

OXIDIZED LOW-RANK COALS - IN SITU IMMOBILIZED HUMIC SUBSTANCES

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Abstract

Properties of oxidized low-rank coals as potential low-cost sorbents of metal ions were investigated. Lignite coal from the Northern Bohemia with a defined range of grain size was oxidized on air at 140 °C for up to 200 hours to increase degree of oxygen functionalities (carboxylic and phenolic groups). For comparison, oxihumolite from the same locality and Aldrich humic acid were used. Influence of coal bitumen (the organic-soluble fraction) was investigated. Changes in composition and structure caused by the laboratory oxidation were studied by elemental analysis and DRIFT spectroscopy, respectively. Proton exchange capacities (PEC) and dissociation of functional groups of the samples were investigated by the Ba(OH)₂ method and potentiometric titration, solubility was checked by spectrophotometry. Sorption of Cs⁺, Co²⁺ and Eu³⁺ cations was studied by batch experiments using radiotracer method.

Introduction

Industrial technologies and energetics are connected with generation of enormous amounts of harmful environmental pollutants, and in agreement with safety regulations require new approaches to waste management. Technologies employed in treatment of waste streams are often expensive and/or insufficient. The nature of some wastes, namely long-life radionuclides, requires their long-term storage in suitable repositories which, in addition to the natural geological barriers within a repository site, need geochemical barriers based on suitable sorbents to immobilize the contaminants in case they penetrate through geotechnical barrier (tanks, vitrifying glass, etc.). Similarly, in situ permeable barriers based on sorbents have a potential for remediation of contaminated ground water. For large-scale use, these materials would be exceedingly expensive. Natural sorbents as zeolites, metal oxides, clays, coal, chitosan, etc. have been considered as promising inexpensive alternative (1). Partial solubility and/or insufficient mechanical stability of sorbent particles deteriorate their utilization especially for dynamic column operations. It is necessary to provide physical support, and preserve or increase accessibility of the binding sites.

Humic substances (HS) are a substantial component of natural organic matter produced by biomass degradation. The complex nature of interaction between cations and HS as heterogenous, polydispersive polyelectrolytes is given by the variety of functional groups (mainly carboxylic and phenolic) located in various chemical environments of the 3-D structure of a macromolecule, and ranges from purely electrostatic, non-specific interactions with the net negative charge on the surface of humic macromolecule to covalent, specific interactions, as in the formation of complexes and chelates with the functional groups (2). Solubility of HS precludes their use as sorbent material without suitable immobilization, although after acid precipitation and drying, humic acid (HA) is fairly stable even in mildly alkaline solutions. In situ immobilization of HS in matrix of low-rank coals, particularly post-sedimentary oxidized coals (oxihumolite or leonardite), represent one of the most abundant natural resources of immobilized HS, and potential low-cost sorbents of toxic metals and radionuclides for use in waste water treatment, groundwater remediation, and construction of active geochemical barriers (3). Since the supply of naturally oxidized coal is limited, it would be convenient to treat the more abundant energetic brown coals to obtain material with sorption properties comparable to oxihumolites. The sorption ability of coal is affected by several factors, as amount and acidity of the oxygen functionalities, their location within coal structure, size and swelling ability of coal particles, pore size distribution. Quantity and/or quality of the exchangeable functional groups can be altered by, e.g., oxidation increasing content of the oxygen functionalities, stripping off metal cations/protonation,

and sulfonation increasing the exchange capacity and extending the exchange range to lower pH. Extraction of the organic-soluble fraction, bitumen, can also affect the sorption properties by influence on the pore system. This work, in continuation of our previous study (4), has been aimed to investigate potential of artificially oxidized low-rank coal (lignite) as a low-cost sorbent of selected radionuclides, in comparison with oxihumolite produced naturally by postsedimentary oxidation of parent coal from the same seam.

Methods

Reagents and sample preparation. All solutions were prepared from analytical reagents without further purification, and ultrapure water. Samples were collected from seam Antonín (Sokolov Basin, Czech Republic) - lignite in Jiří mine, oxihumolite in Marie mine, sieved (0.3-0.5 mm, samples J0 and M, respectively). Sample J0 was oxidized on air at 140°C, samples were withdrawn after 24, 50, 80, 120 and 200 h (J24, J50, J80, J120, J200, respectively). All samples were protonized by 1M HCl. To study the role of bitumen, samples ME, JOE, M200E were prepared from samples M, J0 and J200, respectively, by extraction with toluene/ethanol (1:1) in Soxhlet extractor for 5 days. Aldrich humic acid (HA) was used, purified/protonated according to a procedure described in (5).

Elemental analysis. C, H, N, S were determined by standard methods, O was calculated by the difference.

