), organic matter-bound (OM), manganese oxide-bound (MnOx),
196 amorphous iron oxide-bound (AFeOx), crystalline iron oxide-bound (CFeOx), and residual (Res).
197 The methodological specifics are provided in Table 1.

198

199

Table 1
Successive extraction technique of Singh et al. (1988)

Chemical speciation containing Ni	acronym	Duration of agitation (h)	Extractants	Relative density (g.cm ⁻³)
Exchangeable and soluble	WsEx	2.0	1 M magnesium nitrate (Merck, 98%)	1.10
Carbonate	Car	5.0	1 M sodium acetate (Merck, 99%) (pH=5)	1.04
Organic	OM	0.5	0.7 M sodium hypochloride (pH=8.5)	1.00
Mn oxide	MnOx	0.5	0.1 M hydroxyl amine hydrochloride (Merck, 98%) (pH=2 by nitric acid (Merck, 65%))	1.00
Amorphous Fe oxides	AFeOx	0.5	0.25 M hydroxyl amine hydrochloride (Merck, 98%) + 0.25 M chloridric acid (Merck, 37%)	1.01
Crystalline Fe oxides	CFeOx	0.5	0.2 M ammonium oxalate (Merck, 99%) + 0.2 M oxalic acid (Merck, 99%) + 0.1 M ascorbic acid (Merck, 99.7%)	1.02

201

202 2.5 Release kinetics experiment

203 A 50 ml centrifuge tube was filled with 10 g of soil. After that, 20 ml of DTPA solution
 204 (0.005 M DTPA (Merck, 99%) + 0.1 M tri-ethanol amine (Merck, 99%) + 0.01 M calcium chloride
 205 (Merck, 97%)) (pH: 7.3) (Lindsay and Norvell, 1978) was added to the soil. The soil-DTPA
 206 mixtures were stirred for specific periods of time, i.e. 5, 15, 30, 60, 120, 360, 720 and 1440 minutes
 207 at a constant temperature (25 ± 2 °C). After each stirring time, the soil suspension was centrifuged
 208 (2683 × g) to separate the soil particles from the liquid phase. Atomic absorption spectroscopy
 209 (AAS) (PG 990, PG Instruments Ltd., UK) was used to analyze the Ni concentration in the liquid
 210 phase. The Ni concentration in the liquid phase versus time was plotted to obtain a Ni release
 211 kinetic curve. A total of seven kinetic models namely order models (zero, first, second and third),
 212 parabolic diffusion, power function and simple Elovich were assessed to fit the Ni release data.
 213 The best models for describing the data were selected according to the maximum value of the
 214 coefficient of determination (R²) and the minimum amount of the standard error of estimate (SEE)
 215 (Nasrabadi et al., 2022).

216 2.6 Data analysis

217 The ANOVA test was utilized to assess treatments effects between the individual and
 218 combined biochar and silicon treatments. Additionally, a comparison of means was conducted
 219 using the MSTATC computer program, applying Duncan's test with a significance level of 5%.
 220 Figures were generated using Excel 2013 software. Pearson correlation coefficients among
 221 parameters in the dataset were determined using SPSS 12.0.

222 3 Results and Discussion

223 3.1 Soil characteristics

224 The soil used in the study prior to experimental treatment, exhibited a sandy loam texture
 225 and possessed alkaline properties with significant calcium carbonate content (calcareous soil),
 226 while not being classified as saline (Table 2). The quantity of soil organic matter (OM) and cation
 227 exchange capacity (CEC) were extremely low (Table 2) compared to the values (OM: 1.20-7.10%,

228 CEC: 19.5-55.9 $\text{cmol}_{(+)} \text{kg}^{-1}$) documented by Rassaei et al. (2020) for calcareous soils of Fars
 229 province, southern Iran. The soils in Iran mainly originate from calcareous alluvium under xeric,
 230 ustic or aridic and mesic, thermic or hyperthermic moisture and temperature regimes, respectively.
 231 These soils have varied properties such as calcium carbonate equivalent (1-81%), clay content (1-
 232 75%), EC (0.40-49.0 dS m^{-1}), organic matter (0.10-21.5%) and gypsum content (0-91%) (Ghiri et
 233 al., 2011). Furthermore, it should be noted that the concentration of available Ni extractable by
 234 DTPA in the soil was low (Table 2) compared to the mean value (0.60 mg Ni kg^{-1}) reported by
 235 Jalali et al. (2022) for calcareous soils located at western Iran.

236

Table 2

Certain physicochemical attributes of the soil prior to cultivation.

Sand (%)	58.0
Silt (%)	30.0
Clay (%)	12.0
Soil textural class	Sandy loam
pH _(s)	7.59
EC (dS m^{-1})	2.60
CCE (%)	55.0
OM (%)	0.50
CEC ($\text{cmol}_{(+)}\text{kg}^{-1}$)	11.7
Total Ni (mg kg^{-1})	28.0
Ni-DTPA (mg kg^{-1})	0.39

Notes: EC, electrical conductivity; OM, organic matter; CCE, calcium carbonate equivalent; CEC, cation exchange capacity.

237

238 3.2 Chemical characteristics of the biochars

239 As the pyrolysis temperature rose from 300 °C to 500 °C, the SM biochars demonstrated
 240 elevated pH and EC values, with the highest levels observed at the highest temperature (Table 3).
 241 The elevated levels of alkali salts, which are reflected in the high ash content (Table 3), are the
 242 contributing factor behind this observation in the SM biochars in comparison to the RH biochars.
 243 Plant-based biochars commonly exhibit reduced levels of dissolved solids in comparison to
 244 animal-based biochars (Sun et al., 2014). The SM300 biochar possessed the highest CEC value of
 245 19.70 $\text{cmol}_{(+)} \text{kg}^{-1}$. The observed phenomenon may be attributed to the diminution of surface
 246 functional groups, namely carboxyl and phenol, at elevated pyrolysis temperatures. These groups
 247 are predominantly responsible for facilitating the cation exchange capacity (CEC) of biochars
 248 (Tomczyk et al., 2020). As the pyrolysis temperature increased, there was an observed increase in
 249 the C content of the biochars, and a corresponding decrease in the content of hydrogen, oxygen,
 250 and nitrogen (Table 3). The observed increase in the concentration of C as pyrolysis temperature
 251 rises is consistent with a concomitant rise in the degree of carbonization. The observed reduction
 252 in the levels of H and O might be attributed to the occurrence of dehydration reactions,
 253 decomposition of oxygenated bonds, and the liberation of low molecular weight byproducts rich
 254 in H and O, as recently noted by Zhao et al. (2017). Nitrogen compound volatilization explains the
 255 diminished N content of the biochars at elevated pyrolysis temperatures. The ratios of H:C and
 256 O:C are significant indicators of the aromaticity and polarity of biochars; the lower the ratios the

257 more condensed aromatic C the biochar contains (Chatterjee et al., 2020). The results shown in
 258 Table 3 indicate that the H:C and O:C mole ratios showed a gradual decrease as the pyrolysis
 259 temperature was increased, which can be interpreted as a sign of improved carbonization of the
 260 biochars (Zhao et al., 2017). The Ni content in the biochars derived from rice husk was below
 261 detection, whereas a limited quantity of Ni was detected in the biochars produced from sheep
 262 manure (Table 3).

