A high concentration of cadmium, copper and silver in waters has been identified as a potential health and environmental hazard (Cheremisinoff 1990, Enzminger 1993). The common methods of removal of metals from industrial wastewaters are chemical precipitation, electrolytic extraction, reverse osmosis, evaporative methods, ion exchange and many others (Allen and Brown 1995). The frequent method for decontamination of natural and industrial waters is the adsorption of metals by synthetic ion-exchangers (Enzminger 1993), activated carbons (Newcombe 1994, McKay 1996, Otova et al. 1997), or zeolites (Zamzow and Murphy 1992). Many workers have studied adsorption of soluble metallic species by clays, oxihydroxides or colloids. Khan et al. (1995) studied the adsorption of chromium and silver on bentonite. Fowle and Fein (1999) have studied the adsorption of metals by bacteria. However, these methods are all rather expensive, involving high-priced equipment and energy requirements. Therefore, there is a need for the development of more cost-effective methods. One perspective method is the exploitation of specific natural or industrial waste materials. McKay (1996) reported adsorption properties of activated carbon, peat, lignite or wood. Lignocellulosic materials (kenaf, alfalfa, juniper and aspen) were investigated by Han (1999). Their results show, that these materials are effective as adsorbents of metals (Cd, Cu, Ni, Zn). Removal of copper by apple residues from a solution was described in the report of Lee and Yang (1997). Numerous experiments carried out over many years have proved the suitability of peat and lignite for the improvement of natural waters (Gosset et al. 1986, Kadlec and Keoleian 1986). McLellan and Rock (1988) reported that adsorption of metals by peat increases with increasing metal concentrations and longer contact time. On the other hand, they recommended using peat for the pre-treatment process only.

The primary aim of this research was to determine the adsorption properties of the low-cost natural carbonaceous materials for adsorption of heavy metals from aqueous solutions. The twelve materials used in this study are oxygen-rich adsorbents, humic-rich adsorbents and carbon-rich adsorbents. The goal of this account of our research was to describe the adsorption properties in a continual series of materials, which differ in their degree of coalification, elemental composition, surface oxygen groups content, and structural properties.

MATERIAL AND METHODS

The studied materials were spruce wood, pine bark, cork, peat from Soběslav in Czech Republic (CZ) and coals of different degree of coalification. Brown coals were represented by fusinite, lignite, leonardite (all from Bílina, CZ). Fusinite is com-

Supported by the Ministry of Education, Youth and Sports of the Czech Republic, Project FRVŠ 1718.
posed of highly oxidised phytoclasts. Oxidation at Bílina is related to paleofires. Leonardite is highly oxidised form of lignite. Our sample represents paleoweathered coal. Other studied materials were: bituminous coal from Kladno (CZ) and anthracite from Lhotice (CZ). This series was completed with industrial carbon-rich materials: coke, activated carbon Filtrasorb F-400 and Multisorb\textsuperscript{TM} 100 (Multisorb\textsuperscript{TM} 100 is the peat-based adsorbent manufactured by PEATEC Corporation, USA). All materials were dried at laboratory temperature, disintegrated and sieved. The fraction size of 1–2 mm was used for all adsorption experiments and surface properties characterization. Fine fraction under 1 mm was used for elementary analyses. The elementary composition was determined by pyrolysis accompanied with measurements using a CarboErba microanalysator (Borkovcová et al. 1986). The relative amount of oxygen containing surface functional groups was determined by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded with Nicolet 740 spectrometer using the standard KBr pellet technique (Borkovcová et al. 1986). The relative amount of the carboxylic groups was obtained from the FTIR spectrum by integration of the area in the zone between 1500 and 1800/cm (Yang 1997). The cation exchangeable capacity (CEC) was determined in a leachate of 0.1M BaCl\textsubscript{2} (Plume 1990). The meso- and macroporosity were determined by high-pressure Hg porosimetry (Mayer and Stowe 1965). This method essentially consists of measuring the extent of mercury penetration into the evacuated solid as a function of applied hydrostatic pressure. The Porosimeter 2000 was used for this purpose. The surface area was measured by the Brunauer-Emmet-Teller (BET) method (Brunauer et al. 1938) with Sorptomatic 1800 CarloErba apparatus. The BET method is based on the measurement of nitrogen adsorption isotherm at the liquid N\textsubscript{2} temperature. Adsorption properties of carbonaceous adsorbents were investigated for interaction with toxic metals Cu, Cd and Ag. Solutions of metals were prepared by the dissolution of CdSO\textsubscript{4}, CuSO\textsubscript{4}.5 H\textsubscript{2}O and AgNO\textsubscript{3}. Initial concentrations of metals were chosen 50, 100 and 200 mg/l. The starting pH of solutions was equal to 5. The ionic strength of solution is the parameter affecting the adsorption. The ionic strength of solutions (0.1M) was adjusted using KClO\textsubscript{4}. The kinetic adsorption experiments were made with single component solutions to precede any interactions between metals. Five grams of each adsorbent were shaken with 100 ml of solution for 72 hours. The samples were taken for analysis (Atomic absorption spectrophotometer Varian SpectrAA-200) at regular intervals (0.5, 1, 2, 3, 4, 5, 15, 25, 35, 45, 60 and 72 hours) and pH was measured. The isotherm studies were provided for all materials discussed and the adsorption behaviour was calculated by using the Langmuir equation.

