Sorption of metal ions on lignite and the derived humic substances

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ABSTRACT

The study presents results of sorption of metal ions (Pb^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+}) onto lignite mined in South Moravia, Czech Republic, and solid humic substances (humin and humic acid) derived from it. The efficiency of these sorbents has been studied as a function of contact time, solution pH, and metal concentration. The sorption efficiencies were higher for humin and lower for humic acid samples than for the original lignite. With its high sorption capacities of several mmol/g, particularly for Pb^{2+} and Cd^{2+}, the South Moravian lignite can provide a cheap source material for preparation of sorbents utilizable in removal of toxic metals from wastewaters.

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1. Introduction

Environmental contamination with heavy metals represents a potential threat to humans, animals and plants. The metals do not undergo biodegradation. Many of them are soluble in water, therefore become more available for living systems and accumulate in the environment. Removal of heavy metals from waste streams employs various technologies, which are often either expensive or inefficient, especially when very low residual concentrations compliant with health-based limits are required. Use of inexpensive natural sorbents such as zeolites, metal oxides, fly ash, clays, coal, peat moss, waste biomass, and chitosan has been considered as a promising alternative for this purpose [1].

Lignite as the youngest type of coal is one of the abundant natural resources and its effective utilization other than as fuel has been studied over the past decades. The special merit of lignite and weathered coal (leonardite and oxihumolite) is a high content of exchangeable functional groups that makes them an effective medium for the removal of metals from wastewater, e.g., Refs. [2–8]. The major reservoir of the functional groups in these low-rank coals are humic substances (HS): humic and fulvic acids extractable with strong alkali, and humin—a solid residue remaining after the alkali extraction, which is strongly associated with the coal mineral matrix. Besides coals, HS produced by biomass degradation are a substantial component of natural organic matter in soils, sediments, and waters. They contain heteroatoms, mainly oxygen bound in carboxylic and phenolic hydroxyl groups. Nitrogen and sulfur are less important. The complex nature of interaction between HS and metal cations is given by their heterogeneous, polyelectrolyte and polydispersive character given by the variety of functional groups located in various chemical environments of the three-dimensional structure of HS. The nature of the binding ranges from purely electrostatic, non-specific interaction of metal cation with the net negative charge on the surface of a humic macromolecule to specific interactions at the formation of complexes and chelates with the functional groups. Several interaction models have been proposed, in which the chemical heterogeneity of HS binding sites is usually reflected. The electrostatic effects due to the negative charge of HS molecule are sometimes taken into account. Numerous studies have demonstrated significant capacity of coal derived humic acids for binding metallic cations [9–11]. Also humin has potential for this sorption [12–14].

The present study has been aimed at the potential application of lignites mined in the South Moravian Coalfield, Czech Republic, and HS prepared from it as the sorbents for removal of heavy metals from wastewaters. The sorption tests were carried out with lead, cadmium, copper, and zinc. Many industrial processes including mining and electroplating discharge aqueous effluents containing these heavy metals. Their cations are toxic even at very low levels and are priority pollutants observed in municipal waste. The World Health Organization drinking water guideline values for Pb, Cd, and Cu are 0.01, 0.003, and 2 mg/L, respectively; for Zn, a health-

based guideline value has not been required, but Zn levels above 3 mg/L deteriorate sensoric properties of drinking water [15]. The efficiency of the sorbents has been studied within a broad range of experimental conditions, namely as a function of solution pH and metal concentration.

2. Experimental

2.1. Preparation and characterization of sorbents

Lignite (L) samples were dried and powdered. Lignite and the derived sorbents were characterized by proximate and ultimate analyses, multielement analysis using instrumental neutron and photon activation analyses (INAA and IPAA, respectively), and petrographic optical microscopy.

