Beidellite and other natural low-cost sorbents to remove chromium and cadmium from water and wastewater

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Laboratory experiments were conducted to examine ability of clay minerals and organic matter to remove the cadmium(II) and chromium(III) ions from aqueous effluents. Sample materials for the experiments were taken in Poland and Spain. Their chemical composition, specific surface area, pH in water and potassium chloride, ion exchange capacity and absorption of Cr (III) and Cd (II) have been studied. The clay samples exhibited greater sorption capacity for Cr(III) than for Cd(II) while organic matter, especially brown coal, better sorbed Cd(II) than Cr(III). The Langmuir binding strength parameter (k) was always greater for Cr than for Cd. On the basis of the sequential extraction and microanalysis by SEM it was stated that iron oxides were not involved in the Cd ion binding while their role in Cr(III) binding was essential. Ion binding by Fe oxides and their missing at exchangeable positions yields weak both susceptibility to leaching and mobility of Cr(III) ions. Instead, Cd(II) ions are mainly bound at exchangeable positions, susceptible to leaching.

Keywords: sorbents, beidellite, clays, biolithes, heavy metals, water, wastewater

Beidellita y otros adsorbentes naturales de bajo coste para inmovilizar Cr (III) y Cd (II) en efluentes acuosos

La industria y las urbes descargan sobre los ríos aguas que representan un factor importante en la contaminación medioambiental. La agricultura se ve afectada, siendo uno de los problemas el alto contenido en metales pesados presentes en el suelo o las aguas utilizadas para el riego. En este trabajo se expone la posibilidad de utilizar materiales de bajo costo, minerales arcillosos y carboníferos, tomados en España y Polonia, para remediar esta contaminación. Se ha estudiado su composición química, superficie específica, pH en agua y cloruro potásico, capacidad de intercambio iónica y absorción de Cr (III) y Cd(II). Las muestras arcillosas mostraron mayor capacidad de absorción para el ion Cr(III) que para el Cd(II), mientras que las orgánicas, especialmente la denominada " brown coal" (lignito), fueron mejores adsorbentes del ion Cd. El parámetro k obtenido en las isotermas de absorción según Langmuir, que define la fortaleza del enlace, fue siempre mayor para el Cr que para el Cd. Basándose en los análisis químicos de las extracciones secuenciales efectuadas y en los microanálisis puntuales por Microscopía electrónica de barrido (MEB+EDS) se puede concluir que la presencia de hierro en determinadas microáreas es determinante para la fijación del Cr y sin embargo los iones Cd quedan retenidos por enlaces a posiciones intercambiables y por eso son susceptibles de ser lixiviados.

Palabras clave: Adsorbentes, beidellita, arcillas, lignito, coque, metales pesados, purificación de aguas

1. INTRODUCTION

Discharging industrial and municipal wastewater into rivers and streams is an important factor affecting environmental water quality. Many small factories and workshops applying processes involving heavy metals do not have their own waste treatment facilities. They discharge wastewater directly into municipal sewage systems polluting sewage sludge with heavy metals to such an extend that it cannot be used in agriculture. More than 50% of the sludge is inadequate for agricultural use due to high content of metals[1].

An interesting and realistic solution to the problem seems to be removal of heavy metal ions from industrial wastewater by using various porous adsorbents [2-6]. Mineral and organic adsorbents, rich in clay minerals (smectite) or humic substances, respectively, have been of particular interest for last twenty years.

Clay minerals and organic matter, due to their properties (big specific surface area, porosity, cation exchange capacity and swelling capacity), are highly capable of adsorbing heavy metals and organic molecules.

Minerals belonging to the smectite group (montmorillonite, beidellite) and vermiculite have the highest sorption capacity. Smectite and vermiculite are 2:1 clay minerals, having both interlayer and ionizable hydroxyl sites on their external surface enabling metal cation sorption. Permanent negative surface layer charge resulting from the isomorphous substitution of Mg^{2+} or Fe^{2+} for octahedral Al(III) or Fe^{3+} and Al^{3+} for tetrahedral Si(IV) is the cause of binding of exchangeable cations to the interlayer sites. The cation exchange capacity (CEC) of these minerals is due to substitution within the structure (pH independent) and charges at the edge of the

sheets (pH dependent). The point of zero charge (pH$_{PZC}$) lies about 2.5. The surface of clay minerals is positively charged below this point, and negatively above.

Peat, compost and sewage sludge is abundant in exposed carboxyl and hydroxyl phenolic groups that can bind heavy metals [4, 7-8]. The amount of adsorption sites on organic matter surface is pH dependent due to dissociation of hydrogen ions from these groups. The point of zero charge lies in the interval 2.5-3 [9].

High adsorption of most metal ions is achieved at pH 5 - 6 for both smectite and organic matter.

