



## Utilization of bog iron ores as sorbents of heavy metals

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### ABSTRACT

Sorption properties of bog iron ores with respect to Pb, Cu, Zn, Cr are evaluated at various pH. Maximum sorption determined in the experiments equals to 97.0, 25.2, 25.5, 55.0 mg/g for lead(II), copper(II), zinc(II), and chromium(III), respectively. Chromium(VI) is bound in the amount of up to 10.0 mg/g. The values of desorption indicate that most of the metals remain stably bound to the surface of bog iron ores, indicating that the chemisorption process prevails. The metals are sorbed as cations at the pH values from 4 to 9. Within this pH range up to 100% of the initial metal amount is immobilized. 90–100% of Cr(VI) is sorbed at pH between 3 and 5. Such properties, combined with favorable conditions of shallow mining and resultant low costs, may be regarded as an incentive for local utilization of bog iron ores in the environmental protection practice.

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### 1. Introduction

Heavy metals, such as lead, copper, chromium and zinc, are common pollutants widely found in industrial wastewaters. Methods for removing these elements from solutions include, among others, ion exchange, coprecipitation, reverse osmosis, coagulation, electrochemical treatment and adsorption [1]. Many of these treatments are very expensive, so development of low-cost alternative methods is strongly recommended. At present, there is a growing interest in the readily available unconventional low-cost sorbents [2]. The materials considered have both industrial and natural origin and include clays, zeolites [3], dolomite [4], peat [3,5], soils, fly ash [3,6,7], agricultural wastes, red mud [8–10], manganese nodule residue [11], oxide-coated sands [12–14], etc. Special types of adsorptive solids include ferruginous sediments and wastes. They are rich in amorphous and crystalline iron oxides which have great affinity to metal ions [15].

In this study we evaluate the suitability of bog iron ores for the removal of selected heavy metals: lead(II), copper(II), zinc(II), chromium(III) and chromium(VI) from solutions. Sorption experiments were performed using a wide range of metal concentrations in order to provide a valuable guide for specific removal needs of metal contaminants.

Bog iron ores are one of the varieties of Quaternary iron ores that occur in wet, shallow depressions, several centimeters below the land surface. They can be divided into two main types: fine ores,

representing a loose deposit, and lump (cemented) ores, resembling slag in hand specimens [16]. In the past bog iron ores were used in iron metallurgy, as sorbents (for removing hydrogen sulfide and hydrogen cyanide from flue gases), and as building material [16,17].

Concentrations of two major constituents of bog ores,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , are negatively correlated. Usually higher contents of iron oxides and lower contents of silica characterize fine bog ores. The fine ores exhibit higher lost of ignition than the lump varieties [18]. This results from significantly higher amounts of organic substance and total carbon content. All bog ores are rich in  $\text{P}_2\text{O}_5$  (up to 16 wt.%). Lump bog ores contain also up to about 15 wt.% of  $\text{MnO}_2$ .

The fine ores form cryptocrystalline limonite, which consists of the following primary minerals: hydrated iron oxyhydroxides, ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ), goethite ( $\alpha\text{-FeOOH}$ ), and sometimes lepidocrocite ( $\gamma\text{-FeOOH}$ ). They are accompanied by phosphates (mainly vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and products of its oxidation), carbonates and variable amounts of detrital material (mostly quartz) [19–22]. Quartz-rich lump ores resemble ferruginous sandstones. In addition, lump bog ores contain more poorly crystalline manganese oxides (mainly of the vernadite type) than other ores.

Mineral and chemical composition combined with porous structure of the bog iron ores result in their variegated surface chemistry, large specific surface areas and relatively high ion exchange capacity. Therefore, these mineral raw materials can be used as natural sorbents. In this paper sorption properties of bog iron ores in reference to selected transition metals: Cr(III), Cr(VI), Cu(II), Pb(II) and Zn(II) were investigated. Sorption of these metals was extensively studied on pure, usually synthetic iron oxides (see [15] for review). However, the literature that deals with the sorption properties of

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**Table 1**  
Chemical, physical and mineralogical characteristics of the samples studied

