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# Sorption of complexed and uncomplexed Cu(II), Ni(II) and Zn(II) ions by peat

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Batch experiments of Cu(II), Ni(II) and Zn(II) sorption onto peat were carried out in solutions containing ligands *viz.* glycine, EDTA, tartrate, citrate, and in those without ligands. The presence of ligands in solutions diminished the metal ion sorption onto peat in most cases. At an excess of metal ions in comparison with ligand concentration in solution, the precipitation of insoluble compounds of Cu(II) with EDTA, citrate, tartrate and Zn(II) with citrate and tartrate took place together with metal ion sorption.

**Key words:** sorption, peat, metal ion complexes

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## INTRODUCTION

Nearly all industrial effluents are contaminated with heavy metals. These pollutants are highly toxic, non-biodegradable and may be cancerogenic. The use of metal complexes in industry is the main reason for enormous pollution of the environment with heavy metals. Complexing agents enhance the solubility and bioavailability of metals. Most of heavy metals dissolved in wastewater effluents and surface runoff are complexed. Moderately strong complexing ligands, which consist of a naturally occurring organic matter, are responsible for the complexation of only about 5–20% of such heavy metals as copper and nickel. The remaining part of heavy metals is complexed by synthetic chelating agents [1]. The extent of metal complexation in soil aquatic systems is close to 100% for copper. A significant complexation has been reported for zinc and cadmium [2].

EDTA is one of the synthetic ligands most widely used in industry and household. Besides EDTA, industries use other strong complexing agents such as ethylenediamine, glycine, tartrate, citrate, succinate. As a rule, metal ions from complex solutions are removed after degradation of ligands by oxidation.

The traditional techniques for removing metal ions from aqueous effluents are precipitation with carbonate or hydroxide, filtration, ion exchange, and the use of various sorbents. Cheap and effective technologies or sorbents are required for the treatment of waste water streams contaminated with heavy metals. Natural materials available in large quantities or certain waste products from industry or agriculture are more suitable for this purpose [3].

Peat is one of such sorbents [4–7]. It is a rather complex soil material consisting of organic matter at various stages of decomposition. It contains lignin and cellulose as major constituents. These constituents, especially lignin, contain polar functional groups such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that can be involved in chemical bounding. Due to such properties peat tends to have a high cation exchange capacity and is an effective adsorbent for the removal of heavy metals. Studies of Ni(II), Cu(II), Zn(II) and Cd(II) binding onto moss peat showed that in single-component systems the maximum capacity was similar (180–200 mmol/kg) regardless of the metal nature. However, the pH at which a given percent removal would occur varied. At pH 4.0, 90% of Cu(II) was removed; at pH 4.5, 90% of Ni(II) was removed; at pH 5.6, 90% of Cd(II), and at 6.7, 90% of Zn(II) were removed. For Cu, peat had a maximum sorption capacity of 16.4 mg/g (0.26 mmol/g) and for Ni(II) 9.18 mg/g (0.16 mmol/g), and the value of optimum pH was highest for Ni(II), showing a trend inverse to maximum sorption capacity.

In all cases the adsorption capacity and the values of ion exchange and complexation are dependent on pH, ionic strength, concentration and peat type. There are many different types of peat available, exhibiting different chemical and physical properties. All authors discussing the subject agree that the natural capacity of peat to retain cations is related to pH of the solutions. The optimum pH range for the sorption of most divalent ions onto peat is 3.5–6.5 [4].

Practically, peat investigations are interesting because of peat being an inexpensive sorbent for heavy metals. Theoretically, these investigations can be used to appraise the metal mobility in the environment. However, we did not find in literature any data on complexed metal ion sorption onto peat. Therefore our studies were carried out with the purpose to determine the effect of pH, the initial concentration of Cu(II), Ni(II), Zn(II) and their complexes with EDTA, glycine, citrate, tartrate on the sorption onto peat.