Cadmium Cd(II) and chromium Cr(III) ions are present in industrial wastewater. They are used in electroplating and tanning or in the production of batteries and paints. Combustion of coal is another major source of environmental cadmium and chromium[10-11].

Because cadmium is toxic and highly mobile, it can contaminate as well soil as ground water. In general, cadmium occurs in aqueous solution as mono-atomic divalent ions. Depending on the ionic strength and concentration of ligands in the solution and stability of the metal-ligand interactions, cadmium may also occur in various complex ions, including hydrates, chlorides and organic chelates.

Toxicity of chromium depends on its oxidation state. Hexavalent chromium Cr(VI) is very toxic, poisonous to humans and other mammals, inhaled it can be a carcinogen, whereas trivalent chromium is an essential nutrient, a mineral supplement. Not only toxicity, but also mobility and bioavailability of Cr depend fundamentally on its chemical form. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble trivalent Cr species[12].

Trivalent chromium (CrIII) is more stable oxidation state of chromium in natural conditions. Cr(III) speciation in surface waters shows that aqua/hydroxo complexes are dominant under conditions prevalent in natural waters although Cr(III) exhibits tendency to form many different complexes with naturally occurring organic materials, such as amino, fulvic, humic and other acids[13-14].

Mainly, the adsorption capacity of a particular adsorbent is affected by the contact time, pH, temperature, amount of the adsorbent, concentration and properties of solute, mode of contact between adsorbent and liquid phase.

The aim of this study was to determine the capacity of beidellite-containing clay and alder peat from overburden of brown coal deposits in Belchatow, brown coal from Belchatow Brown Coal Mine (Central Poland), and waste-packing vermiculite from Spain to adsorb Cd(II) and Cr (III) ions, and the effect of ion concentration on this capacity. An attempt at determining the way of binding metals on surfaces of organic and inorganic sorbents was made with the use of the scanning electron microscopy and energy dispersive X-ray analysis.

2. MATERIALS AND METHODS

The adsorbent used in the experiment were two clays and two biolithes coals:

- the **Beidellite**-containing tertiary **clay** occurring in the overburden of brown coal deposits in Belchatow Brown Coal Mine (Central Poland),
- **Vermiculite**, waste-packing, from Spain,

- **Alder peat** occurring in the overburden of brown coal deposits in Belchatow Brown Coal Mine (Central Poland),
- **Brown coal** from Belchatow Brown Coal Mine (Central Poland).

2.1 Physicochemical characterization

The air-dried and homogenized samples were sieved through a 0.5 mm sieve before use. Major physical and physicochemical properties of the samples were determined. Porosity was determined by using mercury porosimeter (Carlo Erba model 2000). The external specific surface area was measured by using BET(N$_2$), the total specific surface area – by using BET(H$_2$O) (Fisons, Sorptomatic 1990). The mineral content of the clay samples was determined by using the X-ray diffraction (XRD, Phillips APD, Cu anode, Ni λ=0.154178 nm filter). The diffraction measurements were conducted within the 2Θ angle of 3-80° at the scanning rate 0.5°. Infrared spectra of clays and peat were obtained on an Fourier transform infrared spectrometer (FTIR) in the 4000 – 400 cm^{-1} spectral range by applying the KBr disc technique (0.4 mg of sample and 200 mg of KBr). Sample pH was measured in deionized water and in 1 M KCl (clay suspension ratio - 1:2.5, organic matter suspension ratio - 1:10), the latter is very useful in soils because it provides the exchangeable H$^+$ in reaction with K $^+$. Chemical composition and initial heavy metals present in native samples were determined by using the XRF method. Free iron oxides (nonsilicate or easily reducible Fe$_d$) were determined by using the citrate-bicarbonate-dithionate (CBD) method[15], noncrystalline forms of Fe (Fe$_o$) - the acid ammonium oxalate method[16], and organic form of Fe (Fe$_p$)- the sodium pyrophosphate method. Cation exchange capacity (CEC) and major cations occupying exchangeable positions were also determined in 1 M NH$_4$OAc at pH 7.

The morphological and chemical analyses in surface of native samples and samples with sorbed Cd(II) and Cr(III) cations were performed on a scanning electron microscope (FESEM, Hitachi Model S-4700) equipped with an energy dispersive X-ray detector system. Before, the powdered samples were dispersed in water, and after sedimentation on a microscope holder, coated with gold in an ionisation chamber.

2.2 Sorption and desorption experiments

The investigations of Cd(II) and Cr(III) sorption were conducted with the use of the batch equilibrium system at constant solution pH = 4, constant contact time (12 h), constant adsorbat/adsorbent ratio (1:10) and metal concentration in the solution ranging between 0.05 and 5000 mg·L^{-1}. Solutions were prepared from CdCl$_2$2.5H$_2$O and CrCl$_3$6H$_2$O salts and distilled water. Initial pH values of the solution in the sorption experiments were adjusted to 4.0 by adding minimum amounts of 0.01 M HCl or KOH. Concentration of cadmium and chromium in initial solution (c_0) and in equilibrium solution (c_{eq}) was measured by atomic emission spectroscopy (ICP-OES) with a Thermo Jarrell Ash model Advantage plasma spectrophotometer. Amount of sorbed metal (S) was calculated as S = (c_0-c_{eq}).v/m, where: m – mass [g], v – volume of metal solution [mL].