Humic acids were prepared by alkaline extraction using two different procedures. In the so-called standard procedure, 50 g of lignite was added to a solution of 500 mL 0.5 M NaOH, stirred 1 h under nitrogen, and closed in a PE bag for 24 h. The samples were then stirred 1 h under nitrogen and the remaining solid (HUM) was separated by centrifugation. Humic acids were coagulated from the supernate by HCl acidification to pH ~1, after 24-h standing centrifuged, rinsed with distilled icy water, centrifuged again, dialyzed through cellophane, and finally lyophilized (HA). In the so-called economically effective procedure (EKO), 60 g of lignite was decanted by 500 mL of 0.05 M NaOH solution, other 500 mL of 0.05 M NaOH was added to the suspension after short stirring. The suspension was stirred overnight, filtered through a rough texture, and rinsed with 500 mL of 0.05 M NaOH. A sieve residue was rinsed with distilled water and dried at an ambient temperature (HUM.EKO). Humic acids were coagulated from the filtrate by addition of 20% HCl to pH ~1, after standing overnight in a refrigerator centrifuged, rinsed with distilled water, centrifuged again and dried at 50 °C (HA.EKO).

To separate humin from the inorganic matrix (mainly clays and oxides), the residue after alkaline extraction should be subjected to deashing, which dissolves a substantial proportion of the mineral matrix without altering significantly the chemical structure of organic compounds [16]. In this work, humin (both HUM and HUM.EKO) represents the untreated solid residue remaining after separation of humic acids.

2.2. Sorption experiments

All experiments were carried out at an ambient temperature of ca. 25 °C in aqueous solutions. The pH of solutions was adjusted by addition of 0.1 M HNO₃ or 0.1 M NaOH, and measured using a pH-meter with a combined glass electrode calibrated against standard pH buffers. Nitrogen was bubbled through the solutions to remove dissolved gasses and to stabilize the pH by preventing further CO_2 dissolution.

The determination of the zero point of charge (ZPC; the pH at which the sorbent particles suspended in water have zero charge) of the sorbents was carried out by a batch procedure according to Ferro-García et al. [17]. Portions (1 g) of sorbent were added to 200 mL of deionized water with pH adjusted to values covering the pH range 2–12 ($pH_{initial}$). The suspensions were allowed to equilibrate by shaking for 24 h, and then filtered. In the filtrates, pH ($pH_{equilibrium}$) was measured.

In the course of sorption experiments, typically 1 g of sorbent was weighed into a glass bottle. Solution (200 mL) of a metal ion nitrate was pH adjusted and added to each sorbent batch. The bottles were placed in a shaker for 6 h to equilibrate. In order to quantify sorption efficiency of the sorbents (percent of metal

adsorbed), suspensions were filtered (filter paper—Filtrak 390) and equilibrium metal ion concentration after sorption was determined in the filtrates by AAS or, in case of very low concentrations, by ICP-OES.

3. Results and discussion

3.1. Characterization of sorbents

The general characteristics of the sorbents are summarized in Table 1. Multielement analysis was made by INAA except for lead determined by IPAA. Besides the major elements, trace elements whose sorption was studied are listed in the table except for cadmium, which was below the detection limit of INAA (typically <2 mg kg⁻¹) in all samples.

Petrographic analysis showed that both humin samples are characterized by comparable maceral composition dominated by huminite (both cca 71 vol.%) and virtually no humic acids, and similar content of mineral matter (HUM 19.6 vol.% and HUM.EKO 14.4 vol.%). On the other hand, the separated humic acids differ significantly; HA contains 100 vol.% of humic acids, whereas HUM.EKO only 54 vol.% of humic acids, 34.8 vol.% of huminite besides other macerals, and 5.4 vol.% of mineral matter. The results of petrographic analysis agree with the characteristics given in Table 1. Again, the differences are much more pronounced for the humic acid samples than for humin samples.

It is obvious that the two extraction procedures yielded materials with significantly different properties, particularly in their mineral matter content reflected by both ash content and elemental composition (namely Si, Al, and Fe). The critical point in the separation procedures with the greatest impact on the sorbent composition is probably the alkali concentration in the first step of the procedures. At the standard procedure, NaOH concentration is sufficient for exceeding the solubility product of sodium aluminosilicates, thus their leaching from coal together with humic acids is significantly suppressed [18]. On the other hand, the ten times lower alkali concentration at the EKO procedure allows dissolution of silicates and aluminates, as well as iron hydroxocomplexes. Aluminum and iron are subsequently co-precipitated with silicic and humic acids at the acidification step.