263

Table 3
 Some physical and chemical properties of the biochars.

	SM300	SM500	RH300	RH500
pH (1:20)	9.96	11.0	9.00	10.3
EC (1:20) (dS m ⁻¹)	3.94	4.28	0.84	1.17
CEC (cmol _c kg ⁻¹)	19.7	18.9	18.9	15.3
C (%)	25.4	31.8	45.0	50.0
H (%)	1.85	0.80	2.28	1.06
N (%)	2.10	1.57	1.30	1.10
Ni (mg kg ⁻¹)	3.00	15.4	Nd	Nd
Moisture content (%)	1.91	1.82	2.65	2.37
Ash content (%)	53.8	60.0	34.2	44.8
H:C mole ratio	0.87	0.30	0.60	0.25
O+S:C mole ratio	0.44	0.09	0.24	0.01

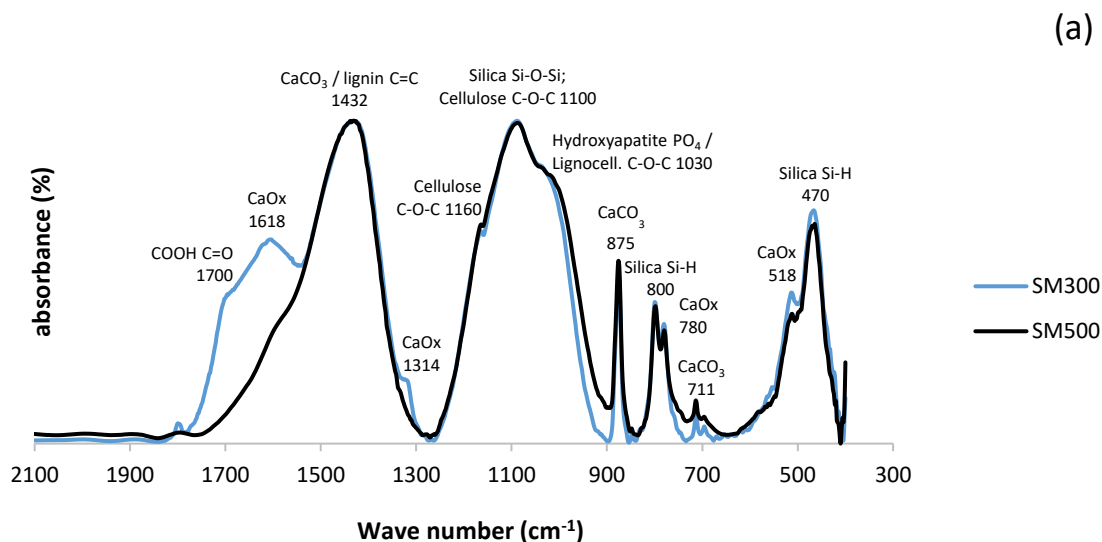
Notes: SM300, sheep manure biochar generated at 300 °C; SM500, sheep manure biochar generated at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice husk biochar produced at 500 °C; CEC, cation exchange capacity; EC, electrical conductivity; Nd, non-detectable.

264

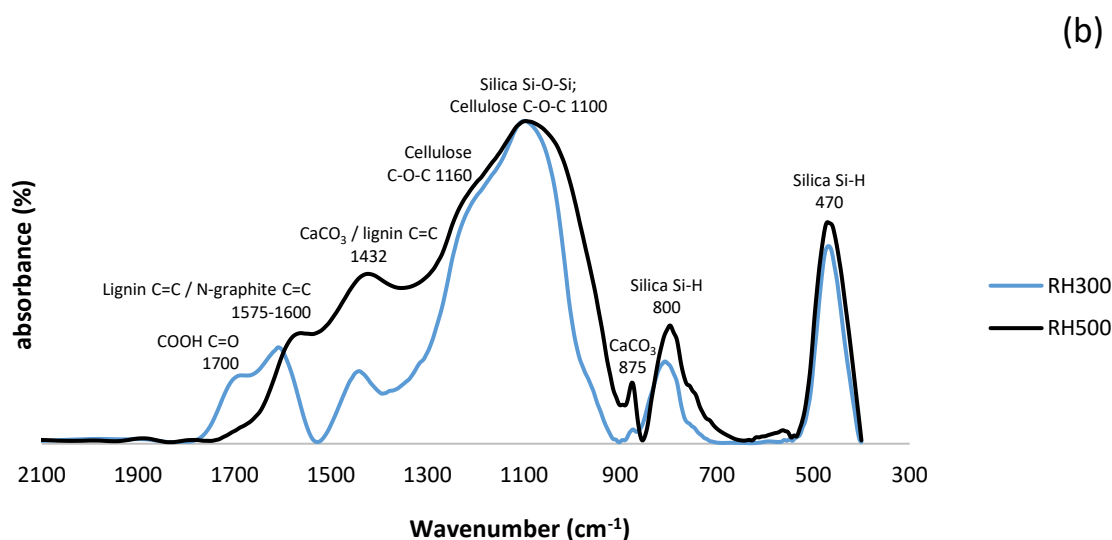
265 3.3 Biochar analysis using FTIR and SEM

266 The FTIR spectra of the SM and RH biochars are shown in Figure 2. The SM and RH
 267 biochars produced at 300 °C contained a higher content of carboxyl groups (1700 cm⁻¹) (Keiluweit
 268 et al., 2010) than the biochars produced at 500 °C, which is in agreement with the O:C values of
 269 the biochars (Table 3). All of the biochars contained absorption bands associated with lignin (1430
 270 cm⁻¹) and cellulose (1030 - 1160 cm⁻¹) (Keiluweit et al., 2010). The SM biochar contained more
 271 calcite than the RH biochar as indicated by the greater intensity of calcite characteristic peaks at
 272 1432, 875, and 711cm⁻¹ (Myszka et al., 2019) in the SM biochars (Fig. 2a). There was also
 273 evidence of the presence of Ca oxalate in the SM biochars, indicated by the characteristic peaks at
 274 1618, 780 and 518 cm⁻¹ (Maruyama et al., 2023). All the biochars contained silica as indicated by
 275 the intense silica absorption peaks at 1100, 800 and 470 cm⁻¹ (Zemnukhova et al., 2015).

