

# Sorption of Metal Ions on Lignite and Humic Acids

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Received 26 November 2002

The adsorption of some heavy metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ ) on modified lignite from South Moravia region was studied. The sorption properties of humic acids isolated from this lignite were also investigated. The kinetics of the adsorption process was described applying the Langmuir theory. The adsorption is considered to be the reaction of the second order, the desorption is described by the first-order kinetics. Nevertheless, the rate constants have to be taken as effective values, where the influence of the size and the shape of particles is included. The sorption capacity of lignites and humic acids was calculated using Langmuir isotherms. The regression analysis confirmed very good accordance of experimental data with the Langmuir relations. Therefore, it can be concluded that heavy metal ions are predominantly chemically bound to the lignite and humic acids. Simultaneously, substantially higher adsorption ability of humic acids was documented, when compared with that of unmodified or modified lignite.

One of the most characteristic properties of humic substances, occurring in soils, some types of coal and water sediments, is their adsorption ability. In natural systems, they bind the contaminating metal ions, and in this way, they influence the effectiveness of the regeneration and purification processes in these systems [1–4]. It is probable that in such systems by the given pH and ionic strength value only definite types of macromolecules of humic substances preferentially react with metal ions [5]. The bond formation between metal ions and humic substances mainly proceeds through carboxylic and phenolic groups. In this case, the multivalent metal ions are able to be complexed by the functional groups of different molecules. Thus, the adsorbent represents the system, where various active sites for the adsorption are available. During the adsorption process these are, according to the strength of the complex, gradually saturated by the interaction with metal ions. The bonding ability of individual functions of humic substances depends on the content of corresponding functional groups, on the size and shape of the macromolecule, and on the experimental conditions [1, 2, 6]. By the increase of pH value, the probability of the complexation of metal ions with humic substances grows [7–9]. By the interaction of humic substances with transition metal ions the bidentate ligands of salicylic and dicarboxylic type play the most important role. As the active site for the binding of metal ions, the carboxylic and phenolic groups can act. These can be situated either on the different aromatic rings of the same macromolecule or on the different macromolecules. Generally, the carboxylic groups dissociate easier than OH groups in aromatic and aliphatic compounds. Phenols

are stronger acids than water and enols, but weaker than most of carboxylic acids. Therefore, the acidic character of humic substances is usually caused by the ionization of COOH and OH group, although the influence of other structures (*e.g.* enol, carbonyl, ether, amino and azo groups) has to be taken into account. The kinetics of the process depends on many parameters. In the solution, the rate of complexation process is significantly influenced by the diffusion coefficient of adsorbate, by the size and shape of adsorbent, as well as by process conditions (convection, temperature, *etc.*). On the solution-adsorbent interface, the rate of the complexation is unequivocally determined by interaction forces between the adsorbent surface and the particle adsorbed.

Commonly, the formation of the monolayer adsorbed species proceeding on equivalent active centres can be described by the Langmuir model [10, 11]. Using this model, in spite of some simplifications, the quantification of many sorption processes can be performed. Eqn (1) represents the linear form of the Langmuir isotherm

$$\frac{c_{\text{eq}}}{a_{\text{eq}}} = \frac{1}{a_{\text{max}} b} + \frac{c_{\text{eq}}}{a_{\text{max}}} \quad (1)$$

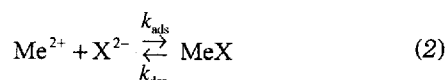
where  $c_{\text{eq}}$  and  $a_{\text{eq}}$  are the concentration and adsorbed amount in equilibrium,  $a_{\text{max}}$  is the maximum of adsorbed amount and  $b$  is the ratio of rate constants for adsorption and desorption, respectively. The kinetics of sorption was described by the equation derived on the basis of the Langmuir model, *i.e.* the rate of adsorption is directly proportional to the metal ions concentration and to the portion of unoccupied active centres,

**Table 1.** Parameters of Langmuir Isotherm for Adsorption of Metal Ions to Lignite and HA

Sample	Co <sup>2+</sup>		Ni <sup>2+</sup>		Cu <sup>2+</sup>	
	$\alpha_{\max}$	$b$	$\alpha_{\max}$	$b$	$\alpha_{\max}$	$b$
	10 <sup>-4</sup> mol g <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>	10 <sup>-4</sup> mol g <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>	10 <sup>-4</sup> mol g <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>
0.2–0.3 mm	2.56	14.0	3.69	21.0	5.42	81.1
0.3–0.4 mm	3.45	22.8	5.09	21.0	8.51	28.5
0.4–0.5 mm	4.11	34.2	7.56	22.7	9.15	26.9
450 °C	2.83	20.8	1.79	12.1	4.26	14.6
550 °C	4.10	26.9	2.34	46.5	6.92	11.5
650 °C	5.42	32.4	3.39	89.8	7.67	24.5
HA	33.32	3.9	51.89	2.0	53.03	2.5

while the rate of the desorption is directly proportional to the fraction of occupied active centres.

