Relationship between soil acidification and zinc fertilization in a model experiment

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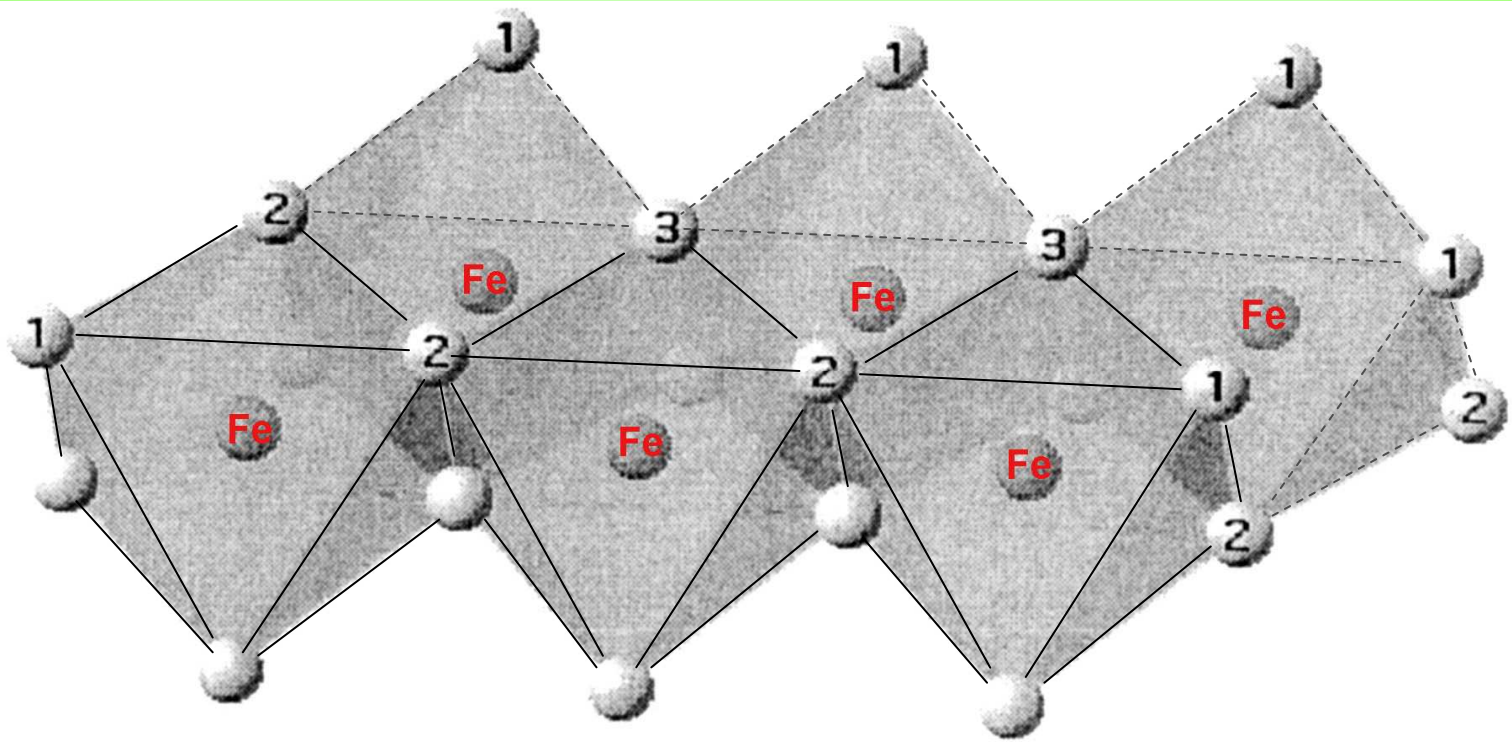
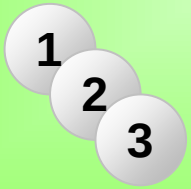
Introduction

- Importance of Zn in organisms
- Zn deficiency – fertilization

- Zn adsorption
- H^+ desorption – acidification?

