

Contribution of Enriched Biochar to the Reduction of the Hydrosoluble Fraction of Some Heavy Metals in an Urban Soil in Ngaoundere, Cameroon

ABSTRACT:

The fertilization by spreading cheap compost coming from unsorted household waste result in the introduction of important quantities of pollutants in the market gardening soils. The soluble fraction of heavy metals existing in the soil can produce important ecotoxicological impacts if its percolation and its transfer in the plant or in the soil water is not restricted. These pollutants substances can therefore generate significant damage to the environment and human health. The aim of the present study is to evaluate the capacity of improved biochar to reduce the hydrosoluble fraction of heavy metals present in a polluted urban soil in Ngaoundere. Different proportion of enriched biochar was incorporating in a polluted soil in order to reduce the hydrosoluble fraction of the four heavy metals (Cadmium, Zinc, Copper and Nickel). Analysis showed that enriched biochar increases the pH at 20%. In addition, the reduction of the hydrosoluble fraction of cadmium is total within one week. Finally, the fixation of the hydrosoluble forms of the heavy metals in the polluted soils can limited their transfers in the plants and the waters.

Keywords: Enriched biochar, Heavy metals, Urban soil, Depollution, Hydrosolubility.

1. INTRODUCTION

Anthropogenic activities in general and those related to intensive agriculture using inputs in particular have increased agricultural yield. However, the amendment by spreading compost from unsorted household waste results in the introduction of significant amounts of pollutants such as heavy metals into agricultural soils [1–5]. Heavy metals occur in polluted soil in potentially bioavailable and non-bioavailable fractions. The bioavailable fraction includes hydrosoluble and exchangeable forms. The potentially bioavailable fraction includes forms bound to carbonates and organic matter. The forms bound to resistant minerals are non-bioavailable [6, 7]. The factors that influence this bioavailability are the pH; the organic matter, carbonate and oxide contents of the soil, as well as its texture and the microbial activity of the microorganisms contained in the soil [6, 8–10].

This bioavailability can be modified upon incorporation of enriched biochar (EB) via several mechanisms [11, 12]. Enriched biochar can be attributed to various effects that can stabilize heavy metals in soils. Direct effects include physical sorption where electrostatic attraction occurs due to the double bonds of the biochar and the heavy metal orbitals. As for the chemical sorption, the molecule links to the surface of the biochar by ionic or covalent bonds. Solid precipitates can also form on the biochar surface with carbonates, phosphates, silicates and hydroxides from the enriched biochar. Direct effects are attributed to the increase in soil pH when the enriched biochar is incorporated. There is also an increase in the cation exchange capacity [13–15], of the soil in the presence of the biochar which helps to stabilize heavy metals present in polluted soils [13, 15–18].

Studies on the stabilization of different types of heavy metals by various types of enriched biochars have been conducted on soils in Belgium [16, 19]. Houben and al.[19] tested the remediation power of enriched biochar by varying its incorporation rate from 1%, 5% to 10% in zinc, cadmium and lead polluted soil in a pot experiment. The levels of bioavailable heavy metals began to decrease after the first hour of incubation and increased throughout the 56-day incubation period. They attributed this reduction mainly to the increase in pH and cation exchange capacity following the incorporation of the different biochar rates. Thus, the introduction of biochar into a soil reduces the mobility of trace metals [15, 20–22]. A strong correlation has been established between pH and water-soluble heavy metal content. Yang and al. [23] tested the stabilizing power of biochar from bamboo and rice stalks in polluted soil in southwest China on

the bioavailable fraction of cadmium, copper, zinc and lead. They reached similar conclusions as Houben et al. [19].

While the contribution to immobilize some trace metal elements in agricultural soils in some regions of the world have been revealed, no study has been conducted on the market garden soils of the city of Ngaoundere (Cameroon). The objective of the present study is to evaluate the capacity of locally produced enriched biochar to reduce the hydrosoluble quantity of some heavy metals present in a market garden soil of Ngaoundere.

2. MATERIALS AND METHODS

2.1. Material

2.1.1. Experimental design

The experimental design shown in Fig. 1 allowed to measure the influence of different proportions of enriched biochar on some physicochemical properties of the soil and to assess the retention of the water-soluble fraction of heavy metals. The properties measured are pH_{water}; pH_{KCl}; electrical conductivity (EC); cation exchange capacity (CEC); organic matter; total cadmium; copper; zinc and nickel content as well as soluble cadmium and copper, zinc and nickel content. The device consists of three series of columns from top to bottom.

2.1.2. Enriched biochar

The enriched biochar used in this study was obtained from a mixture of 53% of sawdust powder of Ayous species "*Triplochiton scleroxylon*", 30% of Wak clay powder and 17% of chicken droppings powder. The choice of these proportions of the components of the enriched biochar was obtained by the response surface analysis by using a method of optimization and the mixing plans. The conditions for biochar production were a temperature of 550°C and a residence time of 2 hours in an electric furnace.

2.2. Methods

2.2.1. Sampling and soil preparation

Sample collection was conducted in accordance with the method described by Beesley and Marmiroli. [24]. Samples were collected to a depth of 20 cm from the surface using a shovel. The quartering allowed to homogenize the samples and select the representative sample. Drying was done in the open air for 24 h.