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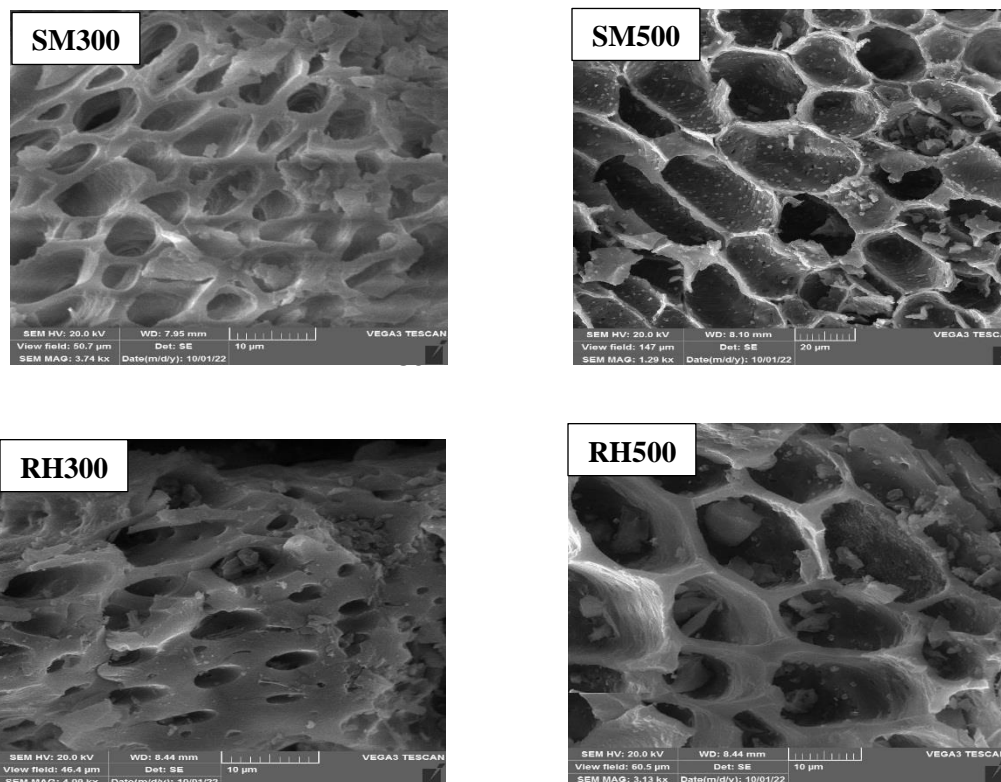


278

279 **Fig. 2.** FTIR spectra the biochars in the wave number range of 400-2000 cm^{-1} . Notes: SM300, sheep
 280 manure biochar produced at 300 °C; SM500, sheep manure biochar produced at 500 °C; RH300, rice husk biochar
 281 produced at 300 °C; RH500, rice husk biochar produced at 500 °C.

282

283 The SEM images of the SM and RH biochars are shown in Figure 3. The morphology of
 284 the biochars became more rigid and porous at higher temperatures, as evidenced by the cell wall
 285 shrinkage attributed to devolatilization of organic tissues (Claoston et al., 2014).



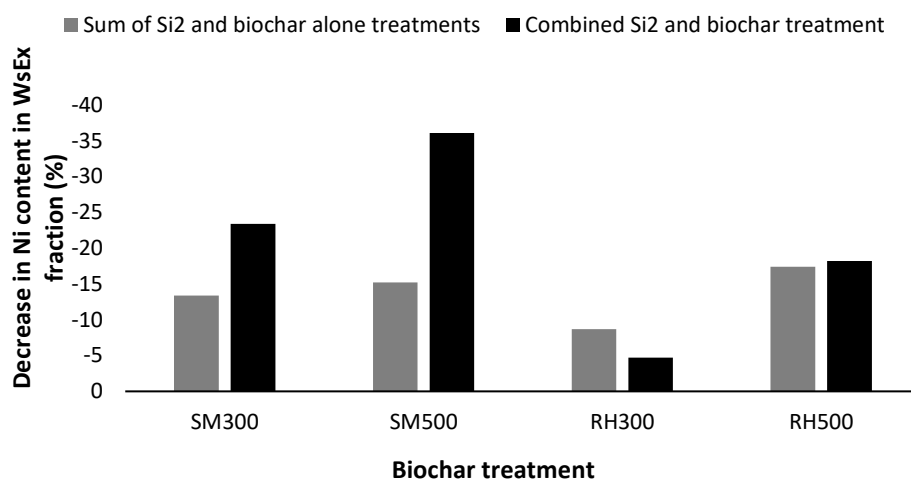
287

288 **Fig. 3.** SEM images of the biochars. Notes: SM300, sheep manure biochar produced at 300 °C; SM500, sheep
 289 manure biochar produced at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice husk biochar produced
 290 at 500 °C.
 291

292 3.4 Nickel content in various soil chemical fractions after the application of Si levels and biochars

293 The interaction of treatments (biochars and Si levels) had a statistically significant effect
 294 ($P < 0.01$) on Ni concentration in all the soil chemical fractions, except for the Car fraction.
 295 Whereas the main effects of individual treatments (biochars and Si levels) on Ni
 296 concentration in all the soil chemical fractions were significant. The Ni concentration in
 297 the WsEx fraction was significantly reduced by the application of Si levels (S_0 to S_2) from
 298 $6.07 \text{ mg Ni kg}^{-1}$ to $5.17 \text{ mg Ni kg}^{-1}$ by 14.8% (Table 4). Among the biochar treatments, the
 299 greatest decrease in Ni content in the WsEx fraction compared to the control was due to
 300 SM500 from $6.04 \text{ mg Ni kg}^{-1}$ to $5.01 \text{ mg Ni kg}^{-1}$ by 17%, while the RH300 treatment had
 301 no significant effect (Table 4). The interaction effects of treatments indicated that the
 302 lowest Ni content in the WsEx fraction was due to the combined treatment of SM500+ S_2
 303 ($4.04 \text{ mg Ni kg}^{-1}$ soil) (Table 4). The combined treatment of S_2 and SM biochars had strong
 304 synergistic effect on reducing Ni content in the WsEx fraction (23-36% reduction)
 305 compared to the sum of the treatments alone (13-15% reduction) (Fig. 4). Whereas this
 306 synergistic effect of the combined treatments was not evident for the RH biochars (Fig. 4).
 307 There was a negative correlation between Ni content in the WsEx fraction and soil pH ($r =$
 308 $-0.66, p < 0.01$) indicating that the reduction in Ni content in the WsEx fraction was
 309 strongly linked to the increase in soil pH due to the amendments (Supplementary
 310 information). Previous studies have also shown that application of biochars and silicates

311 result in increases in soil pH, thus reducing the bioavailability of PTEs and their
 312 conveyance to plant roots (Shen et al., 2020; Ma et al., 2021). Among the applied biochars,
 313 the maximum pH and ash content (Table 3) and calcite (lime) content (Fig. 2) were
 314 attributed to the SM500 biochar. Therefore, the combined SM500+S₂ was most effective
 315 at reducing Ni content in the WsEx fraction, likely due to the higher alkalinity and ash
 316 content of SM500 promoting Ni precipitation and adsorption (Sachdeva et al., 2023). The
 317 increase in soil pH due to Na metasilicate also likely enhanced the precipitation of Ni in
 318 the forms of Ni silicate and hydroxide. Addition of Si in the form of Na metasilicate
 319 increases soil pH due to the hydrolysis of the silicate anion in soil solution which generates
 320 hydroxyl ions (Ma et al., 2021).



