Sorption of heavy metal cations on rhyolitic and andesitic bentonites from Central Slovakia

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Abstract: The main purpose of this work was to determine adsorption characteristics of heavy metal cations on two Slovak bentonites. Adsorption of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} on Jelšový Potok (JP) and Lieskovec (L) bentonites was studied by the batch equilibration technique using solutions of different concentrations. Higher smectite content (81 mass %) and higher cation exchange capacity (CEC) (105 mmol M^+/100 g) of JP bentonite cause higher adsorption of all heavy metals in comparison with L bentonite. JP adsorbed heavy metals in the order $Pb^{2+} >> Cd^{2+} > Zn^{2+} > Cu^{2+}$ while sorption on L was slightly different, $Pb^{2+} >> Cd^{2+} > Cu^{2+} \geq Zn^{2+}$. The Freundlich model of adsorption is more appropriate for adsorption of Pb^{2+} and Cd^{2+} while lower uptake of Cu^{2+} and Zn^{2+} is better described by the Langmuir model. Negative $\Delta G°$ values indicate that the adsorption process of all cations on both bentonites is feasible, spontaneous and exothermic. The decrease in the d_{001} spacings from 14.8–14.9 Å in natural dominantly Ca^{2+}-saturated samples to 13.2–12.6 Å for both bentonites saturated with four heavy metal cations shows the effect of less hydrated exchangeable cations on interlayer spacing. Jelšový Potok bentonite of higher montmorillonite content and greater CEC is the more effective candidate for removal of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} from waste water than Lieskovec bentonite.

Key words: adsorption isotherm, bentonite, lead, zinc, copper, cadmium.

Introduction

With the current awareness of heavy metals as very toxic contaminants, extensive effort has been devoted to investigation of their adsorption by solid surfaces as the most important mechanism for controlling metal content in soil solutions and natural waters (Helios Rybicka et al. 1995). Heavy metals are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in the environment and in food chains (e.g. Farrah & Pickering 1977; Doner 1978; Jain et al. 2004; Bulut et al. 2006). One of the recent environmental applications of bentonites is connected with high-level nuclear waste disposal in underground repositories using a multibarrier system of two basic components, a host rock and an engineered barrier made of metallic containers filled with radioactive waste surrounded by bentonite blocks, as is documented by the results of large scale experiments (e.g. Delay et al. 2007; Pacovský et al. 2007; Stríček et al. 2009). Sorption of radioactive metal cations on the Land JP bentonites has been described recently in detail by Galamboš et al. (2009a,b, 2010).

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters originating from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc. (Kadirvelu et al. 2001; Balistrieri & Blank 2008; Bhattacharyya & Gupta 2008).

The methods used for removal of these and other metals include chemical precipitation, ion exchange, solvent extraction, reverse osmosis, adsorption, and others. Activated carbon is highly effective in adsorbing heavy metals from wastewater but high cost limits its use (Kumar 2006). Various soils were also used for heavy metal adsorption (Fontes & Gomes 2003; Veeresh et al. 2003). Viraraghavan & Kapoor (1994) noted that the abundance and low cost of bentonite make it a strong candidate as an adsorbent for the removal of heavy metals from wastewaters or a retardant of the flow of leachates. Considering the favourable characteristics, adsorption of metal ions and other substances on clays has received considerable attention (e.g. Egozy 1980; Van Bladel et al. 1993; Yong et al. 2001; Abollino et al. 2003; Sezer et al. 2003; Egirani et al. 2005; Kaya & Ören 2005; Stathi et al. 2007; Abu-Eishah 2008; Zhang & Hou 2008; Al-Jlil & Alsewailem 2009).

Illite was shown to adsorb Cd^{2+} (Tanabe 1981) and natural bentonite to eliminate zinc from aqueous solution (Mellah & Chegrouche 1997). Removal of Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} by natural and Na-exchanged bentonites was also reported (Álvarez-Ayuso & García-Sánchez 2003). Strawn et al. (2004) discussed the adsorption of Cu^{2+} by montmorillonite and beidellite, whereas Lin & Juang (2002) used surfactant modified montmorillonite for the removal of Cu^{2+} and Zn^{2+}. Chantawong et al. (2001) studied adsorption of lead on a clay consisting mainly of kaolinite and illite and confirmed that the adsorption efficiency grows with increase in pH. Nevertheless, presence of other ions such as Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and $Cr(VI)$ reduced the lead uptake from aqueous solutions due to the fact that these ions bind strongly with organic matter present in clay to form a complex.

