

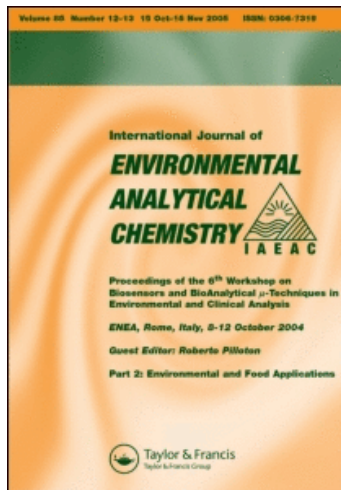
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DESORPTION OF HEAVY METALS FROM TYPICAL SOIL COMPONENTS (CLAY, PEAT) WITH GLYCINE

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Natural organic chelating agents take part in the mobilization and translocation of heavy metals in unpolluted and polluted soils. They also have to be considered as possible extracting agents for the decontamination of heavy metal polluted soils. For an assessment of the desorption capability of glycine, heavy metals (Cd, Cu, Ni, Pb, Zn) were adsorbed onto typical soil components (bentonite and peat). The metal loaded sorbents were resuspended in aqueous solutions of glycine at pH 7.0 and 4.5 and the quantities of the desorbed metals were analysed in the liquid phase. Furthermore, the dependency of the desorption rate on the duration of experiments and the metal content were investigated. The remobilization of heavy metals from bentonite by glycine at pH 7.0 decreases following the order $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Pb}$ and ranges from 95% to 9.5%. The desorption rate was significantly lower at pH 4.5 and in suspensions of peat.

KEY WORDS: Glycine, heavy metals, desorption, soil, bentonite, peat.

INTRODUCTION

Heavy metals are present in native, agriculturally used and contaminated soils. Their concentration, distribution, translocation and speciation in soils depends on their geological origin, pedological transformation and type of their immission as well as on many soil properties and climate conditions.

Organic chelating agents, naturally occurring in the pore water of soils, like aliphatic and aromatic (hydroxy-) carboxylic acids, amino acids, amino sugars, fulvic acids, etc. may play an important role within these processes^{1,2}. They take part in adsorption/desorption and precipitation/solution processes and may change redox potential boundaries for species stability.

As a result of industrial activities, traffic immissions, input of contaminated sludges and wastes, etc., polluted soils have accumulated heavy metals up to some orders of magnitude, compared with background values³.

In this context, the ability of aqueous solutions of complexing agents to remobilize heavy metals has to be considered.

For this purpose, strong synthetic chelating agents like EDTA and NTA have mainly been tested.

The impact of synthetic chelating agents on heavy metals in soils was examined critically as a consequence of the amending of soils with sewage sludges, containing

Table 1 Stability constants ($\lg K_{M_1L_1}$) of selected metal complexes

| Chelating agent | Ni(II) | Cu(II) | Zn(II) | Cd(II) | Hg(II) | Pb(II) | Cr(III) | Fe(III) |
|-----------------|-------------------|-------------------|-------------------|------------------|-------------------|-------------------|---------|---------|
| Citric acid | 5.2 | 5.9 | 4.8 | 3.7 | 10.9 | 4.0 | 7.7 | 10.2 |
| Glycine | 5.8 | 8.2 | 5.0 | 4.7 | 10.3 ^a | 4.7 | 8.4 | 10.0 |
| NTA | 11.3 ^b | 12.7 ^c | 10.5 ^c | 9.8 ^c | 12.7 ^b | 11.8 ^b | — | 15.9 |
| EDTA | 18.6 | 18.8 | 16.4 | 16.5 | 21.8 | 18.0 | 23.4 | 25.0 |

Data sources: Without indices: [11]; a: [12], b: [13], c: [14].

NTA. Some authors reported a significant solubilization of heavy metals after application of NTA in solution or bound on sewage sludge in test series with different types of soils^{4,5}. On the other hand, the effectiveness of synthetic chelators in washing and extracting systems for the decontamination of soils, sludges, and ashes has been proved in several laboratory and pilot scale tests^{6–10}.

