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Immobilization of Heavy Metal Ions on Coals and Carbons

Boleslav Taraba and Roman Maršálek
University of Ostrava
Czech Republic

1. Introduction

Adsorption of heavy metals from the aqueous phase is a very important and attractive separation techniques because of its ease and the ease in the recovery of the loaded adsorbent. For treatment of waste as well as drinking water, activated carbons are widely used (Machida et al., 2005; Guo et al., 2010). Due to an increasing demand on thorough purification of water, there is a great need to search for cheaper and more effective adsorbents. Thus, alternative resources for manufacturing affordable activated carbons are extensively examined (e.g. Guo et al., 2010; Qiu et al., 2008; Giraldo-Gutierrez & Moreno-Pirajan, 2008). Simultaneously, natural coals are investigated as economically accessible and efficient adsorbents to remove heavy metals (Kuhr et al., 1997; Zeledon-Toruno et al., 2005; Mohan & Chander, 2006).

Radovic et al. (2001) published a principal comprehensive review of the adsorption from aqueous solutions on carbons with incredible 777 references. Their analytical survey covers adsorption of both organic and inorganic compounds (including heavy metals) and, certainly, it remains a basic source of information on the topics.

This chapter is concerned with the immobilization of heavy metals on carbonaceous surfaces, and, it attempts to compare adsorption behaviour of activated carbons with that of natural coals. Here, references published in the last decade are mainly reported, the literature findings being immediately confronted with experimental data as obtained from laboratory examinations of two natural coals. First, a brief insight into adsorption kinetics is given, followed by a survey of models to describe adsorption at equilibrium. The issue of thermodynamics of heavy metals adsorption follows. Finally, the possible immobilization mechanisms of heavy metals on carbons/coals are carefully considered and discussed.

2. Sample basis and experimental approaches

A sample of bituminous coals from the Upper Silesian Coal Basin (denoted as OC) and a sample of low rank subbituminous coal (SB) from the North Bohemian Coal District were investigated. Sample OC represents a type of oxidative altered bituminous coal, the occurrence of which is connected with changes in the development of coal seams underground. These changes are due to oxidation and thermal alteration processes, and they took place in the post-sedimentary geological past (Klika & Krausova, 1993). Because of increased content of oxygen, the oxidative altered bituminous coal should be of increased

ability in cation exchange. Thus, their potential to remove heavy metals from aqueous solutions is expected to be comparable with that of subbituminous coal SB, the effectiveness of low rank coals for heavy metals adsorption having already been reported (Kuhr et al., 1997). Basic analyses and properties of the coal are summarised in table 1.

	Sample OC	Sample SC
Ash content (%, dry basis)	11.5	8.0
Elemental composition		
C (%, daf basis)	76.6	74.4
H (%, daf basis)	4.1	6.5
N (%, daf basis)	1.8	1.0
O_{dif} (%, daf basis)	15.1	16.8
S_{total} (%, dry basis)	2.4	1.2
Textural parameters		
Surface area, BET (m^2/g)	1.5	49
Volume of micropores (ml/g)	0.084	0.055
Carbon aromaticity, f_C	0.97	0.50
Iso-electric point, pH_{IEP}	1.6	2.4
Mineral composition in ash (%)		
CaO	22.7	4.0
SiO_2	8.8	51.2
Al_2O_3	7.4	27.5
Fe_2O_3	21.9	6.4
MnO	0.1	0.01
MgO	3.3	0.8
TiO_2	0.1	3.2
V_2O_5	0.03	0.15

Table 1. Analyses and properties of the studied coal samples; BET surface areas were determined from adsorption isotherm of nitrogen at -196°C; volumes of micropores were evaluated from carbon dioxide isotherm at 25°C using Dubinin-Radushkevich model; carbon aromaticities were determined from ^{13}C CP/MAS NMR measurements using Bruker Avance 500 WB/US spectrometer (Germany) at 125 MHz frequency; pH values of iso-electric point were ascertained from zeta-potential measurements by Coulter Delsa 440 SX analyser (Coulter Electronic, USA)

Basic adsorption investigations were performed using lead(II) ion as a representative of heavy metals. Preferential adsorption ability of coals for heavy metals was studied with Cd(II), Cu(II) and Pb(II) cations (nitrate salts). Both for equilibrium adsorption and kinetics examinations, 0.5 g of dried sample (grain size 0.06-0.25 mm) was added to 50 mL of adsorbate solutions of initial concentration to be given. The suspensions were continuously (kinetics measurements) or occasionally (equilibrium adsorption) shaken. The pH value of each suspension was measured using a combination single-junction pH electrode with Ag/AgCl reference cell. Adsorption equilibration usually took 5 days. Then, the coal sample was removed by filtering through a paper filter. Metal concentration of filtered solutions was determined by means of the ICP optical emission spectrometry (Perkin-Elmer Optima 3000 spectrometer). All adsorption measurements were at least duplicated. In addition to

the basic measurements, some other experiments were performed and they are briefly reported in the appropriate sites of this chapter.

3. Kinetics of adsorption of heavy metals on coals and carbons

The study of adsorption kinetics is significant as it provides valuable information (at least) on time required for equilibration of the adsorption system. Thus (e.g. for adsorption of Pb(II) on activated carbons or coal), one can see in literature equilibration time elapsing from one hour (Imamoglu & Tekir, 2008) to two hours (Lao et al., 2005) to 48 hours (Song et al., 2010) or even up to 7 days (Giraldo-Gutierrez & Moreno-Pirajan; 2008). In a more detailed view, the kinetics of adsorption process on porous solid is controlled by three consecutive steps (Baniamerian et al., 2009; Mohan & Chander, 2006; Mohan et al., 2001): (i) transport of the adsorbate from the bulk solution to the film surrounding the adsorbent, (ii) diffusion from the film to the proper surface of adsorbent, and (iii) diffusion from the surface to the internal sites followed by adsorption immobilization on the active sites. Some authors aimed at expressing the kinetics of the individual diffusion steps (e.g. Oubagaranadin & Murthy, 2009; Qadeer & Hanif, 1994). In most cases, however, adsorption kinetics is considered as a global process. To express the adsorption kinetics quantitatively, three kinetic models are mainly used:

i. A simple first-order reaction kinetics (El-Shafey et al., 2002; Kuhr et al., 1997), which can be expressed generally as:

$$\ln(c_t) = \ln(c_o) - k_a \cdot t \quad (1)$$

where c_t is the concentration of metal ions to be adsorbed (mmol/L) at time t (min), c_0 is the initial concentration of the ions (mmol/L) and k_a is the rate constant of adsorption at given temperature (1/min). Plotting the $\ln(c_t)$ versus t, it is then possible to obtain a straight line with the slope corresponding to the value of rate constant k_a.