Bentonite consisting of clay, silt and sand was used in zinc removal (Mellah 1997). The sorption processes usually follow the Langmuir isotherm (e.g. Veli & Alyüz 2007; Sari et al. 2007). Adsorption capacities of 20 mg of Pb^{2+}/g were achieved by bentonite at pH 3.4 (Naseem 2001). Veli & Alyüz (2007) confirmed that pH is a significant factor in adsorption processes of

copper and zinc on bentonite causing electrostatic changes in the solutions. Hydrated hydrogen ions are strongly competing with other adsorbates. The highest removal efficiency in the copper and zinc adsorption with natural clay was obtained at pH >6 (Veli & Alyüz 2007). Sari et al. (2007) calculated changes in thermodynamic parameters, such as Gibbs free energy, enthalpy and entropy. The results showed that adsorptions of Pb^{2+} and Cr^{3+} on clay were feasible, spontaneous and exothermic processes in nature (Fan et al. 2009). Clays could be modified to improve their sorption capacity (e.g. Bailey et al. 1999; Adebowale et al. 2005; Oyanedel-Craver & Smith 2006; Bhattacharyya & Gupta 2006, 2008; Karamanis & Assimakopoulos 2007; Eren & Afsin 2008; Guimarães et al. 2009).

Two bentonite deposits in Central Slovakia underwent different alteration processes. The bentonite from Stará Kremnička-Jelšový potok (JP) developed from rhyolitic tuffs in a lacustrine environment; the main component is an Al-rich montmorillonite (Kraus et al. 1994). The deposit is located in the SW part of the Kremnické Vrchy Mountains in the Western Carpathians and belongs to the Jastrabá Formation. Bentonite from Lieskovec has andesitic pyroclastics as parent rocks and the main mineral is an iron-rich smectite (Andrejkovičová et al. 2006). The Lieskovec (L) deposit, belonging to Abčina Formation, is located in Zvolenská kotlina Basin, only about 25 km east of the JP deposit. In spite of close occurrence of the two bentonites, they differ in mineralogical compositions. JP and L bentonites are well characterized and commonly used. Andrejkovičová et al. (2008) reported recently that the blend containing 65 mass % of Na^+-L and 35 mass % of Na^+-JP bentonites meets all the requirements on bentonites used in geosynthetic clay liners. Smectite content in the blends was the dominant factor affecting their properties. Osacký et al. (2009) investigated in batch experiments stability of four bentonites and one K-bentonite from Slovak deposits in the presence of iron to simulate possible reactions of a bentonite barrier in the contact with a Fe container in a nuclear waste repository. The structure of illite-smectite deteriorated more than the structure of smectites. These results support more extensive application of JP and L bentonites in environmental protection. However, systematic investigation of heavy metals sorption on these materials has not been performed yet. The purpose of this study was to determine adsorption characteristics of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} on these two Slovak bentonites. The experiments were focused on simple adsorption of divalent cations on dominantly Ca^{2+}-bentonites to compare the effect of mineralogical composition including smectite content on adsorption properties. Sorption mechanisms and the effects of ionic strength are not discussed. It is hoped that the results obtained will lead to further environmental applications of these clays.

Materials and methods

Materials

The commercially available JP and L bentonites were supplied by Envigeo, Inc., Slovakia. Raw clays from the deposits were dried and crushed to <3 mm. A pendulum mill (Neuman & Esser PM 05) connected to a cyclone classifier was used to reduce the materials to particle size <250 μm.

Methods

RockJock. Quantitative analysis of bentonites was performed applying the RockJock program (Eberl 2003). The program fits the sum of stored XRD patterns of pure standard minerals (the calculated pattern) to the measured pattern by varying fraction of each mineral using the Solver function Microsoft Excel to minimize the degree of fit parameter between the calculated and measured pattern. Samples for analysis were prepared by adding 0.111 g ZnO (internal standard) to 1.000 g sample. The mixture was ground in a McCrone mill for 5 minutes with 4 ml of methanol then dried and sieved.

The diffraction patterns for RockJock analysis were collected in the 2-theta range from 4° to 65°, using steps of 0.02° 2θ, counting time 2 s per step, on a Philips PW 1710 diffractometer with CuKα (λ = 1.54056 Å) radiation and a secondary beam graphite monochromator PW 1752.

Powder X-ray diffraction (XRD) profiles of pressed powder samples were collected with primary beam monochromatized CoKα (λ = 1.78897 Å) radiation using a STOE Stadi P transmission diffractometer (Stoe, Darmstadt, Germany) configured with a linear position sensitive detector.

Films obtained on slides by evaporation of suspensions were kept for 24 hours at 25 °C in a glass dessicator over saturated magnesium nitrate solution at relative humidity of 53 %. Oriented diffraction patterns were obtained with a Bruker D8 DISCOVER apparatus (Cu-Kα radiation, 40 kV/300 mA) using step of 0.05 2θ and counting time 1 s per step.

Fourier transform infrared (FTIR) spectra were measured in the 4000–400 cm^{-1} region using KBr pressed-disk technique (1 mg of sample and 200 mg of KBr) on a Nicolet Magna 750 spectrometer with a DTGS detector and a KBr beam splitter. Discs were heated in a furnace overnight at 150 °C to minimize the amount of water adsorbed on KBr and the clay samples.