For an estimation of the expectable leaching strength of complexing agents, the corresponding stability constants for the formation of metal complexes in aqueous solutions were often compared.

The stability constants of EDTA and NTA with heavy metals, listed in Table 1, are some orders of magnitude higher than the values of citric acid and glycine. Because other parameters and reactions, which are not reflected by the stability constants, are involved in the removal of metals, the practical relevance of this comparison is limited.

In spite of their weaker stability constants, there are some reasons for the investigation of the desorption capacity of natural chelating agents, namely:

—as natural components of soil solutions and sediment pore waters, they are adapted to environmental self-regulation processes and substance cycles. The risks of hazardous effects, following from their application in remedial actions, seem to be low.

—they are well biodegradable.

—economical sources like agricultural byproducts and wastes, leaf litter, etc. could be tapped for technical formulations.

One class of natural substances with moderate to high complex formation strength are amino acids. They are normally present in soil solutions in the concentration range between one and several mg kg^{-1} (total concentration)¹⁵.

A few studies were undertaken to investigate the leaching effects of higher concentrations of amino acids on metal containing ashes⁶ and sediments^{16,17}. However there still is a lack of information about the removal of heavy metals from typical soil components and soils under the influence of amino acids.

As a step towards this field of research, this study deals with the desorption capability of glycine for five heavy metals, adsorbed onto bentonite and peat. Experimental parameters were the metal content of the sorbents, the pH-value and

the testing period. The extent of adsorption was regulated with reference to the KSV (German sewage sludge act) limit values.

EXPERIMENTAL

Adsorbents

Bentonite (Schwaiba Comp., Germany), a smectite- (esp. montmorillonite) rich mud stone. Cation Exchange Capacity (CEC): 39.25 mval. 100 g⁻¹, pH (0.01 m CaCl₂): 7.54.

Peat, sampled from the upper 30 cm of a Bavarian fen soil, dried at 60°C, 0.56 mm sieved. Organic matter content: 49%, CEC: 82.7 mval 100 g⁻¹, carbonate content: 2.4%, pH (CaCl₂): 5.46.

Metal salts

Analytical grade acetates of Cu (II), Cd (II), Ni (II), Pb (II), and Zn (II), obtained from Merck Comp., Darmstadt (Germany); used in adsorption experiments.

Desorption agents

5% (w/w)-solution of glycine, pH-preadjusted by the addition of HCl and NaOH, respectively. For an adaptation to the inorganic ion content of soil waters, the following salts were added (even in control experiments without glycine): Ca(NO₃)₂ 328.0 mg l⁻¹; CaCl₂ 55.5 mg l⁻¹; MgSO₄ 44.5 mg l⁻¹; K₂SO₄ 29.6 mg l⁻¹; Na₂SO₄ 71.0 mg l⁻¹.

Buffer solutions

pH 7.0: 0.1 M HEPES [N-(2-hydroxyethyl)piperazine-N'-1-ethanesulfonic acid]; pH 4.5: 0.05 M MES[2-(N-morpholino)ethanesulfonic acid], both obtained from Merck, Darmstadt, (Germany).

PROCEDURES

The objective of the adsorption procedure was to realize a metal loading of the sorbents up to the two- and twenty-fold of the KSV limit values for the simulation of a low and a high metal burden.

The adsorption and the desorption experiments were carried out in centrifuge tubes clamped into a rotating apparatus. The solid:liquid ratio was 1:10. During the adsorption step, if necessary, the pH value was adjusted in the suspensions to 4.6–4.8 by the addition of an acetate buffer to prevent the precipitation of metal hydroxides. For the realization of the specific metal uptake, the required amount of the metal salt was determined in previous experiments.

At the end of a shaking period of 18 or 24 hours, the solids were separated from the suspensions by centrifugation and 0.1 μ m membrane-filtration.