Goethite structure

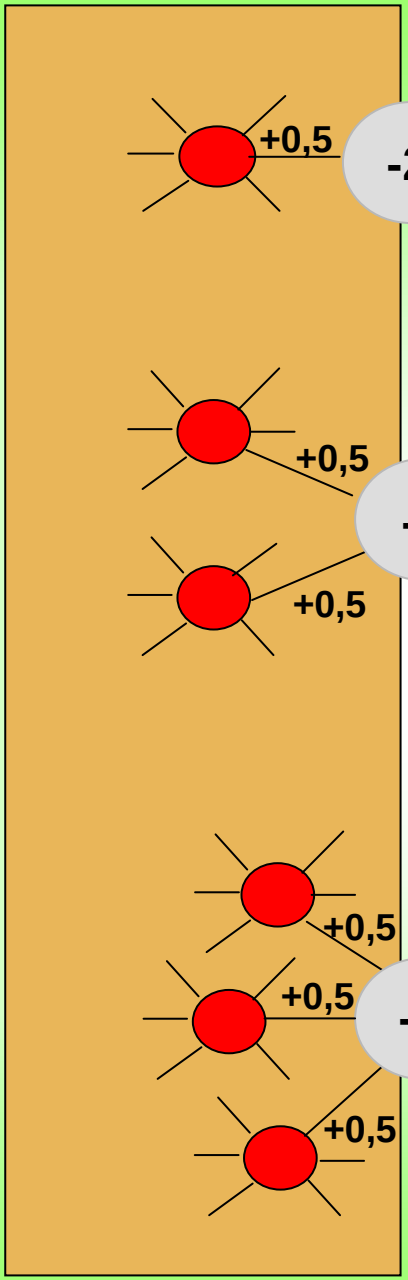




Singly
Doubly
Triply

} coordinated surface oxygen

Goethite surface structure

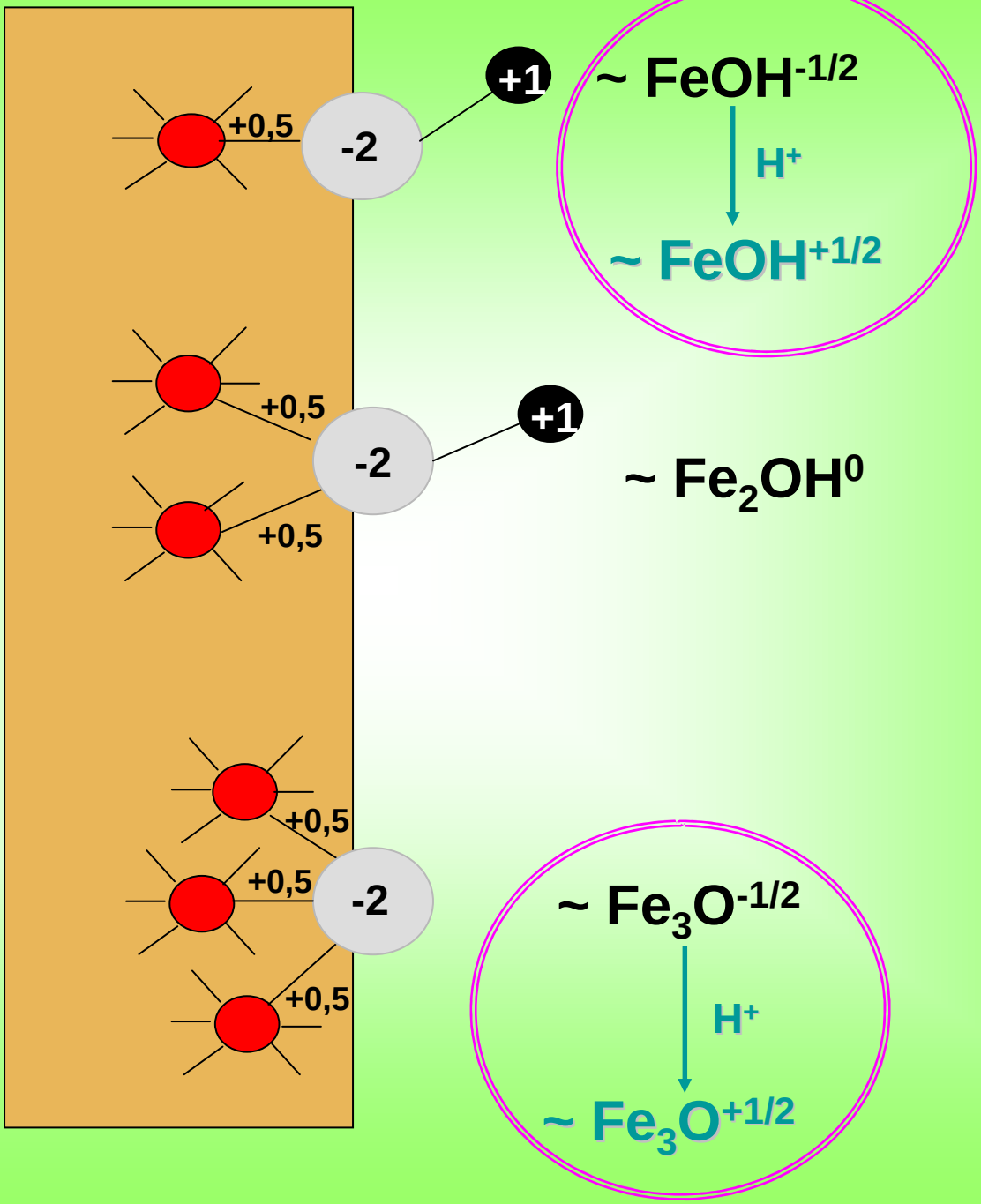


Oxygen

Iron

Hydrogen

Goethite surface structure



Material and Method

Adsorption experiments

0,1 g adsorbent + 50 cm³ „initial" solution —24 hours→ **„equilibrium" solution**

goethite 0 5 7.5 10 12.5 15 20 25 mgZn·dm^{-3}

determined by AAS (213.9 nm)

The difference of Zn concentration between initial solution and equilibrium solution → **adsorbed Zn amount** by adsorbent

The difference of H^+ concentration between initial solution and equilibrium solution (by titration with 0.02 mol·dm^{-3} NaOH) → amount of **desorbed H^+ ions**

Table 1. Changing of Zn and H^+ concentration during the adsorption experiment