It is assumed that the complexation of metal ions proceeds according to the equation



where X<sup>2-</sup> represents one binding site for bivalent ion Me<sup>2+</sup>, MeX is the formed complex. With respect to starting conditions the following kinetic equation was derived

$$-\frac{dx}{dt} = -\frac{dy}{dt} = \frac{dz}{dt} = k_{\text{ads}}xy - k_{\text{des}}z \quad (3)$$

where  $x$ ,  $y$ , and  $z$  are concentration of Me<sup>2+</sup> ions, concentration of binding sites X<sup>2-</sup>, and concentration of the complex MeX. If it is assumed that the starting concentration of the complex MeX is zero ( $z_0 = 0$ ), these relations follow from the law of conservation of mass

$$x_0 - x = z \quad \text{and} \quad y_0 - x_0 + x = y \quad (4)$$

where  $x_0$  and  $y_0$  are the starting concentration of Me<sup>2+</sup> ions and concentration of binding sites X<sup>2-</sup> in the system, respectively. Substituting  $y$  and  $z$  according to eqn (4) and if  $k_{\text{des}} = k_{\text{ads}}/b$ , eqn (3) can be modified

$$\frac{-dx}{k_{\text{ads}}dt} = x^2 + x\left(y_0 - x_0 + \frac{1}{b}\right) - \frac{x_0}{b} \quad (5)$$

For the system in equilibrium, this relation transforms into the quadratic equation

$$\alpha x^2 + \beta x - \gamma = 0 \quad (6)$$

with coefficients  $\alpha = 1$ ,  $\beta = (y_0 - x_0 + 1/b)$ , and  $\gamma = x_0/b$ . Plotting  $\ln \frac{x + x_{\text{eq}} + \beta/\alpha}{x - x_{\text{eq}}}$  vs. time the slope of a straight line having  $s = k_{\text{ads}}\sqrt{\beta^2 + 4\gamma\alpha}$  [12] is

$$\rho = \ln \frac{x + x_{\text{eq}} + \beta/\alpha}{x - x_{\text{eq}}} = st + \text{const} \quad (7)$$

where  $x_{\text{eq}}$  is concentration of Me<sup>2+</sup> ions in equilibrium.

## EXPERIMENTAL

The raw South-Moravia lignite was ground in a ball mill. The grains having the diameter higher than 0.5 mm were separated by sieving. One part of so treated lignite was modified by carbonization in Sapoznikov furnace by the temperatures 450 °C, 550 °C, and 650 °C. The untreated lignite was further separated by sieving. The other part was fractionated using the automatic sieving apparatus (fractions 0.4–0.5 mm, 0.3–0.4 mm, 0.2–0.3 mm). Before using, the sample of lignite was dried by 105 °C to the constant mass.

The ground lignite was treated with the corresponding amount of NaOH ( $c = 0.1 \text{ mol dm}^{-3}$ ) and heated for 24 h at 90 °C under reflux cooler. From the filtrate humic acids were precipitated using the HCl solution ( $c = 0.1 \text{ mol dm}^{-3}$ ), washed with distilled water and dried at 105 °C to the constant mass.

For the study of the sorption properties of humic acids and lignite, the ions Cu<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> were chosen. The aqueous solutions of corresponding chlorides were prepared in the concentration region 0.01–0.5 mol dm<sup>-3</sup>.

For the experimental investigation of the adsorption kinetics, as well as of the adsorption equilibrium, 2 g of adsorbent and 100 cm<sup>3</sup> of the salt solution were employed. The quantity of the adsorbed ions in time  $t$  or in equilibrium was calculated on the basis of the decrease of absorbance (Carl Zeiss SPEKOL 21). The absorbance was measured at  $\lambda = 390 \text{ nm}$  (Ni<sup>2+</sup>),  $\lambda = 510 \text{ nm}$  (Co<sup>2+</sup>), and  $\lambda = 750 \text{ nm}$  (Cu<sup>2+</sup>). Prior to measurements, the calibration curves for the corresponding metal ions were determined.