Table 1
Characterization of sorbents by the proximate and ultimate analyses, and multielement analysis of major and selected trace elements

Sample	L	HA	HUM	HA.EKO	HUM.EKO
Proximate analysis(wt% as received)					
Moisture	30.0	0.55	6.63	0.07	0.13
Ash	14.5	7.01	20.8	36.5	15.9
Ultimate analysis (wt% dry basis)					
C	50.4	57.7	45.8	36.9	50.1
H	4.14	4.31	4.81	3.8	4.82
N	0.72	1.14	0.04	0.74	0.81
S	1.05	1.17	0.56	1.77	1.76
O	23.1	28.6	26.6	18.6	26.5
Multielement analysis(mg kg⁻¹ as received)					
Al	19,020	5850	6,406	55,499	11,924
Si	4,623	5805	10,864	102,560	17,277
Ca	17,351	6039	10,423	1,394	17,623
Mg	4,533	544	1,290	3,267	2,620
Fe	9,109	1212	3,487	15,150	5,732
Na	464	2168	71,034	2,234	15,031
Cl	46.3	3365	<80.8	9,346	470
Cu	46.8	44.6	322	63.2	74.5
Zn	90.5	67.6	128.5	45.8	28.5
Pb	<9	7.82	<13	8.39	3.16
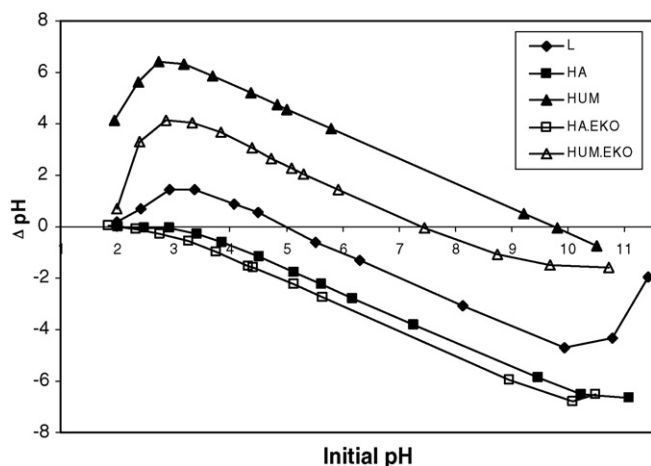
Fig. 1. Dependence of ΔpH (=$pH_{equilibrium}$ − $pH_{initial}$) on the initial pH in the suspensions of the lignite derived sorbents. Conditions: V/m = 200 mL/g, contact time = 24 h.

Fig. 2. Kinetics of metal adsorption onto lignite. Conditions: pH = 5, V/m = 200 mL/g, initial metal concentration = 200 mg/L.

3.2. Zero point of charge

The zero point of charge (ZPC) of slightly soluble compounds is the pH at which their particles suspended in water have zero charge. ZPC is a function of various mineral and organic constituent of a sample. The results in Fig. 1 show the dependence of ΔpH (=$pH_{equilibrium}$ − $pH_{initial}$) on the initial pH. The variation in ΔpH caused by protonation and deprotonation of a sorbent reflects the presence of functional groups and exchangeable cations.

As expected, the sorbents differed in their ZPC. The lignite ZPC corresponding to pH of 5.0 is shifted to higher pH values of 7.5 and 9.8 for humin samples HUM.EKO and HUM, respectively, and to lower pH values of 3 and 2.3 for humic acid samples HA and HA.EKO, respectively. The differences in the ZPC of the sorbents reflect again the differences in both extraction procedures. The exchangeable sites of the humin samples after centrifuging off from the alkaline extract and rinsing remained saturated by Na^+ (replacing mainly Ca^{2+}, Mg^{2+} in the original lignite) to a degree corresponding to amount of alkali applied. On the other hand, the humic (and silicic) acid sites should be protonated after the precipitation with acid. Despite the above-discussed differences of both humic acid samples, their acidobasic character is quite similar.

3.3. Sorption kinetics

The effect of the contact time on metal removal by lignite is illustrated by Fig. 2. The steep sloped initial parts of the curves indicate prompt, dynamic sorption on the large uncovered surface area, the following stage with a slower sorption rate is probably controlled by diffusion of metal ions into the porous structure of lignite. Based on these experiments, the 6-h contact time was applied in all other sorption experiments to sufficiently approach the sorption equilibrium, although in the case of lead, 3 h would be enough to remove it quantitatively from the solution under the conditions given.