Parameter	Sample			
	Biadaszki (BI)	Dębe Małe (DM)	Kolechowice (KOL)	Strzyżew (ST)
<b>Chemical composition</b>				
SiO <sub>2</sub>	3.03	15.00	7.88	16.50
TiO <sub>2</sub>	0.01	0.09	0.02	0.02
MnO <sub>2</sub>	4.23	0.65	0.27	0.18
Al <sub>2</sub> O <sub>3</sub>	0.19	1.62	0.28	0.29
Fe <sub>2</sub> O <sub>3</sub>	70.96	39.16	47.93	37.21
FeO	0.48	0.17	0.49	0.33
CaO	2.36	2.91	2.63	1.22
MgO	0.25	0.20	0.08	0.05
K <sub>2</sub> O	0.01	0.27	0.07	0.06
Na <sub>2</sub> O	0.01	0.12	0.04	0.05
P <sub>2</sub> O <sub>5</sub>	5.19	5.59	3.11	2.76
LOI	13.77	32.97	35.60	39.90
<b>Physical–chemical properties and mineral composition</b>				
CEC (mequiv./100 g)	11.2	38.3	57.2	42.4
BET (m <sup>2</sup> /g)	174	99	125	153
Fe <sub>DCB</sub> (wt.%)	51.38	27.41	31.93	29.26
Fe <sub>OX</sub> (wt.%)	23.00	21.06	24.94	27.16
C <sub>org</sub> (wt.%)	0.50	6.6	3.5	4.9
Mineral composition	<u>Gt</u> , <u>Fh</u> , Mn, Q, S, V, P	<u>Fh</u> , <u>Q</u> , Gt, P, Mn	<u>Fh</u> , <u>Q</u> , Gt, P	<u>Fh</u> , <u>Q</u>

Explanations: LOI: loss on ignition; CEC: cation exchange capacity; BET: surface area; Fe<sub>DCB</sub>: total iron contained in oxides and hydroxides; C<sub>org</sub>: organic carbon; Fh: ferrihydrite; Gt: goethite; Mn: Mn oxides; P: amorphous phosphates; Q: quartz; S: siderite; V: vivianite (main phase underlined).

natural polymineral ferruginous sediments is sparse. Bog ores are an excellent example of such a complex system.

## 2. Materials and methods

### 2.1. Materials

Bog iron samples used in this study were collected at four sites located in various areas of the Polish Lowlands: Biadaszki (BI), Dębe Małe (DM), Kolechowice (KOL) and Strzyżew (ST) [16]. They represent the varieties of bog iron ores that in the initial tests revealed good sorption properties, while at the same time had diversified structures, mineral composition and, subsequently, physical and chemical properties. Chemical and mineral composition of the samples were determined by X-ray fluorescence (Philips PW-2400 sequential XRF analyzer) and X-ray diffraction (Philips APD PW3020 diffractometer, equipped with a graphite reflection monochromator) methods. Cation exchange capacity (CEC) was evaluated by the BaCl<sub>2</sub> method [23]. The surface area was measured by nitrogen adsorption using the BET model. The amount of iron bound in oxides (Fe<sub>DCB</sub>), and in ferrihydrite (Fe<sub>OX</sub>), as well as the organic carbon content were determined by the following methods: dithionite–citrate–bicarbonate method [24], acid ammonium oxalate method [15], and infrared spectroscopy method (LECO analyzer).

The most important parameters which determine sorption properties of four bog iron ores as well as their chemical and mineral composition are presented in Table 1. Ferrihydrite is the dominant mineral in all four samples; its highest amount was found in sample ST. Sample BI represents the sole lump bog ore: it is characterized by the largest specific surface area and the lowest amount of organic substance. Although Fe oxides prevail (the highest values of Fe<sub>DCB</sub>), this sample has the most diversified mineral composition, containing ferrihydrite, goethite, and lower amounts of manganese oxides, phosphates and carbonates. In samples DM and KOL there are higher amounts of organic substance, and they have the lowest specific surface areas and cation exchange capacities among all of the samples. The content of detrital material (mainly quartz) is insignificant in the samples studied.

### 2.2. Preparation of samples

The samples of bog iron ores were used in their natural state for the sorption studies. Representative air-dry samples were sieved through 2 mm sieve and gently crushed in agate mortar. A <0.2 mm fraction was used for experiments.

### 2.3. Sorption studies

Batch sorption experiments were carried out on all samples with respect to copper(II), zinc(II), lead(II), chromium(III), and chromium(VI). A weight of 100 ± 1 mg of crushed and sieved bog iron ore was placed in 8-mL polypropylene tube and filled with 5 mL of solution, containing one of the following metals—Cu(II), Zn(II), Pb(II), Cr(III) in the form of nitrates, or Cr(VI) as potassium dichromate. The ranges of initial metal concentration were 50–2700, 50–3000, 60–3500, 70–3000 and 1–360 mg/dm<sup>3</sup>, respectively. High metal concentrations facilitated comparison of sorption properties of various types of bog ores. Preliminary results indicated that in the range of low metal concentrations (up to 500 mg/dm<sup>3</sup>) bog ores take up 99–100% of the initial quantity of metals and do not show differences among ore types.

The suspensions were shaken (150 rpm) at 25 °C for 24 h, and then centrifuged (10 min/10,000 rpm). The initial and equilibrium concentrations of Cu(II), Zn(II), Cr(III) and Pb(II) were analyzed using absorption atomic spectroscopy (AAS) with a Philips PU-9100x spectrometer. Chromium(VI) was determined by colorimetry with the use of the biphenylcarbazine method [25]. The amounts of metals sorbed were calculated from the difference between their concentrations in solutions before (initial concentration) and after (equilibrium concentration) sorption experiments. pH was also determined in the initial and centrifuged equilibrium solutions.