321
 322 **Fig. 4.** Comparison of the effect of sum of the Si₂ and biochar alone treatment versus the combined
 323 Si₂ and biochar treatments on the reduction of Ni content in the WsEx fraction. Notes: SM300, sheep
 324 manure biochar produced at 300 °C; SM500, sheep manure biochar produced at 500 °C; RH300, rice husk biochar
 325 produced at 300 °C; RH500, rice husk biochar produced at 500 °C.

326 The reduced effectiveness of biochars produced at 300 °C, as compared to those produced
 327 at 500 °C, in decreasing Ni content in the WsEx fraction could also be attributed to the lower rates
 328 of microbial oxidation and mineralization of RH500 and SM500, which is reflected in their greater
 329 environmental stability (as indicated by the lower H/C mole ratio values) (Table 3). Consequently,
 330 biochar produced at 500 °C may not provide sufficient acidic carboxyl functional groups to the
 331 soil to stimulate SOM decomposition, leading to a greater increase in soil pH (Sun et al., 2023).
 332 According to Zhu et al. (2015), the addition of wine lees-based biochar (a material from a wine
 333 processing factory) to a heavy metal-contaminated soil (at levels of 0.5% and 1% w/w) resulted in
 334 an increase in soil pH and a decrease in Ni content in the WsEx fraction.

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 337
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Table 4

Effects of biochars and Si application levels on the Ni concentration (mg kg^{-1}) in different soil chemical fractions after corn cultivation.

	C	SM300	SM500	RH300	RH500	Mean
	WsEx					
S ₀	6.32 a	6.02 a-c	5.91 bc	6.31 a	5.77 c	6.07 A
S ₁	6.03 a-c	5.37 d	5.09 de	6.25 ab	5.28 d	5.60 B
S ₂	5.77 c	4.84 e	4.04 f	6.02 a-c	5.17 de	5.17 C
Mean	6.04 A	5.41 B	5.01 C	6.20 A	5.41 B	
	OM					
S ₀	9.72 a	10.6 a	8.04 d-f	10.0 a	9.02 b	9.40 A
S ₁	9.60 a	9.75 a	7.16 g	8.62 b-d	8.70 bc	8.76 B
S ₂	8.11 c-f	7.94 ef	7.12 g	8.30 c-e	7.63 fg	7.82 C
Mean	9.14 A	9.28 A	7.44 C	8.99 A	8.44 B	
	MnOx					
S ₀	11.6 a	3.77 kl	5.99 f	4.69gh	9.71 c	7.15 A
S ₁	10.3 b	3.50 l	5.00 g	4.57 hi	8.93 d	6.48 B
S ₂	10.3 b	2.98 m	4.28 ij	3.96 jk	7.94 e	5.89 C
Mean	10.7 A	3.42 E	5.09 C	4.41 D	8.86 B	
	AFeOx					
S ₀	11.1 ef	10.4 g	11.8 d	11.0 fg	11.7 de	11.2 C
S ₁	12.2 b-d	10.7 fg	12.0 cd	12.2 b-d	12.7 bc	12.0 B
S ₂	12.8 b	12.2 b-d	12.2 b-d	12.3 b-d	14.2 a	12.7 A
Mean	12.1 B	11.1 C	12.0 B	11.8 B	12.9 A	
	CfeOx					
S ₀	77.3 f	78.0 f	84.0 cd	84.7 cd	79.6 ef	80.7 C
S ₁	77.9 f	82.2 de	86.3 bc	85.1 b-d	83.6 cd	83.0 B
S ₂	79.9 ef	85.5 bc	87.9 ab	85.7 bc	90.4 a	85.9 A
Mean	78.4 C	81.9 B	86.0 A	85.2 A	84.5 A	
	Res					
S ₀	200 c-e	207 a	200 c-e	196 f	198 d-f	200 A
S ₁	200 c-e	204 b	200 c-e	197 ef	195 f	199 A
S ₂	200 cd	204 b	201 c	199 c-e	190 g	199 A
Mean	200 B	205 A	200 B	198 B	195 BC	

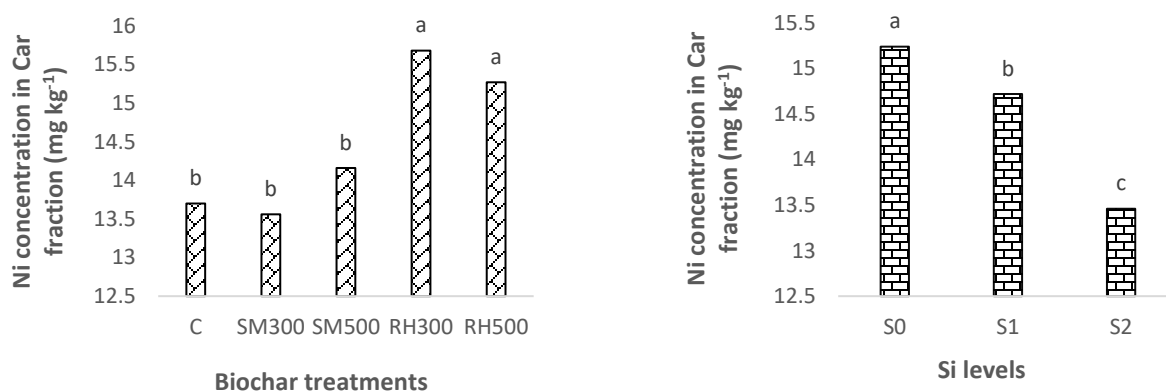
Notes: C, control; SM300, sheep manure biochar produced at 300 °C; SM500, sheep manure biochar produced at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice husk biochar produced at 500 °C; S₀, without Si addition; S₁, application of 250 mg Si kg⁻¹ soil; S₂, application of 500 mg Si kg⁻¹ soil. WsEx, water soluble and exchangeable fraction; OM, organic fraction; MnOx, bound to manganese oxides; AFeOx, bound to amorphous iron oxides; CfeOx, bound to crystalline iron oxides; Res, residual fraction; MF, mobility factor.