By the adsorption experiments on humic acids, the pH value was measured before starting the experiment and in the equilibrium state. The starting materials (lignite and HA), as well as the obtained metal complexes,

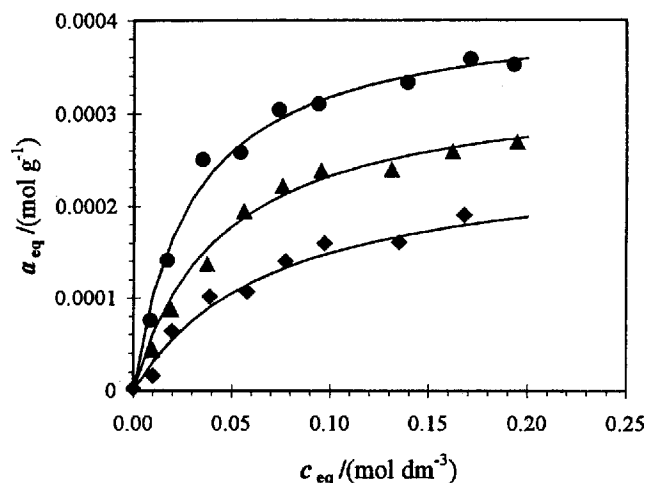


Fig. 1. Adsorption isotherms of  $\text{Co}^{2+}$  ions on unmodified lignite ( $\blacklozenge$  0.2–0.3 mm,  $\blacktriangle$  0.3–0.4 mm,  $\bullet$  0.4–0.5 mm).

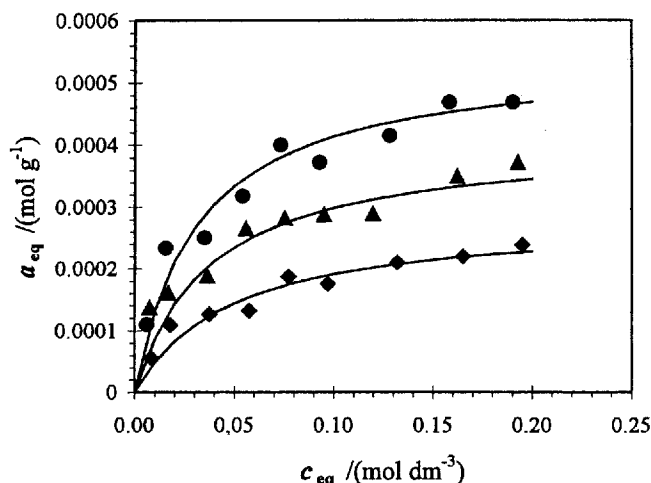


Fig. 2. Adsorption isotherms of  $\text{Co}^{2+}$  ions on lignite modified by carbonization ( $\blacklozenge$  450 °C,  $\blacktriangle$  550 °C,  $\bullet$  650 °C).

were characterized using FTIR spectroscopy (Nicolet Impact 400; KBr pellet).

## RESULTS AND DISCUSSION

### Determination of Adsorption Isotherms

The data obtained by the spectrophotometric measurements before the adsorption and in the equilibrium state were evaluated according to eqn (1). The values  $a_{\text{max}}$  and  $b$  for the individual metal ions were determined by the linear regression and are summarized in Table 1. The examples of adsorption isotherms of transition metal ions on lignite and HA are presented in Figs. 1–4.

In Fig. 1 the adsorption isotherms of  $\text{Co}^{2+}$  ions on three fractions of unmodified lignite are outlined. It is

evident that  $a_{\text{max}}$  value increases when the adsorption was performed by sorbent particles with higher diameter. This effect can be explained by the changes of inner structure during the mechanical processing of crude lignite. In Fig. 2 the adsorption isotherms of  $\text{Co}^{2+}$  ions on lignite carbonized at three different temperatures are shown. Here, the highest sorption capacity was obtained by the lignite heated up to 650 °C. Similar tendencies following from Figs. 1 and 2 were observed also by the simultaneous experiment carried out with  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions.