Bonding strength was evaluated from the degree of desorption. The samples of sorbents after the reaction with metal-containing solutions were washed with 5 mL of desorbing solutions, i.e. 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7) in the case of cationic metal forms and 5 mM KH<sub>2</sub>PO<sub>4</sub> + K<sub>2</sub>HPO<sub>4</sub> (pH 4) for Cr(VI). After 2 h of shaking followed

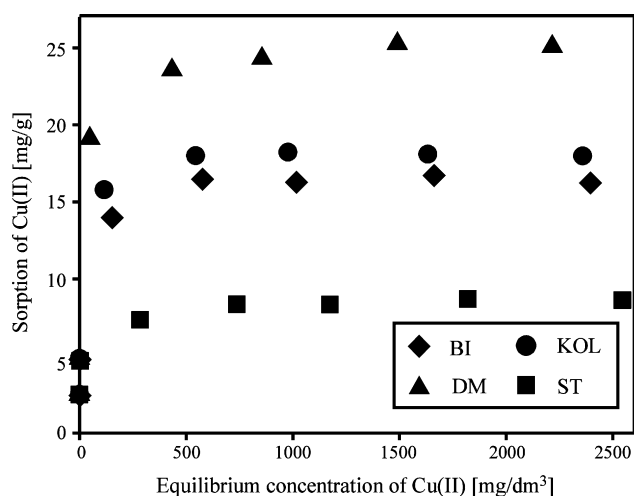


Fig. 1. Sorption isotherm of Cu(II) onto bog iron ores.

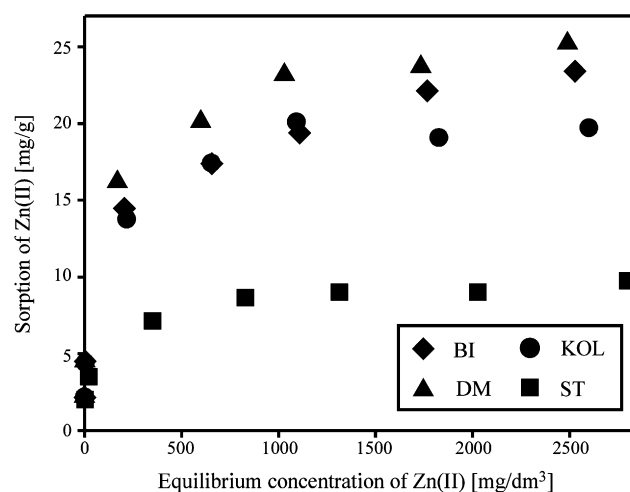


Fig. 2. Sorption isotherm of Zn(II) onto bog iron ores.

by centrifuging, the concentrations of metals in the solutions were analyzed employing the methods described above.

Sorption of Cr(III) and Cr(VI) were assessed in the function of pH and time for sample ST. The sample was shaken with solutions containing Cr(III) or Cr(VI) at concentrations 560 and 10.1 mg/dm<sup>3</sup>, respectively, while initial pH of the solutions was varied from 1.0 to 10.0. When testing the effect of time, the sample was shaken with the solution of the same concentrations of Cr(III) and Cr(VI) as before, and the chromium was assayed within the following intervals: 1, 2, 5, 10, 15, 20, 30, 40, 50, 60, 120, 240, 360, 480, and 600 min.

The experiments were repeated twice and the results constitute arithmetic means.

#### 2.4. Sorption isotherm models

To investigate the sorption isotherms, two equilibrium models, the Langmuir and the Freundlich equations, were applied. The Langmuir isotherm [26] is often used to describe sorption of a solute from a liquid solution. The linear representation of this model for single-component sorption is:

$$\frac{C_{eq}}{S} = \frac{1}{qK} + \frac{C_{eq}}{q}$$

where  $C_{eq}$  is the equilibrium liquid phase concentration (mM/dm<sup>3</sup>),  $S$  is the amount of sorbent adsorbed per unit weight (mM/kg); and  $q$  (mM/kg) and  $K$  (L/mM) are the Langmuir constants related to the sorption capacity and the rate of adsorption, respectively.

The Freundlich isotherm [27] provides an empirical relationship between the sorption capacity and the equilibrium concentration of the adsorbent. Linear form of this model is:

$$\log S = \log K + \frac{1}{n} \log C_{eq}$$

where  $k$  and  $1/n$  are the Freundlich constants related to the sorption capacity and sorption affinity of the sorbent, respectively.