**RESULTS AND DISCUSSION**

**Textural analysis**

The textural properties of adsorbents are presented in Table 1. All investigated materials exhibited

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume of the pores (mm\textsuperscript{3}/g)</th>
<th>BET (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V_{\text{micro}})</td>
<td>(V_{\text{macro}})</td>
</tr>
<tr>
<td>Spruce wood</td>
<td>121</td>
<td>283.7</td>
</tr>
<tr>
<td>Pine bark</td>
<td>89</td>
<td>547.2</td>
</tr>
<tr>
<td>Cork</td>
<td>26</td>
<td>3757.0</td>
</tr>
<tr>
<td>Peat</td>
<td>220</td>
<td>859.2</td>
</tr>
<tr>
<td>Multisorb\textsuperscript{TM} 100</td>
<td>49</td>
<td>213.4</td>
</tr>
<tr>
<td>Lignite</td>
<td>57</td>
<td>45.9</td>
</tr>
<tr>
<td>Leonardite</td>
<td>45</td>
<td>99.9</td>
</tr>
<tr>
<td>Fusinite</td>
<td>112</td>
<td>45.9</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>74</td>
<td>213.4</td>
</tr>
<tr>
<td>Anthracite</td>
<td>64</td>
<td>95.5</td>
</tr>
<tr>
<td>Coke</td>
<td>37</td>
<td>55.5</td>
</tr>
<tr>
<td>Active carbon F-400</td>
<td>270</td>
<td>207.0</td>
</tr>
</tbody>
</table>
a low surface area with the exception of Calgon F-400 activated carbon. The Filtrasorb F-400 carbon is characterised also by important microporosity. Micropores (< 2 nm) and mesopores (2–50 nm) in F-400, in particular, are responsible for adsorption of metallic ions from solutions (Abbasi and Streat 1994). Nevertheless a high volume of micropores was observed for peat, spruce wood and fusinite (Table 1).

The volume of macropores (> 50 nm) was extremely high for cork. The only rate of transport processes in adsorbents is driven by macropores content. The textures of plant materials are macro-pore rich. There is a characteristic macroporosity with pores of about 20–50 micrometers in diameter. The shapes of pores are biologically determined. Open porosity is characteristic for peat and also Multisorb. The porosity of peat is given by a porosity of precursors. Low ranking coals are more compacted. Their pores are elongated and narrower than of previous materials. This feature is related to the development of micro-fractures during coalification. The texture of bituminous coal is created by a net of open pores. Open porosity is related to a high degree of coal transformation, but microporosity is still relatively low. The porosity of coke is not high. Pores are aligned to channels of less than 5 micrometers in diameter.

### Experimental results

Various kinds of wood-based, humic rich materials and coals can be used effectively to remove toxic heavy metals from solutions. Kinetic batch adsorption experiments were made. The decrease of metal concentration in treated solutions was observed for all natural adsorbents (Figure 1). The adsorption curves can be divided into two parts. First is a strong decrease during the first five hours and second is a slow reduction observed in a metal concentration for the next 67 hours. It can be explained by diffusion and transport processes within macropores and subsequently by slow transport within meso- and micropores (Peel and Benedek 1980, Abbasi and Streat 1994). Van Lier (1983) describes three steps of adsorption kinetics, which explains attaining equilibrium. The first step is transporting the bulk of the solution to the outer surface of the particles; the second step is transporting it into the interior of the particles. The third is the proper adsorption step.