Sequential extraction of sorbed metals was performed by applying the chemical extraction method developed by Tessier

et al [17], modified by Kerstner and Forstner[18]. The studied heavy metals were partitioned in the seven-step procedure described by Twardowska and Kyziol[19].

3. RESULTS AND DISCUSSION

3.1 Physicochemical properties

The samples were of high porosity and total specific surface area in ranges 0.46—0.67 and 209-268 $m^2 \cdot g^{-1}$, respectively.

The mineral composition of air-dried clay samples was determined from X-ray diffractograms. The main mineral component of clay from overburden of brown coal deposits was beidellite, also quartz, calcite and kaolinite occurred (Fig. 1). The clay chemical composition was in relation with its mineral one. SiO_2 and Al_2O_3 occurred in the greatest amounts. Content of Fe_2O_3 was 6.45% and the dominating form of iron was iron bound in silicate lattice (96% of total iron); the rest of iron occurred as free iron (4% of total iron).
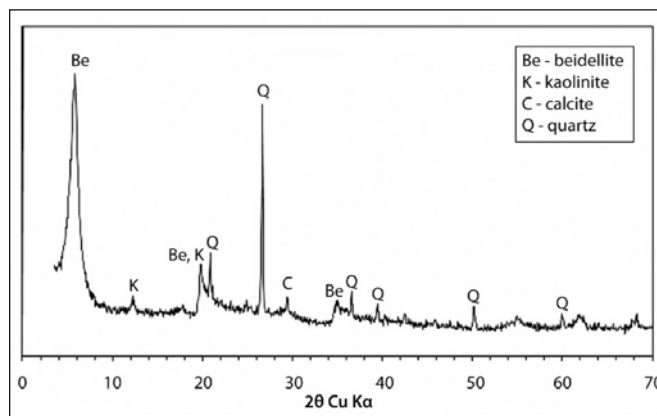

Fig. 1. X-ray diffraction pattern of Beidellite-clay

The content of CaO and MgO was 2.82% and 1.74%, respectively; alkalis were present in trace amounts (Table I). The total background metal concentrations were typical of tertiary clays in Poland.

TABLE I. PHYSICOCHEMICAL PROPERTIES OF THE SAMPLES

Porosity, specific surface area and pH					
Samples	Porosity	Specific surface area (m²/g)		pH	
		External (BET N₂)	Total (BET H₂0)	H₂O	KCl
Beidellite clay	0.46	37.27	208.83	7.85	7.60
Vermiculite	0.8x10⁻⁴	1.33	nd	7.71	6.40
Alder peat	0.52	11.38	218.98	5.62	5.11
Brown coal	0.67	9.98	267.85	5.75	5.01

Chemical analysis (% wt)								
	SiO₂	Al₂O₃	TiO₂	Fe₂O₃	Mn₃O₄	CaO	MgO	Na₂O	K₂O
Beidellite clay	55.81	15.25	0.76	6.45	0.024	2.82	1.74	0.042	0.57
Vermiculite	36.68	8.51	0.99	8.36	0.087	0.17	27.41	0.04	5.90
Alder peat	8.26	2.32	0.113	2.31	0.112	4.57	0.33	0.067	0.213
Brown coal	1.36	0.73	0.055	0.38	0.003	4.98	0.16	0.012	0.016

Trace elements content (mg/kg)						
	Cr	Cu	Cd	Zn	Ni	Pb
Beidellite clay	88.09	16.90	1.47	101.58	52.64	25.32
Vermiculite	111	<0.2	<0.2	82	92	<0.2
Alder peat	23.48	22.07	0.63	11.69	15.27	7.19
Brown coal	0.13	20.09	0.89	0.11	1.89	0.31

Cation exchange capacity								
	CEC₀	CECₜ	Total base saturation (%)	Exchangeable ions cmol(+)/kg. (% of CECₜ)				
	cmol (+) / kg			Ca²⁺	Mg²⁺	Na⁺	K⁺	H⁺
Beidellite clay	81.97	82.42	99.45	72.50 (87.96)	8.56 (10.38)	0.08 (0.09)	0.62 (0.75)	0.45 (0.55)
Vermiculite	68.27	68.65	99.35	5.06 (7.37)	40.04 (58.32)	0.06 (0.09)	23.11 (33.66)	0.38 (0.55)
Alder peat	103.0	125	82.4	95.18 (76.14)	7.14 (5.71)	0.20 (0.16)	0.09 (0.07)	15.5 (12.40)
Brown coal	107.2	136.2	78.7	100.00 (73.42)	6.35 (4.66)	0.28 (0.21)	0.10 (0.07)	29.0 (21.29)