*Numbers followed by same letters in each column and rows, in each section, are not significantly ($P < 0.05$) different

340 As there was no significant interaction effect between biochar type and Si levels on the Ni
 341 concentration in the Car fraction, only the significant individual main effects of biochar and Si
 342 levels are shown in Fig. 5. Changing the Si application levels from S₀ to S₂ significantly decreased
 343 the Ni content in the Car fraction by 11.7% (from 15.2 mg Ni kg⁻¹ soil to 13.5 mg Ni kg⁻¹ soil)
 344 (Fig. 5). The decrease in the concentration of Ni in the Car form with an increase in the Si levels
 345 could potentially be explained by the competition between silicate (SiO₄⁴⁻) and carbonate ions for
 346 binding with Ni²⁺ ions in the soil solution (Sparks et al., 2022). The SM biochars had no significant
 347 effect on the Ni concentration in the Car fraction whereas addition of RH biochars led to a
 348 significant increase in the Ni concentration in this fraction (Fig. 5). Ippolito et al. (2017) found

349 that addition of two biochars (pine [*Pinus contorta*] and tamarisk [*Tamarix* spp.]) to a soil
 350 contaminated by mining activities caused a significant increase in the soil Cd content bound to
 351 carbonates. They concluded that the reduction in Cd bioavailability may have been due to the
 352 ability of biochar to raise soil pH levels and induce the precipitation of CdCO_3 . Similarly, Yuan et
 353 al. (2011) proposed that the decrease in bioavailability of PTEs in soil amended by biochars
 354 derived from different crop residues might have been caused by the creation of metal-carbonate
 355 species and carbonate-surface functional group reactions, which could function as a mechanism
 356 for sequestration.

357



358

359 **Fig. 5.** Main effects of (a) biochar type and (b) Si application levels on the Ni concentration (mg
 360 kg⁻¹) in the Car fraction after corn cultivation. Notes: C, control; SM300, sheep manure biochar produced at
 361 300 °C; SM500, sheep manure biochar produced at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice
 362 husk biochar produced at 500 °C; S₀, without Si addition; S₁, application of 250 mg Si kg⁻¹ soil; S₂, application of 500
 363 mg Si kg⁻¹ soil. * Numbers followed by same letters in each section, are not significantly (P<0.05) different.

364

365 The biochars produced at 300 °C had no significant effect on the Ni content in the OM
 366 fraction compared to control, while the biochars generated at 500 °C significantly decreased it
 367 (Table 4). The greatest reduction in Ni content in the OM fraction (18.6%) was found to be in that
 368 which underwent the SM500 treatment. Lu et al. (2017) explored how the application of bamboo
 369 and rice straw biochars with varying mesh sizes (0.25 and 1 mm) and at three different levels (0,
 370 1, and 5% w/w) affected the distribution of Cd in a contaminated sandy loam soil, using the BCR
 371 (Bureau Communautaire de Référence) sequential extraction method. In contrast to the present
 372 study, they reported that the biochars increased the concentration of Cd in the OM fraction, and
 373 this was closely related to the increase in Cd immobilization. In another study, the application of
 374 sheep manure biochar produced at 500 °C at the rate of 3% wt. to a Cd-contaminated calcareous
 375 soil resulted in a significant increase in Cd content in the OM fraction, whereas the addition of
 376 other biochar treatments (wheat straw, corn straw, rice husk, licorice root pulp) caused a significant
 377 decrease in the concentration of Cd in the OM fraction when compared to the control soil (Boostani
 378 et al., 2018a). In the study conducted by Boostani et al. (2018), the reduction in Cd concentration
 379 in the OM fraction as affected by application of rice husk biochar is in line with our results,

380 however; the increase in Cd content in the OM form with addition of sheep manure biochar is in
381 contrast with the result of the present study. These observations indicate that in addition to the
382 characteristics of biochar and the level of its application (Lu et al., 2017), soil characteristics
383 (calcium carbonate percentage, soil texture, etc.) and the type of heavy metal can also have a
384 substantial role in the binding of PTEs to soil organic matter. Changing the Si levels from S₀ to S₂
385 reduced the Ni concentration in the OM fraction by 16.8% (Table 4). Ma et al. (2021) reported that
386 the application of Si to cultivated soils significantly reduced soil organic matter content, which
387 could explain why the Ni concentration in OM fraction was reduced in the present study. They
388 indicated that Si facilitates the decomposition of organic matter by enhancing soil pH. In this study,
389 the interaction effects of biochars and Si levels showed that the lowest Ni content in the OM
390 fraction was due to the combined treatment of SM500+S₂ (7.12 mg Ni kg⁻¹ soil), which was equal
391 to a 26.7% decrease compared to the control (CS₀) (9.72 mg Ni kg⁻¹ soil) (Table 4).

392 All the biochar treatments caused a significant decrease in Ni content in the MnOx fraction
393 compared to the control, with the greatest reduction caused by the SM300 treatment at 52.6%
394 (Table 4). The lower temperature biochars were more effective than the higher temperature
395 biochars in decreasing the Ni content in the MnOx fraction (Table 4). In agreement with the present
396 study, Boostani et al. (2023c) observed that biochars produced from cow manure, municipal solid
397 waste and licorice root pulp at a lower pyrolysis temperature (300 °C) decreased the Ni content in
398 the MnOx fraction to a greater extent than those prepared at a higher temperature (600 °C).
399 Hydrophobicity of biochar is decreased with increasing pyrolysis temperature (Kameyama et al.,
400 2019). It is well known that, at the same soil water content, the water content of soil pores treated
401 with biochars produced at lower pyrolysis temperatures is higher due to lower absorption of water
402 by the biochars. Therefore, in soils with high soil pore water content and low oxygen conditions,
403 the concentration of MnOx is decreased due to chemical reduction, while concomitantly, the Mn
404 concentration in the exchangeable and water-soluble are increased (Sparrow and Uren, 2014).
405 Furthermore, increasing the Si application levels from S₀ to S₂ significantly decreased the Ni
406 content in the MnOx fraction by 17.6% (Table 4). Compared to the control, which had the highest
407 concentration of Ni in the MnOx fraction (11.58 mg Ni kg⁻¹ soil), the greatest interactive effect in
408 the reduction of this fraction was related to the combined SM300+S₂ (2.98 mg Ni kg⁻¹ soil)
409 treatment by 3.8-fold (Table 4). The concentration of Ni bound to the AFeOx and CFeOx fractions
410 was significantly increased by application of Si levels from S₀ to S₂ by 13.6% and 6.5%,
411 respectively (Table 4). Belton et al. (2012) demonstrated that exogenous silicon application
412 resulted in the attachment of silicate to the surface of iron oxide in the form of a polymer.
413 Following the complexation of ferrosilicon, a significant number of negatively charged functional
414 groups, including silanol, were formed. These groups provided numerous adsorption sites for
415 PTEs, ultimately reducing their bioavailability (Belton et al., 2012). In general, all the biochars
416 caused a significant increase in Ni content in the form of CFeOx, and there were no significant
417 differences among the SM500, RH300 and RH500 treatments (Table 4). However, only the RH500
418 treatment increased the Ni concentration in the AFeOx fraction compared to control (Table 4).
419 Among all the biochars, only the SM300 resulted in a significant increase in the Ni concentration
420 in the Res fraction compared to the control (Table 4). The main (mean) effects of Si application
421 showed that increasing the Si levels from S₀ to S₂ had no statistically significant effect on the Ni
422 content in the Res fraction (Table 4).