2.2.2. Experimental protocol.

Table 1 presents the proportions and mass of soil or enriched soil-biochar mixture. The proportions of 0%; 1%; 5%; 10%; 15% and 20% enriched biochar were applied. A constant mass of soil (500 g) mixed with the different proportions of enriched biochar underwent a drip (Fig. 2).

2.2.3. Characterization of soil and enriched biochar.

The pH water value was performed according to the method of Rajkovich et al. [25] As for the pH_{KCL} analysis, the samples were prepared under the same conditions but in 2/5 (m/v) suspensions. The electrical conductivity of the soil samples was performed according to NF ISO 11265 [26]. The cation exchange capacity (CEC) was determined according to the AFNOR standard method NFX 31–130 [27]. The organic matter content was obtained after calcination of the samples in an oven (550°C, 4 hours). The total content of different heavy metals was determined by atomic absorption spectrometry. The spectrometer used is a VARIAN SpectrAA.20 type operating in flame mode with an air-acetylene mixture. The characteristics of the lamps used are wavelengths of 228.8; 232; 213 and 324 nm respectively for cadmium, nickel, zinc and copper. The analysis of heavy metals was carried out on both the initial soil and the enriched soil-biochar mixtures. The granulometric analysis was applied only on the studied soil and determined according to the Robinson pipette method [28].

2.2.4. Statistical analysis.

The results are statistically analyzed with the software "Statgraphic Centurion" version 18 and Minitab 18. The comparison of the means was done by analysis of variance (ANOVA). Tukey's Honestly Significant Difference (HSD) test was chosen to determine the difference between the means of the treatments. The linear correlation coefficient r measures the strength of the linearity relationship between two variables. The removal rate t (%) (Expressed as a percentage) was used to evaluate the effect of the enriched biochar on the four heavy metals present in the soil. The basis of calculation was always the initial heavy metal content, at the beginning of the remediation (time $t_i=0$) and without incorporation of enriched biochar.

3. RESULTS AND DISCUSSION

3.1. Physical-chemical analyses of urban soils and enriched biochar

Table 2 presents the results of some physicochemical parameters of the soil and enriched biochar. With a pH of 5.96 ± 0.05 , the studied soil is weakly acidic. The soil pH value obtained is similar to those obtained by other

authors who analysed samples from the same site (Adjia et al. 2008). However, this value is lower than that obtained by Ramachandran and D'souza [30] although fertilization was also carried out using compost from organic waste. With a pH of 9.55 ± 0.01 , the enriched biochar is highly basic and falls within the pH range of 6.2 and 9.6 [31]. The high pH value of the enriched biochar is attributable to the enrichment with clay and especially with chicken manure and pyrolysis conditions (moderate temperature and time). In general, the pH of biochar varies with the nature of the substrate used [20, 24, 32, 33].

The pH_{KCL} ranges from 5.2 ± 0.01 (soil) to 8.96 ± 0.01 (enriched biochar). The pH_{KCL} values are all lower than the obtained pH water values. A significant variation ($p<0.05$) was noted between the two substrates studied and the Tukey HSD test also distinguishes two groups representing the two substrates. The calculated coefficient of variation is 26.63% for pH_{KCL} . This variation is also attributed to the comparison between the enriched biochar (highly basic) and the urban soil (weakly acidic). As the mobility and availability of heavy metals is largely dependent on the pH of the medium [14], it is expected that without the incorporation of the enriched biochar, these pollutants will be more mobile and more bioavailable. The electrical conductivity of the studied soil is $26.5\pm 0.3 \mu S.cm^{-1}$ and that of the enriched biochar is 47.75 ± 1.7 . These values are significantly different at $p<0.05$. The soil electrical conductivity values are close to those obtained by Adjia and al. [5] and are less than $60\mu S.cm^{-1}$. They are thus not salty and this is the reason why market gardening is practiced there [34, 35]. The calculated coefficient of variation is 52.74% and reflects the high electrical conductivity of the enriched biochar compared to the studied soil. The cation exchange capacity is $48.85\pm 5 cmol+kg^{-1}$ and $195\pm 5 cmol+kg^{-1}$ for the soil and enriched biochar respectively for a coefficient of variation of 68.05%. The very high coefficient value is attributable to the high cation exchange capacity value measured for the enriched biochar. A significant variation ($p<0.05$) was noted between the two substrates studied and the Tukey HSD test also distinguishes two groups representing the two substrates.

The mean value of organic matter content varied from $15.4\pm 1.1\%$ (soil) and $37.2\pm 1.5\%$ for enriched biochar. The coefficient of variation is 46.26%. These results are far from those of Adjia and al. [5]. This difference could be explained by variations in harvesting season. The high organic matter value of the enriched biochar compared to the soil can be explained by the biological nature of this adsorbent, which is largely composed of sawdust (more than 50%) and chicken manure (more than 15%). A significant variation ($p<0.05$)