Initial Zn concentration $mg \cdot dm^{-3}$	Equilibrium Zn concentration			Adsorbed Zn			Desorbed H^+	
	$mg \cdot dm^{-3}$	error	$mmol \cdot dm^{-3}$	$mg \cdot g^{-1}$	error	$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$	error
0	0	0	0	0	0	0	0	0
5	$6 \cdot 10^{-2}$	0,005	$9,1 \cdot 10^{-4}$	2,46	2,33	$3,7 \cdot 10^{-2}$	0,06	0,007
7,5	$1,8 \cdot 10^{-1}$	0,013	$1,9 \cdot 10^{-4}$	3,65	6,38	$5,5 \cdot 10^{-2}$	0,15	0,010
10	$8,5 \cdot 10^{-1}$	0,058	$8,8 \cdot 10^{-4}$	4,57	29,38	$6,9 \cdot 10^{-2}$	0,21	0,003
12,5	1.8	0,138	$2,1 \cdot 10^{-3}$	5.30	69,00	$8,1 \cdot 10^{-2}$	0,21	0,024
15	3.3	0,409	$4,5 \cdot 10^{-4}$	5,80	204,76	$8,8 \cdot 10^{-2}$	0,42	0,029
20	8.8	0,417	$4,5 \cdot 10^{-4}$	5,58	208,94	$8,5 \cdot 10^{-2}$	0,45	0,090
25	14.1	0,417	$4,5 \cdot 10^{-4}$	5,42	208,88	$8,3 \cdot 10^{-2}$	0,99	0,117