3.4. Effect of pH

Carboxyl and hydroxyl groups are the main exchangeable functional groups that take part in the sorption of metal ions onto the lignite derived sorbents. With increasing solution pH, these functionalities dissociate, i.e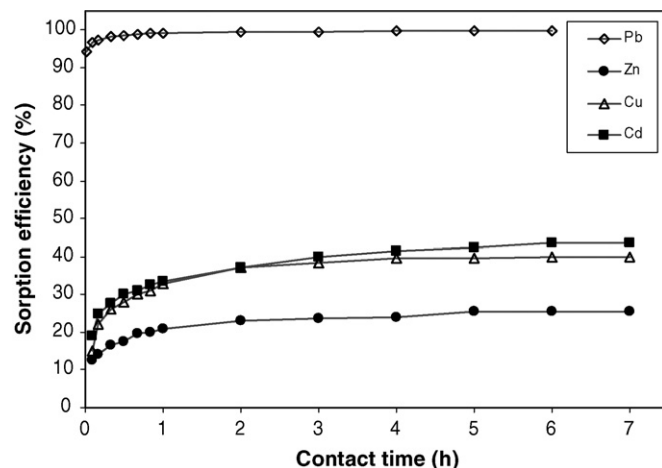., become deprotonated and negatively charged. Dissociation of carboxyl groups of HS proceeds within slightly acidic up to neutral region, dissociation of hydroxyl groups starts at pH above 9–10. The progressive deprotonation and the increasing negative charge of the sorbent surface with the increasing pH promote the sorption of metal cations. During the sorption, H^+ and other exchangeable cations (e.g., Na^+, Ca^{2+}, and Mg^{2+}) are exchanged for metal cations and released from the sorbent to solution.

The shift of an initial pH value to a value measured in equilibrium after metal sorption onto lignite is shown in Fig. 3. Within the initial acidic pH range, the equilibrium pH increases after metal sorption. This shows that, in agreement with the ZPC of lignite of 5.0, both heavy metal and H^+ cations compete for the lignite binding sites with the originally bound exchangeable cations. Within a more basic region (from pH of about 4 for Cu^{2+}, 5 for Cd^{2+} and Pb^{2+}, and 7 for Zn^{2+}), pH starts to decrease after equilibration with metal due to the release of protons exchanged for metal cations. This can be observed as a plateau-buffer region in the dependences of Fig. 3. The height of the plateau should correspond to the amount of exchanged protons. In our case, a comparison between individual metals is not quite illustrative due to non-equimolar concentrations (especially for Pb^{2+}), however, a substantially lower extent of exchange for Zn^{2+} is evident. At higher pH (near-to-neutral region),
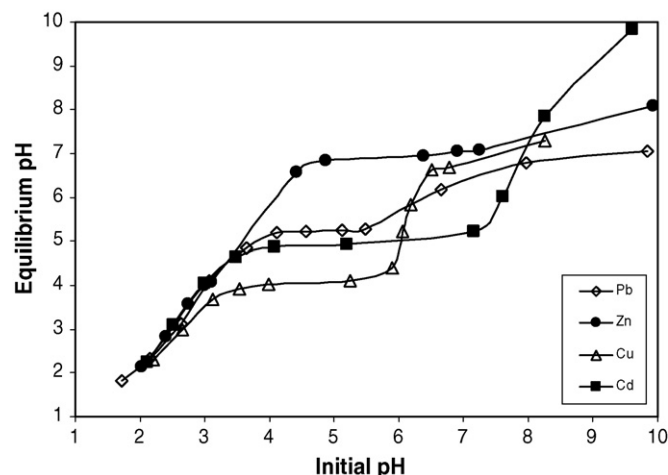