ii. The pseudo-first order kinetic model given by Lagergren equation (Eq. (2)), e.g. Boudrahem et al., 2009; Shibi & Anirudhan, 2006; Erenturk & Malkoc, 2007:

$$\ln(a_e - a_t) = \ln(a_e) - k \cdot t \quad (2)$$

where a_e and a_t are the adsorbed amounts of ions (mmol/g) at equilibrium time and any time t (min), respectively, and k is the rate constant of adsorption (1/min). Again, the rate constant k can be obtained from the slope of $\ln(a_e - a_t)$ versus t plots.

iii. The pseudo-second order model assuming the driving force for adsorption to be proportional to the available fraction of active sites (Oubagaranadin & Murthy, 2009). In the linear form the pseudo-second order rate equation can be expressed as:

$$t/a_t = 1/(k_2 \cdot a_e^2) + t/a_e \quad (3)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mmol.min). Its value can be determined experimentally (together with equlibrium adsorption capacity a_e) from the slope and intercept of plot t/a_t versus t (Li et al., 2009; Shibi & Anirudhan, 2006). As confirmed by the authors that applied several kinetic models to analyse experimental data, the pseudo-second order kinetics usually gives the tightest courses with the adsorption data to be measured (Erenturk & Malkoc, 2007; Li et al., 2009).

Our study of adsorption kinetics of lead(II) ions was performed on subbituminous and bituminous natural coals (SC and OC) at temperatures of 30 and 60°C. For the experiments, solutions with initial concentration of lead(II) ions = 5 mmol/L were used, sample grain size was 0.06 - 0.25 mm. Ratio between mass of the sample and volume of the lead(II) ions solution was 0.5 g/50 mL. Time elapsed during the measurements was 2.5 hours, each dependence being at least triplicated. For the initial stage of lead(II) adsorption, kinetics was found to satisfactorily follow a simple first-order reaction for both temperatures giving coefficients of determination R^2 better than 0.98, cf. fig 1.

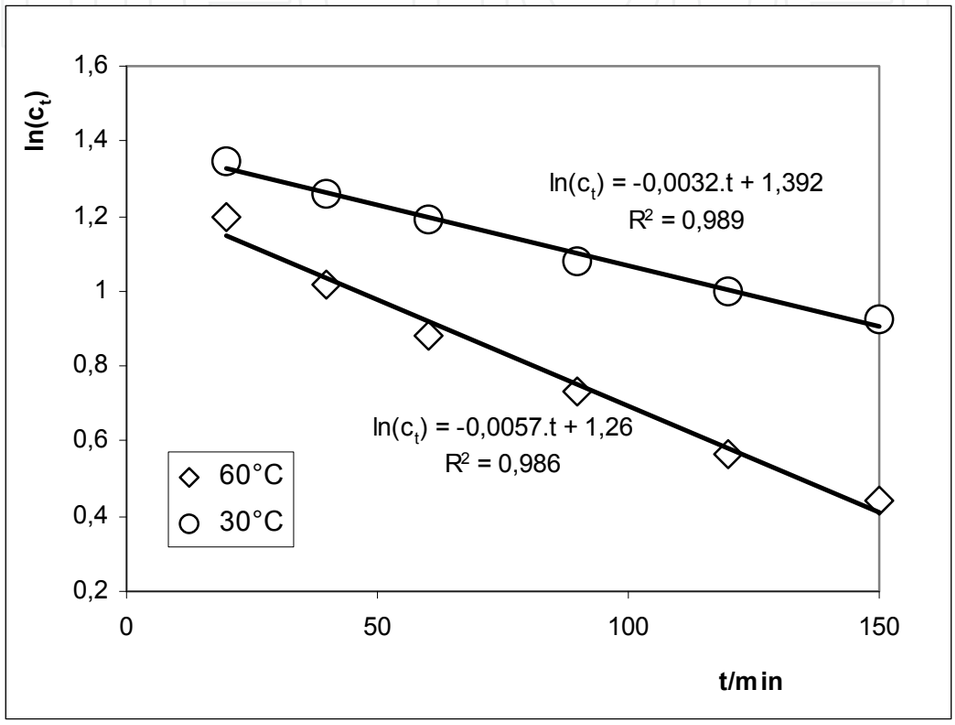


Fig. 1. Kinetic plots of lead(II) adsorption on bituminous coal OC, coal grain size 0.06-0.25 mm, initial concentration of lead(II) ions = 5 mmol/L

From the slopes of the linear plots $\ln(c_t)$ versus t, values of the adsorption rate constant k_a were calculated (see table 2).

Sample	Temperature	Rate konstant k_a (1/min)
SC	30°C	$(4.8 \pm 0.5) \cdot 10^{-4}$
	60°C	$(8.4 \pm 2.5) \cdot 10^{-4}$
OC	30°C	$(3.2 \pm 0.7) \cdot 10^{-3}$
	60°C	$(5.7 \pm 1.5) \cdot 10^{-3}$

Table 2. Rate constants as evaluated from kinetic measurements at 30 and 60°C

We are aware of difficulties in comparing such values of k_a with published data as they depend on experiment conditions, namely on the ratio between mass of adsorbent and the volume of metal solution. Nevertheless, using the Arrhenius equation, the knowledge of the adsorption rate constants at different temperatures enables us to estimate values of the

activation energy of lead(II) adsorption E. Thus, activation energies of 15.7 kJ/mol and 16.2 kJ/mol were found for sample of SC and OC, respectively. Such values of E correspond with the general view on energetics of the adsorption process (Adamson & Gast, 1997), and they are close to 17.1 kJ/mol obtained by Kuhr et al. (1997) for cobalt (II) adsorption on lignite. They are also quite comparable with activation energy 12.3 kJ/mol as was found by Li et al. (2009) for lead(II) adsorption on modified spent grain; however, their interpretation that "positive value of E suggests …the adsorption process is an endothermic in nature" is hardly acceptable.

4. Adsorption of heavy metals on coals/carbons at equilibrium

4.1 Adsorption isotherms

An overwhelming majority of authors correlate their data on metal ion sorption at equilibrium with the Langmuir adsorption model of monolayer coverage (e.g. Mohan & Chander, 2006; Oubagaranadin & Murthy, 2009). In a linear form, the Langmuir equation is given as:

$$c/a_e = c/a_m + 1/(a_m \cdot K) \tag{4}$$

where a_e is the equilibrated amount of the metal ion adsorbed at concentration c (mmol/L) of the ion in solution; K represents monolayer binding constant (L/mmol) and a_m is the monolayer adsorption capacity (mmol/g).