Cation exchange capacity (CEC) was determined using 0.01 M solution of Cu^{2+} triethylenetetramine [Cu Trien]$^{2+}$ prepared according to Meier & Kahr (1999). 200 mg ($\pm$0.5 mg) of clay samples were added to 50 ml of distilled water and 10 ml solution of [Cu Trien]$^{2+}$, then subjected to an ultrasonic treatment for five minutes, filtered and concentration of Cu^{2+} complex was determined in the filtrates by UV-VIS spectrophotometry (Cary 100, Varian) at 578 nm (Meier & Kahr 1999). The amount of adsorbed [Cu Trien]$^{2+}$ was determined using molar absorption coefficient ε = 0.245 mol^{-1}·dm^3·cm^{-1} (Kaufhold & Dohrmann 2003) and the CEC values in milliequivalents of cations per 100 grams of specimen were calculated.

ICP atomic emission spectroscopy. Amounts of adsorbed Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} were calculated from the difference between their initial and final contents in solutions used for sorption experiments. They were obtained with a sequential, radially viewed ICP atomic emission spectrometer Vista MPX (VARIAN).

Morphology of the samples was studied by scanning electron microscopy using a CARL ZEISS-EVO 40 HV micro-

scope. Before the scanning process, all the samples were coated with gold to enhance the electron conductivity. The samples were examined by energy dispersive X-ray analysis (EDX) with spectrometer QUANTAX 400 to analyse the chemical composition in the samples sputtered with carbon.

Adsorption procedure: Adsorption experiments were carried out using a batch method. 100 mg of each sample was added to 10 ml of nitrate solutions of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+}. Five different concentrations for every heavy metal cation solution were used: 0.01 M, 0.005 M, 0.0025 M, 0.00125 M and 0.0005 M. A 24-h contacting period was found to be sufficient to achieve equilibrium sorption. The relatively high pH of solutions with montmorillonites may induce the precipitation of hydroxides of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} as was observed for example, by Barrer & Townsend (1976) and Strawn & Sparks (1999). To avoid possible misinterpretation of exchange selectivity at higher cation concentrations, HNO_3 was added to the stock solutions of these elements to adjust pH to 6 ± 0.1. The theoretical equivalent ratio $[M^{2+}]/[H^+]$ in solution provided values close to 1×10^{-3}, at which possible influence of H^+ ions on the exchange reaction could be neglected. Stock solutions of Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} nitrates were prepared with deionized water. All the chemicals used were of analytical reagent grade and were obtained from Aldrich.

The separation of the liquid from the solid phase was achieved by centrifugation at 20,000 rpm for 30 min. Amounts of adsorbed Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} were calculated from the difference between the heavy metal cation initially added into the system and that remaining in the solution at the adsorption equilibration, as obtained by a ICP atomic emission spectroscopy.

The distribution coefficient K_d ($dm^3 \cdot kg^{-1}$) was calculated using Eq. (1):

$$K_d = \frac{c_{ad}}{c_{eq}}, \tag{1}$$

where c_{ad} ($mol \cdot kg^{-1}$) is the amount of the metal cation adsorbed and c_{eq} ($mol \cdot dm^{-3}$) is the equilibrium concentration of the metal cation in solution.

Change in Gibbs free energy $\Delta G°$ (kJ/mol) was calculated according to Eq. (2) and K_d obtained from Eq. (1):

$$\Delta G° = -RT \ln K_d, \tag{2}$$

where R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$) and T is temperature.

The sorption equilibrium data were applied to the equation based on the Freundlich model:

$c_{ad} = K_F \cdot c_{eq}^{1/n}$, where K_F ($mol \cdot kg^{-1}$) and n ($kg \cdot dm^{-3}$) are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

K_F and $1/n$ were determined from the intercept and slope of linear plot of log c_{ad} versus log c_{eq}, respectively:

$$\log c_{ad} = \log K_F + \frac{1}{n} \log c_{eq}. \tag{3}$$

Sorption capacity K_L according to Langmuir model was calculated from:

$$c_{ad} = \frac{K_L . K_2 . c_{eq}}{1 + K_2 . c_{eq}}, \tag{4}$$

graph $\frac{c_{eq}}{c_{ad}} = f(c_{eq})$ was plotted and K_L ($mol \cdot kg^{-1}$) was calculated by regression of linearized Langmuir isotherm according to Eq. (5):

$$\frac{c_{eq}}{c_{ad}} = \frac{c_{eq}}{K_L} + \frac{1}{K_L . K_2}, \tag{5}$$

where K_2 is an equilibrium constant dependent on sorption energy.

Distribution coefficients were determined using a conventional batch-equilibration technique in which 100 mg of clay was contacted with 10 ml of solution and shaken at room temperature for 24 hours.