Fig. 3. Variation in pH during metal adsorption onto lignite. Conditions: V/m = 200 mL/g, initial metal concentration = 200 mg/L, contact time = 6 h.
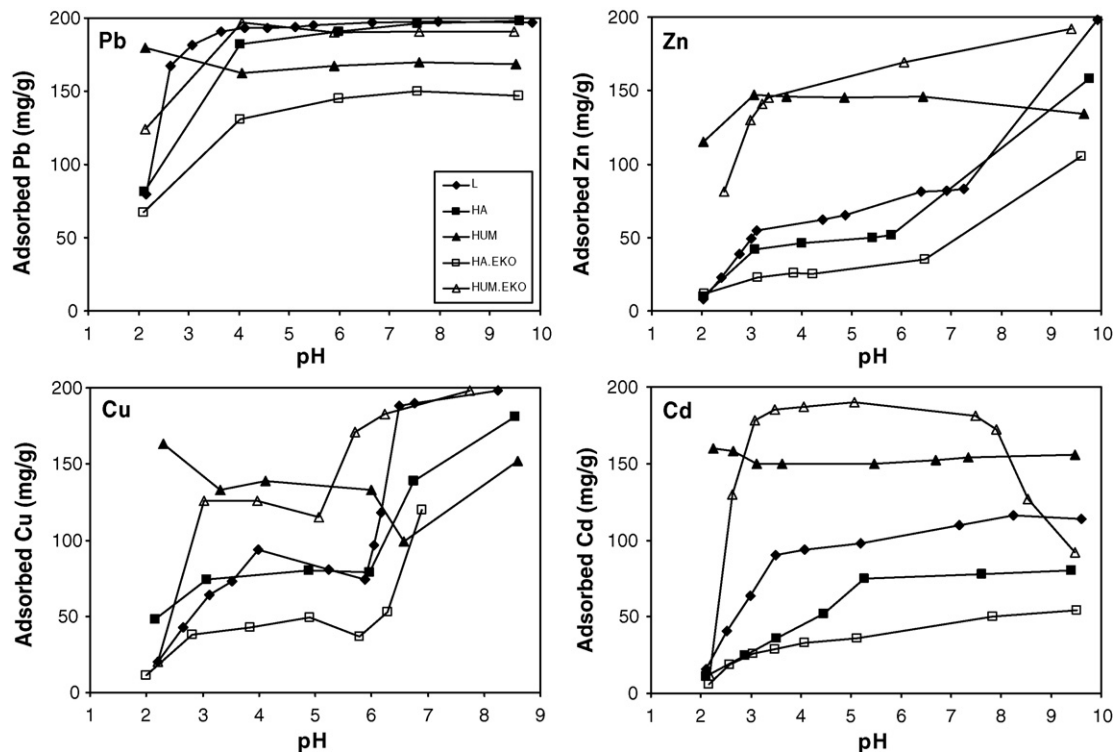
Fig. 4. The effect of pH on metal adsorption onto the lignite derived sorbents. Conditions: V/m = 200 mL/g, initial metal concentration = 200 mg/L, contact time = 6 h.

Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} cations in aqueous solutions are subject to hydrolysis, and at a sufficient metal concentration, their $Me(OH)_2$ hydroxides can precipitate. In the dependences, the hydroxide precipitation is reflected by a steep increase in the equilibrium pH following the buffer region. It starts at pH of about 6 for Pb^{2+} and Cu^{2+}, and at pH of about 7.5 for Zn^{2+} and Cd^{2+}, respectively. This corresponds quite well with speciation calculation performed by the PHREEQC code [19] with an exception of Cd^{2+}, where precipitation should not start below pH of 8. Obviously, completed deprotonation of lignite carboxylic groups is reflected as well.

The effect of pH on metal sorption onto the lignite derived sorbents is illustrated by Fig. 4. With minor deviations, the sorbent efficiency follows the order HUM.EKO ≥ HUM > L ≥ HA > HA.EKO. As expected, the efficiency generally increases with increasing pH for all metals and sorbents, with an exception of the HUM sample, where the effect of pH is indistinctive or even reverse. The increase in the sorption efficiency is most pronounced between pH 2–4

Table 2
Parameters of the Langmuir–Freundlich isotherms (see Fig. 5b) for metal adsorption onto lignite

Metal ion	Q_{max} (mmol/g)	KLF ($(L/mmol)^n$)	n	R^2
Pb^{2+}	2.325	12.12	0.700	0.991
Zn^{2+}	0.993	1.913	0.768	0.999
Cu^{2+}	1.486	3.427	0.841	0.989
Cd^{2+}	3.870	0.239	0.438	0.996

Conditions: pH 5; V/m = 200 mL/g; contact time = 6 h.