A similarly preferred model to analyse adsorption data, as that of Langmuir is the Freundlich isotherm (Li et al., 2005; Erenturk & Malkoc, 2007; Machida et al., 2005). It is also a two-parameter equation that can be, in the linearized form, presented as:

$$\ln(a_e) = (1/n) \cdot \ln(c) + \ln(K_F) \tag{5}$$

where n, K_F are the Freundlich constants. Constant K_F can be denoted as adsorption capacity (Erenturk & Malkoc, 2007; Machida et al., 2005), and its value corresponds to adsorbed amount in the solution with concentration c = 1 mmol/L.

In comparison with Langmuir and Freundlich models, further adsorption isotherms are used with considerably lower frequency. Thus, Sekar et al. (2004) or Erenturk & Malkoc (2007) correlated data on lead(II) adsorption using the Temkin isotherm:

$$a_e = B \cdot \ln(c) + B \cdot \ln(K_T) \tag{6}$$

where K_T is the Temkin constant and B is the parameter related with linear decrease in heat of the adsorption (Asnin et al., 2001). Similarly, also for adsorption of lead(II) ions, Oubagaranadin & Murthy (2009) or Li et al. (2009) used Dubinin-Radushkevich (D-R) isotherm:

$$\ln(a_e) = \ln(a_{mi}) - D \cdot \ln^2(1+(1/c)) \tag{7}$$

where a_{mi} is the D-R adsorption capacity (originally ascribed to adsorption in micropores, (Adamson & Gast, 1997)) and D is the constant related with free energy of adsorption.

In general, it should be stressed that all the above-mentioned adsorption isotherm equations (4) - (7) were originally developed for adsorption of gases (vapours) on solid surfaces (Adamson & Gast, 1997). Thus, their usage to analyse data on adsorption behaviour of metal ions on carbons/coals should be treated carefully, mainly as far as the physical meaning of

the obtained parameters is concerned. This can be demonstrated, for example, by evidently inconsistent values of adsorption heat of lead(II) ions on activated carbon as were published by Sekar et al. (2004). Namely, using parameter B from the Temkin equation (6), heats of adsorption between -125 and -302 J/mol were obtained. On the other hand, using thermodynamic analysis of the same adsorption system, they came to the value of adsorption heat +93 420 J/mol. The most valuable and widely used parameter from the above models is obviously adsorption capacity a_m derived from Langmuir isotherm (4) that enables to quantify adsorption potential of the carbons/coals to individual metal ions. However, also this parameter is certainly "valid for a very limited set of operating conditions (e.g., constant pH)" as pointed out by Radovic et al. (2000).

Based on our measurements of lead(II) equilibrium adsorption on bituminous coal OC at temperatures 30, 60 and 80°C, we have tried to compare consistency of the obtained data with the above-mentioned adsorption models (4) - (7). Experimental courses of the lead(II) adsorption isotherms are graphically presented in figure 2.

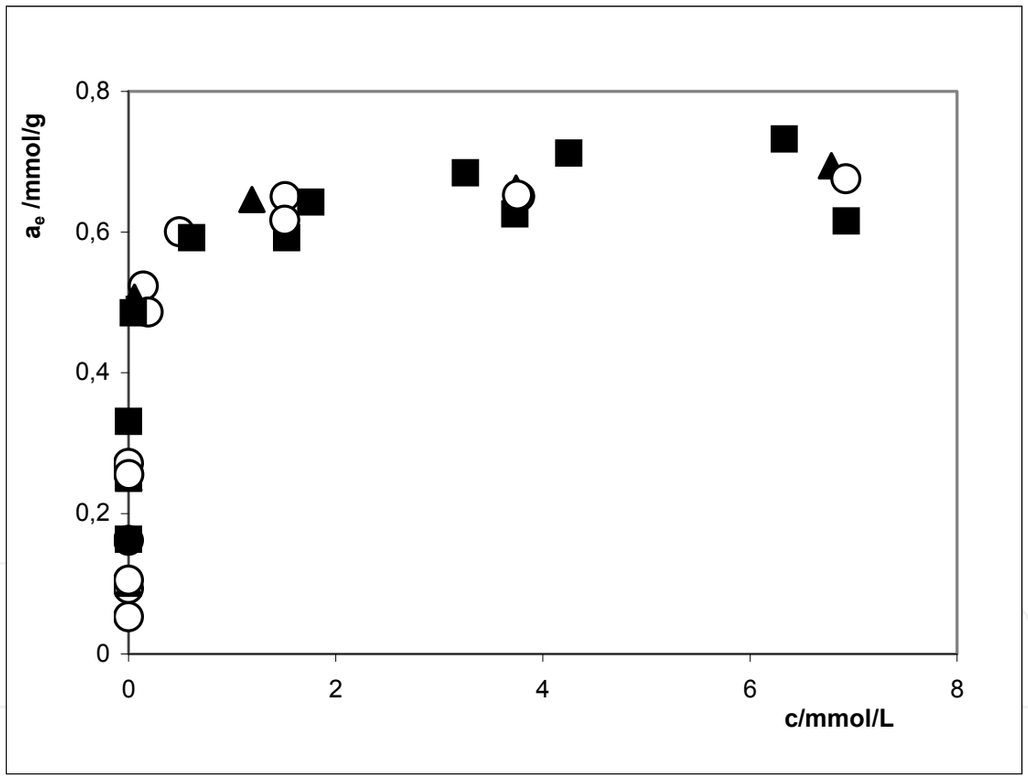


Fig. 2. Adsorption of lead(II) ions on bituminous coal OC at temperatures 30°C (■), 60°C (o) and 80°C (▲), coal grain size 0.06 – 0.25 mm, pH of solution at equilibrium 3.5, equilibration time 120 h.

Linearized forms of the isotherm equations (4) – (7) were applied to regression analysis of the adsorption data. Using the slopes and intercepts of the plots, the adsorption constants and model parameters were then evaluated. The values including coefficient of determination R^2 are given in table 3.