Not only for all types of lignite, but for HA as well, the greatest  $a_{\text{max}}$  value was obtained for  $\text{Cu}^{2+}$  ions. By  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions the ratio of rate constants of the adsorption and desorption ( $b$  value) increases with the size of lignite particles, while by  $\text{Cu}^{2+}$  ions this value decreases. By all types of ions  $a_{\text{max}}$  and  $b$  values increase

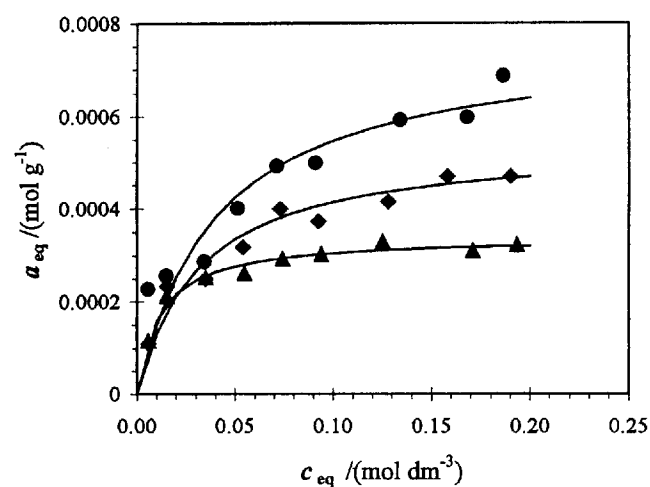


Fig. 3. Adsorption isotherms of metal ions on lignite modified by carbonization at 650 °C ( $\blacktriangle$   $\text{Ni}^{2+}$ ,  $\blacklozenge$   $\text{Co}^{2+}$ ,  $\bullet$   $\text{Cu}^{2+}$ ).

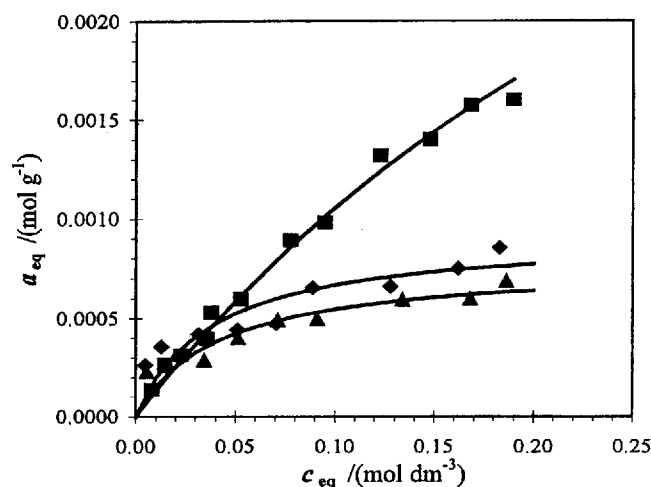


Fig. 4. Adsorption isotherms of  $\text{Cu}^{2+}$  ions on unmodified lignite ( $\blacklozenge$  0.3–0.4 mm), carbonized lignite ( $\blacktriangle$  650 °C), and HA ( $\bullet$ ).

**Table 2.** Rate Constants of Adsorption  $k_{\text{ads}}$  and Desorption  $k_{\text{des}}$ 

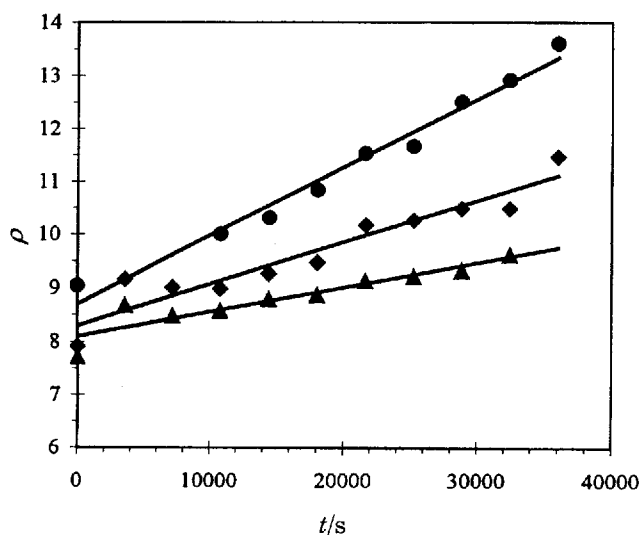
Sample	$\text{Co}^{2+}$		$\text{Ni}^{2+}$		$\text{Cu}^{2+}$	
	$k_{\text{ads}}$	$k_{\text{des}}$	$k_{\text{ads}}$	$k_{\text{des}}$	$k_{\text{ads}}$	$k_{\text{des}}$
	$10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-7} \text{ s}^{-1}$	$10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-7} \text{ s}^{-1}$	$10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-7} \text{ s}^{-1}$
0.2—0.3 mm	8.81	19.73	2.14	1.02	1.35	0.17
0.3—0.4 mm	1.59	0.70	3.11	1.48	2.77	0.97
0.4—0.5 mm	3.37	0.98	3.59	1.58	2.17	0.81
450 °C	4.59	2.20	8.28	6.86	5.57	3.81
550 °C	4.33	1.61	2.23	0.48	8.20	7.15
650 °C	3.55	1.10	0.88	0.07	4.16	1.70
HA	37.21	96.01	29.64	147.22	99.90	401.35