DRIFT. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) utilized a Nicolet 740 spectrometer with a TGS detector and a Spectra Tech diffuse reflectance accessory. Each sample (50 mg) spectrum averaged 512 scans at resolution 2 cm⁻¹.

Titration methods. The proton exchange capacity (PEC) was determined by back titration of excess Ba(OH)₂ equilibrated in suspension (75 mg in 5 mL Ba(OH)₂, 0.1 M) with a sample. Dissociation of acidic functional groups was studied by potentiometric titration using a Radiometer Titralab 80 automatic titrator. Suspension of a sample (150 mg in 30 mL, *I* = 0.1 by NaClO₄) was titrated with 0.1 M NaOH under nitrogen in a cell thermostated at 25 °C, at dosing rate 40 μl per 5 min.

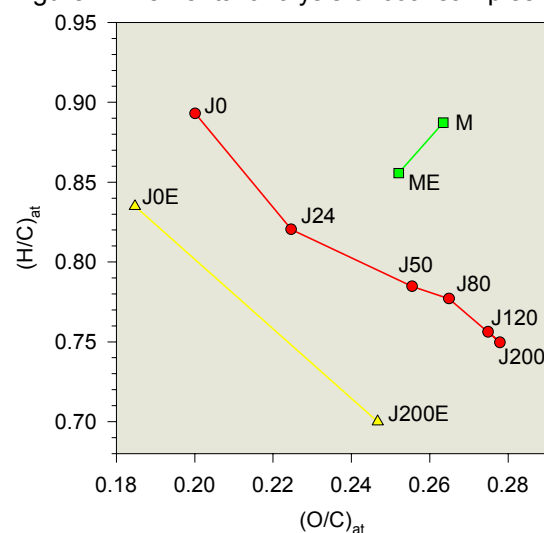
Spectrophotometry. Leaching of HS from the samples was checked by measuring absorbance ($\lambda=254$ nm) of the solution sampled after centrifugation, in quartz cuvettes, after suitable dilution.

Sorption experiments. Batch experiments were performed with radiotracers ¹³⁴Cs, ⁶⁰Co, ¹⁵²Eu (simultaneously) under following conditions: V/m = 100 mL/g, *I* = 0.1 (NaNO₃), Cs, Co and Eu concentration 2.4×10⁻⁵, 2.2×10⁻⁵, 1.6×10⁻⁶ M, respectively, 24 h shaking. Effect of pH was studied. Centrifugation (3500 rpm, 15 min) was used to separate phases. Activities in solution were determined by γ -spectrometry measuring the analytical lines at 122, 605 and 1173 keV for ¹⁵²Eu, ¹³⁴Cs and ⁶⁰Co, respectively.

Results and Discussion

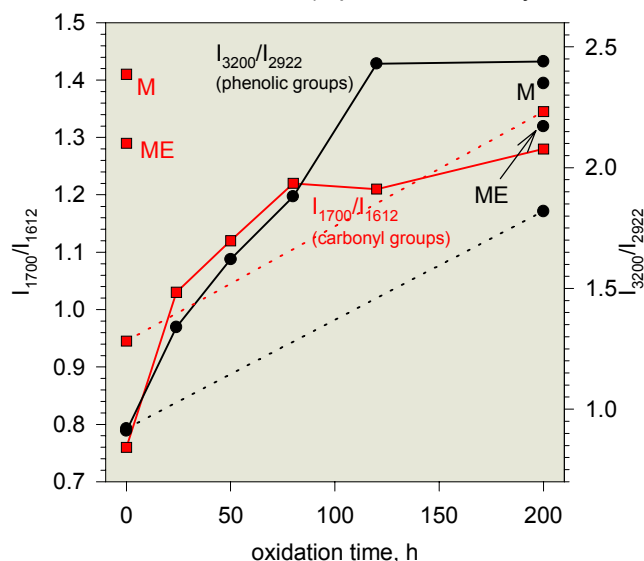
Oxidative changes in coal. The elemental changes are illustrated by the van Krevelen diagram (Figure 1). They are most pronounced during the first 50 hours, the higher O content in M is reached in J after 80 h oxidation. At the same time, H/C atomic ratio decreases due to cleavage of aliphatic C-H bonds (6). Extraction of bitumen (6-8 wt%) decreased content of both O and H by their concentrating in the bituminous fraction.