### 3. Results and discussion

The highest amount of Cu(II) was sorbed by sample DM (25.2 mg/g), lower amounts by samples KOL (18.2 mg/g) and BI (16.8 mg/g), and the lowest amount by sample ST (8.7 mg/g) (Fig. 1). Similar relations have been found for Zn(II), with maximum uptake by sample DM (25.5 mg/g), slightly lower by samples BI (23.7 mg/g)

and KOL (20.0 mg/g), and the lowest by sample ST (10.0 mg/g) (Fig. 2). The highest uptake (85–99%) described as the ratio of the metal sorbed to its initial concentration in the solution, has been noted for Cu(II) and Zn(II), at the initial concentrations of the metals below 200 mg/dm<sup>3</sup>. A further increase of the metal concentration resulted in a sudden drop of uptake effectiveness. This drop of effectiveness was least pronounced for sample DM. At the highest metal concentrations sorption did not exceed 10–20%.

The amounts of Pb(II) and Cr(III) immobilized by all samples are distinctly higher than these for Zn(II) and Cu(II). The amount of Pb(II) sorbed is almost the same for DM, KOL and ST samples within the entire range of concentrations, that is 97.0, 94.4, and 88.9 mg/g, respectively (Fig. 3). The lowest amount of Pb(II) was sorbed by sample BI (71.0 mg/g). Cr(III) was sorbed in significantly higher amounts by samples DM (55.0 mg/g), KOL (51.4 mg/g), and BI (48.8 mg/g) than by sample ST (26.5 mg/g) (Fig. 4). Sorption efficiency of Pb(II) is in the range 95–99% for the initial concentrations below 1300 mg/dm<sup>3</sup>, and that of chromium(III) 80–99% for the initial concentrations below 500 mg/dm<sup>3</sup>. This pertains to all of the samples. Chromium(VI), occurring in the solution as the chromate anion, was sorbed by bog ores in amounts from 4.0 mg/g for sample KOL and 6.5 mg/g for DM to 9.1 mg/g for BI and 10.0 mg/g for sample ST (Fig. 5). The uptake of chromate is more efficient (85–99%) for the initial concentrations below 35 mg/dm<sup>3</sup> than for the maximum initial concentration (30–50%).

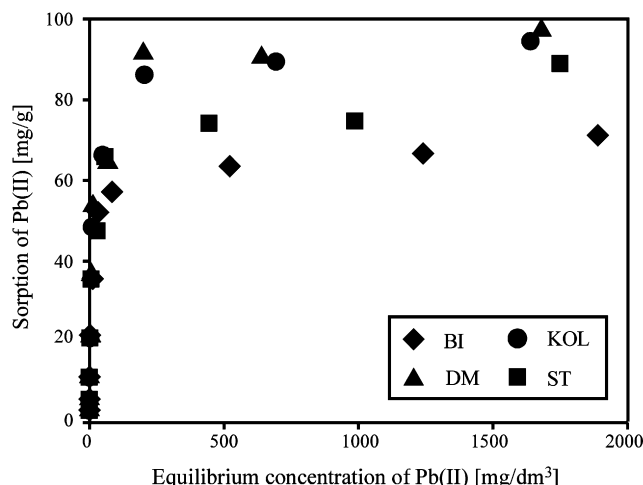


Fig. 3. Sorption isotherm of Pb(II) onto bog iron ores.

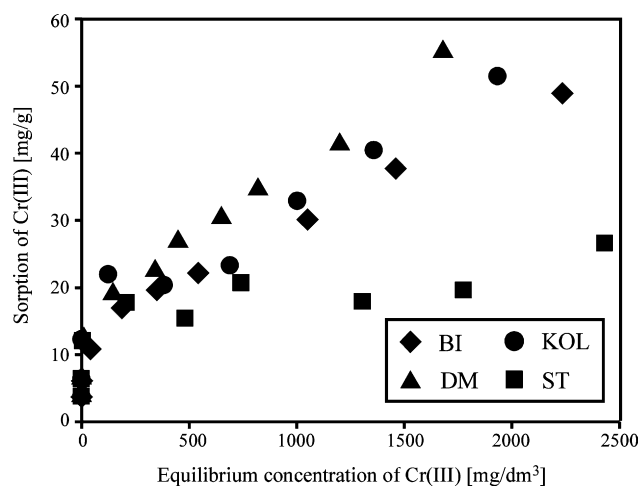


Fig. 4. Sorption isotherm of Cr(III) onto bog iron ores.

Regression coefficient ( $R^2$ ) values presented in Table 2 indicate that the adsorption data for copper, zinc and lead removal fit better the Langmuir isotherm ( $R^2$  above 0.99) than the Freundlich model. However, adsorption data for Cr(VI) fit better the Freundlich model. In the case of Cr(III), adsorption data do not follow neither Langmuir, nor Freundlich isotherms. The  $R^2$  values are almost the same for the Langmuir (0.85–0.94) and the Freundlich (0.86–0.95) model.