Isotherm type	Parameter	30°C	60°C	80°C
Langmuir	a_m (mmol/g)	0.69	0.67	0.69
	K (L/mmol)	14	27	25.5
	R^2	0.992	0.999	0.999
Freundlich	K_F (L/g)	0.60	0.59	0.58
	n	6.5	5.2	5.6
	R^2	0.872	0.880	0.850
Temkin	B	0.053	0.057	0.061
	K_T (L/g)	1.83	1.81	1.84
	R^2	0.970	0.975	0.962
Dubinin - Radushkevich	a_{mi} (mmol/g)	0.67	0.62	0.68
	D	0.0198	0.0199	0.032
	R^2	0.958	0.977	0.968

Table 3. Parameters of isotherm models, adsorption of lead(II) on coal OC (cf. Fig. 2)

As can be deduced from table 3, high values of the coefficient R^2 indicate practical applicability all of the above models. The equilibrium adsorption data are consistent mainly with the Langmuir model giving values of R^2 closest to 1. Conformity of the adsorption data with the Langmuir equation as the best fitting model is usually reported (Erenturk & Malkoc, 2007). However, we are aware that other sophisticated statistical approaches should be used to make the analysis more convincing (Boudrahem et al., 2009). With respect to the parameters resulting from the analysis, it is worth mentioning that the values of monolayer adsorption capacities a_m from Langmuir isotherm are consistent with adsorption capacities a_{mi} from the D-R equation. Simultaneously, they are quite comparable with values of adsorption capacities K_F of the Freundlich model indicating that the adsorption capacities are basically reached at equilibrium concentration c = 1 mmol/L, i.e. according to the shape, the isotherms can be denoted as those of the H-type (high affinity, Qadeer et al., 1993).

4.2 Preferential adsorption of metal ions

What type of metal ion is immobilized on carbon/coal surface more preferably than the other ones is a question of great practical importance. In this respect, the Irving-Williams series is often referred to, showing that the adsorption selectivity of ions follows the stability order of metal – ligand complex formation (Murakami et al., 2001; Kuhr et al. 1997). Guo et al. (2010) confirmed the adsorption of metal ions on carbons to proceed exclusively through surface complexation regarding the importance of acidic functional groups in the complexation reactions. However, published series of metal ions adsorption affinities differ for various types of carbon/coal. For example, for activated carbon from flax shive, El-Shafey et al. (2002) found the following sequence in adsorption capacities: Cu(II) > Pb(II) > Zn(II) > Cd(II). On the other hand, for poultry litter-based activated carbon, Guo et al. (2010) came to the series: Pb(II) > Cu(II) > Cd(II) ≈ Zn(II). Evidently, adsorption selectivity of the ions to carbons/coals should be perceived as a more complex problem reflecting both textural parameters of sorbents and ionic properties such as electronegativity, ionization potential and ionic radius (Lao et al., 2005).

Our experimental study was focused on adsorption selectivity of lead(II), cadmium(II) and copper(II) ions on bituminous coal OC. All the ions were supplied as nitrate salts. Single-ion solutions were applied for the adsorption equilibrium measurements. The obtained

isotherms were analysed using the Langmuir model (4). Adsorption potential for each ion was expressed using its adsorption capacity a_m. Data are summarised in table 4.

pH	Monolayer adsorption capacity, a_m (mmol/g)		
	Pb(II)	Cu(II)	Cd(II)
3	0.37	0.22	0.11
5	0.75	0.61	0.39

Table 4. Adsorption capacities a_m of metal ions on bituminous coal OC at temperature 22°C, coal grain size 0.06 – 0.25 mm.

From table 4, it is obvious that sorption capacities for the ions are in the order of Pb(II) > Cu(II) > Cd(II). The same order could be expected for competitive sorption of the ions from their mixture in solution (Rao et al., 2007). An identical sequence of the three metals was found by Guo et al. (2010) for litter-based activated carbon, and it also agrees with the order published by Rao et al. (2007) for carbon nanotubes.

To elucidate different adsorption behaviour of lead(II), cadmium(II) and copper(II) ions from the point of varieties present in the solutions, we have performed species analysis. Namely, based on the values of the proper stability constants, percentages of hydrolyzed [$Me(OH)^+$] and nitrate [$Me(NO_3)^+$, $Me(NO_3)_2$] species of the studied ions were evaluated. Thus, at a pH of 5, concentrations of hydrolyzed species of all ions were found to be insignificant, with $Me(OH)^+ < 0.2$ %. Similarly, only small amounts of dinitrate species ($Me(NO_3)_2 < 0.8$ %) were ascertained for the ions at maximum concentration of nitrate anions in the solutions to be investigated, i.e. at $(NO_3)^- = 0.02$ mol/L. More significant contents were found only for mononitrate complexes $Me(NO_3)^+$, namely, $Cu(NO_3)^+ \cong Cd(NO_3)^+ \cong 6$ %, and $Pb(NO_3)^+ \cong 23$ %. Thus, evidently, hydrated forms of "free" metallic ions predominate in the solutions with percentages of about 93% for Cu(II) and/or Cd(II) ions, and 76 % for Pb(II). According to the most probable hydration numbers of the ions (Marcus, 1997), the following hydrated species appear to be mainly present in the solutions: $Cu(H_2O)_{10}$, $Cd(H_2O)_{7\text{-}11}$ and $Pb(H_2O)_6$. From this point of view, the greatest adsorption capacity observed for lead could relate to its small hydration shell, the loss of which (during adsorption process) consumes the smallest enthalpic effect in comparison with the other hydrated cations (1572 kJ/mol instead of 1833 and 2123 kJ/mol for $Cd(H_20)_{7\text{-}11}$ and $Cu(H_20)_{10}$, respectively (Marcus, 1997)).

Finally, within the section, we have compared the adsorption potential of the different carbons/coals for heavy metals as were found in the literature. As a representative of the heavy metals, lead(II) ion was chosen because of its evident affinity to carbonaceous surface. Simultaneously, the adsorption behaviour of this very metal ion has been frequently reported in literature (e.g. Machida et al., 2005; Song et al., 2010; Li et al., 2009). Such a comparison is summarised in table 5, adsorption potential of the carbon/coal for lead(II) ion being expressed (again) by monolayer adsorption capacity a_m as evaluated from the Langmuir isotherm.

In general, lower adsorption capacities of activated carbons than those of natural coals can be deduced from the table 5. However, both coals referred to (Leonardite, sample OC) should be stressed to represent low rank coal types with an increased ability to immobilize metal ions. A closer look into the question will be given within section 6 of this chapter.

