

RELATIONSHIP BETWEEN SOIL ACIDIFICATION AND ZINC FERTILIZATION IN A MODEL EXPERIMENT

Gabriella RÉTHÁTI¹ – Ibrahim ISSA² – László TOLNER¹

¹ Szent István University, Department of Soil Science and Agricultural Chemistry, Páter Károly Str. 1. 2103 Gödöllő, Hungary, Tel: +36 28 522 000; Fax: +36 28 410 804, E-mail: rethati.gabriella@mkk.szie.hu

² Sirte University, Sirte, Libya. P. Pox 6742

Abstract: Zinc is an essential nutrient for living organisms. Mobile zinc ions can be taken up by plants in higher amount than their physiological need and herewith can be available for animals and human beings through food chain.

Zinc has a relatively high affinity for the soil particles, however concentration of free zinc ions can increase due to abrupt and intensive acidification. Our examinations were carried out on goethite as an adsorbent. Goethite plays an important role in ion adsorption in soils. Zinc was chosen for our experiment among those heavy metals which have similar adsorption properties.

Zn is necessary for plant growth, but in higher amount can be toxic. Our results are able to describe the parameters determining the soils Zn supply. However, the interval between the plant growth necessary and toxic amount is very narrow and further examinations are necessary for investigate the exact amount of Zn, which is needed by the plant.

Keywords: Zn adsorption, H⁺ desorption, goethite, pH

Introduction

Filep (1998), Csathó (1994), Kádár and Németh (2003) give an overview of the heavy metal contamination of Hungarian soils.

The natural goethite is a peculiar formation of the surface weathering processes. In near-surface sediments and the soil goethite is a building material of the iron particles, iron films and crust, red and brown discolorations. The amorphous coatings crystallise over time (Bohn et al., 1985).

The aqua complex metallic ions of dissolved in the solution connect to the surface through the ligandum, while water molecules distant from the surface dissociate H⁺ ions into the solution. From the aspect of the complex metal ions a ligandum exchange reaction occurs: the free water molecules exchange on the surface to chemically combined water or OH⁻ ions. Following the primary adsorption the combined complexes may chemisorb into stronger ions while water is released, or build into the crystal matrix of the surface. (Kinnibourgh, 1983)

Forbes et al. (1976), Bar-Yossef (1979), Padmanabham (1983), Bruemmer et al. (1988) and Brümmer et al. (1983) have explained the decrease in pH as partly due to hydrolysis of Zn²⁺ to give ZnOH⁺ and H⁺ and partly due to re-adjustment of charge on the soil colloid surfaces as ZnOH⁺ ions are sorbed.

Rimmer and Uygur (1998) examined the Zn absorption of the precipitated ferrous oxide films that form in quantities on the CaCO₃ crystals of the soil. The research proved that the effect of the presence of iron oxide coatings on calcite surfaces is to increase the specific adsorption of the Zn and to decrease the formation of precipitation compared to the un-covered lime surfaces.

Schlegel et al., (1996) examined the goethite crystal-structure during Zn complex adsorption with XAFS - x-ray absorption fine-structure – methods. They concluded that

the adsorbed heavy metal in partly build in the crystal-matrix of the surface while they loose their ligandums.

On the basis of experiments it has been concluded that adsorption of heavy metal on soil was affected by pH (Ioannou et al., 2003; Czinkota et al., 2002.) and Eh (Czinkota et al., 2006).

Material and Method

For this paper we examined the goethite with X-ray diffraction and thermo-analytical methods. The samples were examined original state and after 24 hours of heating on 100°C and 24 hours of heating 200°C. The final samples match the composition of the natural goethite, but it is very probable that a multi-phase iron-hydroxide / iron-oxy-hydroxide system may superpose within the otherwise well-ordered goethite-matrix, similarly to the processes in the nature.

For a proper diagram at least 7 measure points are necessary. With preliminary test experiments we determined the range of concentrations in which reliable results can be achieved. Seven different concentration solutions 0- 5 - 7,5 - 10 - 12,5 - 15 - 20 - 25 mgZn·1000 cm⁻³ as ZnSO₄ - were used for the research. 0,1 g synthetic goethite powder was poured in the 50cm³ zinc solutions, and the sample tubes were shaken for 24 hours. The final solutions were recovered with centrifugation (5 min 5000 min⁻¹ speed) and filtration. The concentrations of the equilibrium solutions were determined with atomic absorption spectrofotometric detection, using a Perkin-Elmer AAS equipment, on the 213.9 nm wavelength that equals the light absorption of zinc. The quantity of desorbed H⁺ ions was determined with titration, by using 0.02 mol.dm⁻³ NaOH solution. The pH was measured with Radelkis OP 210 glass electrode pH meter.