Results and discussion

X-ray diffraction

XRD diffraction patterns of JP and L samples are shown in Fig. 1. Smectite with prevailing Ca^{2+} cation in the interlayer space is the dominant mineral in both samples with basal (001) reflection at 6.68 °2 theta (15.09 Å). The (060) reflection at 73.24 °2 theta (1.49 Å) shows that the main mineral in both samples is a dioctahedral smectite (Brindley & Brown 1980). Identified admixtures include muscovite and kaolinite in JP and quartz, muscovite, kaolinite, cristobalite and orthoclase in L (Fig. 1).

More information on the composition of the materials studied was obtained by RockJock analysis (Table 1). The main differences are related to the smectite and non-clay mineral contents, such as quartz and feldspars. Other non-clay minerals include microcrystalline forms of SiO_2 and possibly also iron oxides/oxyhydroxides.
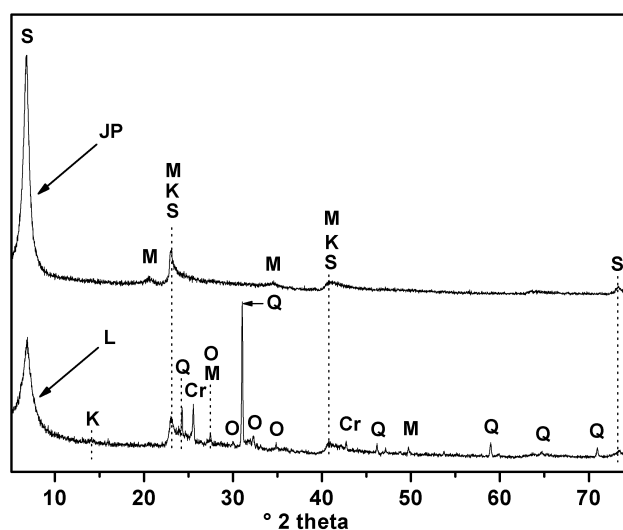

Fig. 1. XRD patterns of JP and L samples (**S** — smectite, **K** — kaolinite, **Q** — quartz, **Cr** — cristobalite, **O** — orthoclase, **M** — muscovite/illite).

Table 1: Mineralogical composition of samples as obtained from the RockJock analysis.

	Sample	
	JP	L
	mass %	
smectite	81	45
kaolinite	1.5	5
muscovite/illite	5	8
quartz	–	13
feldspars	–	11
other non-clay minerals	12.5	18

Infrared spectroscopy

IR spectra provide further information on mineralogical composition of the samples and chemistry of the dominating smectite. The adsorption band near 3624 cm^{-1}, assigned to stretching vibrations of structural OH groups of dioctahedral smectite (montmorillonite), appears in the spectra of both samples (Fig. 2). The broad complex band near 1030 cm^{-1} is related to the stretching vibrations of Si-O groups while the bands at 522 cm^{-1} and 468 cm^{-1} are attributed to Al-O-Si and Si-O-Si bending vibrations, respectively (Farmer 1974). Coupled Al-O and Si-O out of plane bending vibration at 626 cm^{-1} also confirms dioctahedral smectite in the samples (Madejová & Komadel 2001). The characteristic bands of kaolinite at 3698 cm^{-1} and 693 cm^{-1} (Farmer 1974) are clearly visible in the spectrum of L.

The doublet of quartz at 797 and 779 cm^{-1} is overlapped with the band of microcrystalline SiO$_2$ in the spectrum of L sample (Fig. 2). Central atoms in the octahedral sheets of smectite affect the OH-bending bands in the 950–800 cm^{-1} region (Fig. 2). The discrete and relatively intense peak at 915 cm^{-1} corresponds to the AlAlOH bending vibrations of smectite; the OH bending vibrations of kaolinite and illite/muscovite can contribute to this absorption. A higher content of Fe(III) in the octahedral sheets of L is confirmed by the AlFeOH band near 871 cm^{-1}. The AlMgOH vibration near 841 cm^{-1} is not observed in the spectrum of L, thus proving a
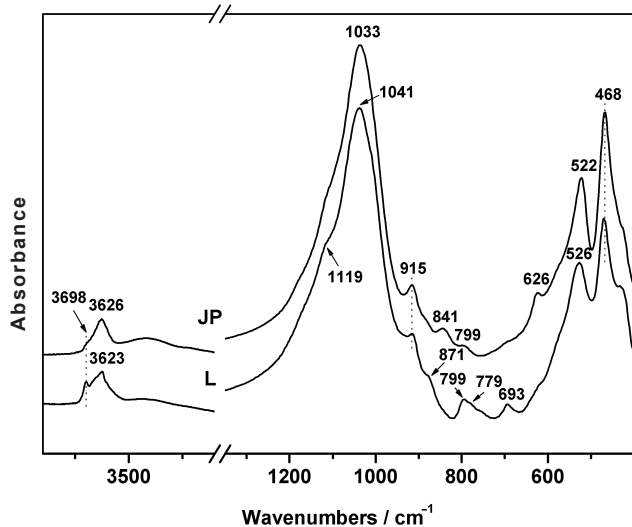
Fig. 2. Infrared spectra of JP and L samples.

relatively low Mg content in the octahedral sheets of the main mineral of Lieskovec bentonite (Andrejkovičová et al. 2006). The spectrum of JP (Fig. 2A) contains a clearly visible AlMgOH bending band near 841 cm^{-1} proving higher isomorphous substitution of Mg(II) for Al(III) in the octahedral sheets of JP than in L and resulting in its higher layer charge. Both XRD and IR results prove a higher smectite content and lower amounts of accessory minerals in JP.