### Elementary analysis

Results of elementary analysis are presented in Table 2. In the direction of coalification the carbon content increased. This increase was accompanied by a decrease in oxygen and hydrogen content. The lowest content of carbon was detected in the peat and the highest in the coke. In some materials clays can play an important role (peat and a variety of coal). The carboxylic groups content of leonardite was the highest from an overall series of investigated adsorbents. This enormous concentration of carboxylic groups is connected with a high degree of oxidation of this material and high humic acids content. The CEC of leonardite was also high (Table 2).

### Table 2. Chemical properties of the adsorbents (au = arbitrary unit)

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>H (%)</th>
<th>Ash (%)</th>
<th>COOH (au)</th>
<th>CEC (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce wood</td>
<td>45.13</td>
<td>47.08</td>
<td>0</td>
<td>6.48</td>
<td>1.31</td>
<td>0.38</td>
<td>8.62</td>
</tr>
<tr>
<td>Pine bark</td>
<td>48.80</td>
<td>42.03</td>
<td>0.19</td>
<td>5.79</td>
<td>3.19</td>
<td>0.81</td>
<td>8.75</td>
</tr>
<tr>
<td>Cork</td>
<td>53.56</td>
<td>37.01</td>
<td>0.66</td>
<td>6.85</td>
<td>1.92</td>
<td>0.59</td>
<td>17.77</td>
</tr>
<tr>
<td>Peat</td>
<td>37.58</td>
<td>34.98</td>
<td>1.49</td>
<td>4.48</td>
<td>21.47</td>
<td>4.03</td>
<td>37.88</td>
</tr>
<tr>
<td>Multisorb TM</td>
<td>45.55</td>
<td>35.52</td>
<td>2.56</td>
<td>5.57</td>
<td>10.80</td>
<td>3.84</td>
<td>47.47</td>
</tr>
<tr>
<td>Lignite</td>
<td>53.47</td>
<td>24.76</td>
<td>0.68</td>
<td>4.80</td>
<td>16.29</td>
<td>4.08</td>
<td>15.73</td>
</tr>
<tr>
<td>Leonardite</td>
<td>55.33</td>
<td>30.72</td>
<td>1.14</td>
<td>4.66</td>
<td>8.15</td>
<td>13.98</td>
<td>31.68</td>
</tr>
<tr>
<td>Fusinite</td>
<td>58.16</td>
<td>25.83</td>
<td>0.67</td>
<td>5.20</td>
<td>10.14</td>
<td>1.78</td>
<td>13.74</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>66.53</td>
<td>15.35</td>
<td>0.99</td>
<td>4.60</td>
<td>12.53</td>
<td>1.20</td>
<td>0.92</td>
</tr>
<tr>
<td>Anthracite</td>
<td>53.74</td>
<td>5.05</td>
<td>1.20</td>
<td>2.10</td>
<td>37.91</td>
<td>0</td>
<td>4.77</td>
</tr>
<tr>
<td>Coke</td>
<td>85.37</td>
<td>3.31</td>
<td>0.93</td>
<td>0.43</td>
<td>9.96</td>
<td>0</td>
<td>2.83</td>
</tr>
<tr>
<td>Active carbon F-400</td>
<td>83.61</td>
<td>8.89</td>
<td>0.32</td>
<td>0.91</td>
<td>6.27</td>
<td>0</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Figure 1: Adsorption behaviour for all metals

Because experiments were done without pH buffering, some exchange in pH was detected during equilibration. The knowledge of these pH modifications is useful for understanding the chemical interactions in solution during equilibration. Many adsorbents exhibited a strong decrease...
in pH from 5 to about 3 to 4. However, materials with high carbon content (anthracite, coke and activated carbon) exhibited an increase in pH to about 10–11.

Spruce wood and pine bark

The metal removal of milled spruce wood was relatively low (Figure 1). Remaining metal content after treatment was high for all initial concentrations. The adsorption capacity was the lowest of all materials examined. The adsorption efficiency of pine bark was slightly higher than that of spruce wood. Remaining concentrations of metals in the solution were lower in comparison with the spruce wood (Figure 1). Low adsorption capacity of the spruce wood and pine bark was related to the low COOH content and low BET-surface.