Langmuir adsorption isotherm

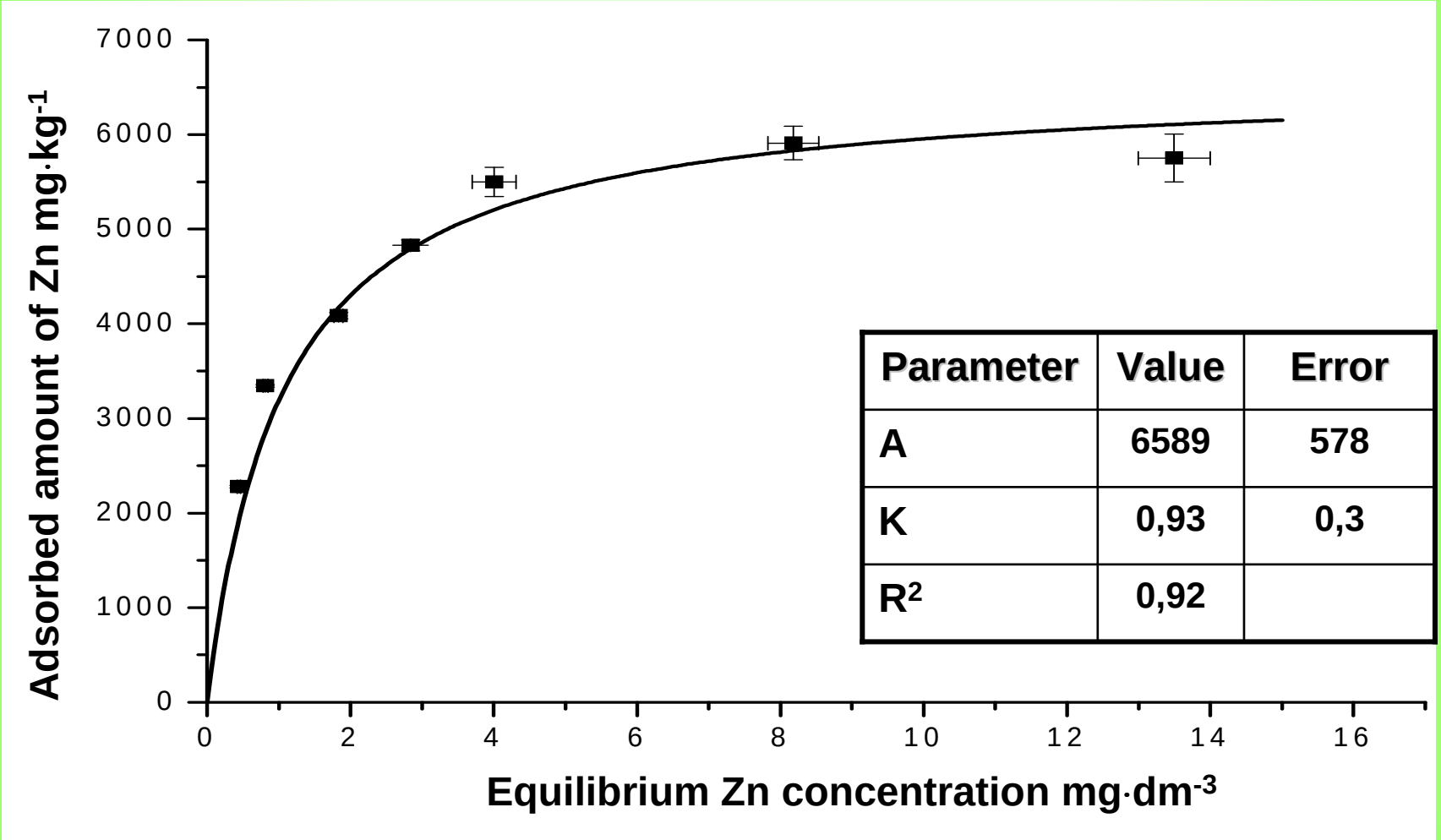
$$Q = \frac{A \cdot k \cdot c}{1 + k \cdot c}$$