was noted between the two substrates studied and the Tukey HSD test distinguishes two groups representing the two substrates. The organic matter present in this soil could not only serve as a nutrient for the plants but also as an absorbent for possible pollutants. The particle size analysis revealed a content of $70.86 \pm 1.2\%$ (sand); $9.35 \pm 1.4\%$ (silt) and $19.85 \pm 1.5\%$ (clay). The particle size analysis classifies the studied soil as sandy loam (SL) soil. Cadmium total analysis reveals a content of $4.72 \pm 0.03 \mu\text{g.g}^{-1}$. This result is close to those obtained by Adjia and al. [5]. This value is outside the European Union standard (ADEME and APCA, 2005) where the cadmium content of soils must be between 0.5 and $1.5 \mu\text{g.g}^{-1}$ whatever the pH considered. The total copper content is $80.98 \pm 5.5 \mu\text{g.g}^{-1}$. This value is slightly lower than those obtained by [5] but is nevertheless within the European Union standard. This standard stipulates that the copper content of agricultural soils must be between 20 and 100 regardless of the pH considered. As for the total zinc content, the soil has a value of $258.42 \pm 9.4 \mu\text{g.g}^{-1}$. The value of the total zinc content of the soil is outside the European norm ($60\text{-}200 \mu\text{g.g}^{-1}$). The last heavy metal studied, nickel, has a value of $40.47 \pm 3.2 \mu\text{g.g}^{-1}$. This value is lower than those obtained by [5] but remains within the standards prescribed by the European Union ($15\text{-}70 \mu\text{g.g}^{-1}$). The sequence of total heavy metal contents in the studied vegetable soil is as follows: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cd}$. This sequence corroborates with that of [5] where the abundance of zinc compared to other heavy metals studied is also noted.

3.2. Influence of enriched biochar on the evolution of pH and hydrosoluble fraction of heavy metal content of soil leachate water.

The choice of a pH evolution study is dictated by the fact that for many authors [14, 19, 36], the increase of pH in a medium is the main cause of the reduction of the amount of immobilized heavy metals. In the case of this study, the increase in pH following biochar incorporation may control the extractability of heavy metals in soils, with the heavy metals being retained more on the soil and biochar particles due to an increase in negative surface charges. The influence of other factors, not studied here, likely plays a secondary role in the short-term immobilization of heavy metals in contaminated soils [36].

3.3. Influence of enriched biochar on soil pH changes.

Fig. 2 shows the evolution of the pH of the leachate water respectively the soil as a function of the proportion of enriched biochar incorporated. In the absence of enriched biochar (control soil),

the pH evolution is almost null and even shows a decrease at the 9th week. The period of evolution of the pH would correspond to the capacity of certain constituents of the soil to reveal the pH of the soil like the presence of certain soluble cations. The decrease in pH after the 9th week may be due to a significant dissolution of iron and aluminum ions and humic acids contained in the soil organic matter. As soon as the enriched biochar is incorporated (1% or more), a pH increase is noticed that is higher than the pH of the control soil of the same period. This finding is generally attributed to the biochar because of its basic nature [19]. During pyrolysis, basic cations such as calcium, magnesium, potassium, and sodium present in the biomass are converted to hydroxides and carbonate [20, 37]. An increase that is more important when it comes to biochar enriched from chicken manure. The change in pH of the mixtures (enriched biochar and soil) reaches its maximum at the 4th week and stabilizes at a constant value throughout the rest of the experiment period. Effects during similar periods have been observed by several authors [19]. According to [20], the increase in pH is also due to decarboxylation of organic anions and ammonification and that the decrease in pH is attributed to nitrification. The impact of biochar in acidic soils has been reported by several stakeholders [14, 19, 24, 32]. The difference in the pH evolution of the mixtures seems to be smaller when the enriched biochar reaches the 15% proportions.

3.4. Influence of enriched biochar on the evolution of hydrosoluble of cadmium content.

Fig. 3 shows the evolution of hydrosoluble cadmium content as a function of the proportions of enriched biochar incorporated and time. The initial soluble cadmium content of the soil was $0.15 \pm 0.02 \text{ mg.kg}^{-1}$. The low values of cadmium compared to other heavy metals studied were also revealed by Adjia and al. [5]. The hydrosoluble fraction of cadmium represents the most soluble fraction because this fraction is extracted with water. The

Table 3 presents the rate of abatement of soluble cadmium. It can be seen that in the absence of the enriched biochar, the final removal rate (after 8 weeks) of the soluble fraction of cadmium present is respectively 19.33. The incorporation of enriched biochar allows a complete depollution after five weeks at a proportion of enriched biochar of 15%. Dumroese et al. [38, 39] obtained similar results with a mixture of peat and biochar after 29 days of experimentation [40]. The effectiveness of

enriched biochar in reducing soluble cadmium is seen as early as 1% incorporation of this adsorbent where an abatement rate of 15 was found. Fig. 4 shows the influence of pH on the quantity of soluble cadmium. It can be seen that the increase in pH due to the incorporation of the enriched biochar leads to a decrease in the soluble fraction of cadmium content. Table 4 represents the results of the correlation analysis. With a correlation coefficient of -0.94, the dependence of soluble fraction of cadmium reduction on pH increase is very strong. The correlation coefficient values are close to that obtained by Houben et al. [19] although their study was not performed on the same type of cadmium fraction nor on the same type of biochar. With a fitted R^2 coefficient of determination close to the R^2 coefficient of determination, we can state that the preferred model is good. This is reinforced by a value of S (sum of squares of residues) close to zero.