nd – not determined
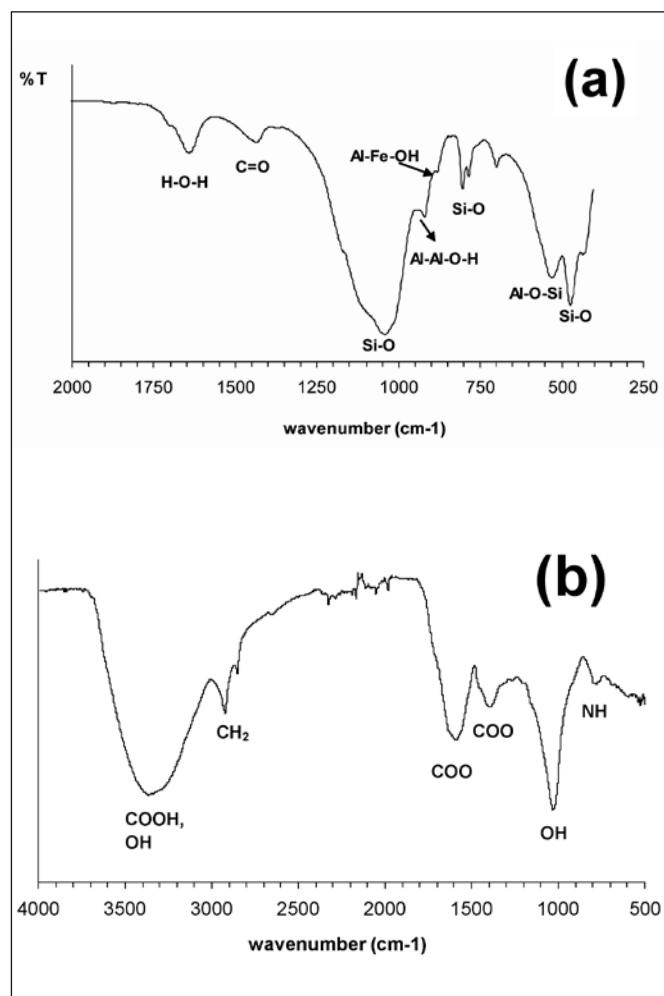
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Fig. 2. FTIR spectra of (a) Beidellite – clay, (b) Alder peat

FTIR spectra of the beidelite-containing clay and peat are shown in Figs. 2a and 2b.

Bands Si-O, Al_2-O-H, Al-Fe-O-H, Al-O-Si and Si-O-Si are characteristic of this clay (Fig.2a). In the clay spectrum, the absorption band at 1032 cm^{-1} and 466 cm^{-1} represents the Si-O stretching vibration of the tetrahedral layer. The characteristic band at 912 cm^{-1} represents the Al-Al-OH stretching in the octahedral layer and the band at 516 cm^{-1} - Al-O-Si stretching mode indicating bond breaking and disordering within the octahedral and between the tetrahedral and octahedral sheets of Ca-rich smectite. The band at 874 represents the Al-Fe^{3+}-OH vibration and bands at 796 cm^{-1} and 778 cm^{-1} are attributed to cristobalite. This clay spectrum also contains a broad band at 1430 cm^{-1} due to the calcite impurity.

In the peat spectrum (Fig. 2b), the region corresponding to high wave numbers shows a broad band at 3200 cm^{-1}. This band is attributed to the O-H vibration of carboxylic and phenolic groups. The bands at around 2930 and 2850 cm^{-1} are assigned to the C-H stretching motions of CH_2 groups. The band at 1600-1550 cm^{-1} is attributed to vibrations corresponding to the COO$^-$ stretching vibration. The band at 1450-1350 cm^{-1} is assigned to salts of COO stretching motions. The band at 1000 cm^{-1} is attributed to vibrations corresponding to the OH groups as -CH_2-OH.

The total cation exchange capacity (CECt) of the air dried beidellite was 82.4 cmol+.kg-1 and its main exchangeable cations were Ca^{2+} (87.96%) and Mg^{2+} (10.38% of exchangeable positions).

Investigated vermiculite has similar CECt but its main exchangeable cations were Mg^{2+} (58.32%) and K$^+$ (33.66% of exchangeable position).

The total cation exchange capacity (CEC$_t$) of the air dried alder peat and brown coal were 125 and 136 cmol$_+$.kg^{-1}, respectively, their main exchangeable cations were Ca^{2+} (76.14% and 73.52%) and Mg^{2+} (5.71% and 4.67% of exchangeable position). Other physicochemical properties are presented in Table I.