## EXPERIMENTAL

The peat used in this study was manufactured by JSC "Durpeta", Šepeta, Kupiškis region, Lithuania. It is of a low degree of decomposition with the following characteristics: pH 5.75–5.85 (in water), pH 3.4–3.5 (in 1 N KCl solution), ash = 3.4%, total organic carbon = 47.9%, total N = 1.6%, total P = 0.02%, inorganic P = 0.004%, moisture content 11–17%.

All experiments were carried out on peat dried at 105 °C and sieved (1 mm<sup>2</sup> mesh). All figures are calculated on the basis of dry peat. The content of ash, carbon, nitrogen and phosphorus in the peat was determined according to standard methods [8]. Incineration was carried out at 600 °C for 3 h, total nitrogen was determined by Kjeldahl method, organic carbon – after oxidation with chromic acid, total and inorganic phosphorus – by oxidation with H<sub>2</sub>O<sub>2</sub> and dissolution in HCl.

All experiments were carried out at room temperature by adding peat to a solution containing metal sulphate salts. The concentrations of metal salts and ligands were selected on the basis of actual concentrations in wastewater streams containing spent solutions in a metal finishing industry and a printed circuit board manufacture. These concentrations can vary in a rather wide range depending on the conditions of production. The effect of the initial concentration of copper, nickel and zinc on adsorption was studied using 1 g dry peat per 100 ml solution. The concentrations of copper, nickel and zinc were studied within a range of 10–200 mmol/l and EDTA 20 mmol/l, glycine 50 mmol/l, citrate 10 mmol/l and tartrate 20 mmol/l. pH was adjusted each 2–3 days by means of NaOH or H<sub>2</sub>SO<sub>4</sub> solutions until the pH value became fixed. It took about 15–20 days. After that the solutions were filtered and analysed.

The concentrations of Ni(II) and Zn(II) in solutions were determined complexometrically by using EDTA as a titrant and appropriate indicators, Cu(II) ions by means of iodide. The concentration

of organic matter was determined by oxidation with permanganate in alkaline solution. The excess of permanganate was retitrated by oxalic acid in acidic solutions [9].

The results on organic matter concentrations are given for both dissolved peat organic matter and ligands.

## RESULTS AND DISCUSSION

**Sorption of free metal ions.** According to the literature data [3, 6], peat acts as a good metal ion sorbent in a rather narrow pH range. First of all, the pH influence on metal sorption onto peat was investigated in order to find out the maximal sorption ability of peat (Fig. 1a). The sorption does not proceed at low pH values. An increase in pH leads to a decrease of residual metal concentrations, *i.e.* to a rise in adsorption. The further increase in pH causes formation of insoluble metal hydroxides, therefore the residual metal concentrations decrease to 0.05–0.2 mmol/l. The increase in metal concentrations in alkaline solutions can be caused by metal ion complexation of dissolved peat organic matter (Fig. 1b). In case of Zn(II) some dissolution of hydroxides takes place at pH 12.

The pH values at which the insoluble metal hydroxides form depending on metal ion concentration are shown in Fig. 1a and tabulated in Table 1. The