The mass balance for the metal distribution between the solid and the liquid phase was calculated from the differences between the initial and final concentrations in the liquid phase. For a critical revision of the results, the metal content of adsorbents was determined several times after digestion with aqua regia. For this purpose, flame and graphite furnace AAS and ICP-AES were used¹⁸. The original metal content of the sorbents was analysed in the same way.

The desorption experiments were carried out as duplicates, resuspending equal amounts (two or five gram) of the dried, metal loaded sorbents in the glycine solutions. All desorption test series were accompanied by at least two control experiments without addition of glycine. The reaction was examined at neutral pH and at pH 4.5.

RESULTS

The initial metal content of the untreated sorbents, the glycine (pH 7.0) extractable amount of this metal fraction and the quantities of experimentally adsorbed metals are summarized in Table 2. The glycine extraction was performed just as described above.

The glycine extractable metal fractions of the untreated peat are higher than the one of bentonite. The heavy metals may be occluded in the mineral lattice of the clay to a high extent. Therefore these detrital metals are not extractable without dissolution of the solid matrix.

Figure 1 shows the reaction pathway of the desorption of heavy metals (twenty-fold KSV values) at neutral pH from bentonite. The final desorption rates range between

Table 2 KSV limit values and metal contents of the sorbents

| | <i>Metals</i> | | | | | <i>Concentration unit</i> |
|----------------|---------------|-----------|-----------|-----------|-----------|---------------------------|
| | <i>Cu</i> | <i>Cd</i> | <i>Ni</i> | <i>Pb</i> | <i>Zn</i> | |
| KSV limit val. | 100 | 3 | 50 | 100 | 300 | mg kg ⁻¹ |
| Bentonite: TC | 10.4 | 0.3 | 8.3 | 24.0 | 88.1 | mg kg ⁻¹ |
| Ex | 1.2 | n.d. | 0.2 | 1.8 | 3.1 | mg kg ⁻¹ |
| LL | 229 | 7.69 | 105 | 230 | 655 | mg kg ⁻¹ |
| | 3.60 | 0.07 | 1.79 | 1.11 | 10.02 | mmol kg ⁻¹ |
| HL | 2403 | 51.4 | 1074 | 3100 | 6240 | mg kg ⁻¹ |
| | 37.81 | 0.46 | 18.29 | 14.96 | 95.46 | mmol kg ⁻¹ |
| Peat: TC | 16.1 | 0.9 | 18.9 | 44.6 | 50.4 | mg kg ⁻¹ |
| Ex | 4.0 | n.d. | 5.2 | 0.9 | 8.8 | mg kg ⁻¹ |
| LL | 246 | 6.48 | 111.3 | 275 | 652 | mg kg ⁻¹ |
| | 3.87 | 0.06 | 1.90 | 1.33 | 9.97 | mmol kg ⁻¹ |
| HL | 2209 | 62.0 | 1072 | 2119 | 6510 | mg kg ⁻¹ |
| | 34.76 | 0.55 | 18.26 | 10.23 | 99.59 | mmol kg ⁻¹ |

Legend: TC: Total metal content (digestion in aqua regia); Ex: Glycine extract; n.d.: not determined; LL: Low load (incl. Ex); HL: High load (incl. Ex).