Adsorption of heavy metal cations

The process of adsorption on the samples is depicted in Fig. 3, where the relationship between the amount of adsorbed metal cation and their equilibrium concentrations in aqueous solutions after adsorption is shown. All experiments were performed in triplicates with standard deviations <2 %. pH was kept at 6±0.1 to avoid precipitation of heavy metal cations at higher pH and undesirable attack on clay layers by protons at lower pH (Strawn & Sparks 1999). JP bentonite with higher smectite content and cation exchange capacity (81 mass % and 105 mmol/100 g, respectively) is a better adsorbent than L bentonite (45 mass % and 51 mmol/100 g). The adsorption curves of Pb^{2+} for both bentonites confirmed the best sorption results. The amount of adsorbed Pb^{2+} for each equilibrium concentration was higher than for the other metal cations, in accord with its lowest ionic potential of 1.60 eV/nm. Both bentonites adsorbed heavy metal cations in a similar order: JP — Pb^{2+}>>Cd^{2+}>Zn^{2+}>Cu^{2+} and L — Pb^{2+}>>Cd^{2+}>Cu^{2+}≥Zn^{2+} (Fig. 3), correlating reasonably well in an opposite manner with the ionic potentials of 1.60, 2.06, 2.70 and 2.74 eV/nm for Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}, respectively.

Adsorption isotherms

Langmuir and Freundlich isotherm models were used to determine correlation between the amounts of adsorbed heavy metal cations on JP and L samples and their equilibrium concentrations in aqueous solution (Fig. 4). The graphs on the left side of Fig. 4 (A, C, E, G) show transformed experimental data to Freundlich model in logarithmic form expressed by Eq. (3), where K_F and $1/n$ constants were determined from the intercepts and slopes of linear plots of $\log c_{ad}$ versus $\log c_{eq}$. The obtained equilibrium data also conformed to the linear form of the Langmuir model (Eq. 5) and are displayed on the right side of Fig. 4 (B, D, F, H). Langmuir adsorption constants (K_L) were calculated from the intercepts and slopes of the linear plots of c_{eq}/c_{ad} vs. c_{eq}.

The adsorption patterns of the metals on JP and L clays were well fitted with both the Langmuir (R^2=0.91–0.99) and Freundlich (R^2=0.86–0.99) models. The Freundlich isotherm represents multi-layer unlimited adsorption. Sorption capacity is achieved at a certain concentration and this phenomenon describes the Langmuir isotherm. Based on the R^2 values, the Freundlich model is better applicable for adsorption of Pb^{2+} and Cd^{2+} while lower uptake of Cu^{2+} and Zn^{2+} is better described by the Langmuir model.

Table 2 shows calculated values for adsorption of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} on both samples, including the distribution coefficient K_d, Gibbs free energy change $\Delta G°$, sorption
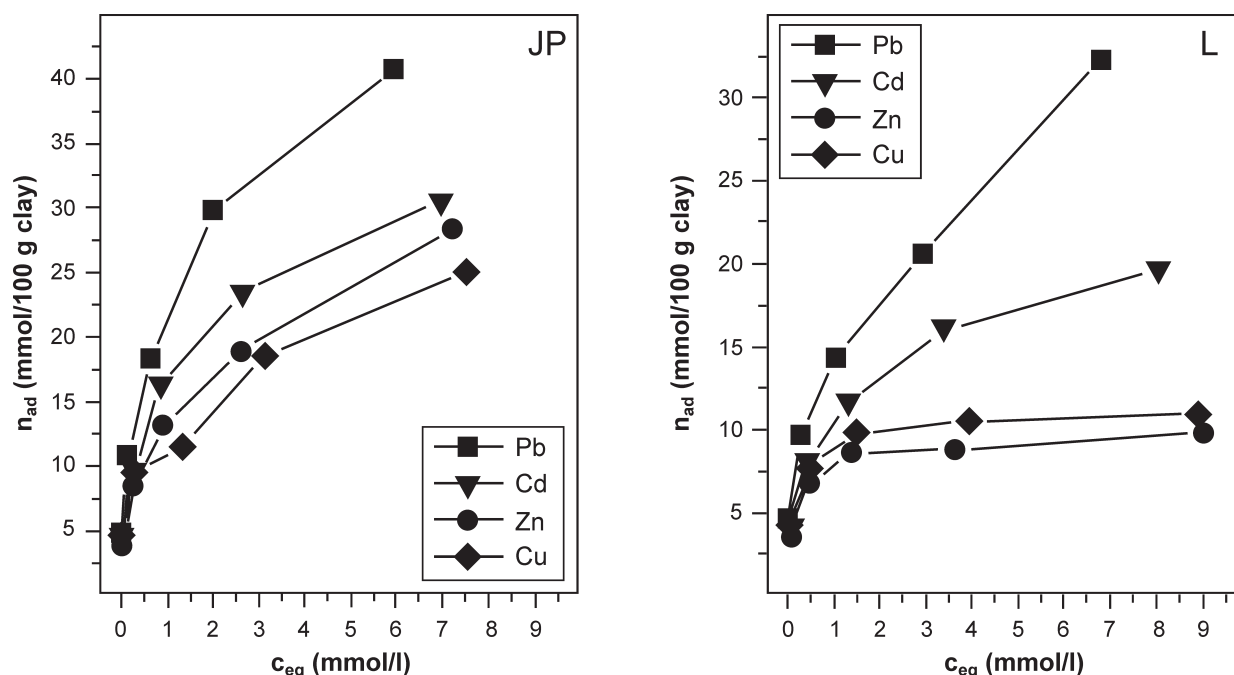
Fig. 3. Adsorption of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} on JP and L bentonites as a function of equilibrium concentration of the metal cation.