The relative durability of bonding between the metal and the ore can be measured in terms of the metal desorption. The measurements have shown that most of studied metals remain permanently bound to the surfaces of bog ores, indicating that chemisorption processes prevail. Around 20–30% of the Cu(II) sorbed is released back into the solution. Desorption of zinc is higher (40–50%), while desorption of lead distinctly lower (5–15%). The lowest desorption was found for chromium(III), and did not exceed 2%. Desorption of Cr(VI) varies: the amounts of chromium(VI) released from the surface of bog iron range between 10 and 25%.

Sorption of Cr(III) by bog ore increases gradually with increasing pH of the equilibrium solution from 1 to 9 (Fig. 6). A further increase of pH above 9.0 is accompanied by a small decrease (to 95%) of the amount of the chromium adsorbed. Similar to bivalent cationic forms of transition metals, Cr(III) is sorbed mainly at the pH values from 4 to 9. At this pH range, up to 100% of initial amount is immobilized. The maximum amount of the Cr(III) immobilized by

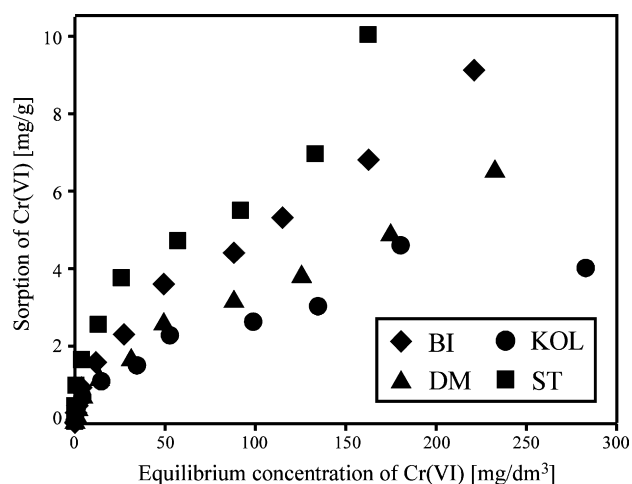


Fig. 5. Sorption isotherm of Cr(VI) onto bog iron ores.

Table 2  
Langmuir and Freundlich model coefficients for metals-bog ore isotherms

Sample	Langmuir isotherm			Freundlich isotherm		
	$q$	$K$	$R^2$	$n$	$K$	$R^2$
<b>Cu(II)</b>						
BI	256.41	0.05	0.9996	0.15	171.00	0.9726
DM	400.00	0.20	0.9997	0.20	229.19	0.9696
KOL	285.71	0.03	0.9999	0.16	182.77	0.9754
ST	136.99	0.36	0.9994	0.12	92.98	0.9775
<b>Zn(II)</b>						
BI	370.37	1.52	0.9894	0.23	161.40	0.9931
DM	384.62	1.00	0.9961	0.27	162.89	0.9849
KOL	312.50	0.66	0.9980	0.27	134.12	0.9782
ST	151.52	1.14	0.9968	0.23	69.92	0.9811
<b>Pb(II)</b>						
BI	333.33	0.07	0.9983	0.27	264.73	0.8535
DM	476.19	0.05	0.9991	0.32	373.51	0.8809
KOL	454.54	0.04	0.9995	0.32	369.83	0.8767
ST	416.67	0.12	0.9917	0.29	309.96	0.8725
<b>Cr(III)</b>						
BI	909.09	5.45	0.8932	0.25	270.33	0.9552
DM	1000.00	4.20	0.9341	0.18	385.12	0.9205
KOL	909.09	4.40	0.8541	0.19	364.75	0.8680
ST	454.55	2.00	0.9452	0.14	252.00	0.8946
<b>Cr(VI)</b>						
BI	175.44	0.91	0.8532	0.62	70.62	0.9858
DM	125.00	1.00	0.8497	0.60	48.12	0.9922
KOL	83.33	0.59	0.9221	0.44	39.60	0.9945
ST	161.29	0.32	0.8719	0.39	94.25	0.8992

the bog ore (99–100%) coincides approximately with its maximum amount precipitating as the hydroxide. Therefore, it is difficult to assess without any doubt the contributions of Cr(III) sorption and the hydroxide precipitation. The maximum amount (90–100%) of the Cr(VI) is sorbed between pH values 3 and 5. When pH falls below 3, the amount of the chromate sorbed decreases to 80%. Also, any increase of pH above 5 results in the decrease of the amount of the Cr(VI) immobilized and at pH 8–9 sorption falls to 10–30%. A decrease in the amount of the Cr(VI) sorbed at low pH values is a result of reduction of Cr(VI) to Cr(III) which is the process competitive to sorption. Organic substance contained in bog ore acts as a reducing agent. It has been reported that Cr(VI) can be rapidly reduced to Cr(III) by organic matter under acidic conditions [28].

