

SORPTION OF Fe^{2+} , Fe^{3+} AND Mn^{2+} IONS IN AN UNOXYGENATED MATERIAL OF LOESSIAL SOIL

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Abstract. This study examined courses of sorption and of leaching with distilled water of ions Fe^{2+} , Fe^{3+} , and Mn^{2+} in non-deoxidized and un-oxygenated loessial soil material. The sorption was measured using a dynamic method. ODR and Eh were measured as indices of soil oxygenation. It was found that un-oxygenation of loessial soil material increases the sorption of ions Fe^{2+} , Fe^{3+} , and Mn^{2+} in samples of pH 4.8, while in samples having pH 6.5 an increased sorption was only found for Fe^{3+} ions.

INTRODUCTION

The problem of contamination hazard of soils by heavy metals is closely connected with conditions of such metals' accumulation [6,7,8]. The conditions of metal accumulation determine their mobility and indirectly their toxicity in the environment. In future they may also determine soil conditions and plant yield as well as the salubrity of humans and animals [1].

The present paper constitutes a continuation of model studies aiming at the evaluation of the effects of un-oxygenated conditions in loessial soil material on the sorption processes of Fe^{2+} , Fe^{3+} , and Mn^{2+} ions [2,3,4,5].

MATERIALS AND METHODS

An air-dry loessial soil material, sieved through a 1 mm sieve, was taken for examination. The loessial soil contained 36 %

fine particles and 2.1 % organic C. The soil had a specific surface area of 24 m²/g and quartz content of 72 % [2].

The experiment was carried out with soil samples having acid reaction (pH 4.8) and a reaction modified to pH 6.5. The latter was obtained by treating the soil samples with 0.3 % suspension of CaCO_3 for four months. The un-oxygenated samples were obtained by percolating through the soil material pure nitrogen from a cylinder at a rate of about 50 cm³/min for two hours. Simultaneously the soil sample was shaken up to ensure better access to nitrogen of the entire soil sample mass. Next the sample was incubated for 24 h in a nitrogen atmosphere.

Then a 100 g portion of soil material was poured into an organic glass column 44 mm in diameter and 100 mm long, and wet with distilled water by the method of capillary rise. On to the surface of such prepared material the solution of a given cation with concentrations of 0.05 M Fe^{2+} and Mn^{2+} or 0.033 M Fe^{3+} were instilled at a constant pressure of 96 hPa. Those solutions were introduced at a rate of 2 cm²/min until 140 cm³ effluents were collected. Ions that had been retained in the intergranular spaces or those weakly sorbed by the soil

sorptive complex were washed out with 140 cm³ of distilled water. In the effluent, collected as individual 10 cm³ portions, the contents of metal cations were analyzed with the atomic absorption spectrometer AAS-1. All the procedures were run at a temperature of 293 °K±2°. The oxygen diffusion rate (ODR) and redox potential (Eh) values were chosen as the soil aeration indices. The measurements were performed, after tightening the column with water, by using an ODR-Eh apparatus constructed by Malicki and Walczak [5].

RESULTS AND DISCUSSION

The values of oxygen microdiffusion (ODR) and of redox potential (Eh) in soil samples obtained during the experiment are given in Tables 1 and 2. The data indicate that due to percolation of nitrogen through the soil material and to incubation of soil samples in the nitrogen atmosphere, a state

Table 1. Values of ODR (in $\mu\text{g O}_2\text{m}^{-2}\text{s}^{-1}$)

pH			
4.8		6.5	
I	II	I	II
75.0	40.0	76.1	41.6
75.6	44.0	75.3	39.0
76.0	47.0	74.6	45.0
75.2	43.6	74.3	41.9

I - non-deoxidized samples; II - unoxxygenated samples.

Table 2. Values of Eh (in mV)

pH			
4.8		6.5	
I	II	I	II
451.3	318.0	481.3	352.3
457.9	321.2	484.7	350.2
448.7	320.4	489.1	351.4
452.6	319.8	485.0	351.3

Explanations as in Table 1.

of oxygen deficiency (under-oxygenation or unoxxygenation state) in the soil sample was obtained. Although the treatments applied caused a decrease in Eh, they did not lead to a reduction of O₂, NO₃⁻, MnO₂ or iron oxides. During the saturation of both the non-deoxidized and unoxxygenated loessial soil samples of pH 4.8 with the metal solutions, Fe²⁺ and Mn²⁺ ions were sorbed to a greater amount by the material in the state of oxygen deficiency (Figs 1 and 3). The unoxxygenation of soil samples of pH 4.8 did not exert any significant effect on the quantity of sorbed Fe³⁺ ions (Fig. 2). While saturating the unoxxygenated soil samples of pH 6.5 the ions Fe²⁺, Fe³⁺, and Mn²⁺ were sorbed to lesser amounts as compared to the non-deoxidized samples. Leaching the metal ions with distilled water out of the unoxxygenated loessial soil samples of pH 4.8 resulted in higher losses of Fe²⁺ and Mn²⁺ and lower losses of Fe³⁺ as compared to the losses from the non-deoxidized soil samples.