423 Mailakeba and Bk (2021) studied the addition of kunai grass biochar (0.75%) to a soil with
424 different Ni contamination levels (0, 56, 100, and 180 mg Ni kg⁻¹ soil). They found that the

425 application of the grass biochar increased Ni content in the Res fraction and reduced Ni in the other
426 fractions in the soil. In another study, Boostani et al. (2023c) demonstrated that the application of
427 biochars (cow manure, municipal compost and licorice root pulp each at 3%(w/w)) to a Ni-
428 contaminated soil increased Ni concentration in the fractions of OM and Res, and decreased Ni
429 content in the fractions of WsEx, Car, and Fe/Mn oxide. Whereas, Boostani et al. (2023b) found
430 that the application of manure and compost biochars (3% w/w) to Pb-contaminated soil did not
431 significantly affect the content of Pb in the Res fraction but did decrease the WsEx fraction.
432 Therefore, it seems that the effect of biochars on the changes of chemical fractions of PTEs in soil
433 depends on the raw materials and production conditions of the biochar, the soil application levels,
434 type of PTEs, the degree of soil contamination with PTEs, the selection of sequential extraction
435 procedure and the soil properties (Mailakeba and Bk, 2021; Boostani et al., 2023b, a; Boostani et
436 al., 2021).

437 In summary, the application of biochars in the present study resulted in the transfer of Ni
438 in soil from more bioavailable and mobile fractions (WsEx, MnOx, OM) into other stable fractions
439 (AFeOx and CFeOx). These changes were more evident in the WsEx fraction when SM biochars
440 were applied in conjunction with Si (23-36% reduction in Ni content in the WsEx fraction
441 compared to 13-15% when applied alone), indicating that the simultaneous application of these
442 two substances is much more effective than applying them separately.

443 3.5 Ni concentration in corn (*Zea mays L.*) shoots as affected by treatments

444 The main effects of biochars, Si application levels and their interactive effects were statistically
445 significant ($P < 0.01$) on the Ni concentration in corn shoots. The main (mean) effects of Si
446 application levels showed that changing the Si levels from S_0 to S_2 resulted in 32% decrease in the
447 Ni concentration in shoots from 8.56 mg Ni kg⁻¹ dry matter (DM) to 5.82 mg Ni kg⁻¹ DM (Table
448 5). In addition, the Ni concentration in shoots was significantly decreased by application of all the
449 biochar treatments compared to the control (with no biochar addition) (Table 5). The interactive
450 effects of treatments indicated that the lowest Ni concentration in shoots was observed in the
451 combined treatment of SM500+S₂ (4.45 mg Ni kg⁻¹ DM), which showed a 57.2% decrease
452 compared to the control (CS₀: without Si and biochar addition) (10.4 mg Ni kg⁻¹ DM) (Table 5).
453 The Ni content in shoots had a significant and positive correlation with the Ni content in the WsEx
454 fraction ($r = +0.62$, $P < 0.01$) while there were a significant and negative correlation between
455 the soil pH ($r = -0.60$, $P < 0.01$) and Ni content in the CFeOx fraction ($r = -0.50$, $P < 0.01$)
456 (Supplementary information). This indicates that the application of Si and biochar can reduce the
457 Ni content in shoots by increasing soil pH and, as a result, reducing the amount of Ni in the fraction
458 of WsEx and increasing the Ni content attached to the CFeOx fraction. Boostani et al. (2019a)
459 reported a significant reduction in the concentration of Ni in spinach (*Spinacia oleracea L.*) shoots
460 due to the application of rice husk and licorice root pulp biochars (2.5% w/w) in a Ni-contaminated
461 calcareous soil. Additionally, they reported that the biochars produced at 350 °C were more
462 effective at reducing crop Ni uptake and promoting plant growth than the biochars produced at
463 550 °C. The most significant factors that contribute to the uptake reduction of PTEs by plants in
464 contaminated soils that have been amended with biochars include adsorption of heavy metals by
465 surface functional groups, increased soil pH, reducing the mobility of PTEs by changing soil redox
466 conditions, improved physical and biological properties of the soil, changes in the activity levels
467 of antioxidant enzymes, and a decrease in the transfer of PTEs to the plant shoots (Zeng et al.,

2018; Rizwan et al., 2016). Several studies have investigated the effect of Si application on Ni concentration in shoots and other heavy metals in various plant species. Khaliq et al. (2016) observed a notable increase Ni concentration and accumulation within the leaf, stem, and roots of cotton after Ni application. Whereas, Si application was observed to induce a significant reduction in Ni concentrations across these respective plant components. In another study, Maryam et al. (2024) concluded that addition of Si caused an increase in the growth indices of maize through reducing the Pb concentration in shoots. One possible explanation for the reduction of Ni concentration in shoots is that Si can compete with Ni for uptake by plant roots. Silicon has a similar ionic radius to Ni, which means that it can occupy the same binding sites on root cell membranes and reduce the uptake of Ni. Additionally, Si can induce the expression of genes that are involved in Ni transport and homeostasis, which may contribute to the reduced Ni concentration in shoots (Hossain et al., 2012; Liang et al., 2005).

480

Table 5

Ni concentration (mg Ni kg⁻¹ DM) in corn shoots as affected by biochars and Si application levels.