Sorbent	pH	d (mm)	t (°C)	a_m mmol/g)	Reference
AC from sal wood	4	-	30	0.04	Oubagaranadin, 2009
Modified spent grain	5.5	< 0.355	25	0.165	Li et al., 2009
Coal-based AC	5.5	0.125-0.25	25	0.15	Machida et al., 2005
Oak-based charcoal	5.5	0.125-0.25	25	0.096	Machida et al., 2005
Coconut-based AC	5.8	< 60 mesh	25	0.11	Song et al., 2010
AC from coffee res.	5.5	< 0.063	25	0.31	Boudraham et al., 2009
AC from hazelnut husk	5.7	0.5 - 2	18	0.063	Imamoglu et al., 2008
AC from sugar cane husk	5	0.2 – 0.3	Lab.	0.41	Giraldo-Gutierrez, 2008
Low rank coal -Leonardite	5-6	0.09 – 0.2	Lab.	1.21	Lao et al., 2005
Bituminous coal (OC)	5	0.06–0.25	22	0.75	This study (cf. table 3)

Table 5. Comparison of carbons/coals abilities to lead(II) adsorption as published in the literature, d – grain size diameter, t – temperature, a_m – monolayer adsorption capacity, AC – activated carbon

5. Thermodynamics of heavy metals adsorption

Thermodynamic analysis should provide information on the energetics of the adsorption process. As basic thermodynamic parameters, changes in Gibbs energy ΔG (J/mol), enthalpy ΔH (J/mol) and in entropy ΔS (J/(mol · K)) for the adsorption process are usually calculated. As a rule, such calculations arise from fundamental thermodynamic equation for Gibbs energy:

$$\Delta G = - R \cdot T \cdot \ln(K_a) \tag{8}$$

where R is the universal gas constant (8.314 J/(mol K), T is temperature (K) and K_a is the thermodynamic equilibrium constant.

Enthalpy change ΔH and change in entropy ΔS is possible to evaluate from the slope, respectively from the intercept of the linearized dependence of equilibrium constant K_a on temperature in coordinates ln(K) versus 1/T:

$$\ln(K_a) = - \Delta H/(R \cdot T) + \Delta S/R \tag{9}$$

Formula (9) is known as van´t Hoff equation, and it was derived provided that ΔH as well as ΔS are invariables within the temperature interval to be studied.

Both of the above equations (8) and (9) deal with thermodynamic equilibrium constant K_a of the adsorption process. Thus, of course, the result of such thermodynamic analysis strongly depends on reliability of the K_a determination. In literature, several possibilities to evaluate the equilibrium constant of adsorption have been published; however, not one of them was generally accepted and recommended for such thermodynamic analyses.

As equilibrium constant K_a, most of the authors accept the value of the Langmuir constant K ascertained from the Langmuir model applied to equilibrium adsorption data (Kuo, 2009; Mohan et al., 2001; Shibi & Anirudhan, 2006; Kuhr et al., 1997; Mohan & Chander, 2006). Although the "proper" thermodynamic equilibrium constant K_a should be dimensionless, Klucakova & Pekar (2006) indicate the way how to consider the Langmuir constant (with usual dimension L/mmol, cf. eq. (4)) even for the thermodynamic analysis.

Another approach to estimate the value of equilibrium constant K_a arises from determination of the ratio (denoted also as distribution coefficient K_D) between adsorbed amount a_e and concentration c of the metal ion in equilibrium, $a_e/c = K_D$ (Li et al., 2009; Erenturk & Malkoc, 2007). However, a more sophisticated procedure to estimate equilibrium constant K_a using the coefficient K_D appears to be plot a_e/c versus a_e and extrapolate it to zero a_e. The approach was used by Li et al. (2005) and Sekar et al. (2004) for thermodynamic analysis of lead(II) adsorption.

As resulted from the literature studied, analyses of all adsorption systems confirmed negative values of changes in Gibbs energy giving thus thermodynamic evidence of feasibility and spontaneous nature of metal ions adsorption on carbons/coal. Concerning changes in enthalpy ΔH and entropy ΔS, however, the situation is not so clear. Practically only for immobilization of mercury(II) on activated carbon (Mohan et al., 2001), the adsorption was confirmed to be exothermic (ΔH= - 23.6 kJ/mol) and entropy decreasing (ΔS = - 20.5 kJ/mol·K [sic]) process. In principle, such changes in enthalpy and entropy are consistent with the "classical" view on the thermodynamics of the adsorption process. For all other cases, adsorption of metal ions was found to cause an increase in entropy with values of ΔS from + 26 J/mol · K (adsorption of Pb(II) on carbon nanotubes, Li et al., 2005) to + 312 J/mol·K (adsorption of Pb(II) on activated carbon, Sekar et al., 2004). As a rule, the positive value of ΔS is explained by increased randomness at the solid-solution interface during adsorption of the metal ion on a carbon/coal surface (Li et al., 2009; Erenturk & Malkoc, 2007; etc.). On the other hand, it is not so easy to explain endothermicity of the process, as was thermodynamically confirmed e.g. for adsorption of Cu(II) ions (Kuo, 2009), Fe(II) ions (Mohan & Chander, 2006), Cd(II) ions (Shibi & Anirudhan, 2006) or Pb(II) ions (Li et al., 2005; Sekar et al., 2004; etc.). Most of the authors give no comment to the finding. Erenturk & Malkoc (2007) as did Qadeer et al. (1993) see the reason of the endothermicity in the change of hydration shells in the environment of the adsorbed and non-adsorbed metal ions. However, as Radovic et al. (2001) indicate, the solution of the aspect appears to be more complicated.

Our study in the field consisted in thermodynamic analysis of the experimental data on Pb(II) ions adsorption on bituminous coal sample OC at temperatures 30, 60 and 80°C (cf. fig. 2). In addition, we have explored our experience with calorimetric techniques, and we have measured values of adsorption enthalpy ΔH to make their comparison with calculated ones possible.

The usage of Langmuir constants K as values of equilibrium constants for the thermodynamic analysis of the Pb(II) ions adsorption on OC sample unfortunately failed. The reason was an unconvincing (non-monotonous) trend in the Langmuir constants with increasing temperature, see table 3. Thus, as equilibrium constants at given temperatures, extrapolated values of a_e/c to zero a_e were evaluated, according to Sekar et al. (2004). For better reading, the dependences of a_e/c versus a_e were plotted in coordinates $\ln(a_e/c)$ versus a_e , see figure 3.

