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Examination of zinc adsorption capacity of soils treated with different pyrolysis products

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Abstract: Organic matter input into soils is essential regarding agricultural, environmental and soil science aspects as well. However, the application of the pyrolysed forms of biochars and materials with different organic matter content gained more attention in order to decrease the emission of the green house gases (CO_2, N_2O) from the soil. During pyrolysis, the materials containing high organic matter (biomass-originated organic matter) are heated in oxygen-free (or limited amount of oxygen) environment. As a result, the solid phase, which remains after eliminating the gases and liquid phase, is more stable compared to the original product, it cannot be mineralized easily in the soil and its utilization is more beneficial in terms of climatic aspects. Furthermore, it can improve soil structure and it can retain soil moisture and cations in the topsoil for long periods of time, which is very important for plants. In our experiment, the effects of biochar and bone char were examined on soils by zinc adsorption experiments. Based on our experiments, we concluded that the pyrolysis products can have significant Zn adsorption capacity compared to the soil. Bone ash can adsorb more Zn than the charcoal product. The Zn adsorption capacity of soils treated by pyrolysis products can be described by Langmuir adsorption isotherms. However, based on the amount of pyrolysis products, one or two term Langmuir isotherm fits well on the experiment data, which depends on the time the pyrolysis product has spent in the soil.

Keywords: biochar, bone char, Zn adsorption

1. Introduction

The pyrolysed biomass products have high carbon content and their chemical structures differ greatly. Thus, the weakly charred organic materials, such as the biochar and the soot, also belong to this group [1]. Depending on the temperature of the pyrolysis, different structural changes occur in the organic macromolecules. By the effect of the lower temperature, the chemically bound water will leave; then, as the temperature increases, the functional groups, the amount of oxygen and hydrogen will decrease, which might result in an aromatic and polyaromatic structure [2]. This type of organic matter can resist the mineralization processes in the soil for a long period of time (even for 100 years); thus, it decreases the amount of greenhouse gases (CO_2, N_2O), leaving the soil in the atmosphere. Their role is essential from climatic aspects, but they also improve soil structure, moisture and the nutrient holding capacity of soils.

In our experiments, we compared the Zn retention capacity of two types of pyrolysed organic substances (biochar, bone char), and we examined the effect of incubation on the Zn retention capacity in soil-biochar systems with different composition.

2. Materials and methods

Incubation

The soil that was used in our experiment (Tab. 1) was mixed with 0, 1, 2.5, 5 and 10% pyrolysed products (biochar, bone char). Soil moisture was adjusted by adding distilled water to 50% of field capacity; then it was incubated for two weeks. After this, the samples were dried and sieved (2 mm), and adsorption experiments were carried out.

Tab. 1. Parameters of the test soil (brown forest soil, Gödöllő)

K_A	pH (KCl)	pH (H_2O)	Humus %	Total C%	Total N%	AL-P_2O_5 mg/kg
25	4.9	5.2	1	0.58	0.58	33

Tab. 2. Parameters of the pyrolysed products

	pH	Bulk density kg/m^3	Total C%	TOC%	Total N%	Total P_2O_5 %	AL-P_2O_5 %	Zn(EDTA) mg/kg	Total PAH mg/kg
Biochar	8.3	360	80	70	0.7	0.2	0.05	73.8	4.8
Bone char	7.5	320	10	9	1.8	31	5.63	3.6	0.4