probably reflecting progressive deprotonation of carboxylic groups. In the case of HUM sample, these functionalities have been substantially removed by the alkali extraction. Another steep increase in the sorption efficiency can be observed for Zn^{2+} and particularly Cu^{2+} at pH > 6, probably connected with starting hydrolysis and precipitation of the metal hydroxides. On the other hand, in the case of
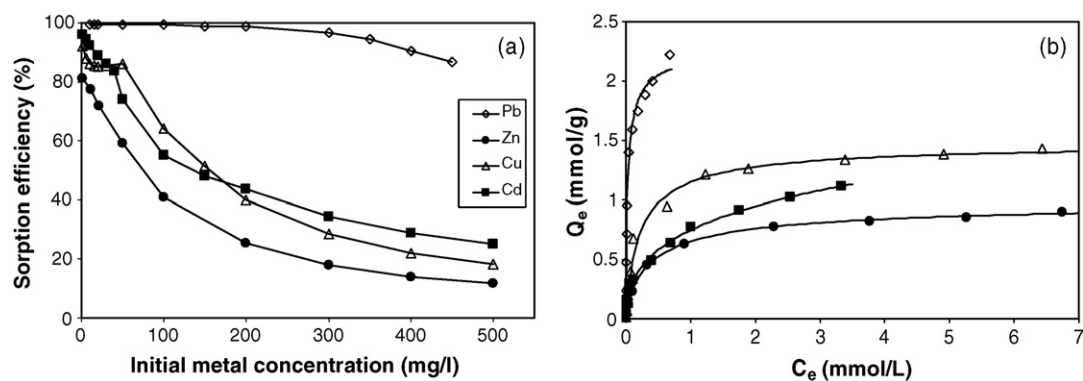

Fig. 5. The effect of metal concentration on metal adsorption onto lignite: (a) Sorption efficiency as a function of initial metal concentration, and (b) sorption isotherms fitted using the Langmuir-Freundlich model. Conditions: pH = 5, V/m = 200 mL/g, contact time = 6 h.

Table 3
Reported adsorption capacities (mmol/g) of lignite and humic acid based sorbents in comparison with the South Moravian lignite studien in the present work

Material	Reference	Isotherm[a]	pH	Pb	Zn	Cu	Cd
Lignite	Present work	L–F	5.0	2.32	0.99	1.49	3.87
Lignite	Klučáková and Omelka [10]	L	4.5			58.15	
Lignite	Pehlivan and Arslan [6]	L	4.5	0.39; 0.50		0.41; 0.44	
Oxihumolite	Janoš et al. [7]	L	3.5–4.5	0.34	0.14	0.18	0.18
		L–F		0.42	0.17	0.30	1.37
Humic acid	Čežíková et al. [9]	L*	1–4	1.70	0.43	0.59	0.56
Humic acid	Klučáková and Omelka [10]	L	4.5			2.93	
Humic acid	Klučáková and Pekař [22]	L	4.5			3.06	
Humic acid	El-Eswed and Khalili [23]	L	3.7			0.97	
Humic acids	Coles and Yong [21]	E	4.0	2.19			3.71
Humin	Alvarez-Puebla et al. [14]	L	3.2			1.8	

[a] L, Langmuir; L–F, Langmuir–Freundlich; L*, Langmuir-type model accounting for dissociation/protonation of binding sites; E, experimental value.

Cd^{2+} sorption onto the HUM.EKO sample, the sorption efficiency decreases in the basic region. Although it is not clear why a similar effect did not take place with other sorbents and Zn^{2+} on the same sorbent, we ascribe it to possible leaching of HS from the HUM.EKO sample, which would retain Cd^{2+} in solution as a humic complex and suppress hydroxide precipitation.

3.5. Effect of metal concentration and sorption isotherms

A wide range of metal concentration (1–500 mg of metal per litre at pH of 5) was inspected to investigate the effect of metal loading on the efficiency of the lignite derived sorbents and their sorption capacities. These experiments were carried out only with lignite in the view of previous results (see the previous paragraph), which demonstrated its good sorption capability without further chemical treatment, thus promising its highly economical utilization.

The results presented in Fig. 5 show that the South Moravian lignite is an effective sorbent material for removing Pb, Zn, Cu and Cd from contaminated wastewater. The uptake was almost quantitative or very high at low metal concentrations. According to their affinity for the sorption onto lignite, the studied metals follow the order $Pb \gg Cu \geq Cd > Zn$. This order corresponds with the affinity series published previously (e.g., Refs. [7] and [9]).