3.5. Influence of enriched biochar on the evolution of hydrosoluble of zinc content.

Fig. 5 shows the evolution of the hydrosoluble zinc content. The initial value of soluble zinc is $2.28 \pm 0.3 \text{ mg.kg}^{-1}$. Zinc ions have a strong affinity with the adsorption sites of the enriched biochar compared to cadmium ions. Table 5 represents the removal rate in the soil. The control soil constituents provide an abatement rate of 11.23. The incorporation of enriched biochar even at low proportions (1%) allows a reduction of 3.36% from the contact between this adsorbent and the contaminated soil. The incorporation of enriched biochar, even at the highest rates studied in this work, does not completely remove the soluble zinc present in the two soils. At the highest rates of incorporation (20% enriched biochar incorporated) and for the longest periods (9 weeks), the removal rate was 58.33. This is explained by the initial high levels of this heavy metal and the release from the zinc contained in the soil fractions. From a phyto-nutritional point of view, a complete removal of soluble zinc could even be detrimental to the plant, since at low proportions it is rather a trace element necessary for plant growth [19].

Fig. 6 shows the relationship between pH and soluble zinc content. Increasing pH results in a reduction in soluble zinc content.

Table 6 shows the results of the correlation analysis. The correlation coefficient between pH and hydrosoluble zinc is -0.74 respectively. These values are low compared to the coefficients calculated for soluble cadmium, but

nevertheless represent a strong dependence of soluble zinc reduction on pH. Both calculated correlation coefficients are less than -0.7. In studies by Houben et al. [19], the authors obtained a correlation coefficient of -0.94 for the pH dependence of exchangeable zinc on CaCl_2 . This difference can be explained by the nature of the zinc fraction studied and to the type of biochar used. The proposed regression model for the pH dependence of soluble zinc in both soils has a low coefficient of determination and a low adjusted coefficient of determination compared to the hydrosoluble cadmium study.

3.6. Influence of enriched biochar on the evolution of hydrosoluble of nickel content.

Fig. 7 shows the evolution of the hydrosoluble fraction of nickel content as a function of the incorporation rate of enriched biochar and time. The initial soluble nickel content is $1.23 \pm 0.02 \text{ mg.kg}^{-1}$. The soluble nickel value is lower than the soluble fraction values of the other heavy metals studied except for the soluble fraction of cadmium. Similar comparisons were obtained by Adjia and al. [5],[29]. Constituents of control soils provide a 23.58 reduction. Dumroese et al. [41] obtained concentrations of less than 0.01 mg.kg^{-1} after 29 days of experimentation. The difference with these results can be explained in part by the low soluble nickel content at baseline (less than 6%) and the associated substrate at baseline which was peat.

Table 7 shows the rate of soluble nickel removal. The enriched biochar removes nickel after four weeks (100% removal rate) in the Bali soil for a 20% incorporation of enriched biochar or after eight weeks at a 15% incorporation rate. Fig. 8 shows the dependence of soluble nickel. Like the soluble fraction of the first two heavy metals, the increase in pH is inversely proportional to the soluble nickel content. Table 8 presents the correlation analysis between pH and soluble nickel content. The correlation coefficients obtained are -0.68. The preferred model of hydrosoluble nickel dependence on pH has low values where the coefficient of determination is 47.21%. Nevertheless, with a sum of squares of

residues equal to 0.12 and close to 0, we can validate the proposed model [40, 42].

3.7. Influence of enriched biochar on the evolution of hydrosoluble of copper content.

Fig. 9 represents the evolution of hydrosoluble copper as a function of the enriched biochar incorporated and the soil. Of all the heavy metals studied, the soluble copper fraction is the most important. A soluble copper content of $4.01 \pm 0.2 \text{ mg.kg}^{-1}$. In the absence of enriched biochar, the constituents responsible for soluble copper retention provide an abatement rate of 16.81.

Table 9 shows the abatement rate. Upon incorporation of 1% enriched biochar, nearly 4% of the soluble copper content is retained. Incorporation of 15% and 20% enriched biochar eliminates the presence of soluble copper for four weeks. Being a trace element, a total elimination of soluble copper may represent a deficiency of this chemical element for the plants. Fig. 10 shows the correlation between pH and the amount of soluble copper. As for the other three heavy metals studied, it is noticed that the content of soluble copper decreases when the pH increases. Table 10 represents the results of the correlation analysis between the pH and the soluble copper content. The correlation coefficient is -0.85. This strong coefficient shows the dependence of the decrease in the soluble fraction of this heavy metal on pH. The preferred model for the dependence of soluble copper on pH has a sum of squares of residues greater than 0.5. However, the coefficients of determination and the fitted coefficients of

determination are greater than 70%. This may allow us to validate the model.

4. CONCLUSION

The objective of the present study was to evaluate the capacity of improved biochar to reduce the hydrosoluble fraction of heavy metals present in a polluted urban soil in Ngaoundere. It appears that the incorporation of improved biochar raises the pH by more than two units and increases the cation exchange capacity. In addition, the incorporation of enriched biochar significantly reduces the content of bioavailable heavy metals. Enriched biochar had better performance for the fixation of soil heavy metals related to the higher surface areas and more functional groups and had enough binding sites to combine heavy metal ions. By using the mechanism of electrostatic sorption, the action of the surface complexation and precipitation of functional groups and free π electrons on the surface of carbon materials. At high incorporation rates of enriched biochar, the content of bioavailable heavy metals can be below the values allowed by the European standard. The stabilization of the most ecotoxicologically toxic fraction, the hydrosoluble fraction, is reduced, especially for cadmium. Thus, for this heavy metal, the abatement rate is total. There is a complete absence of hydrosoluble fraction of cadmium after one week. The strong correlation between the pH and the hydrosoluble contents of the studied heavy metals allows us to affirm that between all the mechanisms that can stabilize metals, the pH is the most important. The pH contributes more strongly to the stabilization of heavy metals than the direct effects by chemical sorption, physical sorption or precipitation. There is a strong affinity between enriched biochar and the hydrosoluble fraction of cadmium, followed by the hydrosoluble fractions of copper, nickel and finally zinc.