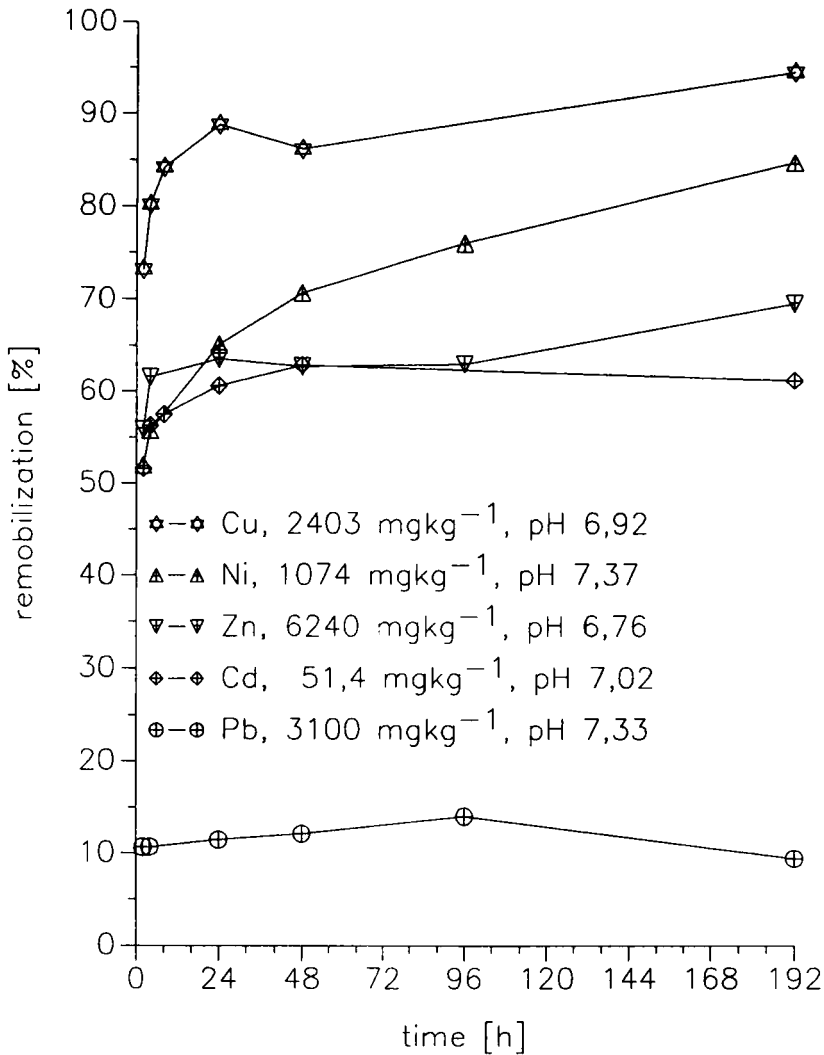


Figure 1 Desorption of heavy metals from high loaded bentonite.

94.7% (Cu) and 9.4% (Pb). The desorption rates increase following the order Pb < Cd < Zn < Ni < Cu. Between 61% (Ni) and 100% (Pb) of the totally removed amount of metals have been released during the first two hours. Three different types of the time-depending reaction course can be distinguished.

a) Reaching the approximate final values within 24 or 48 hours (Cd, Pb, Cu).

b) Increase of the desorption rate during the whole time span, with a progressive decrease in the desorption increments with the duration of the experiment; describable by a first order reaction term-with exception of the first two hours (Ni).