Where

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

Results /1

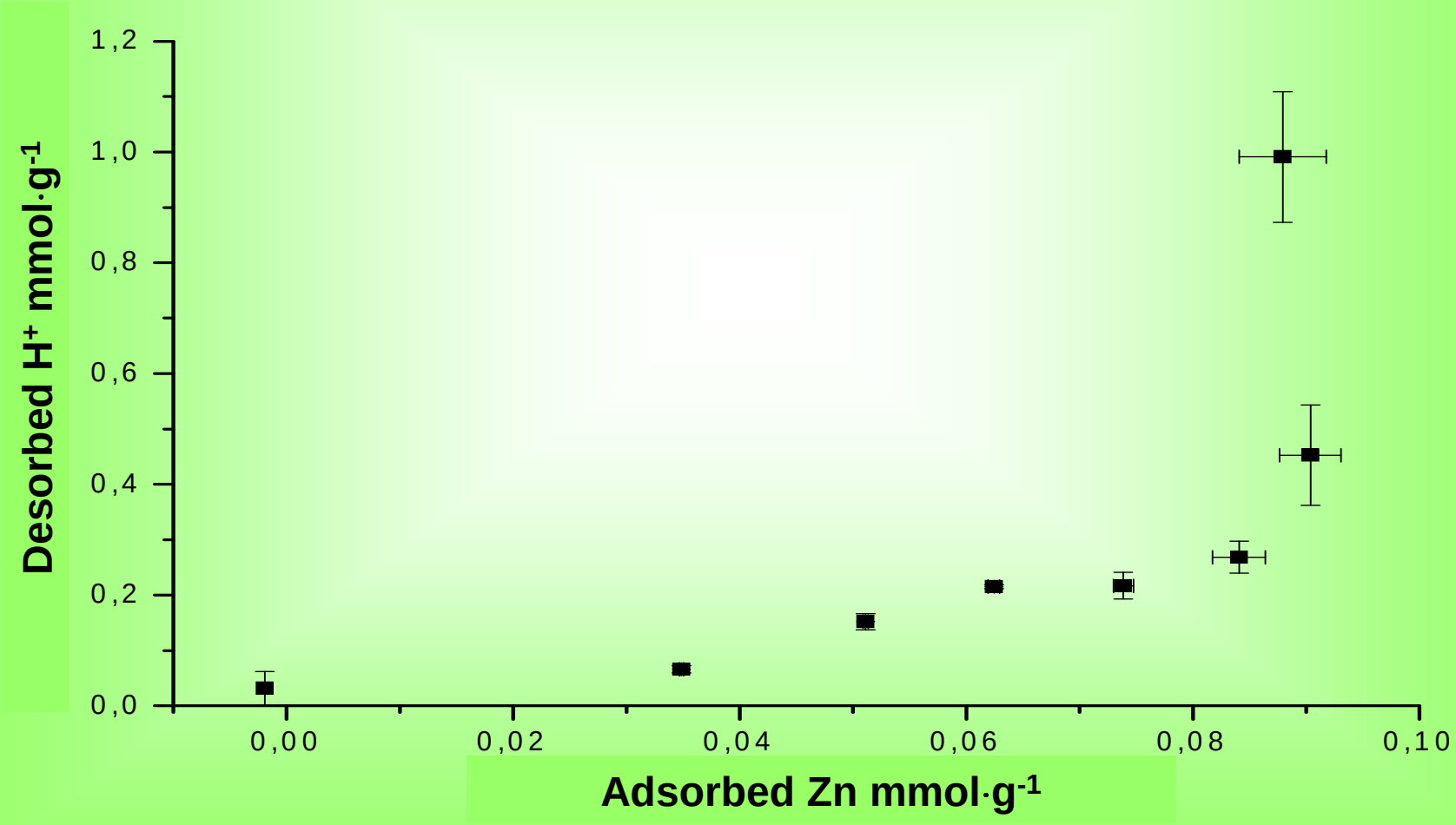
Figure 1. Adsorption isotherm of the Zn adsorption on goethite surface