In addition to the a_e/c versus a_e dependences, we have adapted the alternative approach to calculate the distribution coefficient reported earlier by Qadeer & Hanif (1994). Namely, instead of a_e/c extrapolation to zero a_e, ratios $(c_0 - c)/c$ were evaluated and extrapolated to zero uptake (c_0 is the initial concentration of the ions). A certain advantage of such a procedure can be seen in the dimensionless character of the obtained value of equilibrium constant K. Results of the thermodynamic analysis applied to Pb(II) ions adsorption on OC

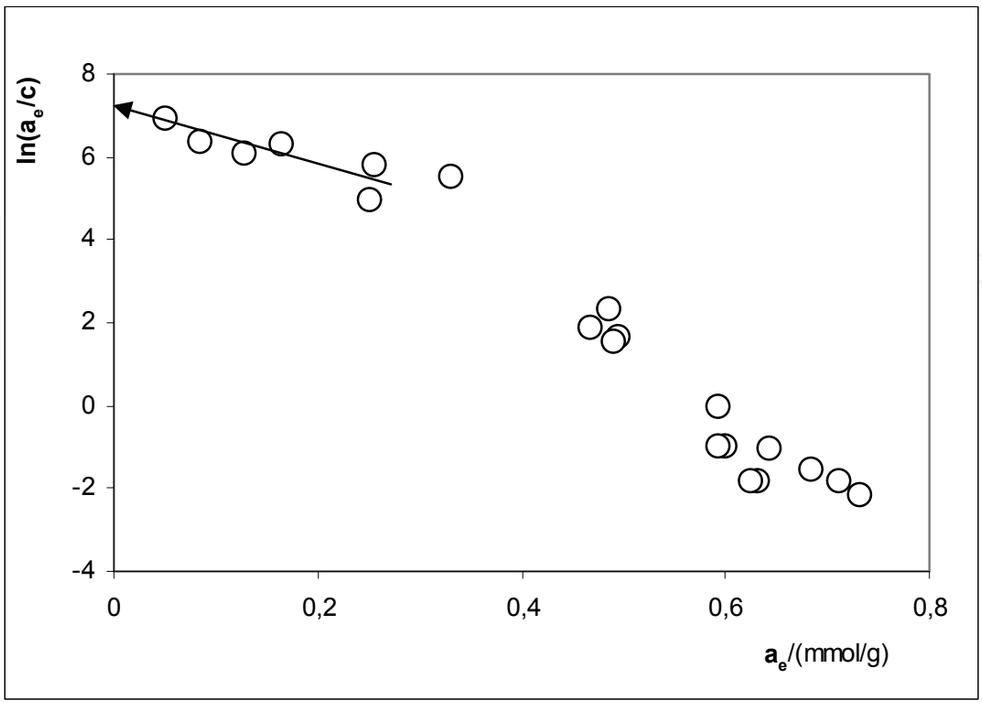


Fig. 3. Dependence of a_e/c versus a_e as obtained for lead(II) adsorption on sample OC at 30°C

sample using both the above-mentioned procedures are summarised in table 6. It is also worth mentioning that regression coefficients R^2 of the plots in coordinates ln(K) versus 1/T to evaluate enthalpy and entropy changes were 0.856 and 0.925, respectively.

	a_e/c extrapolated to $a_e = 0$				$(c_o - c)/c$ extrapolated to $a_e = 0$			
temp. °C	K L/g	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol·K	K	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol·K
30	1095	-17.5	- 28.5	-34.5	11000	-23.5	-30	- 20.5
60	665	-18			5500	-24		
80	200	-15.5			1900	-22		

Table 6. Thermodynamic analysis of Pb(II) ions adsorption on OC sample

Irrespective of the different values of "equilibrium constants" K, comparable values of changes both in enthalpy ΔH and (more or less) in entropy ΔS were obtained from the procedures. Quite opposite to the published data, however, values of both parameters were found to be evidently negative. In the context with literature that has been studied, it is the first time when adsorption of Pb(II) ions on carbonaceous surface proved to be exothermic.

In order to check the thermodynamic finding of exothermicity of Pb(II) ions adsorption, we have performed direct calorimetric determination of the adsorption enthalpy. For this purpose, a SETARAM C80 calorimeter equipped with percolation vessel was used. The flow calorimetric technique was adapted when the flow of water (percolating through sample) was changed for flow of Pb(II) ions solution. The corresponding heat effect (related to Pb(II) adsorption) was then determined. Subsequent changeover of Pb(II) ions solution flow back

for water flow then enabled to evaluate desorption heat of the Pb(II) ions from the sample. For the experiments, natural coal samples of OC and SC were used. In addition, a representative sample of activated carbons (denoted as HS3) was investigated. Typical shape of Pb(II) adsorption/desorption calorimetric curve as obtained for subbituminous coal SC is illustrated in figure 4.

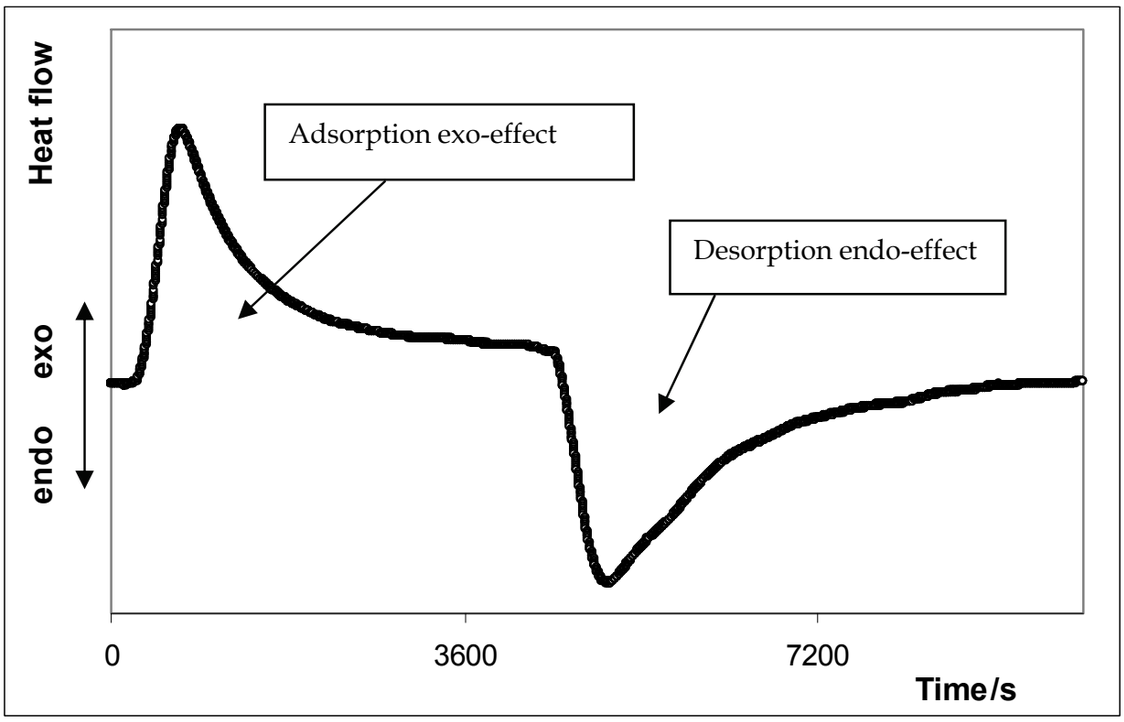


Fig. 4. Calorimetric curve of Pb(II) ions adsorption/desorption cycle ascertained for sample SC, grain size = 0.06 –0.25 mm, temperature = 30°C, Pb(II) ions concentration = 20 mmol/L, flow rate = 0.4 ml/min

No doubt, the performed calorimetric investigations clearly confirmed exothermicity of the Pb(II) ions adsorption (as well as endothermicity of the Pb(II) ions desorption process) for all investigated samples. Comparison of the calorimetric results with adsorbed amounts of the Pb(II) ions determined from adsorption isotherms then made it possible to estimate values of the molar enthalpy changes ΔH. The results are tabulated in table 7.