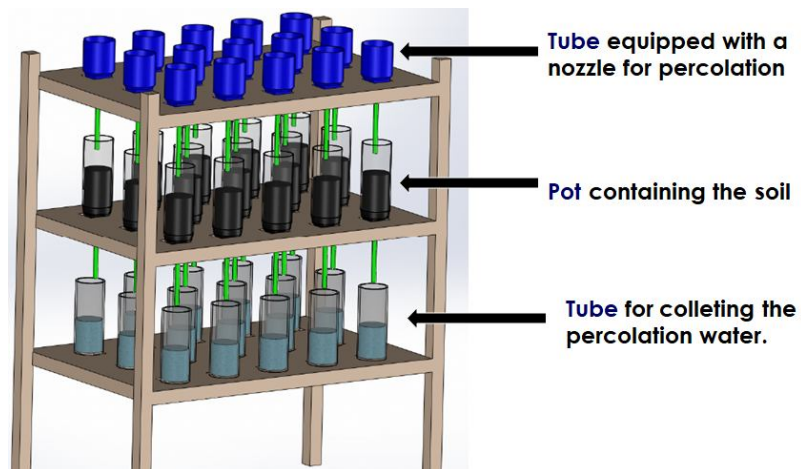


Fig. 1 :Percolation apparatus.

Table 1: Soil and different enriched soil-biochar mixtures for the leaching setup.

Matrix	Control	N°1	N°2	N°3	N°4	N°5
Soil [g]	500	500	500	500	500	500
Biochar [Wt%]	0	1	5	10	15	20
Biochar [g]	0	5	25	50	75	100
Total [g]	500	505	525	550	575	600

Table 2: Physiochemical analysis of soil and enriched biochar.

Parameters	Soil	Enriched Biochar
pH _{water}	5.96±0.05 ^b	9.55±0.01 ^a
pH _{KCl}	5.20±0.01 ^b	8.96±0.01 ^a
EC _{1/5} [$\mu\text{S}\cdot\text{cm}^{-1}$]	26.56±0.3 ^b	47.75±1.7 ^a
CEC [$\text{cmol}\cdot\text{kg}^{-1}$]	48.85±5 ^b	195±5 ^a
OM [%]	15.4±1.1 ^b	37.2±1.5 ^a
<i>Granulometric Analysis</i>		
Sand content [%]	70.86±1.2	nd
Silt content [%]	9.35±1.4	nd
Clay content [%]	19.85±1.5	nd
Soil texture	S-s	nd
<i>Heavy metals (Total)</i>		
Total Cd [$\mu\text{g}\cdot\text{g}^{-1}$]	4.72±0.03	nd
Total Cu [$\mu\text{g}\cdot\text{g}^{-1}$]	80.98±5.5	nd
Total Zn [$\mu\text{g}\cdot\text{g}^{-1}$]	258.42±9.4	nd
Total Ni [$\mu\text{g}\cdot\text{g}^{-1}$]	40.47±3.2	nd

Values followed by the same small letters are not significantly different at $p < 0.05$ p =probability; OM=organic matter; EC=electrical conductivity; CEC=cation exchange capacity; Cd=cadmium; Zn=Zinc; Ni=Nickel; Cu=Copper; nd=not determined; S-s=sandstone.

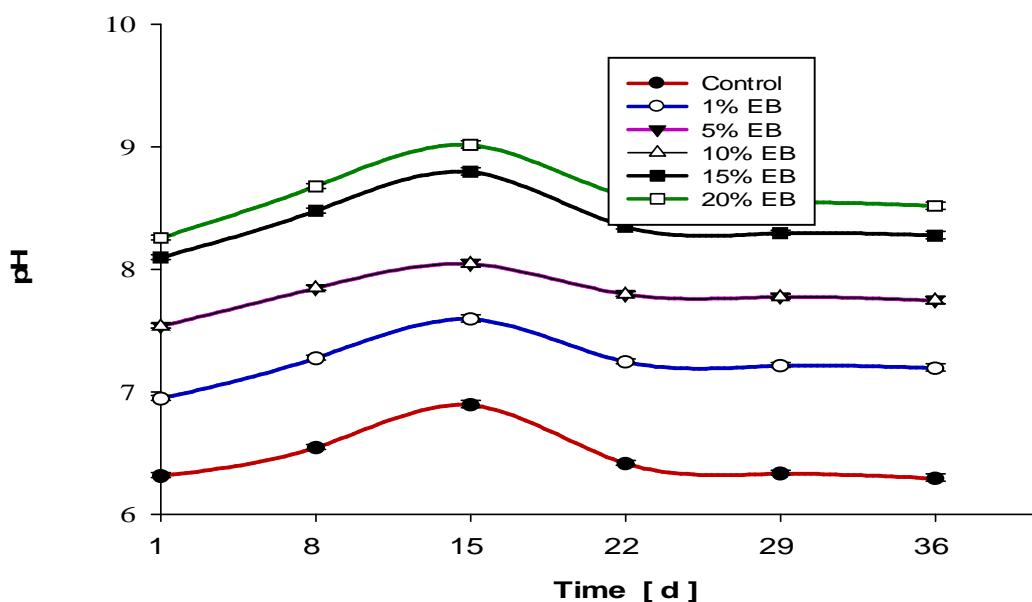


Fig. 2: Evolution of pH as a function of time and the proportion of enriched Biochar incorporated.

