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AFFINITY OF THE SOUTH MORAVIAN LIGNITE FOR FLUORIDE ANION

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Abstract
Adsorption-desorption behaviour of fluoride anion onto natural lignite is tested in a wide concentration range. The lignite shows a remarkable affinity for this ion. Fluoride bound is relatively tight, especially under low fluoride concentration that is, however, still above the limit for drinking waters. Natural lignite is a potential cost-effective defluoridation agent that could be used also for the in situ remediation of fluoride-contaminated soils

Keywords: fluoride, lignite, sorption

1. Introduction

Lignite represents the youngest type of coal. It belongs to caustobiolites, substances coalified to various degrees of the original phytomass. According to the degree of coalification lignite is found between the peat and brown coal on the scale. The fact that lignite is a relatively young caustobiolite is reflected by its outstanding qualitative properties, e.g. by its high sorption ability and relatively high content of humic acids.

The lignite is almost solely used as a lower quality fuel. Similarly to any coal burning, the lignite burning represents wastage of a valuable raw material[1]. Besides alternative use of the lignite after suitable chemical or physico-chemical transformations, it can be used outside the electrical power production industry also in its native state, which is the most cost-effective way. In this case specific surface properties of lignite particles or its relatively high contents of humic substances are exploited. Although, e.g., sorption capacity of untreated lignite may not be as high as that of thermally activated carbon materials, natural lignite may still has advantageous ratio price/efficacy. Various ecological technologies may serve as examples of the most important non-fuel applications of lignite. The lignite thus could undoubtedly serve as a material for treating or preventing ecological accidents.

Non-energy or non-fuel applications of the lignite should be based on its specific chemical and physical properties. Among them its remarkable surface activity, i.e. sorption ability has very important position. Studies on sorption properties of the lignite or coals in general are being continuously published. For example, Lakatos[2] studied various potential materials for the low-cost reactive barriers for environmental protection and their affinity for several heavy metal ions. Venkata Mohan et al.[3] investigated colour removal of trisazo direct dyes by charfines, lignite, bituminous coal and activated carbon. Pehlivan et al.[4] reported on adsorption and desorption of several heavy metals on three different lignite samples. Binding was only 5-30% reversible, indicating that ion exchange is not dominating. Hanzlík et al.[5] studied twelve carbonaceous materials, including the lignite and leonardite, for the adsorption of Cd, Cu and Ag. The best results were obtained for materials in an intermediate degree of carbonisation with a high adsorption of metals. McKay and Allen[6] give an overview of applications of low-cost adsorbents including lignite with an emphasis on the continuous processes. In our laboratory, sorption properties of the lignite mined in the South Moravia (Czech Republic) are studied[7, 8].

Fluoride anion, especially dissolved in water, belongs to the elements of potential risk for the environment or human health. Although it has positive effect on the protection of teeth, too high concentration becomes harmful. The optimum fluoride level in drinking water set by The World Health Organization is between 0.5 and 1.5 mg/l, concentrations above the 1.5 mg/l (i.e., about $7.9 \cdot 10^{-5}$ mol/l) can lead to fluorosis[9, 10]. Fluorides can penetrate into the environment from phosphate fertilizer plants, glass etching units, aluminum smelters, and the fluorine industry. Various approaches to the water defluoridation have been developed and published. The major techniques include precipitation, adsorption and ion exchange. Some of them, e.g. the precipitation, are not so effective at low, but still above the limit, fluoride concentrations (due to the relatively high solubility product), other may be cost-demanding. Studies on low-cost, effective defluoridation agents are being continuously reported[11-14].

This work reports on the first results from our study aimed at investigation of the South Moravian lignite affinity for the fluoride anion and potential application of the lignite as a defluoridation agent.

2. Experimental

Lignite from the Mikulčice locality (Czech Republic) was used throughout the study. Detailed characterization has been published elsewhere[15-17]. It was obtained as a crushed material and the fraction which was captured between the 0.1 and 0.2 mm sieves was used.

Adsorption and desorption experiments were done in a batch arrangement at the laboratory temperature (25±1°C). The lignite was weighted into a plastic centrifuge test tube and 10 ml of the fluoride solution were added. The suspension was shaken over the desired time period, the solid was then centrifuged and concentration of fluorides in the liquid supernatant was determined. If also desorption tests followed, then the solid in the test tube was washed with 5 ml of deionized water, centrifuged and 10 ml of deionized water were added to the solid residue. The suspension was then shaken over the desired time period and, after centrifugation, concentration of fluorides in the liquid phase was determined.