capacities K_F, K_L and Freundlich coefficient (1/n). The distribution coefficients K_d increase while $\Delta G°$ values decrease with decreasing concentration of heavy metal in solution for all investigated cations (Table 2). The negative values of $\Delta G°$ indicate that the adsorption process of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} and on JP and L is feasible, spontaneous and exothermic in nature (Fan et al. 2009).

The most spontaneous processes are connected with adsorption of all heavy metals from the less concentrated solutions. The $\Delta G°$ values are between –16.1 and –18.3 for JP and –14.6 and –16.8 kJ/mol for L. The most feasible is adsorption of Pb^{2+} on JP from 0.0005 M solution with the lowest $\Delta G°$ of –18.3 kJ/mol. The values of Gibbs free energy change decrease in the order $Pb^{2+}>Cu^{2+}>Cd^{2+}≥Zn^{2+}$ for both JP and L at the lowest concentration of heavy metal cations of 0.0005 M. The adsorption process from the most concentrated solutions of heavy metals (0.01 M, Table 3) differs in some way compared to adsorption from 0.0005 M solutions. L adsorbs the cations with $\Delta G°$ in the order $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}$. This is in good accordance with the results of Helios Rybicka et al.

Table 2: Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} adsorption parameters for JP and L samples, c is concentration of metal cations in initial solutions.