The chief components of the mineral fraction of organic samples (peat and brown coal) were SiO_2 (8.26% and 1.36%), CaO (4.57% and 4.98%), Al_2O_3 (2.32% and 0.73%) and Fe_2O_3 (2.31% and 0.38% respectively). Iron occurred mainly as free non-crystalline iron and iron bound to organic matter (Table II).

TABLE II. CONTENT (MG/KG) OF THE DIFFERENT FORMS OF FE IN EACH SAMPLE. PERCENTAGE RESPECT OF TOTAL FE IN BRACKETS

Samples	Fe$_{total}$	Fe free Fe$_d$	Fe noncryst. Fe$_o$	Fe cryst. Fe$_d$ - Fe$_o$	Fe organic Fe$_p$	Fe in silicate Fe$_{total}$ – Fe$_d$
Beidellite clay	45150 (100)	1786.7 (3.96)	634.5 (1.41)	1152.2 (2.56)	nd	43363.3 (96.04)
Alder peat	16170 (100)	9795 (60.57)	9792.7 (60.56)	2.3 (0.014)	6371 (39.40)	4.09 (0.024)
Brown coal	2660 (100)	1752.7 (65.89)	1731.5 (65.09)	21.2 (0.79)	904 (39.40)	3.3 (0.124)

nd – not determined

3.2 Sorption of Cd(II) and Cr(III) ions

The plot of Cd(II) and Cr(III) sorbed by investigated mineral and organic samples (mg·kg^{-1}) against equilibrium concentration of the metals (mg·L^{-1}) in solution is presented in Fig. 3. The sorption of Cd (II) and Cr (III) increases as its initial concentration in solution increases until equilibrium is reached. Sorption capacity of investigated samples for Cd(II) represented the descending order: brown coal > alder peat > beidellite > vermiculite. The maximum sorption capacity changed from 22720 mg/kg for vermiculite to 55750 mg/kg for brown coal. This order is in agreement with the CEC value for these samples. In all cases Cd(II) ions were sorbed below CEC of samples.

Sorption capacity of the samples for Cr(III) represented the descending order: Alder peat >> beidellite> vermiculite > brown coal. Low ability to bind the Cr(III) ions by brown coal should be mentioned. It is probably due to low content of iron oxides (Table II) for which strong affinity Cr(III) ions have and form bindings $(Cr_x.Fe_{1-x})(OH)_3$ in these oxides presence (where x is the mole fraction of Cr)[20].

In all cases amounts of Cr(III) ions sorbed were greater than doubled CEC of studied samples.The Cd(II) equilibrium solution pH for clay samples was relatively high and varied between 7.75 and 5.48, while for peat and coal was from 7.35 to 4.2 and 7.45 to 4.4, respectively. The pH value of Cr equilibrium solution for all samples varied similarly between 7.70 and 4.60.

The linear fits of experimental data obtained by using Freundlich $S = K_F C_{eq}^n$ and Langmuir isotherms $S = K_L Q C_{eq}/(1+QC_{eq})$ for beidellite clay are presented in Figure 4.
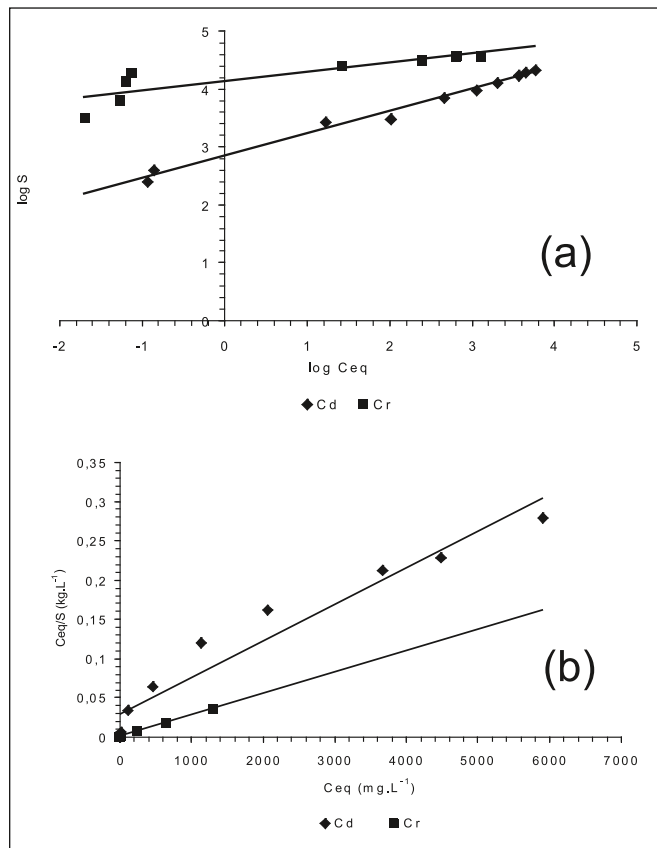