	C	SM300	SM500	RH300	RH500	Mean
S ₀	10.4 a	7.35 bc	9.85 a	7.55 bc	7.65 b	8.56 A
S ₁	7.65 b	6.90 bc	6.60 cd	7.05 bc	7.35 bc	7.11 B
S ₂	7.20 bc	5.05 ef	4.45 f	5.80 de	6.60 cd	5.82 C
Mean	8.41 A	6.43 C	6.96 BC	6.80 BC	7.20 B	

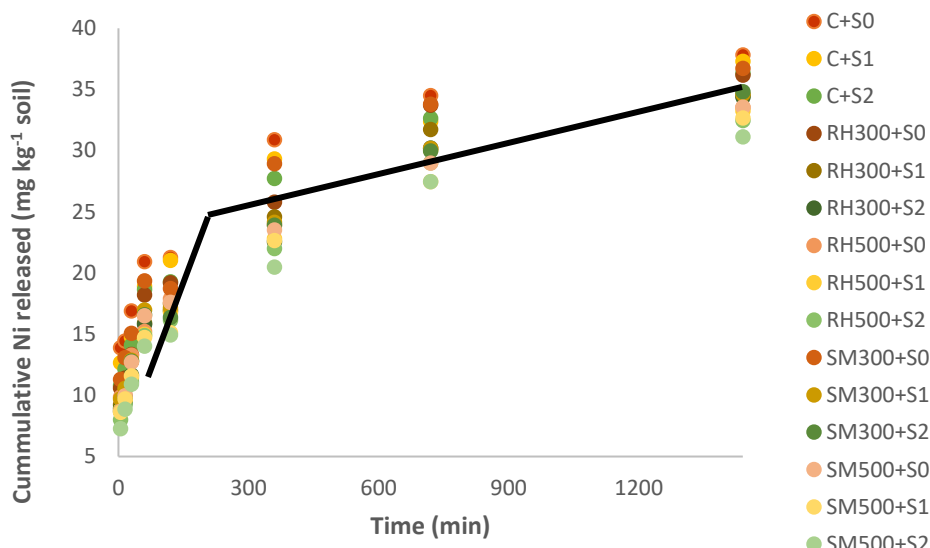
Notes: C, control; SM300, sheep manure biochar generated at 300 °C; SM500, sheep manure biochar generated at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice husk biochar produced at 500 °C; S₀, without Si application; S₁, addition of 250 mg Si kg⁻¹ soil; S₂, addition of 500 mg Si kg⁻¹ soil. Numbers followed by same letters in each section, are not significantly (P<0.05) different.

481

482 3.6 Ni desorption in soil as affected by Si application levels and biochars

483 The cumulative Ni desorption (extracted by DTPA) in the soil as a function of time are
 484 shown in Figure 6. The release of Ni from the soil initially proceeded at a much higher rate during
 485 the first hour, and then proceeded at a much slower rate during the next 24 hours, as illustrated by
 486 the trend-line in Figure 6. This two-stage process of releasing heavy metals from soil has also been
 487 reported by other researchers (Sajadi Tabar and Jalali, 2013; Boostani et al., 2023b). It is likely
 488 that the first stage of Ni release is related to forms that are less strongly attached to soil particles,
 489 including WsEx and Car, while the second stage of Ni desorption is likely from soil chemical
 490 fractions with less bioavailability, such as FeOx and Res (Saffari et al., 2015). In general, the
 491 amount of Ni desorption in the soil was reduced by addition of biochars and Si levels (Fig. 6). In
 492 addition, the effects of biochars produced at the higher pyrolysis temperature (500 °C) on reducing
 493 Ni release was more than those generated at the lower pyrolysis temperature (300 °C) in the soil.
 494 The highest amount of Ni release was due to the control (CS₀: without biochar and Si application)
 495 (37.84 mg Ni kg⁻¹ soil) while the lowest was observed in the combined application of SM500 and
 496 S₂ (31.13 mg Ni kg⁻¹ soil) treatment.

497



499

500 **Fig. 6.** Cumulative Ni desorption (extracted by DTPA) (mg kg^{-1}) in the soil as affected by different
 501 treatments. Notes: C, control; SM300, sheep manure biochar produced at 300°C ; SM500, sheep manure biochar
 502 produced at 500°C ; RH300, rice husk biochar produced at 300°C ; RH500, rice husk biochar produced at 500°C ; S₀,
 503 without Si addition; S₁, application of $250 \text{ mg Si kg}^{-1}$ soil; S₂, application of $500 \text{ mg Si kg}^{-1}$ soil.

504 3.7 Fitting of Ni release data to kinetic models

505 The Ni release data during 24 hours for all the biochar and Si treatments were evaluated by
 506 seven different kinetic models (Table 6). The effectiveness of the various kinetic models to
 507 describe the observed Ni desorption in the soil was analyzed by considering the coefficient of
 508 determination (R^2) and standard error of estimate (SEE), so that the highest value of the R^2 and the
 509 lowest value of the SEE were set as the criteria. As seen in Table 6, the order kinetic models did
 510 not adequately describe Ni release in the soil, and with the increase in the order of the kinetic
 511 model (from zero to third), the value of the R^2 decreased. This has also been found by other
 512 researchers for the release of heavy metals from soil (Boostani et al., 2019b; Ghasemi-Fasaee et
 513 al., 2006). Whereas, the non-order kinetic models, including power function, parabolic diffusion
 514 and simple Elovich, acceptably described the Ni release in the soil amended with various
 515 treatments (Table 6). Among them, the power function model was the best according to the highest
 516 value of R^2 (0.98) and the lowest value of SEE (0.055). Boostani et al. (2018a) also reported that
 517 the power function was the best kinetic model to describe Cd desorption in a Cd-contaminated soil
 518 treated with biochars and zeolite.

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Table 6

The range of coefficients of determination (R^2) and standard error of estimate (SEE) of applied kinetic models to all the soil treatments.

Kinetic models	R^2		SEE	
	Range	Mean	Range	Mean
Zero order	0.79-0.87	0.80	3.36-4.67	3.67
First order	0.69-0.75	0.75	0.22-0.29	0.25
Second order	0.53-0.61	0.52	$(1.10-2.60) \times 10^{-2}$	1.80×10^{-2}
Third order	0.39-0.51	0.41	$(1.30-5.20) \times 10^{-3}$	3.00×10^{-3}
Parabolic diffusion	0.94-0.98	0.96	1.26-2.44	1.85
Power function	0.97-0.99	0.98	0.05-0.06	0.05
Simple Elovich	0.92-0.97	0.95	2.04-2.78	2.50

525

526 3.8 Using the parameters of power function model to investigate the effect of treatments on Ni
527 desorption in soil

528 As the power function model ($q = at^b$) described the Ni release data the best, its
529 parameters (a and b) were used to investigate the effect of biochar application and Si levels on the
530 release of Ni in the Ni-contaminated soil (Table 7). The main effects of biochars and Si levels and
531 their interactions on the 'a' and 'b' parameters were significant ($P < 0.01$). As Dang et al. (1994)
532 reported, in this kinetic model, a decrease in parameter 'a' and an increase in parameter 'b' indicates
533 a decrease in the rate of heavy metal desorption from the soil. The main effects of the treatments
534 showed that addition of all 4 biochars caused a significant decrease in the 'a' parameter compared
535 to the control while the 'b' parameter was significantly increased (Table 7). The same trend was
536 observed for all the Si treatment levels (Table 7). Therefore, it can be concluded that the use of all
537 the biochars and Si levels caused a decrease in the rate of Ni release in the Ni-contaminated soil.
538 Generally, there was a greater decrease in Ni desorption in biochar treatments prepared at the
539 higher temperature (Table 7). The interactive effects indicate that the most effective combined
540 treatment in reducing the rate of Ni release in the soil was SM500+S₂ which had the lowest value
541 of parameter 'a' (4.52) and the highest value of parameter 'b' (0.26) among the treatments.