|	$c/10^{-3}$ (mol/dm^3)	JP					L				
		10	**5**	**2.5**	**1.25**	**0.5**	**10**	**5**	**2.5**	**1.25**	**0.5**
Pb	K_d (Henry) (dm^3/kg)	68.6	148.3	278.2	635.3	2178	47.6	70.2	135.0	338.2	1147
	$\Delta G°$ (kJ/mol)	–10.1	–11.9	–13.4	–15.4	–18.3	–9.2	–10.1	–11.7	–13.9	–16.8
	K_L (Langmuir) (mol/kg)			0.44					0.35		
	K_F (Freundlich) (mol/kg)			3.15					1.87		
	1/n (kg/dm^3)			0.39					0.37		
Cd	K_d (Henry) (dm^3/kg)	44.1	88.5	187.7	341.7	911.2	24.5	47.4	87.4	182.1	507.4
	$\Delta G°$ (kJ/mol)	–9.0	–10.7	–12.5	–13.9	–16.2	–7.6	–9.2	–10.6	–12.4	–14.8
	K_L (Langmuir) (mol/kg)			0.33					0.21		
	K_F (Freundlich) (mol/kg)			2.35					1.09		
	1/n (kg/dm^3)			0.39					0.34		
Zn	K_d (Henry) (dm^3/kg)	39.6	72.6	138.3	303.8	846.1	10.9	24.4	62.3	148.5	459.0
	$\Delta G°$ (kJ/mol)	–8.8	–10.2	–11.7	–13.6	–16.1	–5.7	–7.6	–9.8	–11.9	–14.6
	K_L (Langmuir) (mol/kg)			0.31					0.10		
	K_F (Freundlich) (mol/kg)			1.91					0.28		
	1/n (kg/dm^3)			0.39					0.20		
Cu	K_d (Henry) (dm^3/kg)	33.5	59.0	85.0	310.5	1188	12.3	26.6	64.3	162.2	645.8
	$\Delta G°$ (kJ/mol)	–8.4	–9.7	–10.6	–13.7	–16.9	–6.0	–7.8	–9.9	–12.1	–15.4
	K_L (Langmuir) (mol/kg)			0.27					0.11		
	K_F (Freundlich) (mol/kg)			1.07					0.30		
	1/n (kg/dm^3)			0.31					0.19		
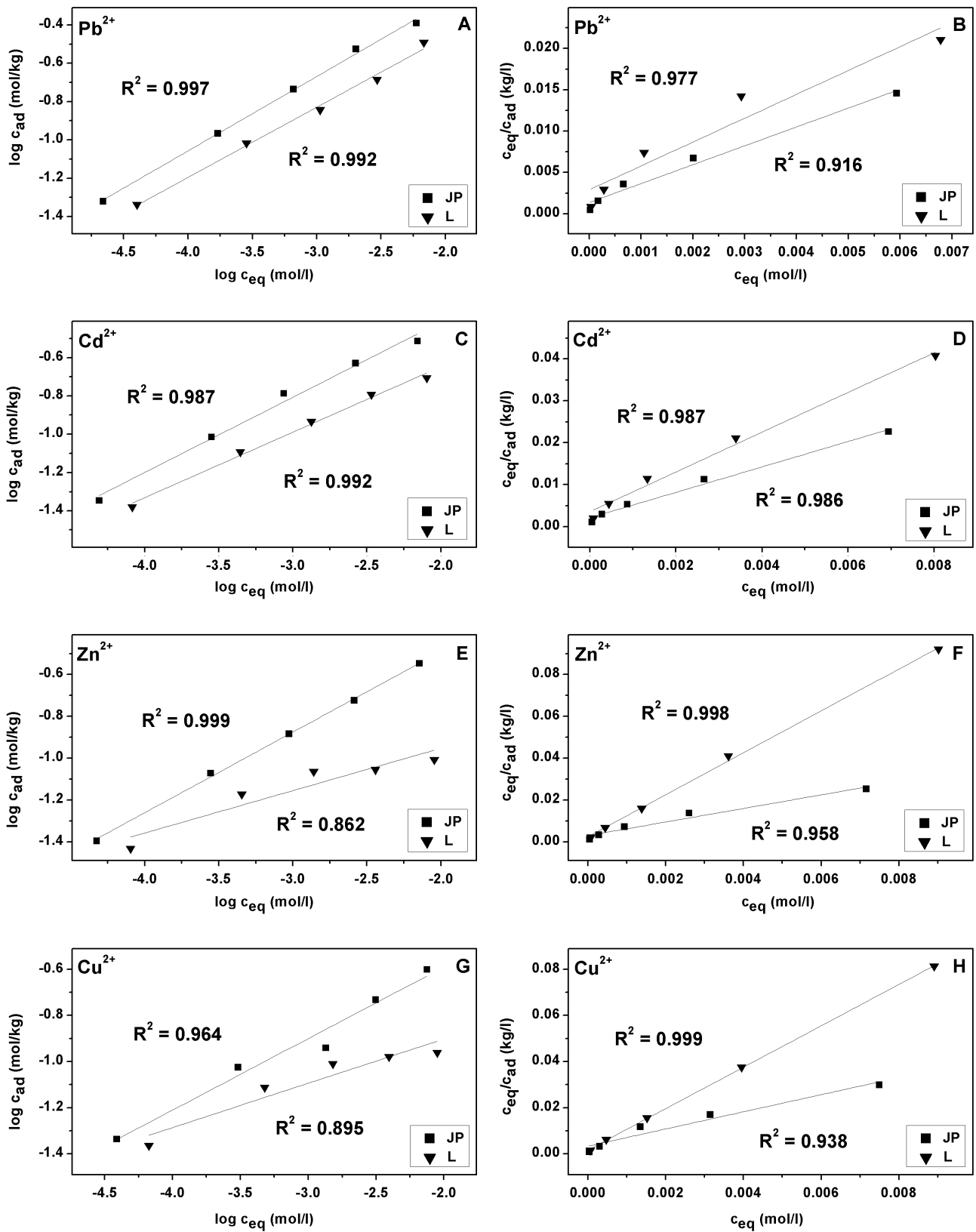
Fig. 4. Linear plots of Freundlich (left) and Langmuir (right) isotherms of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} adsorption on JP and L bentonites.
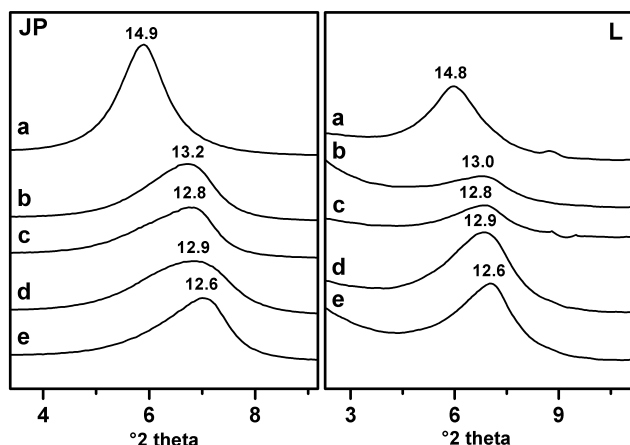
Fig. 5. Oriented XRD patterns of JP and L samples: (**a**) native samples, (**b**) Cd^{2+}-saturated, (**c**) Pb^{2+}-saturated, (**d**) Zn^{2+}-saturated and (**e**) Cu^{2+}-saturated, d_{001} values in Å.