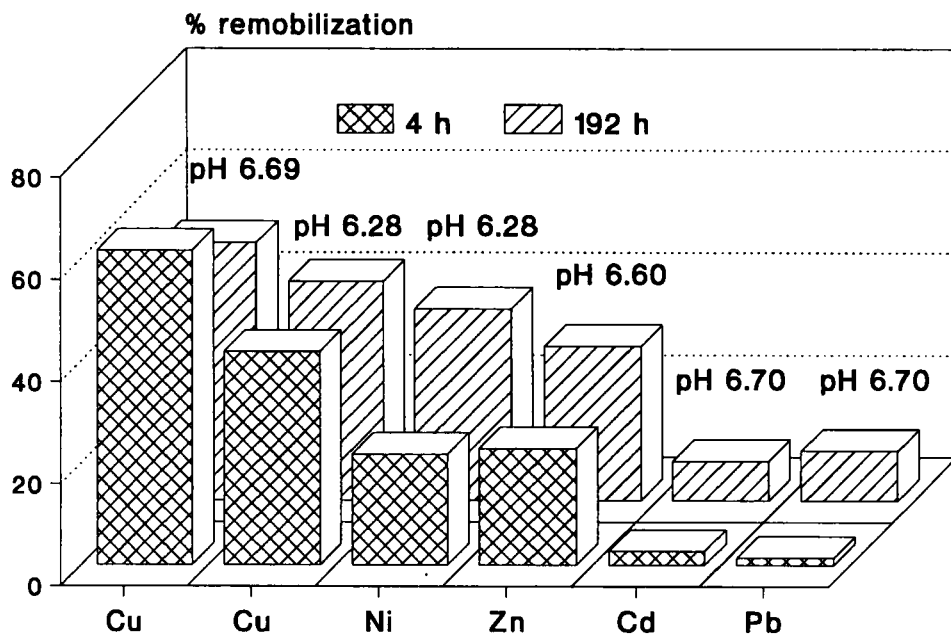


Figure 2 Desorption of heavy metals from peat.

c) Fast reaching of a plateau, followed by a second increase of the remobilization rate after some days (Zn).

Figure 2 shows the results of the corresponding tests with peat. Compared with the results of the desorption from bentonite, smaller amounts of metals (decrease of the Cu, Ni and Zn desorption of about 50 per cent) were desorbed. The effect is especially noticeable in the case of Cd: The remobilization rate dropped down from 61.3% to 7.7%. The order of leachability changes into the following sequence: $\text{Cd} < \text{Pb} < \text{Zn} < \text{Ni} < \text{Cu}$. Due to the self-buffering properties of peat, the reaction pH is somewhat shifted towards lower pH values (pH differences to the bentonite experiments between 0.16 and 1.05 units, mean difference 0.48 units). The influence of the pH value is evidenced in the Cu experiments. Partially the time course of the reaction deserved another feature: The solute concentrations of Cu and Ni were reduced at the second or third measuring and increased afterwards. This correlates with synchronous pH drifts in the Ni and Cu (mean pH: 6.28) test series, but it does not correlate with the Cu tests at the higher pH level.

Additional information about the metal desorption from high loaded sorbents at neutral pH is given in Table 3. The removal efficiency of glycine is clarified not only by the percentages of solubilized metals, but also by the term "final metal concentration in the glycine solution" divided by "final concentration in the buffer solution" (enrichment factor). This underlines the strong solubilization effect of glycine on adsorbed Cu and Ni and elucidates the remarkable increase of desorbed Pb in the bentonite suspension.

Table 3 Data survey: Desorption at neutral pH and high metal content

| | Metal ions | | | | |
|------------------------------------------|------------|-------|-------|------|------|
| | Cd | Cu | Ni | Pb | Zn |
| Bentonite: | | | | | |
| C _{s,i} [mg kg ⁻¹] | 51.4 | 2403 | 1074 | 3100 | 6240 |
| C _{s,f} [mg kg ⁻¹] | 19.9 | 127.4 | 162.2 | 2809 | 1897 |
| C _{e,f} [mg l ⁻¹] | 3.21 | 240.2 | 98.5 | 23.6 | 451 |
| C _{e(gly)} /C _{e(buf)} | 12.8 | 155 | 63.1 | 56.6 | 20.4 |
| Rem. [%] | 61.3 | 94.7 | 84.9 | 9.4 | 69.6 |
| Peat: | | | | | |
| C _{s,i} [mg kg ⁻¹] | 62.0 | 2209 | 1072 | 2119 | 6510 |
| C _{s,f} [mg kg ⁻¹] | 57.2 | 1096 | 671.1 | 1914 | 4544 |
| C _{e,f} [mg l ⁻¹] | 0.54 | 106.5 | 44.3 | 24.7 | 213 |
| C _{e(gly)} /C _{e(buf)} | 15.8 | 52.7 | 42.6 | 15.9 | 34.1 |
| Rem. [%] | 7.7 | 50.4 | 37.4 | 9.7 | 30.2 |

Legend: C_s: Concentration in the solid phase; C_e: Concentration in the liquid phase; i.: initial; f.: final; buf.: buffer.

A direct comparison of the influence of various reaction parameters on the desorption process was made for the elements Cu, Ni, Cd and Zn. Lead could not be desorbed to a higher extent than 10%, independently of the tested metal covering and pH.