with the temperature of carbonization. By HA the highest  $b$  constant was unambiguously achieved by  $\text{Co}^{2+}$  ions. The good accordance of experimental data with the Langmuir model is confirmed by the high value of correlation coefficient. The greatest deviation from the Langmuir relation was found by thermally unmodified lignite. Therefore, it can be assumed that these metal ions are linked to the surface of lignite and HA particles mainly by chemical bonds, *i.e.* the complexation reaction proceeds. Only the small portion of ions can undergo the unspecific sorption. Based on the quantum-chemical calculations of interaction energy of HA with some metal ions [2] the following sequence of the stability of HA complexes  $\sigma$  was determined:  $\sigma(\text{Cu}^{2+}) > \sigma(\text{Fe}^{3+}) > \sigma(\text{Mn}^{2+}) > \sigma(\text{Cd}^{2+}) \approx \sigma(\text{Mg}^{2+}) \approx \sigma(\text{Ca}^{2+})$ . The authors in Ref. [13] have postulated the increase of  $\sigma$  of HA complexes with different metal ions in the sequence:  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ . The sorption of three transition metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and

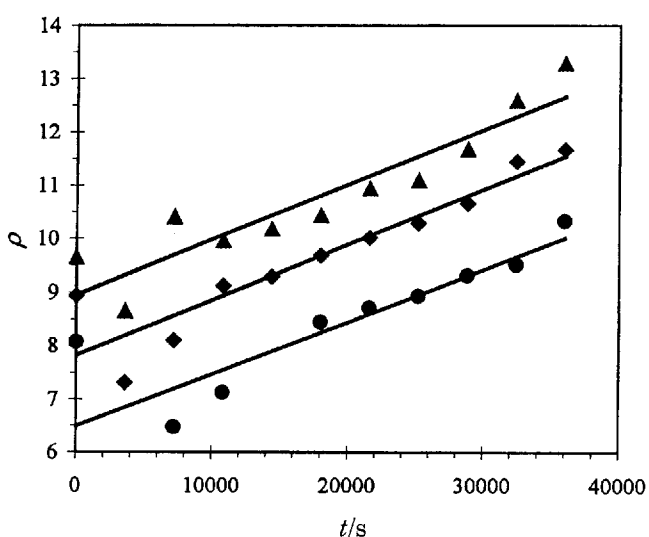
$\text{Cu}^{2+}$ ) on HA reported in this work is fully in accordance with this order. By some types of lignite another sequence was found by  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions. Nevertheless, by  $\text{Cu}^{2+}$  ions the most effective adsorption was confirmed by all samples used.

The rate constants of the adsorption and desorption determined from the experimental data and eqn (5) are involved in Table 2. The rate constants of the adsorption  $k_{\text{ads}}$  were calculated from the slope and the function  $\rho = f(t)$ , the rate constants of the desorption  $k_{\text{des}}$  were calculated from the adsorption coefficients  $b = k_{\text{ads}}/k_{\text{des}}$  in Table 1 and commonly, they are 10 times lower than those of the adsorption. According to the determined rate constants the rate of the adsorption on HA is higher than that observed on the lignite. Thus, HA can be considered as the dominant components of lignite for the sorption of metal ions.

In Fig. 5 the experimental data obtained for  $\text{Ni}^{2+}$  ions and three fractions of lignite are fitted by eqn (6).