542 If it is differentiated from the power function equation ($q = at^b$) with respect to time (t)
543 ($dq/dt = ab t^{b-1}$), when $t = 1$ s = 0, the ratio of dq/dt becomes 'ab'. This parameter indicates the
544 amount of heavy metal desorption in the initial time (Dalal, 1985). The 'ab' parameter was affected
545 by the application of Si levels and biochars, so that this parameter was significantly decreased
546 compared to the control with addition of all the biochars (12.4%, 24.2%, 15.4% and 21.3% for the
547 SM300, SM500, RH300 and RH500, respectively) and Si application levels (13% from S₀ to S₂),
548 (Table 7). This finding also confirmed the effect of applied treatments in reducing the amount of
549 Ni release. The greatest reduction was observed in the combined treatment of SM500+S₂ by 33.5%
550 compared to the control (Table 7).

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Table 7

The coefficients of the power function model as affected by biochars and Si application levels in a Ni-polluted calcareous soil after corn cultivation.

	C	SM300	SM500	RH300	RH500	Mean
	a (mg Ni kg ⁻¹ h ⁻¹) ^b					
S ₀	9.15 a	7.39 c	5.56 gh	6.49 e	5.95 f	6.91 A
S ₁	7.92 b	6.01 f	5.23 i	5.66 g	5.21 i	6.00 B
S ₂	6.90 d	5.39 hi	4.52 k	5.22 i	4.84 j	5.38 C
Mean	7.99 A	6.27 B	5.11 E	5.80 C	5.34 D	
	b (mg Ni kg ⁻¹) ⁻¹					
S ₀	0.20 g	0.22 e	0.25 b	0.24 c	0.24 c	0.23 C
S ₁	0.21 f	0.24 c	0.25 b	0.25 b	0.25 b	0.24 B
S ₂	0.23 d	0.25 b	0.26 a	0.26 a	0.26 a	0.25 A
Mean	0.21 C	0.24 B	0.25 A	0.25 A	0.25 A	
	ab					
S ₀	1.79 a	1.68 c	1.37 h	1.54 e	1.41 g	1.55 A
S ₁	1.69 b	1.43 f	1.29 k	1.41 fg	1.32 j	1.42 B
S ₂	1.59 d	1.37 h	1.19 m	1.34 i	1.27 l	1.35 C
Mean	1.69 A	1.48 B	1.28 E	1.43 C	1.33 D	

Notes: C, control; SM300, sheep manure biochar produced at 300 °C; SM500, sheep manure biochar produced at 500 °C; RH300, rice husk biochar produced at 300 °C; RH500, rice husk biochar produced at 500 °C; S₀, without Si addition; S₁, application of 250 mg Si kg⁻¹ soil; S₂, application of 500 mg Si kg⁻¹ soil.

* Numbers followed by same letters in each column and rows, in each section, are not significantly (P<0.05) different

The correlation between the parameters of the fitted power function model with Ni content in various soil chemical fractions, Ni concentration in corn shoots and soil pH are shown in Table 8. The 'a' and 'ab' parameters had a positive correlation with the Ni content in the WsEx, OM and MnOx fractions, while these parameters had a negative correlation with the Ni content in the AFeOx and CFeOx fractions. This trend was inverse for the 'b' parameter of the power function model. These correlations verified that the application of Si and biochar to the Ni-contaminated calcareous soil led to a decrease in the rate and amount of Ni release by reducing the Ni concentration in chemical forms with higher bioavailability including WsEx, OM and MnOx. Furthermore, the 'a' and 'ab' parameters were negatively correlated with soil pH. Whereas there were positive correlations between these parameters and Ni concentration in shoots (Table 8). These findings once again confirmed that the increase in soil pH due to the application of Si and biochar can cause a decrease in bioavailability of Ni in the soil and, as a result, a decrease in the concentration of Ni in aerial parts of the plant.

Table 8

The Pearson correlation coefficients (r) among the power function model parameters (a, b, ab) with Ni content in soil chemical fractions, Ni concentration in corn shoots and soil pH.

	WsEx	Car	OM	MnOx	AFeOx	CFeOx	Res	Ni content in shoots	Soil pH
a	0.63**	0.02 ^{ns}	0.70**	0.53**	-0.44**	-0.80**	0.27 ^{ns}	0.62**	-0.52**
b	-0.59**	0.03 ^{ns}	-0.68**	-0.54**	0.46**	0.83**	-0.28 ^{ns}	-0.63**	0.51**
ab	0.68**	0.04 ^{ns}	0.74**	0.46**	-0.46**	-0.80**	0.29 ^{ns}	0.06**	-0.51**

Notes: WsEx, water soluble and exchangeable fraction; OM, organic fraction; MnOx, bound to manganese oxides; AFeOx, bound to amorphous iron oxides; CFeOx, bound to crystalline iron oxides; Res, residual fraction.

** and ^{ns} indicate significance at the 0.01 probability level and non-significant, respectively.

570 **4 Conclusions**

571 The application of biochars and Si in the present study resulted in the transfer of Ni in soil
 572 from more bioavailable and mobile fractions (WsEx, MnOx, OM) to more stable forms (AFeOx
 573 and CFeOx). These changes were particularly evident in the WsEx fraction when SM biochars
 574 were applied in conjunction with silicon, indicating a strong synergistic effect related to soil pH
 575 increase. Application of all biochars and Si reduced DPTA-extractable Ni release in the soil, which
 576 was most strongly associated with the increase in Ni content in the CFeOx fraction. Application
 577 of all the biochars and Si decreased corn Ni uptake, with the combined SM500+S₂ being the most
 578 effective. The decrease in corn uptake was correlated with the decrease in Ni content in the WsEx
 579 fraction and increase in the CFeOx fraction. SM500 was likely the most effective biochar due to
 580 its higher alkalinity and ash content, and lower acidic functional group content which enhances Ni
 581 sorption reactions with Si. Future research is needed to better understand the mechanisms
 582 underlying the interaction effects of Si and biochar application on the distribution of Ni in different
 583 soil chemical fractions and to optimize Si application strategies for sustainable Ni management in
 584 agricultural and natural ecosystems. It is suggested that the interactive effects of Si and biochar on
 585 the Ni content in soil chemical fractions and its release in aged Ni-contaminated soils should also
 586 be investigated and compared, as this study was limited to a recently Ni-contaminated soil.

587

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 589 Validation A.G.H. Writing - Review & Editing M.N. Project administration, Visualization E.B.
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