The concentration of fluorides was determined with the combined fluoride electrode (Theta’90, Czech Republic). TISAB buffer solution necessary for the fluoride determination was purchased also from Theta’90, sodium fluoride of p.a. quality from Fluka.

3. Results and discussion

In order to get overall information on the lignite affinity, as broad as possible fluoride concentration range was used, i.e. the range of the electrode used to determine the fluoride concentration. Preliminary experiments were done directly with the fluoride calibration solutions prepared in the TISAB solution. The residual concentration was examined after 24 h, 3, 4, and 7 days of the sorption. Although the majority of fluoride ions was adsorbed during the first day, here we report on 4-days results to ensure attaining sorption equilibrium. Figure 1 shows the relative uptake for solutions of different initial concentration of fluorides. The relative fluoride uptake increases with decreasing initial concentration and lignite turns out to be very effective sorbent especially at the low fluoride concentrations. Because of utilizing the TISAB solution, the pH of fluoride solutions was maintained between 5.1-5.3 during the sorptions.

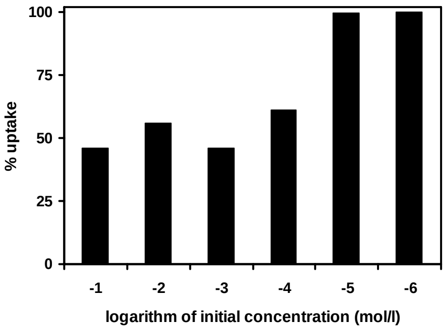

Fig. 1: Results of the fluoride sorption on lignite from the TISAB solutions of various concentrations

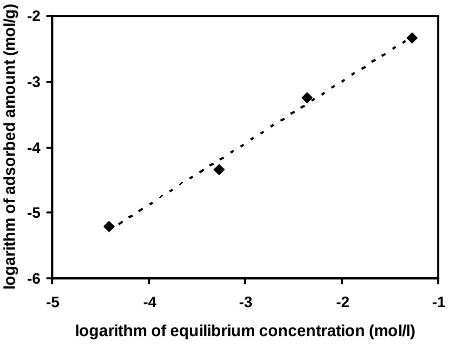

Fig. 2: Adsorption isotherm for the fluoride sorption on lignite from the TISAB solutions in the linearized Freundlich coordinates

Due to the wide concentration range it is not easy to present an illustrative figure of the adsorption isotherm. Surprisingly, the data did not show saturation of the lignite with the fluoride despite of its high concentrations tested. Specifically, the data do not correspond to the Langmuir adsorption isotherm whereas they can be fitted by the Freundlich isotherm as Figure 2 illustrates (the two points of the lowest concentration were excluded because the equilibrium concentration was below the detection limit). From the linearised fit the following equation of the adsorption isotherm was finally deduced: $a = 73.1\times10^{-3}c_{eq}^{0.938}$ (the adsorbed amount *a* is in mol/g, the equilibrium concentration c_{eq} in mol/l). Because the saturation sorption capacity has not been attained we can report only on the highest measured capacity, which was 4.6 mmol/g.

The promising preliminary tests continued in experiments which used solutions of NaF, i.e. the solutions free of buffering ions, in a little bit narrower concentration range that should be more relevant for practical applications. Figure 3 indicates that the percentage uptake is somewhat lower that in the preceding case but the lignite still remains an effective sorbent, especially at the low concentrations. The influence of other ions (from the TISAB solution) indicates that electrostatic interactions would have some (and positive) effect on the fluoride sorption, as expected, but their influence seems to be relatively modest. The data also do not indicate a saturation of the lignite surface, the highest measured sorption capacity was about 2.5 mmol/g.