The first information pairing was made for Cu and Ni (see Figure 3). Besides the already discussed differences between the desorption from bentonite and peat at

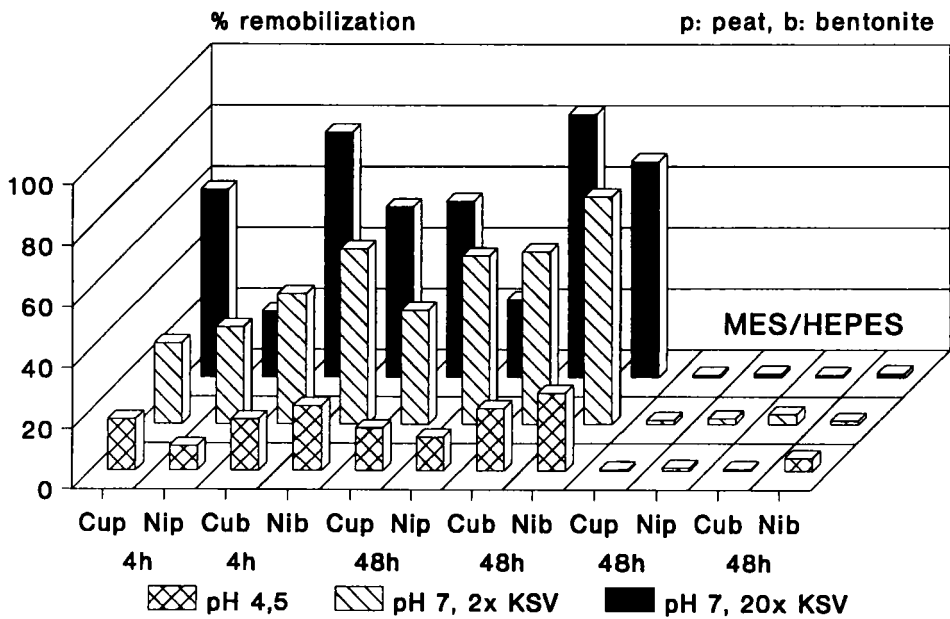


Figure 3 Remobilization of Cu and Ni from bentonite and peat.

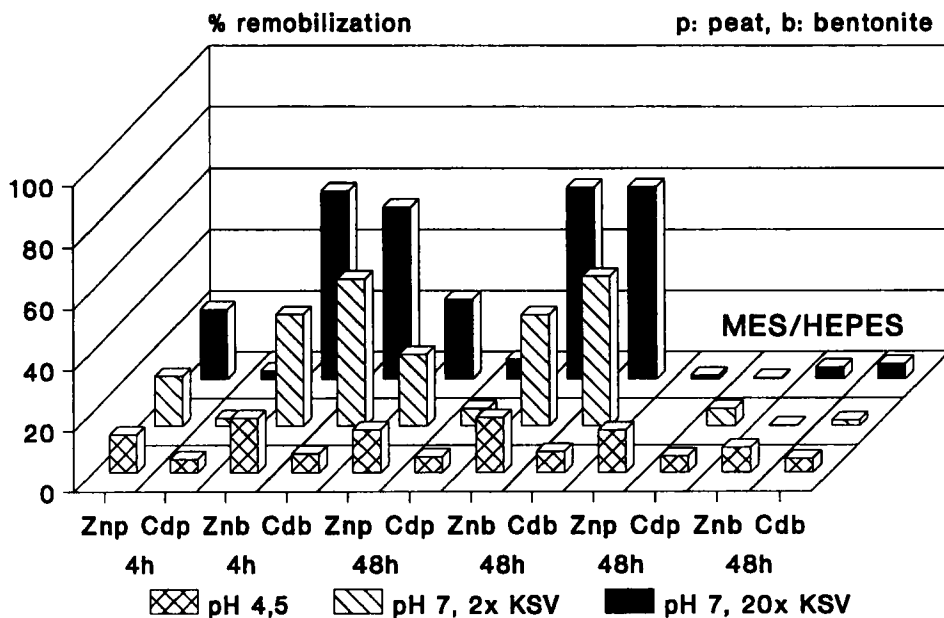


Figure 4 Remobilization of Zn and Cd from bentonite and peat.

pH 7.0, the reduced desorption of the elements from both sorbents at pH 4.5 is conspicuous. The sorbents effect is still recognizable at pH 4.5. The copper desorption increases with the increase of the metal load of both sorbents, whereas a revised relation was found for nickel. The metal solubilization in the buffer solutions remains below two percent, typically.