Results and conclusions

All of concentrations (initial and equilibrium) were applied in two different dimensions (mg·dm⁻³, mmol·dm⁻³). The adsorbed quantities were calculated as the decrease in concentration of solution while the process of adsorption (*Table 1.*).

Table 1. The Zn concentration of the solutions, the quantity of adsorbed Zn and desorbed H⁺-ions

Initial Zn concentration mg·dm ⁻³	Equilibrium Zn concentration			Adsorbed Zn			Desorbed H ⁺	
	mg·dm ⁻³	error	mmol·dm ⁻³	mg·g ⁻¹	error	mmol·g ⁻¹	mmol·g ⁻¹	error
0	0	0	0	0	0	0	0	0
5	6·10 ⁻²	0,005	9,1·10 ⁻⁴	2,46	2,33	3,7·10 ⁻²	0,06	0,007
7,5	1,8·10 ⁻¹	0,013	1,9·10 ⁻⁴	3,65	6,38	5,5·10 ⁻²	0,15	0,010
10	8,5·10 ⁻¹	0,058	8,8·10 ⁻⁴	4,57	29,38	6,9·10 ⁻²	0,21	0,003
12,5	1,8	0,138	2,1·10 ⁻³	5,30	69,00	8,1·10 ⁻²	0,21	0,024
15	3,3	0,409	4,5·10 ⁻⁴	5,80	204,76	8,8·10 ⁻²	0,42	0,029
20	8,8	0,417	4,5·10 ⁻⁴	5,58	208,94	8,5·10 ⁻²	0,45	0,090
25	14,1	0,417	4,5·10 ⁻⁴	5,42	208,88	8,3·10 ⁻²	0,99	0,117

Zn adsorption on goethite fitted to the Langmuir adsorption isotherm (*Figure 1.*). The form of the equation used was:

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

Where Q = the amount of adsorbed Zn (mg.kg^{-1})
 c = the equilibrium Zn concentration (mg.dm^{-3})
 A = the Langmuir adsorption maximum (mg.kg^{-1})
 k = the Langmuir energy constant ($\text{dm}^3.\text{mg}^{-1}$)

Figure 1. shows the curve matches the points of the results of the measures. As expected, Zn sorption increased with increasing added Zn concentration for goethite. Zinc and hydrogen are concurring during the adsorption process. The adsorption become less effective due to acidification caused by the hydrogen desorption. In other words the adsorption balance shifting toward desorption because of the higher quantity of the H^+ -ions, i.e. less zinc can be adsorbed.

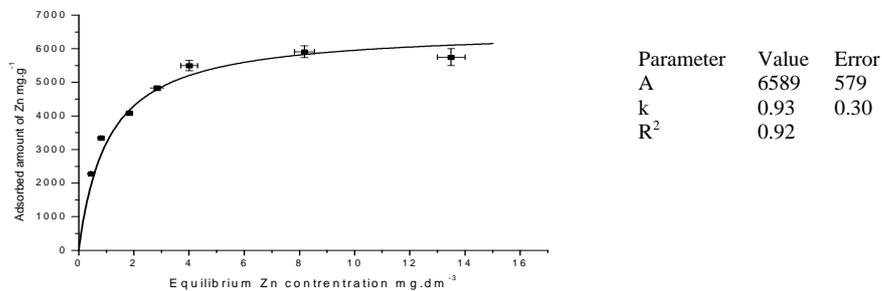


Figure 1. The adsorption isotherm of the Zinc adsorption on the surface of the goethite and parameters of the Langmuir adsorption isotherm

Delineating the quantity of desorbed H^+ ions in relation of the adsorbed Zn the first linear stage is followed by an exponential increasing step (Figure 2.) Greater adsorption of Zn, that is showed by increasing of H^+ concentration, led to precipitation as $\text{Zn}(\text{OH})_2$ which was evidenced by the rising of slope in the isotherm. The explanation of this phenomenon requires further research.

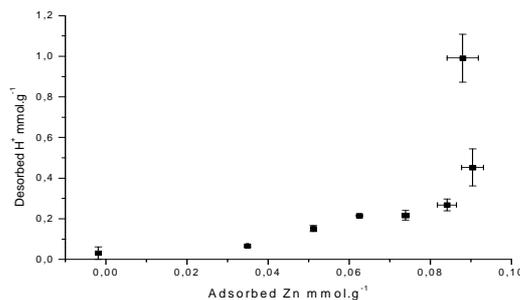


Figure 2. The quantity of desorbed H^+ ions from the surface of the goethite, in relation of the quantity of the adsorbed Zn

The rise of the curve about the initial stage of the ion-exchange is gradient ~ 2 , (Figure 3). An explanation for the expected two may be the proportion of the valences. The presumed process is: $\text{SURFACE}=\text{Zn} + 2 \text{H}^+ > \text{SURFACE}=\text{H}_2 + \text{Zn}^{2+}$