The equilibrium data in the logarithmic form give not so good linear fit as in the preceding case, the squared correlation coefficient is 0.987comparing to 0.994 in the case of the sorption from the TISAB solutions. Freundlich isotherm becomes here: $a = 10.0\times10^{-3}c_{eq}^{0.668}$. An alternative and perhaps a better description is obtained with a double-linear fit especially in the linearized Langmuir coordinates (Figure 4) where the equilibrium concentration has been normalized to c_{eq}/a, as usual. This is an indication that there are two principal sites for the fluoride adsorption on the lignite surface. Estimated parameters of their adsorption isotherms are given in Table 1. The site operating preferably at low concentrations is stronger (high value of the equilibrium adsorption constant *K*) and of lower capacity than the site operating at higher concentrations.

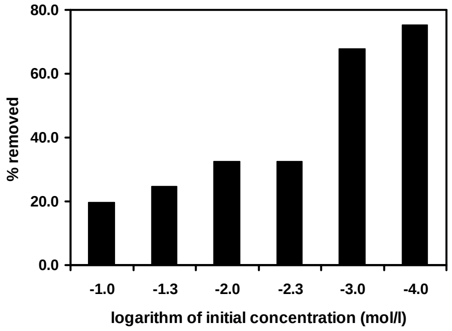

Fig. 3: Results of the fluoride sorption on lignite from the NaF solutions

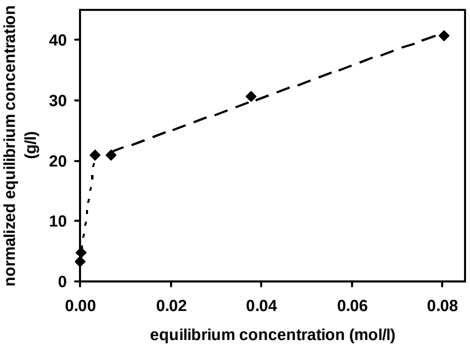

Fig. 4: Adsorption isotherms for the fluoride sorption on lignite from the NaF solutions in the linearized Langmuir coordinates

Table 1 Parameters of the two Langmuir isotherms fitted to the data on the sorption from NaF solution, cf. Figure 4

Parameter	Isotherm	
	1st	2nd
a_{max} (mmol/g)	0.191	3.73
K (l/mol)	1684	13.70

In this case no special provision to control solution pH was made. Therefore, the sorptions were made from the natural pH of fluoride solutions. After the fluoride sorption, pH decreased in about 0.3-0.7 units, indicating a decrease of hydroxyl ion concentration.

Our data indicate that the lignite maximum capacity for the fluoride anion should be in orders of milimols per one gram, at least, i.e. tens to hundreds of miligrams per one gram which is several times higher than reported for other types of carbonaceous sorbents[18].

After the sorption from the NaF solutions, desorption experiments started, i.e. back-leaching with deionized water. Results of 19-days leaching are given in Figure 5 and show that most of the adsorbed fluoride is tightly bounded to the lignite surface, especially at low concentrations, and that the fluoride adsorption is only partially reversible. The causes of the high lignite affinity to the fluoride anions are not fully explained. In general, the lignite surface contains many acidic functional groups, mainly of the carboxylic or phenolic types, that can definitely bound metal and hydrated metal ions in a variety of ways as confirmed by a detailed quantum chemistry modelling. However, binding of the fluoride ion with the opposite charge is not so clear-cut. Siwasamy et al.[18] suggest that fluoride can be bound to the coal surface by the ion exchange with the hydroxyl ions or through the hydrogen bonds to the hydrogen atoms of the surface functional groups. Ion exchange could be responsible for the reversible part of the fluoride adsorption but observed decrease of pH during the sorption does not indicate exchange with hydroxyls. The fluoride anion is known to form firm hydrogen bonds which could explain the irreversible part. Halogenide anions generally act as donors of electron pairs and form various complexes. Consequently, various forms of ligand binding on the lignite surface can be suggested participating probably both in the irreversible and reversible parts of the sorption. Interactions of the fluoride anion with carboxyl and phenolic groups attached to various model molecules would deserve computer modelling study similar to that published in the ref.[19].