The characteristics of the cadmium and zinc remobilization from bentonite largely correspond to the copper example (see Figure 4). For every experimental condition, Cd shows greatest differences between the desorption from bentonite and peat. The desorption of Cd from peat does not exceed 10%. Glycine however has a slight effect of the solubilization of Cd from high loaded peat at pH 7.0. At pH 4.5 (high metal burden) and pH 7.0 (low metal content), the remobilization in the buffer solutions reached the same level as in the amino acid solution, approximately.

Relative high amounts of Zn were desorbed at pH 4.5, especially from peat. Reflecting the Zn concentrations in the MES-solutions at pH 4.5, one has to consider cation exchange reactions as a driving force for the metal release. With minor importance, this seems to be the case for Cd, too.

DISCUSSION

The comparison of the removal of elements under the viewpoint of the stabilities of formed glycine complexes as regulating factors is handicapped by the nonequivalent

metal load of the sorbents. Since the variation of the metal load within one order of magnitude has a lower effect on the metal solubilization for the majority of the elements than the change of the sorbent, a first attempt in this direction could be made. In fact, the order of remobilization rates is in good agreement with the order of stability constants. An exception is lead which should be removed approximately equal to cadmium. On closer examination, this seems to be a result of the higher lead content of the sorbents and the very low solubility of the lead hydroxide which could not be compensated by glycine to a higher extent.

A better correspondence with the order of stability constants is obtained by taking the enrichment factors of the metals $[C_e(\text{gly})/C_e(\text{buf})]$ in the peat suspensions as a basis for the interpretation. This clarifies the impact of complexation on the distribution of the metal ions between the solid and the liquid phase.

The adsorption/cation exchange capacity of peat mainly belongs to its organic matter. Alternatively, the adsorption itself can be interpreted as a complexation by macromolecular humic substances at isolated coordination groups, similar to the one of glycine. Thus the release of heavy metals from peat is the result of the competition of both ligands for the metal ions. Therefore, the equilibrium of the ligand exchange reaction strongly depends on the concentration and stability constants of all included ligands.

The specific complexation by organic matter explains the higher metal fixation on the peat particles compared to the adsorption onto the clay mineral which bounds cations by electrostatic attraction mainly.

Within the observed pH range, the increase of the proton concentration reduces and does not enhance the metal solubilization, as it was reported for EDTA⁹. Due to its amphoteric character and according to its isoelectric point of 6.07, glycine is positively charged at a pH value below 6.07, predominantly. This alleviates the complexation capacity of glycine and favours complex species with M:L-ratios of 1:2 or 1:3 which easily undergoes ligand exchange reactions. The positive charged glycine molecules as well as the positive charged complex species can be (re-)adsorbed.

The decrease of the remobilization rate of most elements with the decrease of the metal content in the solid phase may be caused by the relatively higher contribution of primarily occupied sorption sites with higher bonding energies. Another possibility may be the increasing formation of better adsorbable multi-ligand species, due to the higher excess of glycine.

CONCLUSIONS

—Under equal experimental conditions, the remobilization of heavy metals from bentonite by glycine exceeds the corresponding results from tests with peat.

—Desorption at neutral pH is more effective than at acidic pH.

—In most cases, the desorption rate increases with the increase of the metal content.

—Considering the reduction of ecotoxicological equivalents of heavy metals from typical soil components, the following order of remobilization rates, as affected by glycine, could be made : $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Pb}$

—Despite the different metal burdens of the sorbents, the order of remobilization rates approximately corresponds to the order of the metal-glycine stability constants.

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