To describe experimental results of metal sorption on various natural sorbents, the simple Langmuir or Freundlich sorption isothermal models are often successfully employed. The Langmuir model assumes that the sorption process takes place on a homogenous surface composed of a fixed number of non-interacting monodentate sites of equal sorption energy, and proceeds until a monolayer coverage is obtained. On the other hand, despite its empirical sense, the Freundlich model describes sorption onto an energetically heterogeneous surface not limited by a monolayer capacity [20]. Both models were tested in fitting our experimental data with the former model providing better fit for all metals studied. However, the Langmuir model has not been able to describe well the high sorption affinity of lignite for Pb^{2+}. In agreement with the results published by Janoš et al. [7], a better fit for Pb^{2+} as well as for the other metals has been obtained using Langmuir–Freundlich model. The Langmuir–Freundlich isotherm usually takes the form:

$$Q_e = \frac{Q_{max}K_{LF}C_e^n}{1 + K_{LF}C_e^n}$$

where C_e (mmol/L) is the equilibrium metal concentration in solution, Q_e (mmol/g) is the amount of the metal adsorbed onto a sorbent at equilibrium, Q_{max} is the maximum sorption capacity (mmol/g) of the sorbent, K_{LF} is a constant characterizing sorption energy ((L/mmol)^n), and n, usually called a heterogeneity parameter, reflects heterogeneity of the sorbent surface and/or sto-

ichiometry of the surface complexation/ion exchange reaction [7]. In the case of a homogeneous surface ($n = 1$), the model reduces to the Langmuir model, at low metal concentrations it converges to the Freundlich model.

The experimental isotherms with the fitted curves are depicted in Fig. 5 and the parameters of the Langmuir–Freundlich isotherm are presented in Table 2. As seen from the graph, the model fits closely all data, although for Pb it still underestimates the observed maximum sorption capacity. The model parameters are quite informative in comparing the sorption affinity of Pb, Zn, and Cu; both Q_{max} and K_{LF} follow the observed affinity order. The heterogeneity parameter n, on the other hand, is similar for all three metals.

In the case of Cd, the model provides extremely high maximum sorption capacity, which may be unrealistic considering typical range of carboxylic cation exchange capacities (CEC) in HS (2–5 mmol/g; [21]). At the same time, K_{LF} value is substantially lower, as well as n. Similar result for Cd in comparison with Pb, Zn and Cu has been observed by Janoš et al. [7], who considered it overestimated because of an extrapolation beyond the examined concentration range, which has been also the case in our study. On the other hand, similar sorption capacity (experimental value) for Cd exceeding even the CEC value of the sorbent (humic acid) at given pH has been reported by Coles and Young [21]—see Table 3. This repeatedly observed results for Cd may point to a particular way of binding, characterized by a higher degree of heterogeneity and a lower sorption energy than the specific site binding, e.g., electrostatic, non-specific interaction with the net negative charge on the sorbent surface.

Table 3 compares the sorption capacities determined for the South Moravian lignite with the capacities reported in literature for lignite and humic acid based sorbents. The comparison demonstrates a very good capability of the South Moravian lignite for metal sorption. Although a direct comparison of the lignite with other sorbents is difficult due to the different experimental conditions applied, it has been found that its sorption capacities are very high also in comparison with different sorption materials like mine overburden [24], chars [25], red mud [26], sunflower leaves [27], activated carbon [28], fir [29], and others [30].

4. Conclusion

The present work has studied the sorption of heavy metal cations, Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+}, from aqueous solutions onto lignite mined in the South Moravian Coalfield, Czech Republic, and onto the sorbents derived from it by two alkali extraction procedures—humic acids and the untreated solid residue remaining after their separation, humin. The two extraction procedures differing mainly in the alkali concentration provided materials

with significantly different composition and sorption properties. The sorbents have shown their ability to adsorb the metals with various efficiencies, which were higher for humin and lower for humic acid samples than for the original lignite. Yet, the raw lignite demonstrated a good sorption efficiency promising its highly economical utilization without necessity of further chemical treatment. Its sorption capacity, particularly for the highly toxic metals lead and cadmium, is high compared to the capacities reported in literature for related sorbents. This has indicated a high suitability of the South Moravian lignite as a readily available, inexpensive, and effective material for the removal of heavy metals from wastewaters and polluted natural waters.

Acknowledgement

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