In conditions of oxygen deficiency in soil samples there is a high peak on the leaching curve of Fe³⁺ ion (Fig. 2), which points to a low binding force of these ions in sorption processes. From the unoxxygenated soil samples of pH 6.5 sorbed with the metal solutions tested, the distilled water washed out less Fe²⁺ and Fe³⁺ and much more Mn²⁺. The occurrence of a peak on the leaching curve of Mn²⁺ denotes the sorption of low binding forces for the said ion (Fig. 3).

The deoxygenation of the loessial soil samples of pH 4.8 appeared to be a factor increasing the sorption of Fe²⁺ ions from 29.1% to 35.4%; Fe³⁺ from 41.87% to 47.87%, and Mn²⁺ from 14.78% to 30.18%, as compared to the sorption in the non-deoxidized soil material (Fig. 4).

In soil samples of pH 6.5 the deoxygenation caused an increase in sorption of Fe³⁺ ions from 65.49% to 72.27%, and a decrease in sorption of Fe²⁺ ions from 51.69% to 47.87%, and Mn²⁺ ions from 31.76% to 23.86% in comparison with the sorption in non-deoxidized samples.

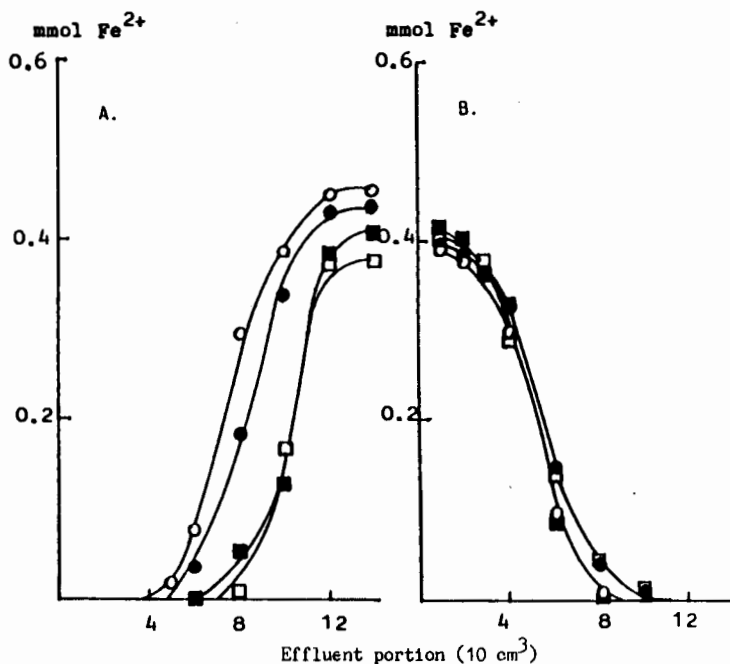


Fig. 1. Course of sorption (A) and leaching out with distilled water (B) of Fe^{2+} ions from the loessial soil sample under different oxygen and pH conditions. Explanations: 1-pH 4.8, non-deoxidized; 2-pH 4.8, unoxxygenated; 3-pH 6.5, non-deoxidized; 4-pH 6.5, unoxxygenated.

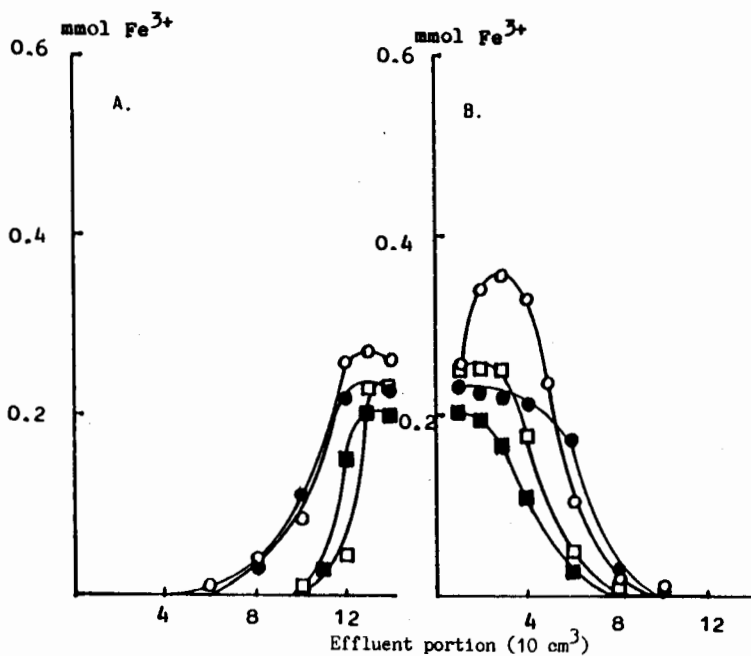


Fig. 2. Course of sorption (A) and leaching out with distilled water (B) of Fe^{3+} ions from the loessial soil sample under different oxygen and pH conditions. Explanations as in Fig. 1.