**Fig. 5.** Experimental data of adsorption of  $\text{Ni}^{2+}$  ions on unmodified lignite fitted by eqn (7) ( $\blacktriangle$  0.2—0.3 mm,  $\blacklozenge$  0.3—0.4 mm,  $\bullet$  0.4—0.5 mm).



**Fig. 6.** Experimental data of adsorption of  $\text{Ni}^{2+}$  ions on carbonized lignite fitted by eqn (7) ( $\bullet$  450 °C,  $\blacklozenge$  550 °C,  $\blacktriangle$  650 °C).

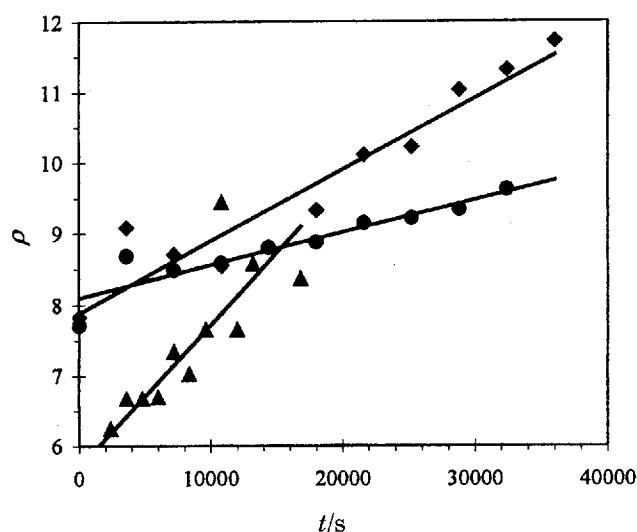
We can see that very good agreement between eqn (4) and experimental data was achieved and the slope of these lines increases with the diameter of sorbent particle. The example of kinetic data for adsorption of  $\text{Ni}^{2+}$  ions on lignite carbonized at three different temperatures is presented in Fig. 6. In this case, the influence of heating temperature on adsorption kinetics is not strongly evident. Similar results were obtained for  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions (see Table 2). In Fig. 7 the dependences  $\rho = f(t)$  for unmodified lignite, carbonized lignite, and HA are compared. It is evident that carbonization positively influences the rate of sorption process and the steepness of presented lines is the highest for HA.

Generally, the acid-base properties of the medium play very important role in sorption processes. Because of its adsorption and binding ability, the presence of HA can influence the determination of heavy metals in the solution. While copper forms the complexes with HA also at low pH values, the ions of cadmium and cobalt are complexed in neutral and alkaline medium [14, 15]. Although according to Klučáková *et al.* [2] the alkaline medium is the most suitable one for the formation of the complex metal—HA, for the solutions of ecological problems the sorption processes proceeding in neutral and acid medium are more relevant. Within this work, the pH values of the salt solutions were not additionally treated. As the starting point for the investigation of pH changes during the complexation, the values observed in aqueous solutions of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{CuCl}_2$  were taken. These depend on the concentration of the salt, as demonstrated in Table 3. Here, the experimental pH values for five concentrations of salt are shown. Simultaneously, the equilibrium pH values in the system composed of 2 g of solid HA and 100  $\text{cm}^3$  of the solution of the corresponding ions are presented. The experimental pH values can also be influenced by the

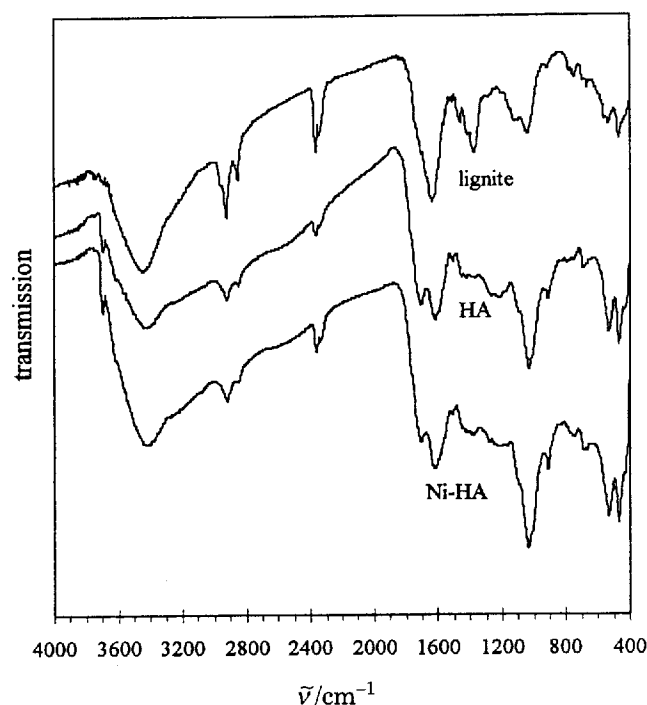
**Table 3.** pH Values Measured before Adsorption ( $\text{pH}_0$ ) and in Equilibrium ( $\text{pH}_{\text{eq}}$ )