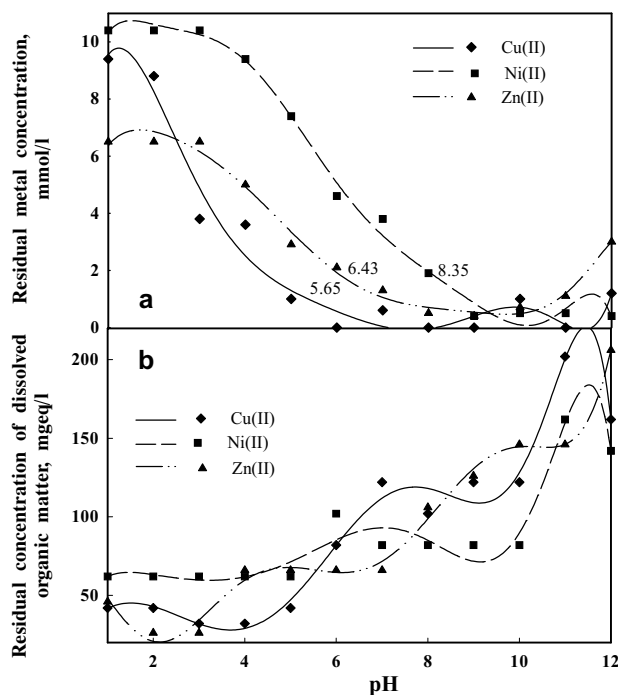


Fig. 1. Dependence of residual metal (a) and organic matter (b) concentrations on pH after sorption. 1,1' – Cu(II), 2,2' – Ni(II) and 3,3' – Zn(II). Initial concentrations (mmol/l): Cu(II) – 9.6, Ni(II) – 10.4, Zn(II) – 6.5

Table 1. Calculated pH values at which insoluble metal hydroxides form depending on metal ion concentration

Metal hydroxides	Solubility product [10]	Concentration, mmol/l	pH of beginning of precipitation
Cu(OH) <sub>2</sub>	5.0·10 <sup>-20</sup>	10	5.65
		50	5.00
		100	4.85
		200	4.70
Ni(OH) <sub>2</sub>	2.0·10 <sup>-15</sup>	10	8.35
		50	7.30
		100	7.15
		200	7.00
Zn(OH) <sub>2</sub>	7.1·10 <sup>-18</sup>	10*	6.43
		50	6.08
		100	6.08
		200	6.22

\* The beginning of dissolution of Zn(OH)<sub>2</sub> takes place at pH 10.5, the complete dissolution occurs at pH 12–13.

pH of the beginning of precipitation was calculated according to the equation:

$$\text{pH} = 14 - \lg \left( \frac{\text{SP}}{\text{Me}^{2+}} \right)^{1/2}$$

where SP is the solubility product of insoluble metal hydroxides.

The quantities of dissolved organic matter increase with an increase in pH and considerably exceed the metal ion concentration at all pH investigated (Fig 1b). According to reference [6], the composition of dissolved organic matter strongly depends on pH. In mildly acidic and neutral solutions the dissolution of low molecular weight organic acids such as oxalic, citric, gallic etc. is possible, meanwhile in alkaline solutions the dissolution of high molecular weight compounds such as tannin, lignin humic and fulvic acids proceeds. These high molecular weight compounds act as complexing agents for metal ions. It partly explains the retarding effect of pH on metal ion sorption on peat in alkaline solutions, meanwhile low molecular weight organic compounds are known as precipitants for metal ions [11].

During the sorption process the solution pH, as a rule, decreased. Therefore it was adjusted with NaOH. However, due to the complicated sorption process, the role of pH was not thoroughly studied.

The estimation of peat sorption ability is most reliable at the pH values when no hydroxide precipitation takes place. Therefore the further investigations were carried out at pH 4 for Cu(II), and pH 5 for Ni(II) and Zn(II). The peat sorption ability for Cu(II), Ni(II) and Zn(II) depends on the metal concentration in solution and increases with its increase. The free metal ion sorption onto peat is in good agreement with the solubility of the metal hydroxides and decreases in the following order: Cu(II) > Zn(II) > Ni(II) (Fig. 2). Actually, this order is similar for all the sorbents containing functional groups with oxygen [12, 13]. Our data are in good agreement with the well-known explanation of metal ion sorption onto peat by functional groups containing oxygen. Besides, the sorbed amounts of metal ions are similar to those described in literature [4].