Adsorption Experiment

One gram of the above-mentioned treated soil samples and the pyrolysis products were placed in centrifuge tubes. They were mixed with Zn solution (shaking solution) with different concentrations (0, 25, 50, 75, 100, 200, 250, 500, 600, 750, 1000 mg dm^{-3}) in a ratio of 1 g to 10 cm^3 during 12 hours in rotary shaker at constant temperature (20±1°C). After completing the shaking, centrifugation (5,000 rpm, 5 minutes) and filtration were carried out; then, with proper dilution, the Zn concentrations of the filtrate (hereinafter: equilibrium solutions) were measured by Perkin Elmer 303 AA spectrophotometer. Knowing the concentration of the shaking and the equilibrium solution, we calculated the amount of adsorbed Zn on the solid phase. Then we illustrated the amount of adsorbed Zn (mg kg^{-1}) as a function of the concentration of the equilibrium solution. We fit the Langmuir adsorption isotherm onto the obtained experimental points, which mathematical form is the following:

$$q = \frac{A \cdot k \cdot c}{1 + k \cdot c} + b$$

q = the amount of Zn adsorbed by the soil (mg/kg)
A = maximum amount of Zn that can be adsorbed by the soil
k = equilibrium constant of adsorption (dm^3/mg)
c = Zn concentration of equilibrium solution (mg/dm^3)
b = constant (mg/kg)

3. Results and discussions

The bone char adsorbed a large amount of Zn (Fig. 1), which can be explained by the high phosphate content of the bone char (Tab. 2). In this case, the Zn is not adsorbed in an exchangeable form, but precipitation occurred, since poorly-soluble Zn-phosphates were produced.

This is also proved by the equilibrium constant (k) of the process and the steepness of the isotherm curve calculated in different points and the buffering capacity values as well (Tab. 3).

Thus, the bone char mixed into the soil significantly increased its Zn retention capacity; even when 5% bone char was mixed in, it doubled the maximum amount of Zn that can be retained.

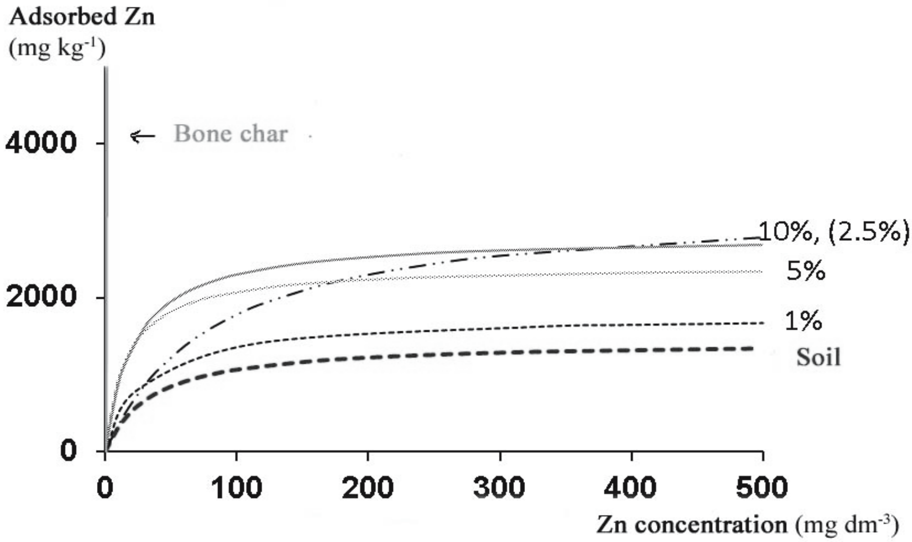

Fig. 1. Zn adsorption capacity of bone char and soils treated with bone char (Langmuir isotherms)

The Zn retention capacity of biochar and soils treated with biochar was significantly lower compared to the bone char. The maximum amount of Zn that the soil can retain is nearly seven times higher than the amount the biochar can retain. This is probably due to the fact that chemical changes occurred within the structure of the biochar during the pyrolysis, which destroyed its cation retention capacity.