Fig. 4. Freundlich (a) and Langmuir (b) isotherms of Cd(II) and Cr(III) ions for beidellite-containing clay and vermiculite
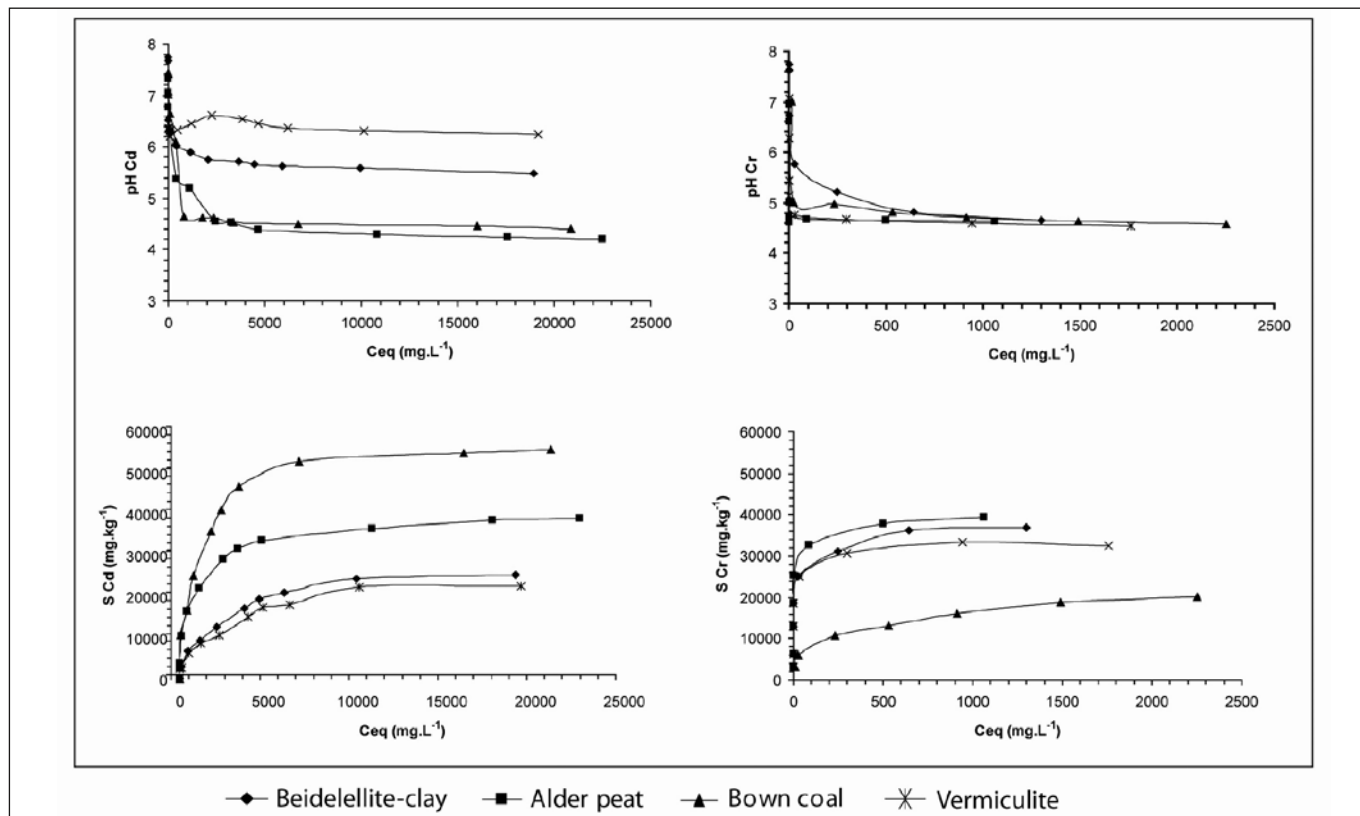

Fig. 3. Experimental isotherms for sorption of Cd(II) and Cr(III) ions from chloride solution onto studied samples and pH changes in equilibrium solutions

From the Langmuir isotherm the maximum sorption Q (mg·kg⁻¹) and the bonding energy coefficient (mg·L⁻¹) were calculated, and from Freundlich isotherm - the k and n (constants). They are presented in Table III. A good fit of the theoretical isotherm, determined from the formula, to the experimental isotherm was observed. It is in accordance with the high determination coefficient R^2 (Table III). Metal ions were bound by the sample sorption complex in compliance with the Langmuir equation. Also other autors[21-23] observed better Langmuir model relevance to process of binding metals by peats and mineral sorbents.

3.3 Susceptibility to leaching of sorbed metal ions

Sequential extraction of Cd(II) and Cr(III) sorbed onto mineral and organic samples revealed diversity in binding mechanisms of these metals.