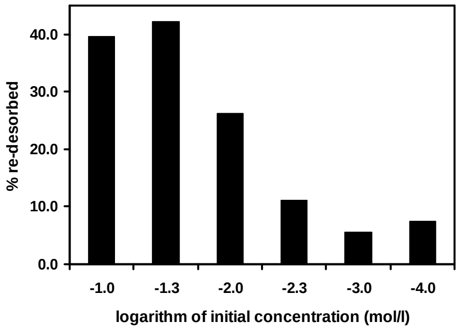

Fig. 5: Results of the fluoride leaching after its sorption on lignite from the NaF solutions

Finally, we tested the effect of the ratio lignite:fluoride solution on the efficacy of the fluoride removal. The experiments were made with NaF solutions containing 10^{-3} and 10^{-4} mol/l of the fluoride, i.e. the amounts slightly above the drinking water limit where other fluoride removal methods may not be effective. Results are given in Table 2 and confirm the high lignite efficiency especially in solutions of low fluoride concentration (but still above the limit).

Table 2 Effect of lignite:solution (10 ml) ratio on the sorption from NaF solutions of various concentrations

Lignite amount (g)	Initial concentration (mol/l)	% removed
0.5	10^{-3}	76.3
	10^{-4}	93.6
1	10^{-3}	89.9
	10^{-4}	99.9
2	10^{-3}	96.6
	10^{-4}	100.0

4. Conclusions

Lignite mined in the South Moravia region of the Czech Republic has a remarkable affinity for the fluoride anion, under various solution chemistries and in its natural state. The bound of fluoride to the lignite is relatively tight. The lignite is therefore a potential cost-effective defluoridation agent that could be used also for the in situ remediation of fluoride-contaminated soils where it can serve also as a soil organic matter and plant nutrition support due to its high contents of humic substances.

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References

[1] Pekař, M., Klučáková, M.: CHEMagazín 2003, 13(1), 8.
[2] Lakatos, J., Brown, S.D., Snape, C.E.: Fuel 2002, 81(5), 691.
[3] Mohan, S.V., Rao, N.C., Karthikeyan, J.: J. Hazard. Mater. 2002, 90(2), 189.
[4] Pehlivan, E., Richardson, A., Zuman, P.: Electroanalysis 2004, 16(16), 1292.
[5] Hanzlík, P., Jehlička, J., Weishauptová, Z., Šebek, O.: Plant Soil Environ. 2004, 50(6), 257.
[6] McKay, G., Allen, S.J.: Low-Cost Adsorbent in Continuous Processes. In Biosorbents for Metal Ions, Taylor&Francis: London, 1997, p. 183.
[7] Klučáková, M., Omelka, L.:Chem. Pap. 2004, 58(3), 170.
[8] Pekař, M., Klučáková, M.: Affinity of natural lignite for mercury and lead. In 9th Conference on Environment and Mineral Processing. Ostrava: VŠB-TU Ostrava, 2005, Part I, p. 93.
[9] Díaz-Nava, C., Solache-Ríos, M., Olguín, M.T.: Sep. Sci. Technol. 2003, 38(1), 131.
[10] Chubar, N.I., Samanidou, V.F., Kouts, V.S., Gallios, G.G., Kanibolotsky, V.A., Strelko, V.V., Zhuravlev, I.Z.: J. Colloid Interface Sci. 2005, 291(1), 67.
[11] Sinha, S., Pandey, K., Mohan, D., Singh, K.P.: Ind. Eng. Chem. Res. 2003, 42(26), 6911.
[12] Jamode, A.V., Jamode, V.S., Chandak, B.S., Rao, M.: Poll. Res. 2004, 23(2), 239.
[13] Jamode, A.V., Sapkal, V.S., Jamode, V.S.:J. Indian Inst. Sci. 2004, 84(5), 163.
[14] Fan, X., Parker, D.J., Smith, M.D.: Water Res. 2003, 37(20), 4929.
[15] Sýkorová, I., Michna, O.: Zesz. Nauk. Polit. Slas. 2001, 249, 177.
[16] Honěk, J. et al.: Trans. VŠB-Technical University Ostrava, Mining and Geology Series, Monograph 3, 2001, 47, 272 pp. (in Czech)
[17] Kučerík, J., Pekař, M., Klučáková, M.: Petroleum and Coal 2003, 45(1-2), 58.
[18] Sivasamy, A., Singh, K.P., Mohan, D., Maruthamuthu M.:J. Chem. Technol. Biotechnol. 2001, 76(7), 717.
[19] Klučáková, M., Pelikán, P., Lapčík, L., Lapčíková, B., Kučerík, J., Kaláb, M.: J. Polym. Mater. 2000, 17, 337.