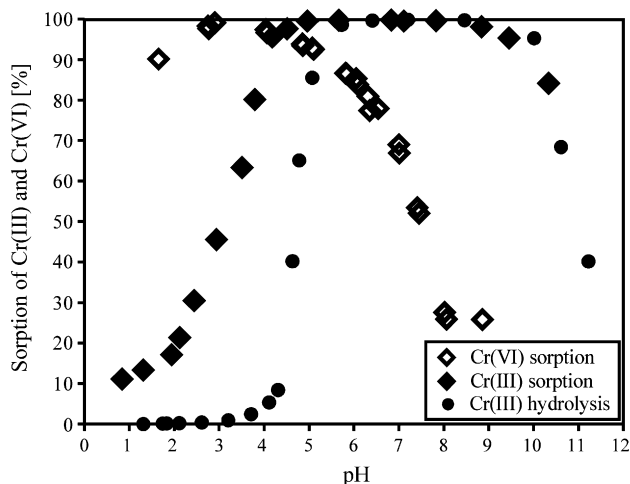
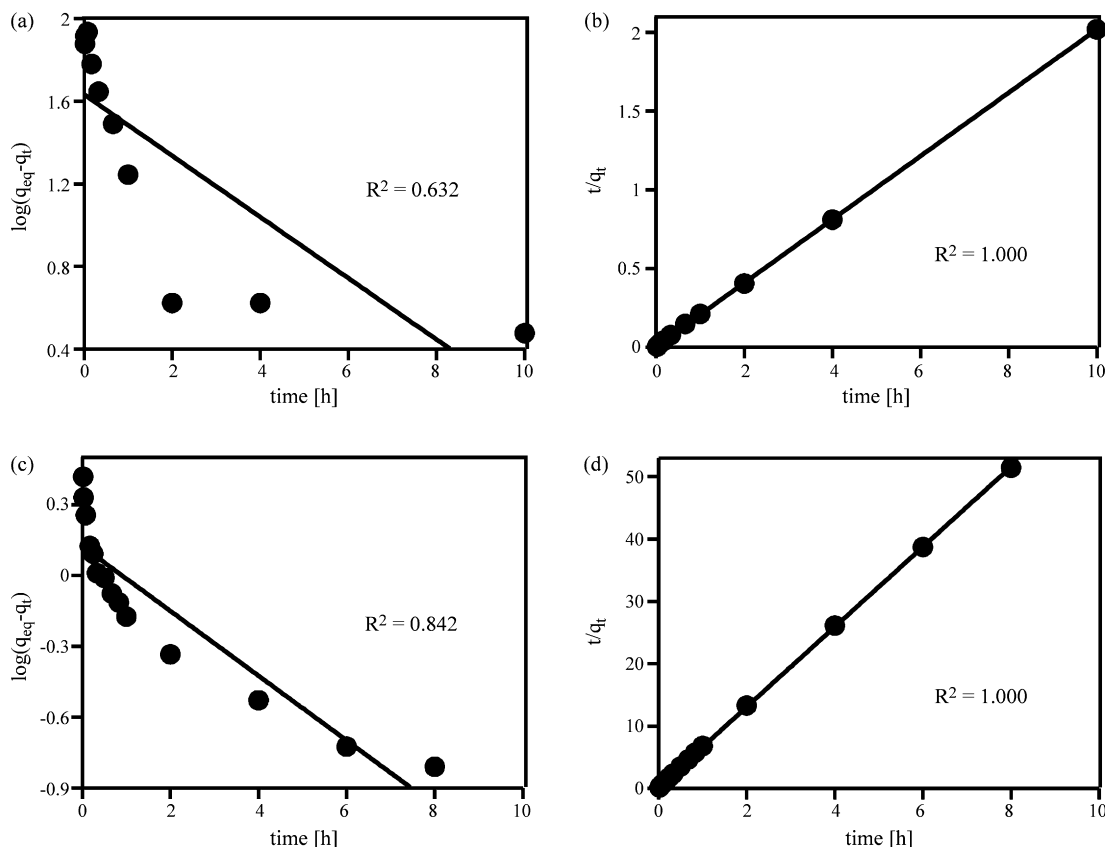


Fig. 6. Sorption of Cr(III) and Cr(VI) by the sample ST as the function of pH of an equilibrium solution against the background of the hydrolysis curve of Cr(III). Initial concentrations of Cr(III) – 560 mg/dm<sup>3</sup>, Cr(VI) – 10.1 mg/dm<sup>3</sup>.



**Fig. 7.** Pseudo-first and pseudo-second order sorption kinetics of Cr(III) (a) and (b) and Cr(VI) (c) and (d) on sample ST. (a) and (c) data represent the pseudo-first order sorption rate. (b) and (d) data represent the pseudo-second order sorption rate. Initial concentrations of Cr(III) – 560 mg/dm<sup>3</sup>, Cr(VI) – 10.1 mg/dm<sup>3</sup>.