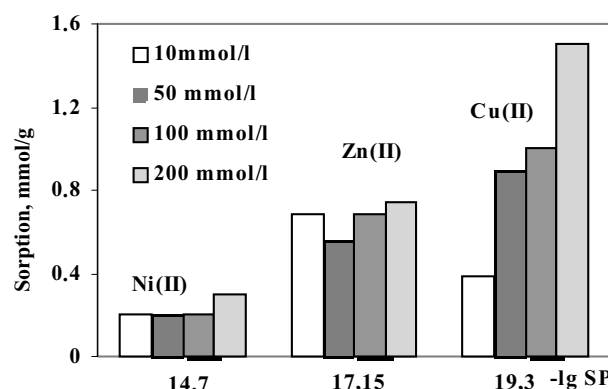


Fig. 2. Effect of solubility product on metal ion sorption onto peat at different initial metal concentrations

Table 2. Sorbed amount of metal ions onto peat, mmol/g

Metal ions concentration, mmol/l	Ligand					
	Without	Glycine	EDTA	Tartrate	Citrate	
Cu (II)	9.6	0.4	0.1	0.5	0.6	0.2
	48	0.9	0.4	3.3*	1.6*	1.5*
	96	1.0	0.4	7.8*	1.8*	0.4
	192	1.5	0.6	5.6*	2.4*	0.4
Ni (II)	10.4	0.2	0.1	0.04	0.1	0.05
	52	0.2	0.1	0.2	0.3	0.1
	104	0.2	0.2	0.3	0	0
	208	0.4	0.2	0.3	0	0
Zn (II)	10.6	0.7	0	0	0.1	0.1
	53	0.6	0.3	0.5	1.7*	0.2
	106	0.7	0.4	0.8	1.9*	8.8*
	212	0.9	0.4	1.2	2.4*	4.5*

\* Formation of light precipitates different from peat

**Sorption of complexed metal ions.** The presence of ligands in solutions considerably changes the metal ions sorption ability of peat (Table 2, Figs. 3–6). In most cases inspection of peat after filtration showed that the peat to contain light crystalline precipitates. They are indicated in Table 2. Glycine, as a rule, reduces the sorption of all investigated metal ions onto peat (Fig. 3a). The presence of EDTA (Fig. 4a) considerably increases the supposed Cu(II) sorption at higher metal concentrations. Only when the EDTA concentration exceeds the Cu(II) concentration, the retarding effect of EDTA on Cu(II) sorption is seen. The further investigation showed that at pH 4 the precipitation of insoluble  $\text{Cu}_2\text{EDTA}\cdot 4\text{H}_2\text{O}$  took place when the Cu(II) concentration exceeded that of EDTA [14]. However, the presence of peat considerably changed the completeness of Cu(II)-EDTA precipitation. In case of Ni(II) and Zn(II), when the precipitation with EDTA did not proceed, the sorption of metal ions was much lower than that without ligands.

The formation of insoluble metal compounds of tartrate and citrate with an excess of Cu(II) and Zn(II) is well known. However, the presence of tartrate (Fig. 5a) and citrate (Fig. 6a) remarkably reduces the Ni(II) sorption onto peat. It is worth noting that in case of Cu(II) and Zn(II), when no insoluble precipitates appear, the metal ion sorption

is much lower in comparison with sorption without ligands.

The residual concentrations of organic matter remarkably increase when insoluble precipitates are formed (Figs. 3b–6b). When changes in residual metal concentrations are small, changes in organic matter concentrations are small, too. Such changes arise due to the sorption process. The considerably decreased metal ion concentrations as well as a decreased organic matter content show, as a rule, the formation of insoluble metal compounds. The exception is citrate provided by a high (200 mmol/l) Cu(II) concentration (Fig. 6). In this case the residual organic matter concentration and the metal sorption are low, and the precipitates do not form.

A comparison of the results of peat interaction with the complexed and uncomplexed metal ions showed that in case of complexed metal ions the interaction was more complicated due to a precipitation of insoluble metal ion compound with ligands. When the precipitation did not take place, the presence of ligands decreased the metal ion sorption. Such a distinct effect was observed for Cu(II), Ni(II) and Zn(II) complexes with glycine, and Ni(II) complexes with EDTA, citrate and tartrate.