Parameter	Value	Error
A	6589	578
K	0,93	0,3
R^2	0,92	

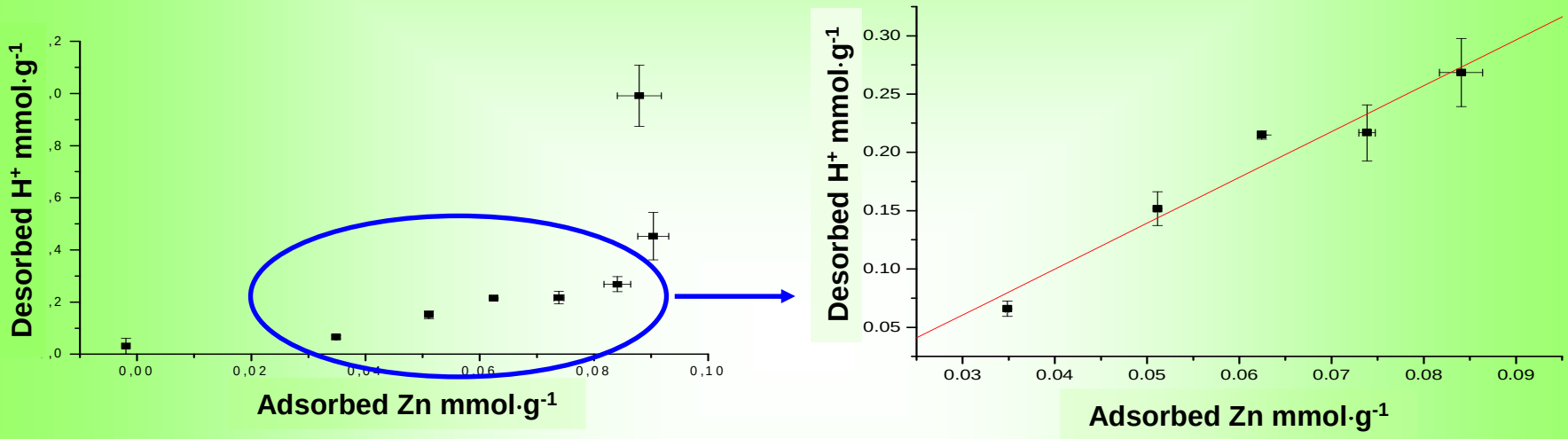
Results /2

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



Results/3

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



Parameter	Value
Intersection	-0,02
Gradient	2.42
R	0.96

Conclusion

- Langmuir adsorption isotherm can be successfully applied to model the process
- The adsorption capacity of goethite is 6589 mg Zn/kg
- The decreasing of pH leads to decreasing of Zn adsorption

  (competition between Zn ions and H+ ions for site of adsorption)
- The relationship between Zn adsorption and H^+ desorption shows two phenomenas:
  - The first is a simple $H^+ \rightarrow Zn^{2+}$ ion-exchange (Gradient $\cong$ 2)

$$\mathbf{SURFACE{=}H_2 + Zn^{2+} \rightarrow SURFACE{=}Zn + 2\ H^+}$$

  - The exponential rising of curve may be caused by acid hydrolysis of unadsorbed and desorbed Zn^{2+}.

$$\mathbf{Zn^{2+} + H_2O \rightarrow ZnOH^+ + H^+}$$


Thank You