$c_0$ mol $\text{dm}^{-3}$	$\text{Co}^{2+}$		$\text{Ni}^{2+}$		$\text{Cu}^{2+}$	
	$\text{pH}_0$	$\text{pH}_{\text{eq}}$	$\text{pH}_0$	$\text{pH}_{\text{eq}}$	$\text{pH}_0$	$\text{pH}_{\text{eq}}$
0.01	5.61	2.77	7.11	2.75	5.10	2.66
0.05	5.31	2.61	6.73	2.69	4.32	2.46
0.20	4.79	2.46	6.76	2.43	4.00	2.28
0.35	4.60	2.40	6.59	2.32	3.67	2.20
0.50	4.37	2.31	6.39	2.25	3.46	2.12

relative acidity of deionized water ( $\text{pH} = 6.9$ ) and laboratory conditions. The acid-base properties of the medium significantly influence the above described sorption processes. In Ref. [16] the influence of pH of copper salts on their sorption by HA was investigated. It has been found that the value of adsorption coefficient decreases with the increased acidity, the  $\alpha_{\text{max}}$  value having been kept at the level of the same order. By  $\text{pH} = 1.4$  the sorption was not measurable. As confirmed by pH measurements during the sorption, the increase of acidity of the solution occurs, *i.e.* the  $\text{H}^+$  ions are released from the molecules of HA. It can be supposed that the formation of the complex metal—HA proceeds by two mechanisms, either by the mutual exchange of  $\text{H}^+$  and metal ions or by the binding of metal ions to the suitable dissociable function group (binding site).



**Fig. 7.** Comparison of experimental data fitted by eqn (7) for sorption kinetics of  $\text{Cu}^{2+}$  ions on unmodified lignite ( $\bullet$  0.4—0.5 mm), carbonized lignite ( $\blacklozenge$  650  $^{\circ}\text{C}$ ), and HA ( $\blacktriangle$ ).



**Fig. 8.** FTIR spectra of unmodified lignite, HA, and complex Ni—HA.

In Fig. 8 FTIR spectra of lignite, HA and their complexes with Ni<sup>2+</sup> ions are shown. From the measured spectra the decrease of the intensity of bands at  $\bar{\nu} = 1724 \text{ cm}^{-1}$  and  $1205 \text{ cm}^{-1}$ , resulting from the deprotonation of carboxylic groups, is evident. The simultaneous increase of bands at  $\bar{\nu} = 1615 \text{ cm}^{-1}$  and  $1383 \text{ cm}^{-1}$  relates to the complexation of metal ions and can be ascribed to the symmetric and asymmetric vibrations of metals coordinated to these groups. The decrease of the intensity at  $3400 \text{ cm}^{-1}$  following from the reduction of OH groups cannot be practically proved. This can be explained by the effect of the humidity, which cannot be fully removed, although the samples were thoroughly dried by the temperatures  $90 \text{ }^\circ\text{C}$  for 5 h. Similar changes of characteristic bands were observed in the spectra of complexes of HA with Co<sup>2+</sup> and Cu<sup>2+</sup> ions.

### CONCLUSION

The experimental results obtained in the framework of this paper confirmed that lignite and humic acids are suitable sorption materials for transition metal ions. HA can be unambiguously considered as the most effective because their sorption capacity is substantially higher in comparison with lignite. In the case of application, however, the fact has to be taken into account, if this advantage is in accordance with the costs for their isolation from lignite. The carbonization in Sapoznikov furnace resulted in the increase of rate constants of the adsorption process on lignite. Nevertheless, the enhancement of sorption capacity by this procedure was not confirmed.

*Acknowledgements.* This work was supported by the Grant Agency of the Czech Republic, Project No. 104/02/D036.

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