Metals bound to the fractions F0 (metals in pore solution), F1 and F2 (metals at exchangeable sites) are mobile and easily removable, metals occurring in the fractions F3 (bound to Mn oxides) and F4 (associated with Fe oxides) are mobilizable. Metals occurring in the fractions F5 (in organic complexes) and F6 (in crystal lattice) are very strongly bound and not releasable.

The retention capacity of pore solution (F0) for the metal ions was low, while the immobile fraction F6 in the organic samples did not occur. The most important fractions determining the metal mobility were thus F1 and F2 where metal binding was predominantly due to Ca^{2+} ion exchange [24]. In this study, Cd(II) was distributed between two major fractions F1 (40-
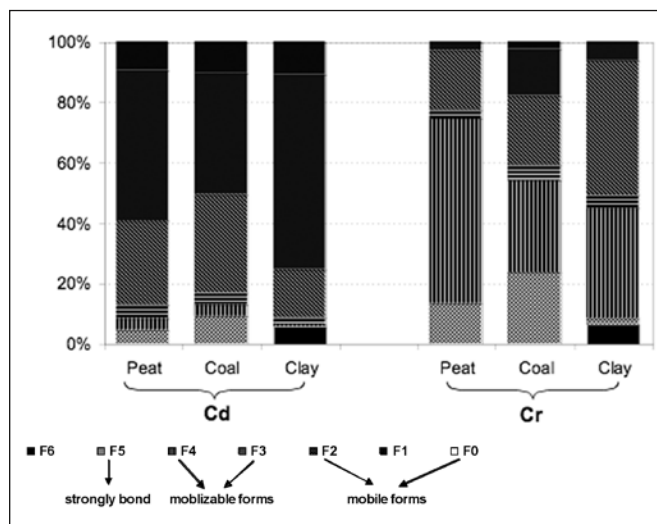

Fig. 5. Distribution of Cd(II) and Cr(III) ions among the fractions collected during sequential extraction. Strength of Cd- and Cr-samples interactions ranges from very weak in F0 to very strong in F6

65%) and F2 (16-33%). Other fractions, especially F4 (to 4%) and F5 (to 10%) were poorly enriched in Cd(II).

The pattern of distribution of Cr(III) between fractions shows that only for organic samples there was significant enrichment of fractions of higher binding strength in Cr(III), especially fractions F4 (30-60%) and F5 (14-25%). For beidellite-containing clay, the fraction F2 enrichment in Cr(III) was significant (44%).

TABLE III. PARAMETERS OF THE ISOTHERMS OF SORPTION OF CD(II) AND CR(III) IONS FOR INVESTIGATED SAMPLES

		Freundlich isotherm			Langmuir isotherm			
	Samples	n	k	R^2	Maximum of sorption	Q	k	R^2
					mg/kg	mg/kg	dm³/kg	
CdCl₂	Beidellite clay	0.38	700	0.9887	25 402	25 641	0,0014	0.9381
	Vermiculite	0.68	38.48	0.9735	22 720	26 316	0.0003	0.9858
	Alder peat	0.41	1 037	0.9367	39 171	40 000	0.0023	0.9978
	Brown Coal	0.41	1 417	0.9700	55 750	55 856	0.0021	0.9967
CrCl₃	Beidellite clay	0.16	13 245	0.7300	37 000	37 037	0.1098	0.9988
	Vermiculite	0.15	12 473	0.6912	32 400	33 333	0.3875	0.9997
	Alder Peat	0.19	12 792	0.6927	39 372	40 000	0.2101	0.9995
	Brown Coal	0.32	1 705	0.9630	20 760	21 739	0.0051	0.9911

TABLE IV. ELEMENTS CONTENT IN NATIVE SAMPLE OF BEIDELLITE-CONTAINING CLAY (SEM-EDS)

atom %	O	Mg	Al	Si	Ca	Fe
Average concentration	63.72±0.10	0.79±0.03	8.04±0.09	21.69±0.78	2.31±1.68	3.45±1.61
Bulk concentration	64.20	0.51	7.32	23.03	1.21	2.89

Also the parameter k for the Langmuir batch isotherm, expressing binding energy of ions, was higher for Cr(III) than for Cd(II) (Table III) what corresponded with metal partitioning data (Figure 5).

3.4 Electron probe X-ray microanalysis

Beidellite-containing clay sample was analysed on a scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector system (EDS). The clay appeared to have irregularly shaped particles of size generally between 0.1 and 2 μm (Fig. 6). Average chemical composition computed for native sample with the use of the point analysis is presented in Table IV where also the bulk concentration is given. The greatest differences are for Ca and Fe.

The chemical composition was determined at several points of clay with Cd(II) ions, adsorbed from solution of initial ion concentration 250 mg·L^{-1} and 5000 mg·L^{-1}, and with Cr (III) ions adsorbed from solutions of initial ion concentration 5000 mg·L^{-1}. The concentrations for selected points are given in Table V. The Cd distribution, dependent on its initial concentration, proves that even at low Cd(II) concentrations these ions are bound onto a surface. It is exchangeable reaction Ca - Cd. When concentration of Cd is maximum all Ca is removed from exchangeable sites of minerals, when concentration of Cd is small - only same parts of Ca is.