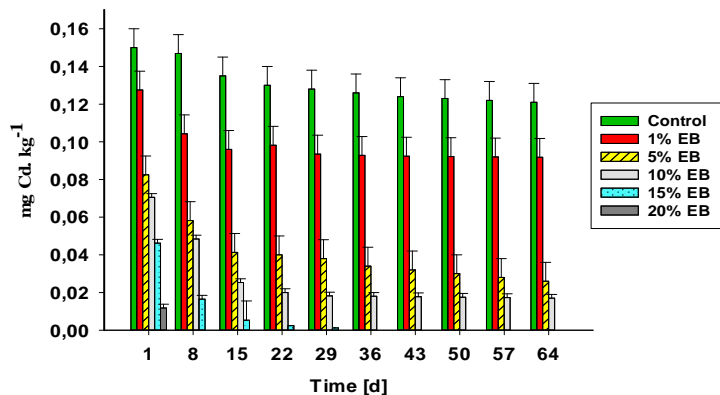


Fig. 3: Evolution of the hydrosoluble Cadmium content as a function of the proportion of enriched biochar incorporated and time.

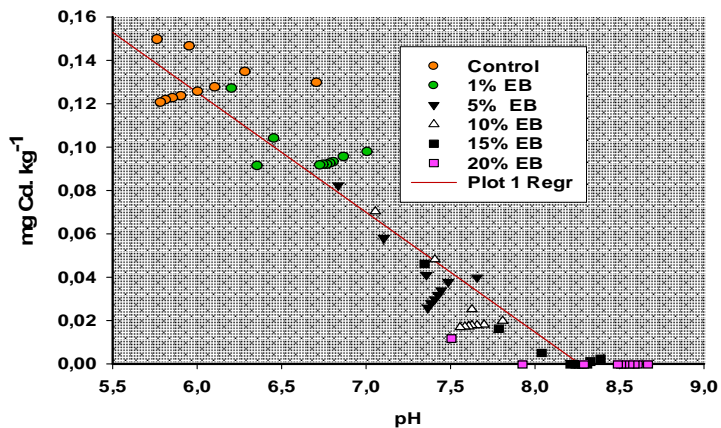


Fig. 4: Influence of pH on hydrosoluble Cadmium content.

Table 3: Hydrosoluble Cadmium removal rates as a function of the proportion of enriched biochar incorporated and time.

Time [d]	Control	1%EB	5%EB	10%EB	15%EB	20%EB
1	0.00	15.00	45.00	53.00	69.2	92.13
8	2.07	30.47	61.2	67.73	89.00	100.00
15	10.00	36.00	72.47	83.13	96.47	100.00
22	13.33	34.53	73.33	86.67	98.40	100.00
29	14.67	37.67	74.67	87.87	99.20	100.00
36	16.00	38.13	77.33	88.00	100.00	100.00
43	17.33	38.4	78.67	88.13	100.00	100.00
50	18.00	38.53	80.00	88.33	100.00	100.00
57	18.67	38.67	81.33	88.47	100.00	100.00
64	19.33	38.80	82.67	88.67	100.00	100.00

EB=proportion of enriched Biochar

Table 4: Correlation and variance analysis of hydrosoluble fraction Cadmium content as a function of pH.

Term	Coeff.	p	r	S	R ²	R ² ajus	VIF
Value at the beginning	0.457						
Gradient	-0.055						
Statistics		0.000	-0.94	0.015	90.92%	90.76%	1.00

Coeff=coefficient, p=probability; r=linear correlation coefficient; S=sum of squares of residuals, R²=coefficient of determination; R²ajus=adjusted coefficient of determination, VIF=variance inflation factor

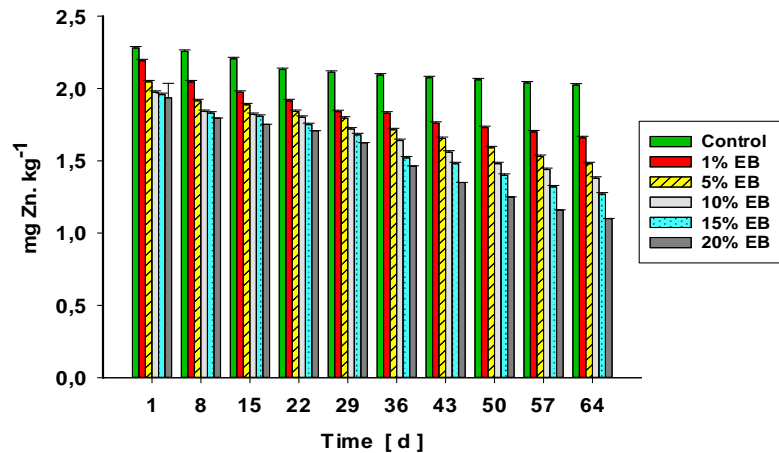


Fig. 5: Evolution of the hydrosoluble Zinc content as a function of the proportion of enriched biochar incorporated and Time.