Sample	Adsorption heat J/g	Adsorbed amount mmol Pb(II)/g	Molar enthalpy ΔH kJ/mol
Coal sample OC	- 1.65	0.7	- 2.5
Coal sample SC	- 0.55	0.09	- 6
Activ. carbon HS3	- 6.3	0.21	- 30

Table 7. Values of molar enthalpy of Pb(II) ions adsorption as estimated from calorimetric and Pb(II) ions uptake measurements at 30°C.

Surprisingly low molar enthalpies for natural coals in comparison with ΔH of activated carbon are evident from the table 7, indicating quite different immobilization mechanisms of

the samples. For highly microporous activated carbon HS3 (volume of micropores = 0.48 mL/g, D-R isotherm of CO_2 adsorption), preferred adsorption in the micropores could be suggested. On the other hand, as will be discussed in more detail in the next section, interaction of the Pb(II) ions with natural coals OC and SC is expected to proceed mainly through oxygen functional groups. Irrespective of the evident disagreement between calorimetrically determined values of ΔH and these calculated from thermodynamic analysis (table 6), the experimentally obtained enthalpies for natural coals OA and SC are quite comparable with values of ΔH as resulted from metal ion versus oxygen group simulations using a semiempirical method of quantum chemistry "INDO", $\Delta H \approx -3$ kJ/mol (Klucakova et al., 2000).

6. Considerations on immobilization mechanism of heavy metals on coals

Radovic et al. (2001) in their analytical review summarize that immobilization of metal ions on carbons is largely governed by electrostatic adsorbate-adsorbent interactions. At values of pH exceeding the level of iso-electric point of carbon (pH_{IEP}), carbonaceous surface gains negative charge and its interactions with positively charged metals begin to be of an attraction character. Thus is reflected a significant role of pH on metal ions uptake, an evident rise in adsorption capacity of carbons to metals with increasing pH being generally known. For analysed coals OC and SC in this case, the influence of pH on lead(II) uptake is illustrated by fig. 5.

As a type of the electrostatic interactions, mainly cation exchange is mentioned, even for range of pH above the value of the iso-electric point (Radovic et al., 2001). A governing role of the ion exchange was confirmed both for activated carbons (Sekar et al., 2004; El-Shafey et al., 2002) and coals (Murakami et al., 2001; Burns et al., 2004). In addition to cation exchange, other possible mechanisms for metal ion immobilization such as surface precipitation or physical adsorption have been mentioned (Le Cloirec & Faur-Brasquet, 2008; Mohan & Chander, 2006). However, as the most probable alternative to cation exchange, surface complexation of metals is referred to (Guo et al., 2010; Zeledon-Toruno et al., 2005; Klucakova et al., 2000). The question thus arises as to the proportion between the cation exchange and the other mechanisms taking part in metal ions immobilization on carbon/coal.

The original way to understand the actual role of the cation exchange offers measurement of the change in pH in adsorbate solution during equilibration process (Burns et al., 2004; El-Shafey et al., 2002; Klucakova & Pekar, 2006). Namely, in the case of exclusive cation exchange between bivalent metals Me(II) and protons H^+, twice the amount of protons should be released from carbon into solution in comparison with the metal uptake. Indeed, a value of 2 was found for adsorption of cadmium(II) both on activated carbon (El-Shafey et al., 2002) and on low-rank Australian coals at pH 6 (Burns et al., 2004). Mohan & Chander (2006) then showed that during the sorption of Fe(II), Mn(II) or Fe(III) ions on lignite, calcium ions were mainly released to the solution. In this case, the ratio between released ions and the metal(s) bound to lignite was proved to even exceed the theoretical value (Mohan & Chander, 2006). On the other hand, quite a low amount of released H^+ ions was found when copper(II) was adsorbed on lignite-based humic acids at pH 2.8 (Klucakova & Pekar, 2006), proving thus only a minor role of cation exchange. For cation exchange as well as surface complexation of metals, it is reasonable to expect that surface acidic oxygen-containing groups such as carboxyl or hydroxyl play a decisive role (Klucakova et al., 2000). Experimental findings that metal uptakes on carbons are of very tight correlations neither

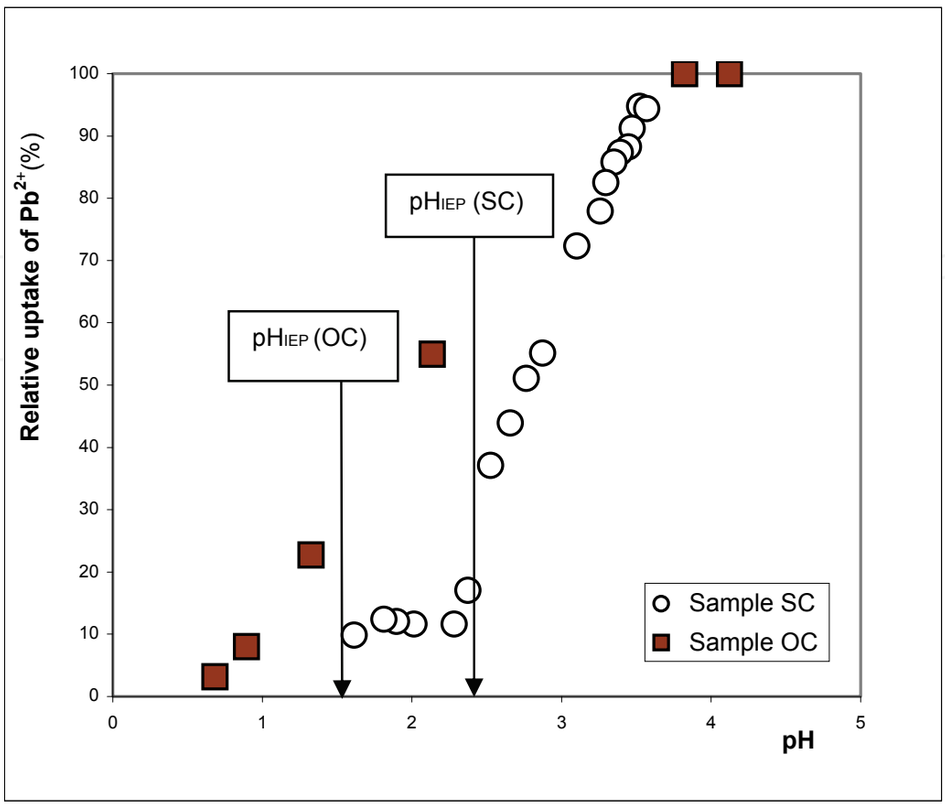


Fig. 5. Influence of pH on adsorption of lead(II) on coal samples SC and OC at 30°C; initial concentration of lead(II) nitrate was 1 mmol/L and 5 mmol/L, respectively; pH_{IEP} = value of iso-electric point

with specific surface area nor pore volume, but with the amount of the acidic oxygen functionalities thus support the leading role of these immobilization mechanisms (Song et al., 2010; Giraldo-Gutierrez & Moreno-Pirajan, 2008).