Investigations of the dependence of sorption of the Cd(II) ions on Fe content in samples prove that Fe is only involved in the Cr ions binding (Table V). Instead, an essential role ($R^2 = 0.7879$) in the Cr ion binding oxides of Fe play, what is also in support of results from the sequential extraction.

4. CONCLUSIONS

Studied mineral and organic samples were good adsorbents for use in purification processes designed to remove cadmium and chromium ions from solutions. The maximum sorption capacity of investigated sorbents for Cd(II) ions changed from 22720 mg·kg^{-1} (vermiculite) to 55750 mg·kg^{-1} (brown coal), and for Cr (III) ions – from 20200 mg·kg^{-1} (brown coal) to 39370 mg·kg^{-1} (Alder peat).

Because the cadmium ions were weakly bound onto the samples, they could be easily removed from sorbents extracted. The easy extraction means the possibility of the sample regeneration and use in further purification cycles.

Instead, Cr(III) ions were strongly bound to the adsorption centres, thus unsusceptible to leaching. Iron oxides play an important role in binding the Cr(III) ions.
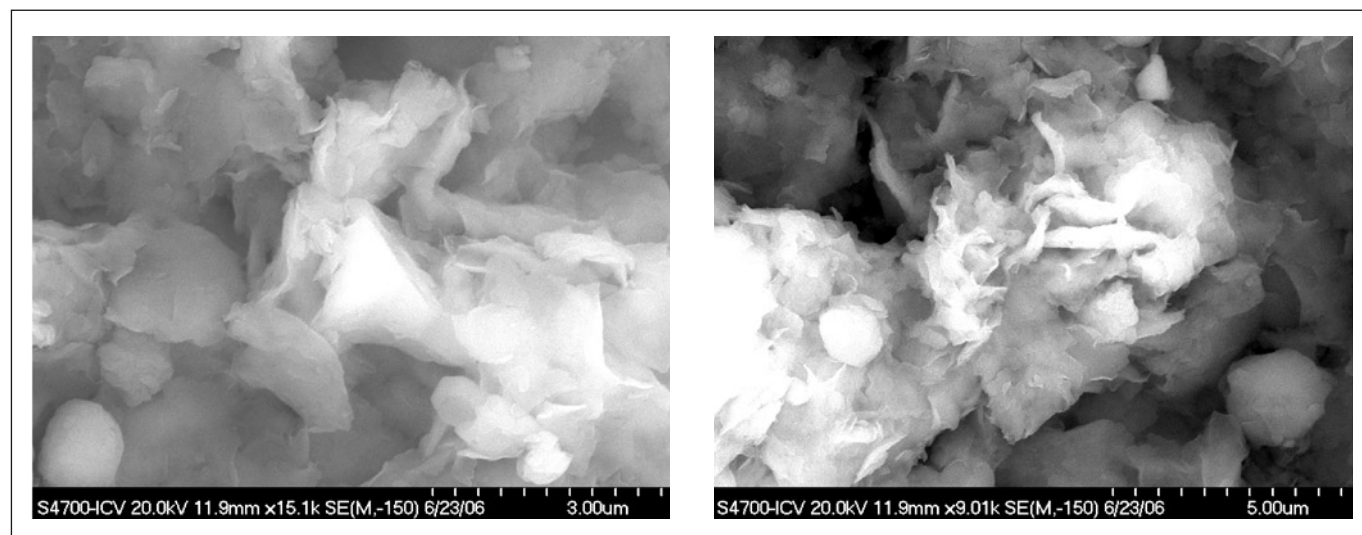
TABLE V. Fe, Ca and Cd content by SEM-EDS in beidellite-clay after Cd(II) and Cr(III) sorption.

Initial concentration	Ca	Fe	Cd
Cd 250 (mg·L^{-1})	atom %		
	9.58	2.27	0.45
	2.06	3.92	0.33
	1.06	3.14	0.31
	2.83	3.53	0.33
	4.36	4.18	0.15
Cd 5000 (mg·L^{-1})	<dl	3.44	1.27
	<dl	4.04	1.25
	<dl	5.98	1.03
	0.13	3.39	1.14
	<dl	4.13	2.21
	<dl	5.53	1.34
Cr 5000 (mg·L^{-1})	Ca	Fe	Cr
	4.11	5.10	11.29
	7.07	1.95	3.03
	4.98	9.87	12.71
	4.18	8.70	10.62
	3.21	5.39	7.63
	4.18	10.17	13.54
	1.98	4.12	5.57
	3.91	3.88	2.47

dl – determination limit

Fig 6. Scanning electron micrograph of native Beidellite-clay

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