Spruce wood and pine bark is not acceptable for being used as adsorbent of toxic metals. However, it contradicts results of Teles de Vesconcelos and Beca (1994) for lead. Although Han (1999) emphasises that various wood-based fibres can be used to filter toxic heavy metals from stormwater (but the kenaf bast fibres only were unmodified; other materials were sulfonated). He concludes that hemicellulose and lignin make minimum contributions to ion exchange and hemicellulose and extractives are the major players. Chelation is another possible reaction in the presence of flavonoids.

Cork

Cork is the last unmodified plant material. The adsorption capacity was higher than that of the two previous materials. Chemisorption and physisorption are low because of very low COOH content and low BET-area.

Peat

This natural material was proposed as a very good adsorbent of all metals used. The adsorption was satisfying for all initial concentrations but the adsorption ability decreased with increasing concentrations of metals in the solution. Our results correlate with studies of Gosset et al. (1986) for adsorption of Cu, Cd, Zn and Ni. Kadlec and Keoleian (1986) also obtained comparable results for peat. Peat is a material with high amounts of humic substances and many oxygen-rich (mainly carboxylic) groups. They are able to dissociate, and released hydrogen can be exchanged for metal ions (Gosset et al. 1986). It also correlates with strong decrease in pH of solution during the adsorption. Moreover the CEC is high (Table 2). In view of this fact we can suppose that chemisorption plays a dominant role in metal recovery by peat.

Multisorb

Although Multisorb is a specially manufactured product obtained from peat, the adsorption capacity was comparable to raw peat. In the case of Ag the adsorption efficiency was higher than for peat, while for Cd and Cu it was slightly lower. Multisorb was identified as an excellent material to remove silver from solutions at higher concentrations (Figure 1). The COOH content was slightly lower than for peat and CEC was the highest from all materials used. The surface area was very small (< 1 m²/g) therefore a dominant process was chemisorption.

Lignite

Lignite exhibited a better capability to remove metals than all plant materials. Using lignite as adsorbent of metals from waters is advanced mainly for silver and copper at lower initial concentrations (lower than 200 mg/l). Lafferty and Hobday (1990) or Allen and Brown (1995) have stated that brown coal could be used for removing a range of metals from solutions. Lignite was characterised by a high content of oxygen-rich functional groups similar to Multisorb and its CEC was equal to 15.7 meq/100 g. The BET area was higher than this parameter of all raw biological materials (7.6 m²/g). In this case both chemisorption and physisorption are adsorption-driving mechanisms.

Leonardite

The adsorption capacity of leonardite for Ag and Cd was comparable to cork, however in the case of copper it was much higher. The adsorption of copper was comparable or slightly better than of activated carbon. The best adsorption of Cu was reached for lower initial concentrations of copper (50–100 mg/l). The carboxylic groups content was the highest in the overall series of investigated adsorbents. This enormous concentration of carboxylic groups is connected with a high degree of oxidation of this material and high content of humic acids. CEC of leonardite was also high (Table 2) and the BET surface area was relatively low. Hence chemisorption was the dominant process of adsorption. The ion exchange between metal ions and hydrogen ions released from surface groups was
accompanied by strong decrease in pH of solution during the equilibration.

**Fusinite**

The Ag and Cu removal in diluted solutions was only slightly lower for fusinite than for Multisorb. The adsorption of Cd was low (comparable to cork). The fusinite can be used as an adsorbent of metals from waters mainly for silver and copper at lower initial concentrations. The CEC of fusinite was about 13.7 mg/100 g (as with lignite) and a dominant role in ion exchange played ions Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\). The amount of COOH groups was medium and the BET area was equal to 6.3 m\(^2\)/g. Because of an insignificant number of carboxylic groups and amount of surface area, it cannot be determined which kind of adsorption (chemisorption or physisorption) was the driving mechanism.

**Bituminous coal**

This material was identified as a very bad medium for removing cadmium in all initial concentrations and copper in high concentrations (100 and 200 mg/l). Recovery of Ag was comparable to lignite. Bituminous coal displayed a relatively high BET surface area but the content of COOH groups was low. The CEC was negligible. In this case the physiosorption plays a significant role.

**Anthracite**

Anthracite was the second worst material for removing of Cd (nearly equal to bituminous coal). The recovery of Cu was comparable to cork. However, the extremely high efficiency was observed for silver. Overall low efficiency regarding Cd can be attributed to higher ionic radii of Cd in comparison to Cu or Ag. The content of carboxyls was undetectable and the surface area was relatively low (comparable to fusinite).