The results presented show that peat is a useful sorbent of free metal ions. Metal ions in the pre-

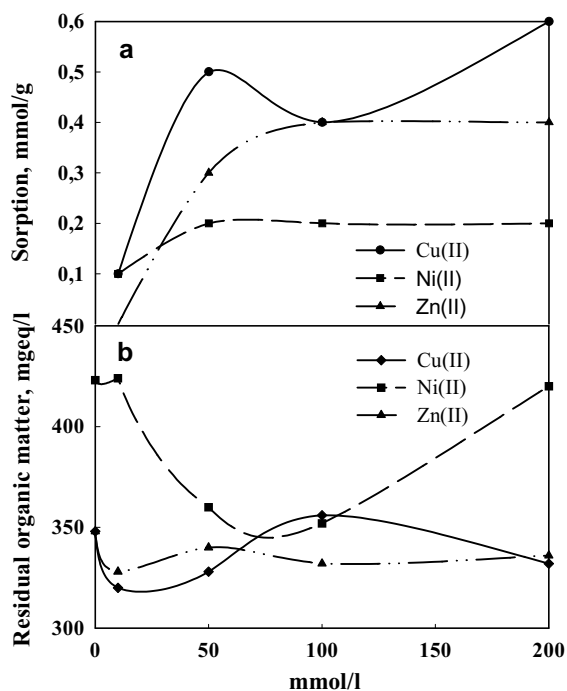


Fig. 3. Dependence of sorbed quantities of metal ions (a) and residual organic matter (b) on initial concentration of metal ions at pH 4 for Cu(II) and pH 5 for Ni(II) and Zn(II) in presence of glycine

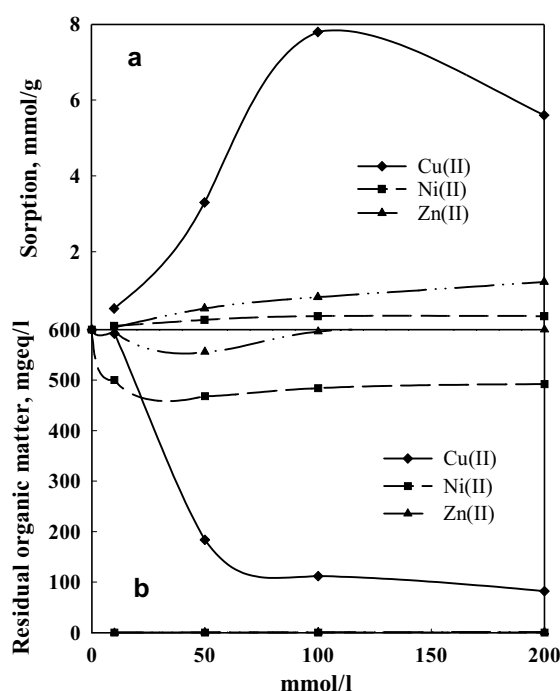


Fig. 4. Dependence of sorbed quantities of metal ions (a) and residual organic matter (b) on initial concentration of metal ions at pH 4 for Cu(II) and pH 5 for Ni(II) and Zn(II) in presence of EDTA

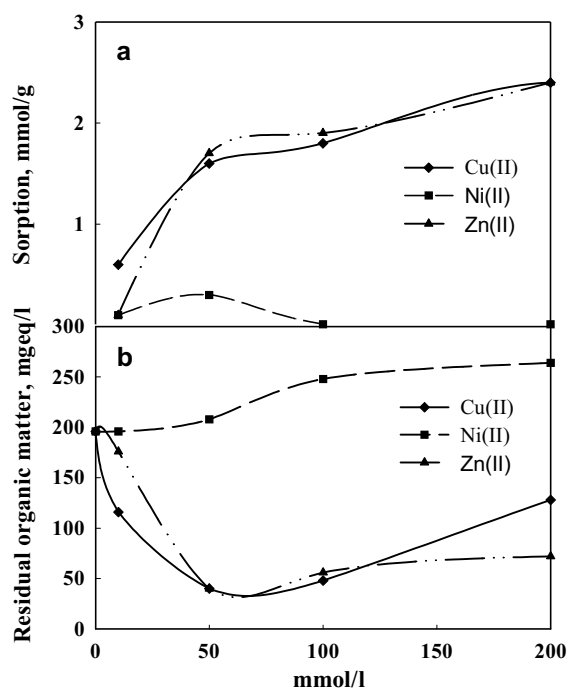


Fig. 5. Dependence of sorbed quantities of metal ions (a) and residual organic matter (b) on initial concentration of metal ions at pH 4 for Cu(II) and pH 5 for Ni(II) and Zn(II) in presence of tartrate