Metals are bound to the surface of bog ore relatively fast: in the first 15 min up to 90% of the initial Cr(III) amount and up to 80% of the initial Cr(VI) amount are removed from the solution. Theoretical models of sorption kinetics have been presented by Ho and McKay [5,29]. Sorption kinetics of metal cations on soils is often described using the pseudo-first or pseudo-second order models [5]. Therefore these two models are compared herein. The lines that result from plotting  $\log(q_{eq} - q_t)$  versus  $t$ , and  $t/q_t$  versus  $t$  indicate the degree of fitting of the metal sorption to the pseudo-first and pseudo-second order rate kinetics model, respectively (Fig. 7). Kinetic data of Cr(III) and Cr(VI) sorption can be more appropriately defined using the pseudo-second order sorption rate model (Fig. 7b and d) rather than the pseudo-first order model (Fig. 7a and c) because  $R^2$  (correlation coefficient) values are higher for the pseudo-second order model.

Considering the uptake of heavy metals, the sorption properties of bog iron ores appear to be very good, although quite diversified due to variability of their mineral and chemical composition. The uptake of metal by bog ores is controlled first of all by iron oxides. In case of pure iron oxides and oxyhydroxides, adsorption in an aqueous environment involves functional surface hydroxyl groups with singly coordinated (terminal) hydroxyl groups being the most important [15]. Cationic heavy metals are specifically sorbed, through interaction with deprotonated surface hydroxyl groups to form mono- and binuclear inner sphere complexes [15,30]. Surface hydroxyl groups also have the capability of binding anions (like chromate) via ligand exchange reaction with the ion which displaces  $\text{OH}^-$  from coordination positions on the surface [31].

Relatively good fit of experimental results with the Langmuir sorption model indicates that the ores, being fine crystalline mate-

rials with weakly ordered internal structures, have highly specific surface areas, as well as many active centers homogeneously distributed over the surface. The character of the bond between oxide surface and the sorbed metal may be, however, considerably modified by ions (mainly anions) associated with the mineral surface [15,32]. They also affect the surface charge value and the size of the specific surface area. Such interactions are often observed in bog ores, where phosphates, silicates and organic ions are bound to the surface of iron oxides.

Mineral and chemical composition does not clearly correlate with surface properties (as BET and CEC) and sorption capacity for the samples studied. Such disappointing fact can be explained by complex composition of the material. Various properties of bog iron ores are influenced by various components. For example, CEC is related to organic matter content (estimated by organic carbon concentration). For this reason, the CEC value is the lowest for sample BI (containing only 0.5 wt.%  $C_{org}$ ), and the highest for sample KOL, (containing much more organic matter). On the other hand, iron oxides can also affect cation exchange capacity. This effect is weaker than in the case of organic matter. However, individual iron phases (goethite, ferrihydrite, and lepidocrocite) reveal different surface properties. Furthermore, these properties vary significantly with structural factors such as particle size and shape, crystallinity, chemical impurities, etc. (see [15] for review). Ferrihydrite usually reveals better sorption properties (and, thus, higher CEC values) than more crystalline compounds such as goethite. The total  $\text{Fe}_2\text{O}_3$  and even  $\text{Fe}_{DCB}$  values do not reflect iron phases mineralogy, and this fact can explain the lack of clear relations between iron content and sorption properties of CEC.

Complex mineralogy affects also surface area relation to the composition of bog ores. In this case, iron oxides play (an essen-

**Table 3**  
Uptake of metals by bog iron ores and other natural mineral sorbents

Metal	Sorbent type	$C_0$ (mg/dm <sup>3</sup> )	$S_{max}$ (mg/g)	References
Cr(III)	Bog iron ore	10–7800	55.0	This paper
	Peat	10–7800	167.5	[33]
	Smectite claystone	10–7800	53.6	[33]
	Zeolite	10–1900	14.6	[34]
Cr(VI)	Bog iron ore	0.1–360	10.0	This paper
	Peat	104	2.6	[35]
	Bentonite	104	0.5	[35]
	Smectite claystone	0.1–100	0.2	[33]
	Kaolinite	0.05–5.2	18	[36]
Cu(II)	Bog iron ore	10–7000	25.2	This paper
	Peat	25–2000	14.3	[29]
	Smectite–zeolite claystone	1–5500	14.0	[37]
	Zeolite	1–5500	11.0	[37]
Pb(II)	Bog iron ore	10–7300	97.0	This paper
	Peat	35–210	24.6	[29]
	Bentonite	100–200	28.0	[38]
	Zeolite	10–3100	28.3	[37]

Experiments under static conditions ( $C_0$ : initial metal concentration;  $S_{max}$ : maximum metal sorption).

tial) the most important role. As a result, BI sample, having the highest Fe content, reveals the highest surface area, and sample DM with the lowest Fe concentration, has the lowest surface area. However, this trend can be modified by structural factors discussed above. Having said that, ST sample, with slightly lower Fe content than KOL sample, has higher surface area compared to the latter.