**Coke**

Coke can remove metals from solutions. The efficiency was excellent for Ag and diluted solutions of Cd and Cu. With an increasing initial concentration of Cd or Cu the efficiency decreased. It is evident (Table 1) that physiosorption (which is connected with the internal surface area) does not play any role in removing metals from solution. The BET area was under the detection limit for this material. The CEC can play a minor role but a possible mechanism is the precipitation of metal salts (shift in pH to 11). In solutions with pH > 10 begin the precipitation of otavite (CdCO\(_3\)) for example. The precipitation of new phases also gives account of the almost absolute recovery of silver, which was seen regarding coke and anthracite (mainly at lower initial concentrations).

**Activated carbon**

This globally-available material displayed unique adsorption properties for Ag and Cd in all concentrations. The efficiency in adsorption of Cu was identical to the efficiency of leonardite. Our studies show that activated carbon is the best adsorbent from an examined series of materials. Similar outcomes have been obtained by many authors (Corapcioglu and Huang 1987, Wilczak and Keinath 1993). It was discovered that activated carbon can remove silver, copper and cadmium from water (in concentrations of 50 to 200 mg/l) if the proportion of carbon/solution is 1/20. Adsorption properties of activated carbon are connected mainly to the high specific surface area of activated carbon (Table 1). Carboxyls were absent due to a high degree of carbonisation and the cation exchangeable capacity was very low. The adsorption properties of activated carbon are governed by physiosorption. Another possible mechanism of metal uptake could be the precipitation of new phases because of an observable increase in pH during equilibration.

The order of metals (in view of the adsorption affinity) was not the same for all materials. With oxygen-rich materials (spruce wood, pine bark, cork), leonardite and peat was the order: Cu > Cd > Ag. The order of adsorption Cu > Cd was in conformity with order of adsorption for humic acids (Kerndorff and Schnitzer 1980). About presence of humic acids in low carbonified materials we can infer from analysis of the carboxylic groups. Moreover, the order of adsorption capacity of lignite in a single-component system after Allen and Brown (1995) is identical (Cu > Zn > Cd). The majority of other adsorbents exhibit an affinity of adsorption for metals in the order Ag > Cu > Cd. Coke and activated carbon F-400 are characterised by this order: Ag ≥ Cd > Cu.

**Isotherm calculations**

Computer calculations of Langmuir isotherms including adsorption capacities of investigated materials were made. Calculations for spruce wood and pine bark show a low ability to adsorb cadmium and copper. Adsorption isotherms for adsorption...
of silver onto wood and bark are of the linear-type. With linear isotherm it is impossible to determine the maximal uptake (adsorption capacity). The highest adsorption capacities of all used metals were calculated for Multisorb (Figure 2). Despite the fact Multisorb is produced from peat, peat displayed a significantly lower capacity than Multisorb for all metals. Nevertheless peat displayed good results for silver and copper. The adsorption capacity for Ag of peat was similar to that of cork (Figure 2). The adsorption capacity of lignite was comparable to peat for Cu. Results for lignite, leonardite and fusinite for Ag were similar. The effectiveness of removing metal ions was the lowest in case of highly carbonified materials (bituminous coal, anthracite). Our results are in agreement with findings of Ong and Swanson (1966), who stated that the adsorption capacity of bituminous coal is much times less than that of the lignite. The adsorption capacity calculations of activated carbon were not done well because of the precipitation of metals in solution.

The findings of our laboratory studies are encouraging and should be applicable to potable and industrial wastewaters. Some natural materials (in view of good adsorption properties and low cost) can effectively substitute actually used adsorbents.

Acknowledgement

We would like to thank V. Machovič for his study of COOH groups and elementary analysis.

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Adsorpce mědi, kadmia a stříbra z vodních roztoků na přírodní uhlikaté materiály


Klíčová slova: adsorpce; měď; kadmium; stříbro; dřevo; rašelina; uhlí; aktivní uhlí

Corresponding author:

RNDr. Jan Jehlicka, Dr., Ústav geochemie, mineralogie a nerostných zdrojů, Přírodovědecká fakulta,
Univerzita Karlova, Albertov 6, 128 43 Praha 2, Česká republika
phone: + 420 221 951 503, fax: + 420 221 951 496, e-mail: jehlicka@natur.cuni.cz