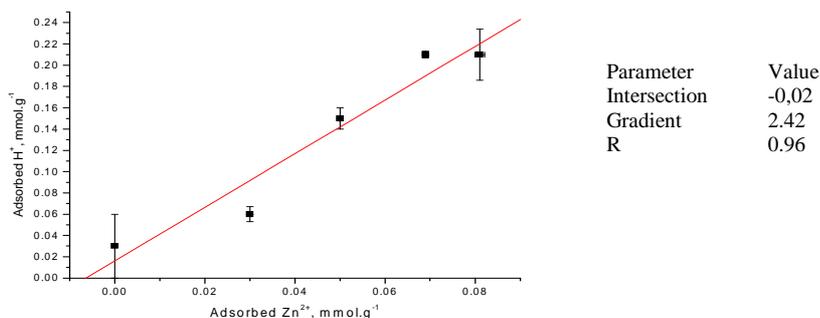


Figure 3. The quantity of desorbed H^+ ions from the surface of the goethite, in relation of the quantity of the adsorbed Zn, the linear section of curve

References

- Bar-Yossef, B.: 1979. pH-dependent zinc adsorption by soils. *Soil Sci. Soc. Am. J.*, **43**: 1095–1099.
- Bohn, H. L. - McNeal, B.L. - O'Connor, G.A.: 1985. *Talajkémia. Mezőgazdasági Kiadó-Gondolat Kiadó. Budapest. 363.*
- Bruemmer, G.W. - Gerth, J. - Tiller, K.G.: 1988. Reaction kinetics of the sorption and desorption of nickel, Zn and cadmium by goethite. I. Sorption and diffusion of metals. *J. Soil Sci.*, **39**: 37–52.
- Brümmer, G. - Tiller, K.G. - Herms, U. - Clayton, P.M.: 1983. Adsorption-desorption and/or precipitation-dissolution processes of Zn in soils. *Geoderma* **31**: 337-354.
- Csathó, P.: 1994. A környezet nehézfém szennyezettsége és az agrártermelés (temazikus szakirodalmi szemle). A Környezet-és Területfejlesztési Minisztérium és az MTA Talajtani és Agrokémiail Kutató Intézete kiadványa, Budapest. 176 p.
- Czinkota, I. - Ioannou, A. - Dimirkou, A. - Füleký, G. - Papadopoulos, P.: 2002. Egyensúlyi modell a proton/nehézfém felületi reakciók leírására goethit, kaolinit és goethit-kaolinit rendszerben. In: *Talaj és környezet. Debrecen, Magyarország, 2002 pp. 224-232.*
- Czinkota, I. - Issa, I. - Rétháti, G. - Kovács, B.: 2006. Determination of the Behaviour and the Transport Parameters of Chromium in Soil-Water System *Agrokémia és Talajtan*, **55**: 287-294.
- Filep, Gy.: 1988. *Talajkémia. Akadémiai Kiadó, Budapest. 293 p.*
- Forbes, E.A. - Posner, A.M. - Quirk, J.P.: 1976. The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite. *J. Soil Sci.*, **27**: 154–166.
- Ioannou A. - Tolner L. - Dimirkou A. - Füleký Gy.: 2003. Copper adsorption on bentonite and soil as affected by pH. *Bulletin of the Szent István University. 2003. Gödöllő, 74-84.*
- Kádár, I. - Németh, T.: 2003. Mikroelem-szennyezők kimosódásának vizsgálata szabadföldi terheléses tartamkíséletben. *Agrokémia és Talajtan*, **52**: 315-330.
- Kinniburgh, D.G.: 1983. The H^+ and Me^{2+} exchange stoichiometry of calcium and zinc adsorption by ferrihydrite. *Soil Sci. Soc. Am. J.*, **34**: 759-768.
- Padmanabham, M.: 1983. Comparative study of the sorption-desorption behaviour of copper(II), Zn(II), cobalt(II) and lead(II) at the goethite solution interface. *Aust. J. Soil Res.*, **21**: 515–525.
- Rimmer, D.- Uygur, V.: 1998. The effect of surface coatings of iron oxide on the sorption and precipitation of zinc on calcite surfaces. *World congress of Soil Science, Montpellier, France. Symp. 6. N° 250.*
- Schlegel M.L. - Manceau A. - Charlet L.: 1996. EXAFS Study of Zn and ZnEDTA Sorption at the Goethite (a-FeOOH)/Water Interface (X-Ray Absorption Fine Structure (XAFS) Spectroscopy) *Proceedings of the 9th International Conference on X-Ray Absorption Fine Structure 26-30 August, Grenoble, France C2-823*