Our investigations of immobilization mechanisms focused on lead(II) adsorption on natural coals OC and SC. Namely, both the studied samples are of very similar elemental composition including oxygen content (see table 1). Infrared and ^{13}C CP/MAS NMR spectroscopies then confirmed hydroxyl and carboxyl groups as prevailing oxygen functionalities for both the sample. However, adsorption capacities a_m of the samples to lead(II) ions were found to be considerably different, giving values of 0.69 mmol/g for OC coal and 0.089 mmol/g for SC (at 30°C, pH 3.5). To elucidate the possible reason of the discrepancy, measurements of the pH changes in solutions during the lead(II) adsorption were performed first. With this respect, it is worth pointing out that before the adsorption measurements, the samples were repeatedly water leached in order to avoid release of other cations than H^+ during lead(II) adsorption. Experimentally obtained dependences of lead(II) uptake and H+ released from OC coal are demonstrated in figure 6.

Based on the measurements, average values of H^+/Pb(II) ratios were found to be 0.15 for the OC sample and 0.9 for SC coal, thus showing a more pronounced role of ion exchange for sample SC. Such a value for the SC sample indicates that a bit more than 50 % of lead(II) ions is immobilized by a way other than cation exchange. In this case, complexation fixation

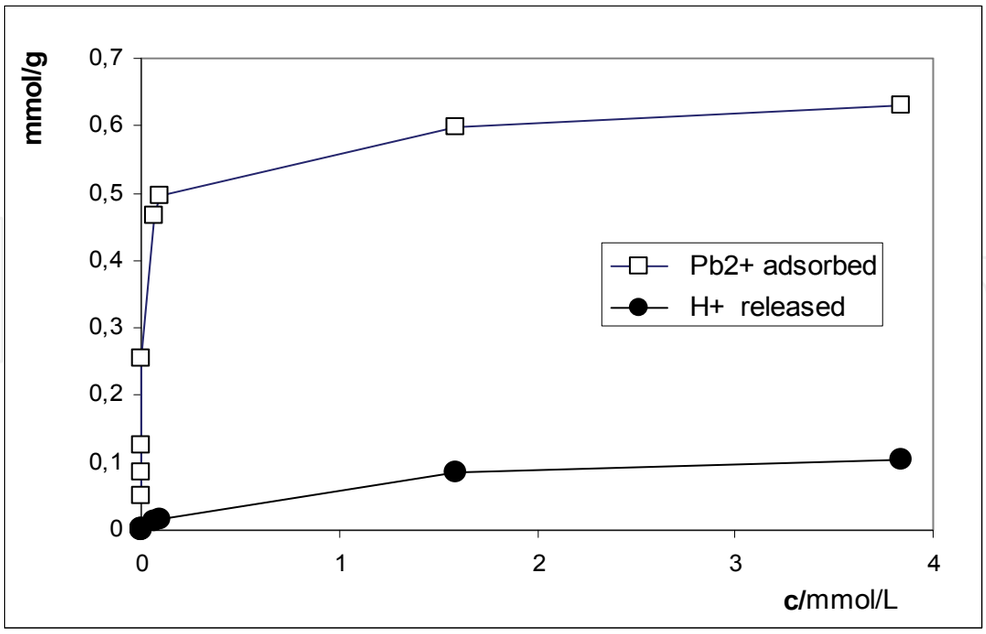


Fig. 6. Comparison between amounts of adsorbed lead(II) and H^+ released from OC coal, 30°C, initial pH = 4.2

of the ions appears to be the most probable alternative, simultaneous combination of both the immobilization mechanisms being already recognised (Klucakova et al., 2000). However, such an immobilization alternative can hardly explain about 90 % of cation non-exchanged lead(II) for sample OC. After some considerations on the possible influence of different aromaticity of the samples (see table 1), we have concluded that the reason of increased ability of OC sample to lead(II) probably lies in the composition of the inorganic parts of the sample. Namely, increased content of Mn and Mg oxides in ash of OC coal (see table 1) has been anticipated to be the main cause of the different adsorption behaviour of the coal, since these two very oxides were ascertained as effective solids for heavy metal adsorption (Machida et al., 2005). To recognize the role of ash in the lead(II) immobilization, adsorption measurements with ashes (0.15 g) prepared from both coal samples were performed at 30°C using the solutions of lead(II) at initial concentration 1.5 mmol/L (50 mL). Based on the investigations, markedly enlarged adsorption potential of OC ash for lead(II) was confirmed, more than one order exceeding that of SC ash. Namely, 0.58 mmol/g for OC ash instead of 0.032 mmol/g for SC ash was found to be adsorbed at equilibrium pH 4.
Thus, one can conclude that the differences in binding forces of the ashes toward Pb(II) were the main reason of the different adsorption behaviour of the coal samples.

7. Conclusion

Natural coals proved to have great potential in the immobilization of heavy metal ions with adsorption capacities usually exceeding the level of those referred for activated carbons. Especially for low rank coals of high ash, there is a possibility of synergy leading to a considerable increase in the adsorption affinity to heavy metals. The synergic effect results both from high concentration of oxygen functionalities on the coal surface and from the

propitious composition of the inorganic parts, namely the presence of metals such as Mg or Mn.

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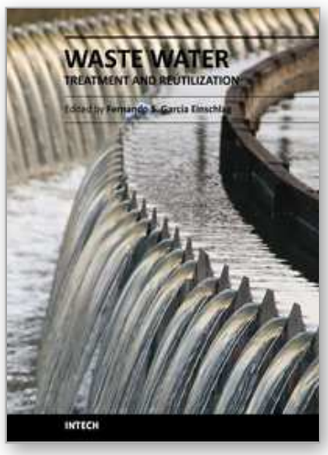
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51000 Rijeka, Croatia
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Unit 405, Office Block, Hotel Equatorial Shanghai
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
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