Table 3: EDX analysis for Ca and Pb in JP and L, c is concentration of metal cations in initial solutions.

		JP					L				
$c/10^{-3}$ (mol/dm³)		10	5	2.5	1.25	0.5	10	5	2.5	1.25	0.5
Mass %	Ca	1.85	0.57	0.95	1.16	1.32	1.80	0.86	–	–	0.43	0.58	0.63
	Pb	–	6.72	5.53	3.64	2.45	1.04	–	3.64	2.77	3.00	1.99	0.58

The type of cation in the interlayer space of a smectite influences its d_{001} value. Figure 5 shows changes in interlayer distances after adsorption of individual heavy metals from the 0.01 M solutions for both clays. The d_{001} values decrease progressively from ~ 14.9 Å obtained for native samples with Ca^{2+} as the prevailing cation to values in the 12.6–13.2 Å range for smectites with heavy metal cations which are less hydrated than Ca^{2+}. These numbers are in accord with the data of Auboiroux et al. (1996) and Brigatti et al. (1995) for Pb^{2+} and Zn^{2+}-saturated Wyoming and Cheto montomorillonites, respectively. The change in d_{001} is a function ion exchange also depending on solution concentration or heavy metal cation content available for ion exchange. No changes in d_{001} values were observed after treatments with 0.0005 M solutions because of an insufficient amount of heavy metal cation to get adsorbed on montmorillonite and substitute substantial amount of Ca^{2+} in the interlayers, thus the final d_{001} of 14.9 Å was the same as that obtained for the parent Ca^{2+}-saturated montmorillonites.

Bentonites after adsorption of heavy metal cations were studied by EDX analysis to determine the contents of adsorbed cations. Table 3 provides data on Pb and Ca in the starting materials and samples treated in particular solutions. Ca^{2+} content in raw JP (1.85 %) was more than twice as high as in L (0.86 %). With increasing Pb^{2+} amount in solution, Pb contents in treated bentonites increased and Ca^{2+} decreased. As expected, more Pb^{2+} got adsorbed on JP than on L from solutions of all concentrations. No Ca^{2+} remained in L after Pb^{2+} adsorption from 0.01 M and 0.005 M solutions; it was quantitatively exchanged with Pb^{2+}.

Conclusions

The adsorption process of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} on both bentonites is feasible, spontaneous and exothermic in nature. Modified Langmuir and Freundlich equations are suitable to characterize the adsorption of heavy metal cations on the studied bentonites. The adsorption patterns of metal cations on JP and L bentonites are well fitted with the Langmuir and Freundlich models, providing slightly better fits for the Langmuir ($R^2 = 0.91$–0.99) than for the Freundlich ($R^2 = 0.86$–0.99) model. The greatest adsorption amounts are obtained on both bentonites for Pb^{2+}, followed by Cd^{2+} and Zn^{2+} or Cu^{2+}. Higher smectite content and higher cation exchange capacity are the crucial factors affecting the bentonite adsorption properties generally and causing the superior properties of the Jelšový Potok bentonite in comparison with the Lieskovec bentonite.

(1995) obtained for Cheto montmorillonite and for JP in a similar order except for the exchanged last two members: $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$.

K_d values were calculated according to the Henry isotherm model (Eq. 1) confirming monolayer adsorption of metal cations of low concentration in solution. As expected, K_d values decrease in the same order as $\Delta G°$ values $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ for 0.0005 M solutions and are higher for JP than for L. K_d values for 0.01 M solutions also decline in the same way as $\Delta G°$ values do in the order of $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ and $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$ for JP and L, respectively (Table 2).

The Freundlich adsorption capacity K_F is the highest for Pb^{2+}, with values of 3.15 and 1.87 mol/kg for JP and L, respectively. L has comparable values of K_F for Zn^{2+} and Cu^{2+} of 0.28 and 0.30 mol/kg, respectively. The K_F values decrease for JP in the order $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ while for L in order $Pb^{2+} > Cd^{2+} > Cu^{2+} \geq Zn^{2+}$. Moreover, the Freundlich coefficients 1/n are lower than 1 and indicate that the adsorption of all heavy metal cations on JP and L is favourable under the studied conditions.

Sorption capacity values (K_L) provide information on maximal sorption capacity of the materials in given conditions. Both bentonites have maximum sorption capacities for Pb^{2+}, 0.44 mol/kg and 0.35 mol/kg for JP and L, respectively. The lowest K_L has L for Zn^{2+} (0.10 mol/kg) and JP for Cu^{2+} (0.27 mol/kg). K_L values decrease for JP and L in the same order as K_F values: $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ and $Pb^{2+} > Cd^{2+} > Cu^{2+} \geq Zn^{2+}$, respectively.

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