Tab. 3. Parameters of the Langmuir isotherms of bone char and soils treated with bone char

	Langmuir isotherm parameters		**Buffering capacity** (dm^3/kg)			
	A **mg/kg**	**k** **dm^3/mg**	**0**	**0.1**	**1**	**10**
Bone char	20 193	0.7768	15 688	13 508	4 968.8	204.0
Soil	1 378	0.0290	41.7	41.4	39.3	25.0
1% bone char	1 768	0.0337	59.7	59.3	55.9	33.4
2,5% bone char	3 236	0.0120	39.6	39.5	38.7	31.4
5% bone char	2 416	0.0604	146.1	144.4	129.9	56.7
10% bone char	2 804	0.0460	129.2	128.0	118.06	60.5

Probably, hydrophobic, aromatic structures were formed which are able to adsorb only a few cations. It is interesting, however, that when this material was mixed into the soil and was shortly incubated, the Zn retention capacity increased.

When 5% was mixed, the maximum amount of Zn that can be retained doubled. This phenomenon is probably due to the activated biological processes in the soil in such a short time.

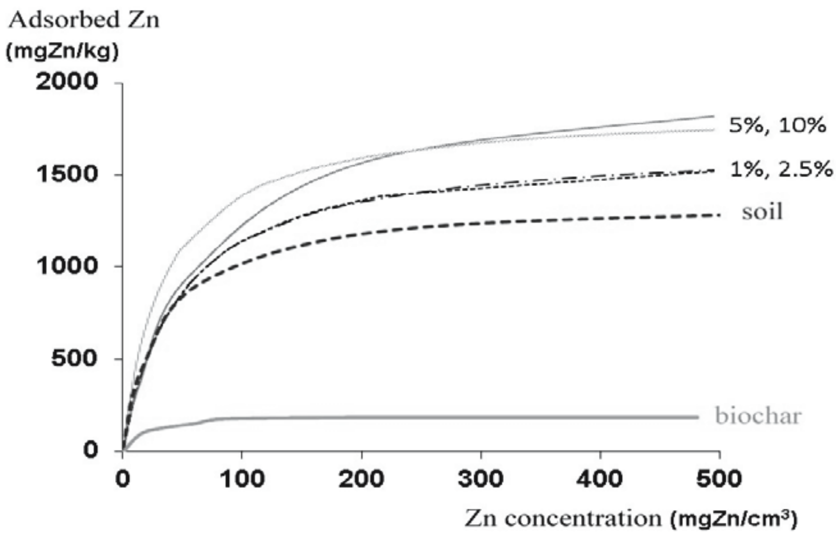

Fig. 2. Zn adsorption capacity of biochar and soils treated with biochar (Langmuir isotherms)

Tab. 4. Parameters of the Langmuir isotherms of biochar and soils treated with biochar

	Langmuir isotherm parameters		**Buffering capacity** (dm^3/kg)			
	A mg/kg	**k** dm^3/mg	**0**	**0,1**	**1**	**10**
Biochar	197.2	0.0601	11.9	11.7	10.5	4.6
Soil	1 378	0.0300	41.4	41.1	39	24.5
1% biochar	1 689	0.0208	35.2	35.0	33.8	24.1
2,5% biochar	1 668	0.0215	35.8	35.7	34.4	24.3
5% biochar	2 083	0.0150	31.3	31.2	30.4	23.7
10% biochar	1 867	0.0287	53.6	53.3	50.7	32.4

4. Conclusions

The soil microorganisms attach onto these organic substances that have very high surface area and they change their structure during their metabolism. Functional groups that are able to adsorb cations are formed especially on the edges, which are easily accessible.

This is the reason why the pyrolysed organic substances that are able to resist mineralization and sometimes contain toxic material (PAHs) can change into a harmless and useful soil component [3].

Acknowledgements

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References

[1] Masiello, C. A. (2004), New direction in black carbon organic geochemistry. *Marine Chemistry* 92, 201–213.

[2] Knicker, H. (2011), Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments. *Quaternary International* 243, 251–263.

[3] Haritash, A. K., Kaushik, C. P. (2009), Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): A review. *Journal of Hazardaous Matematics* 169, 1–15.