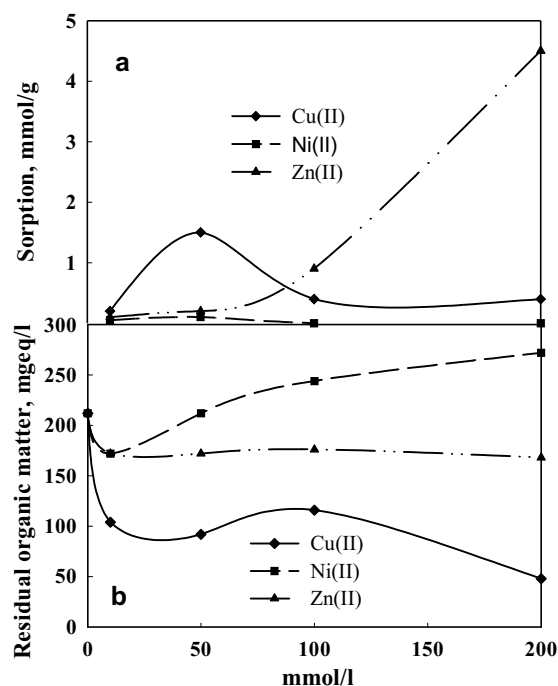


Fig. 6. Dependence of sorbed quantities of metal ions (a) and residual organic matter (b) on initial concentration of metal ions at pH 4 for Cu(II) and pH 5 for Ni(II) and Zn(II) in presence of citrate

sence of ligands are sorbed onto peat much less. At an excess of metal ions in comparison with ligands the sorption onto peat as a rule increases for both

free and complexed metal ions. In some cases precipitation of insoluble metal compounds takes place simultaneously with sorption.

## CONCLUSIONS

1. The sorption of free metal ions onto peat decreases in the following order: Cu(II) > Zn(II) > Ni(II).

2. The sorption of metal ions onto peat in the presence of ligands is much lower.

3. An increase in metal ion concentration:

a) leads to an increase in the sorption of both complexed and uncomplexed metal ions;

b) causes the formation of insoluble Cu(II) compounds with EDTA, citrate and tartrate and insoluble Zn(II) compounds with citrate and tartrate.

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**KOMPLEKSINIŲ IR NEKOMPLEKSINIŲ Cu(II), Ni(II) ir Zn(II) JONŲ SAŲEIKA SU DURPĖMIS**

**S a n t r a u k a**

Buvo tirta laisvų Cu(II), Ni(II) ir Zn(II) jonų ir jų kompleksų su glicinu, EDTA, tartratu ir citratu sorbcija durpėse. Ligandai dažniausiai mažina metalų jonų sorbciją tirpaluose ant durpių. Su metalų sorbcija, esant jų pertekliui, vyksta ir netirpių junginių, Cu(II) su EDTA, citratu, tartratu ir Zn(II) su citratu ir tartratu, nusėdimas.

**И. Айкайте, О. Гилене, М. Шалкаускас**

**ВЗАИМОДЕЙСТВИЕ КОМПЛЕКСНЫХ И НЕКОМПЛЕКСНЫХ ИОНОВ Cu(II), Ni(II), Zn(II) С ТОРФОМ**

**Р е з ю м е**

Исследована сорбция торфом свободных Cu(II), Ni(II) и Zn(II) ионов и их комплексных соединений с глицином, ЭДТА, тартратом, цитратом из растворов. Лиганды, как правило, снижают сорбцию металлов торфом. При избытке свободных ионов металлов образуются нерастворимые соединения Cu(II) с ЭДТА, тартратом, цитратом и Zn(II) с тартратом и цитратом.