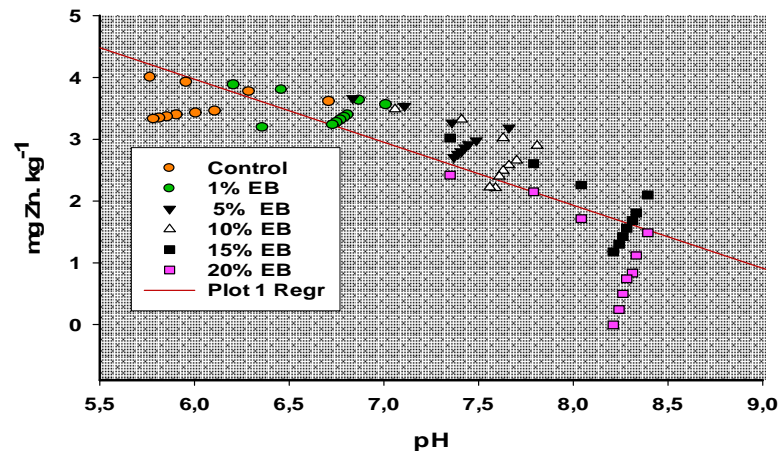


Fig. 6: Influence of pH on hydrosoluble Zinc content.

Table 5: Hydrosoluble Zinc removal rates a function of the proportion of enriched biochar incorporated and time.

Time [d]	Control	1%EB	5%EB	10%EB	15%EB	20%EB
1	0.00	3.86	10,26	13.42	14.12	15.09
8	1.01	10.26	16,01	19.25	19.74	21.27
15	3.25	13.42	17,24	20.13	20.7	23.16
22	6.54	13.43	19,25	21.01	23.25	25.09
29	7.37	13.44	21,27	24.56	26.32	29.61
36	8.2	13.45	24,78	28.07	33.33	35.79
43	8.99	13.46	27,46	31.58	35.09	41.67
50	9.65	13.47	30,26	35.09	38.6	47.37
57	10.61	13.48	32,89	36.84	42.11	53.51
64	11.23	13.49	35,09	39.47	44.3	58.33

EB=proportion of enriched Biochar

Table 6: Correlation and variance analysis of hydrosoluble fraction of Zinc content as a function of pH.

Term	Coeff.	p	r	S	R ²	R ² ajus	VIF
Value at the beginning	3.63						
Gradient	-0.256						
Statistics		0.000	-0.74	0.193	56.62%	55.87%	1.00

Coeff=coefficient, p=probability; r=linear correlation coefficient; S=sum of squares of residuals, R²=coefficient of determination; R²ajus=adjusted coefficient of determination, VIF=variance inflation factor

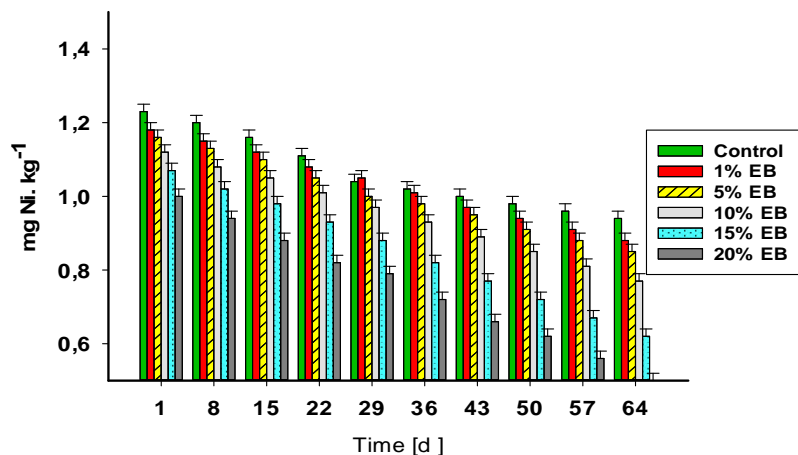


Fig. 7: Evolution of the hydrosoluble Nickel content as a function of the proportion of enriched biochar incorporated and time.

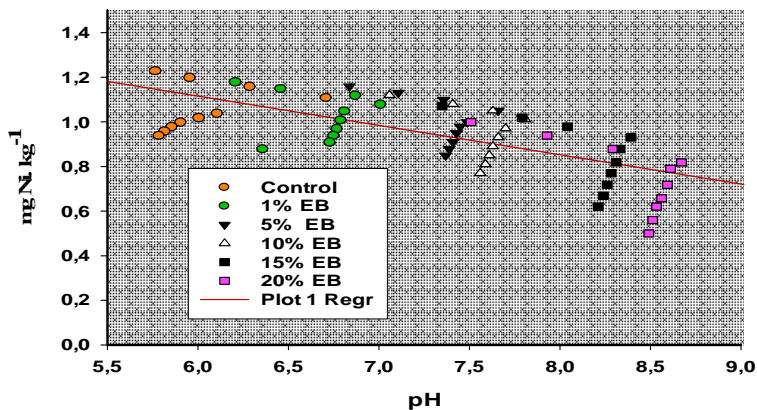


Fig. 8 : Influence of pH on hydrosoluble Nickel content.