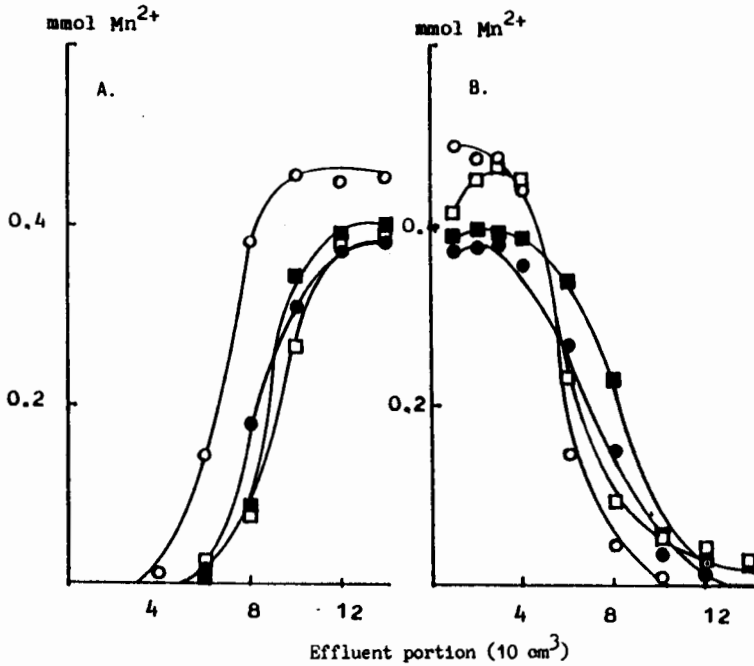


Fig. 3. Course of sorption (A) and leaching out with distilled water (B) of Mn^{2+} ions from the loessial soil sample under different oxygen and pH conditions. Explanations as in Fig. 1.

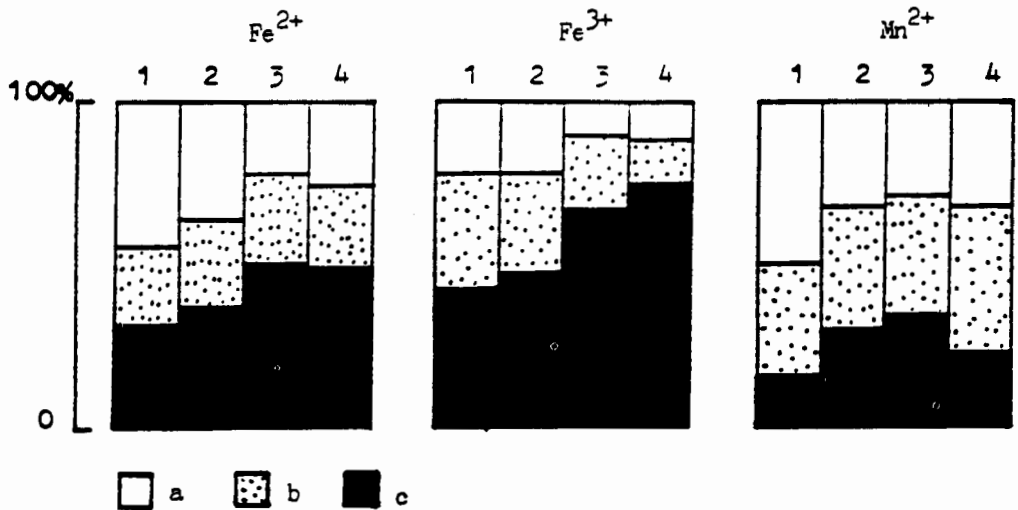


Fig. 4. Distribution of ions Fe^{2+} , Fe^{3+} , and Mn^{2+} in consecutive stages of the experiment. Explanations: a-in the effluent after saturation; b-after leaching with water; c-residue; other explanations as in Fig. 1.

CONCLUSIONS

The experiments carried out allow us to draw the following conclusions.

1. The deoxygenation, i.e. the state of oxygen deficiency of loessial soil samples of

pH 4.8, constitutes a factor increasing the sorption of Fe^{2+} , Fe^{3+} , and Mn^{2+} ions.

2. The deoxygenation of loessial material of pH 6.5 is a factor responsible for increased sorption only for Fe^{3+} ions.

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SORPCJA JONÓW Fe^{2+} , Fe^{3+} I Mn^{2+} W
NIEDOTLENIONYM MATERIALE GLEBY
LESSOWEJ

Zbadano przebieg sorpcji jonów Fe^{2+} , Fe^{3+} i Mn^{2+} i wymywania ich wodą destylowaną, w materiale gleby lessowej - nieodtlenionym i niedotlenionym. Sorpcję przeprowadzono metodą dynamiczną. Jako wskaźniki natlenienia mierzono ODR i Eh. Stwierdzono, że niedotlenienie materiału gleby lessowej zwiększa sorpcję jonów Fe^{2+} , Fe^{3+} i Mn^{2+} w próbkach o pH 4,8 a w próbkach o pH 6,5 jedynie jonów Fe^{3+} .