The sorption mechanisms are further complicated by the presence of substances other than Fe oxides, such as manganese oxides and organic matter. These substances are also capable of binding metals. Therefore, sorption of particular trace elements depends strongly on mutual interaction of components of bog iron ore. These components form a complex organic–mineral system, which provide various types of active centers that take part in sorption processes. However, further study using greater number of samples is needed to find statistic correlations.

As was mentioned above, there exist no clear relations between composition of the samples and their sorption properties. The initial tests showed, however, that bog iron ores rich in ferrihydrite ( $Fe_{OX} > 10$  wt.%) and ones that contain relatively high levels of  $Fe_2O_3$  (>25 wt.%) and low of  $SiO_2$  (<35 wt.%), revealed distinctly better properties than the others. All the samples studied in this work fulfill these restrictions.

Regardless of the uptake mechanism, bog ores have sorption properties comparable or even better than other natural mineral sorbents (Table 3). Such properties, combined with favorable conditions of shallow, low cost mining, seem to be an incentive for local utilization of bog iron ores in environmental protection practice. Taking into account the diversity of structural and textural features and a silty nature of bog ores, the possibility of their utilization as classical industrial sorbents is low. However, the authors predict their applicability as geomembrane for the lining of landfills. It could be combined with bentonite or other clay, which has a very low hydraulic conductivity. Taking into account almost 100-percent metal sorption at the initial concentrations up to several tens of mg/dm<sup>3</sup>, application of bog ores guarantees a very high degree of decontamination of disposal sites effluents.

To our knowledge, there are no procedures for treatment and utilization of spent bog ore, i.e. the ore loaded with heavy metals that were sorbed. Disposal of a waste seems to be possible but only after carrying out tests on chemical stability of the metals that it contains and after taking into account the conditions of the dump site. The mechanisms of bonding described in the literature indi-

cate that the bonds between the metals and the spent bog ore are relatively strong.

Desorption experiments reveal that most of the analyzed metals remain permanently bound to the surfaces of bog ores. Consequently this indicates that chemisorption processes prevail. Thus contaminated bog iron ores could be regenerated in the first step to remove the weakly sorbed metals. Since chemisorbed metals form a non-leachable (non-water soluble) complex with the sorbent, bog ores can be disposed as non-hazardous conventional waste, (e.g., land filled). But this matter requires additional research.

#### 4. Conclusions

- (1) Bog iron ores exhibit good sorption capacity with regard to heavy metals. Among the metals studied, Pb was incorporated with the highest amount—up to 97.0 mg/g. The maximum amount of sorbed chromium(III) was 55.0 mg/g, while sorption of zinc, copper and chromium(VI) equaled to 25.5, 25.2, 10.0 mg/g, respectively. Sorption selectivity reflected by the maximum sorption capacity (expressed in mg/g) follows the order  $Pb > Cr > Zn \approx Cu$ . Sorption effectiveness determined on the basis of maximum amounts of the cations taken up, (expressed in mg/g), is in order  $DM > KOL \approx BI > ST$ . In turn, sorption effectiveness of anions, evaluated on the basis of chromate, is different:  $ST > BI > DM > KOL$ .
- (2) Adsorption of copper, zinc and lead fit the Langmuir isotherm better than the Freundlich model. Adsorption data for Cr(VI) fit better the Freundlich model. In the case of Cr(III), adsorption data does not fit either Langmuir, or Freundlich isotherms.
- (3) Desorption experiments indicate that most of the analyzed metals remain permanently bound to the surfaces of bog ores, indicating that chemisorption processes prevail.
- (4) Process of sorption of metals on surface of bog ore is relatively fast (quick, rapid). After the first 15 min of the reaction, 90% of the initial Cr(III) amount and up to 80% of the initial Cr(VI) amount were immobilized.
- (5) Cr(III), similar to bivalent cationic species of transition metals, is sorbed mainly at the pH values from 4 to 9, at which up to 100% of its initial amount is immobilized, although the maximum sorption (99–100%) coincides approximately with its maximum amount of precipitated as the hydroxide. The maximum amount (90–100%) of the anionic form of Cr(VI) is sorbed between pH values 3 and 5. A decrease of the amount of the

Cr(VI) sorbed at low pH values, results from reduction (transformation) of Cr(VI) to Cr(III) as this process is competitive to sorption within these ranges of pH.

- (6) The uptake of metal by bog ores is controlled primarily by iron oxides. Due to the variability in chemical and mineral composition, structures and textures, other mechanisms of metal uptake are possible as well.
- (7) Very good sorption properties of bog iron ores, combined with favorable conditions of shallow mining and resultant low costs, seem to be an incentive for local utilization of these sediments for environmental protection technologies.

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