Table 7: Hydrosoluble Nickel removal rates as a function of the proportion of enriched biochar incorporated and time.

Time [d]	Control	1%EB	5%EB	10%EB	15%EB	20%EB
1	0.00	4.07	5.69	8.94	13.01	18.7
8	2.44	6.5	8.13	12.2	17.07	23.58
15	5.69	8.94	10.57	14.63	20.33	28.46
22	9.76	12.2	14.63	17.89	24.39	33.33
29	15.45	14.63	18.7	21.14	28.46	35.77
36	17.07	17.89	20.33	24.39	33.33	41.46
43	18.7	21.14	22.76	27.64	37.4	46.34
50	20.33	23.58	26.02	30.89	41.46	49.59
57	21.95	26.02	28.46	34.15	45.53	54.47
64	23.58	28.46	30.89	37.4	49.59	59.35

EB=proportion of enriched Biochar

Table 8: Correlation and variance analysis of hydrosoluble fraction Nickel as a function of pH.

Term	Coeff.	p	r	S	R ²	R ² ajus	VIF
Value at the beginning	1.9						
Gradient	-0.123						
Statistics		0.000	-0.68	0.12	47.21%	46.3%	1.00

Coeff=coefficient, p=probability; r=linear correlation coefficient; S=sum of squares of residuals, R²=coefficient of determination; R²ajus=adjusted coefficient of determination, VIF=variance inflation factor

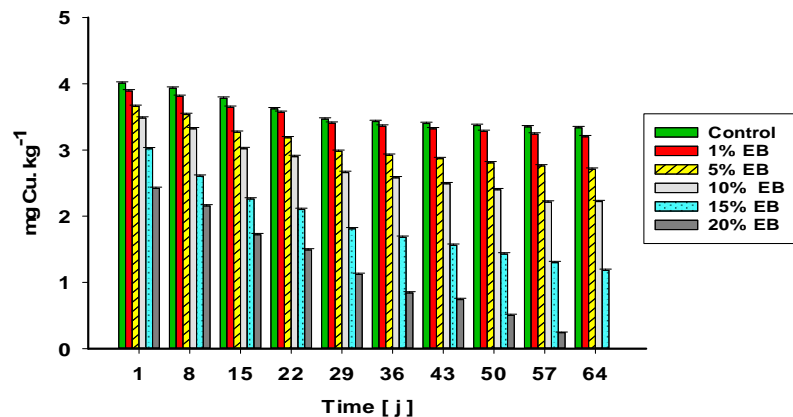


Fig. 9 : Evolution of the hydrosoluble Copper content as a function of the proportion of enriched biochar incorporated and time.

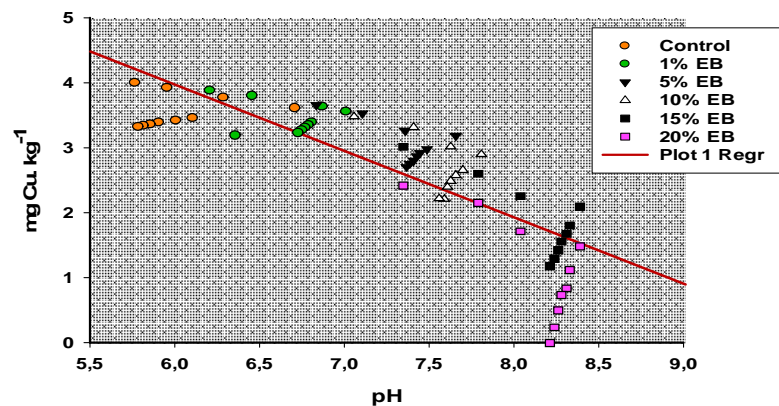


Fig. 10 : Influence of pH on hydrosoluble Copper content.

Table 9: Hydrosoluble Copper removal rates as a function of the proportion of enriched biochar incorporated and time.

Time [d]	Control	1%EB	5%EB	10%EB	15%EB	20%EB
1	0.00	2.94	8.78	13.17	24.74	39.65
8	1.90	4.99	11.82	17.21	35.06	46.28
15	5.69	9.130	18.50	24.69	43.64	57.11
22	9.68	11.02	20.6	27.68	47.63	62.84
29	13.57	15.11	25.69	33.67	54.91	72.07
36	14.46	16.21	27.18	35.66	58.1	79.05
43	15.21	17.21	28.43	37.91	61.1	81.55
50	15.96	18.2	30.02	40.15	64.39	87.53
57	16.46	19.2	31.17	44.84	67.63	94.01
64	16.81	20.2	32.42	51.02	70.57	100.00

EB=proportion of enriched Biochar

Table 10: Correlation and variance analysis of hydrosoluble fraction Copper as a function of pH.

Term	Coeff.	p	r	S	R ²	R ² ajus	VIF
Value at the beginning	10						
Gradient	-1.002						
Statistics		0.000	-0.73	0.51	73.67%	73.22%	1.00

Coeff=coefficient, p=probability; r=linear correlation coefficient; S=sum of squares of residuals, R²=coefficient of determination; R²ajus=adjusted coefficient of determination, VIF=variance inflation factor

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