Figure 1: Elemental analysis of coal samples - van Krevelen diagram



Structural changes in oxygen functionalities can be followed by the DRIFT spectroscopy using interpretation of the spectra as shown on Figure 2. The increase of content of carboxyl functionalities with oxidation time is reflected by increasing ratio of peak intensities at 1700 cm^{-1} (stretching vibrations of carbonyl groups) and 1612 cm^{-1} (aromatic C=C bonds). The gain in phenolic groups is followed by the ratio of 3200 (phenolic -OH) and 2922 cm^{-1} (aliphatic C-H bonds) peak intensities. Effect of extraction is ambiguous. For oxihumulite (M vs. ME), it slightly decreases content of both types of O functionalities as expected. For extracted coal samples (J0E, J200E), decrease is observed only in phenolic groups, content of carbonyl increases with extraction, particularly for the non-oxidized sample. Possibly, oxidation takes place during extraction with hot solvents on air, and/or content of aromatic structures decreases increasing the I_{1700}/I_{1612} intensity ratio.

Figure 2: Relative content of carbonyl and phenolic groups determined by DRIFT spectroscopy, as function of oxidation time (squares – carbonyl, circles – phenolic, broken lines – extracted J samples)



Changes in acidobasic properties of coal samples due to oxidation are illustrated by titration curves (Figure 3) and proton exchange capacities (Table 1). Increase in O functionalities due to oxidation is reflected by shift of the curves to higher NaOH consumption, and increase in the PEC values. Comparing the PEC values with NaOH consumption at the end of titration ($\text{pH} > 10$ -11), the latter is significantly lower. Obviously, titration was not slow enough to reach equilibrium after each titrant addition due to a worse accessibility of HS functional groups in coal mineral matrix. In case of the purified (demineralized) HA, the PEC corresponds quite well with the titration curve. Extraction of bitumen changed character of titration curve and decreased PEC, especially in case of oxihumulite (M vs. ME) and strongly oxidized coal (J vs. J200E).

Figure 3: Titration curves

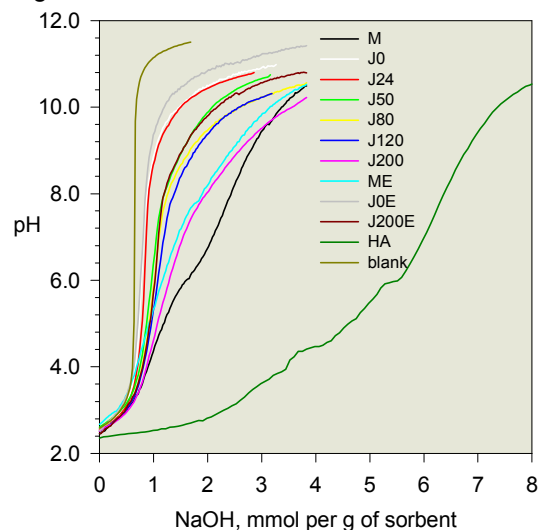
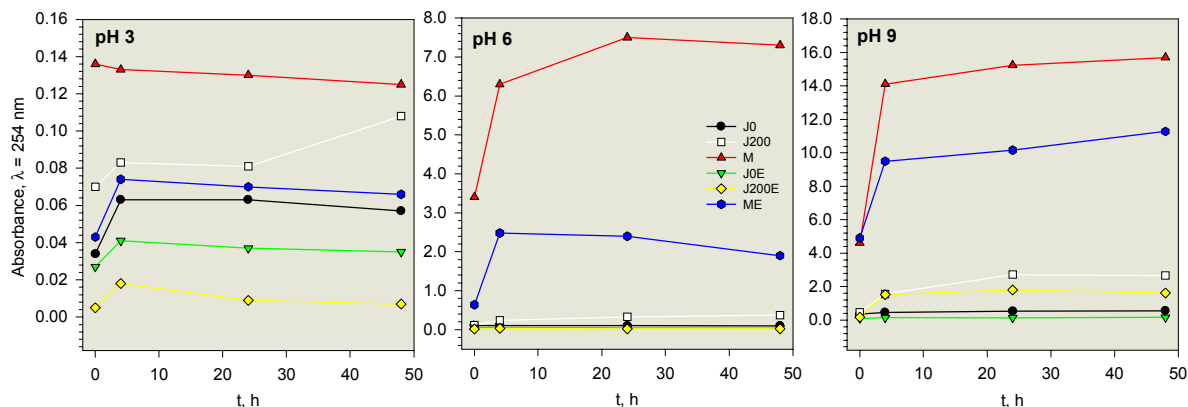


Table 1: Proton exchange capacities

| Sample | PEC (mmol/g) |
|--------|-----------------|
| M | 6.02 ± 0.38 |
| J0 | 4.63 ± 0.17 |
| J24 | 5.90 ± 0.01 |
| J50 | 6.22 ± 0.11 |
| J80 | 6.35 ± 0.04 |
| J120 | 6.67 ± 0.01 |
| J200 | 7.07 ± 0.00 |
| ME | 5.60 ± 0.14 |
| J0E | 4.53 ± 0.14 |
| J200E | 6.35 ± 0.21 |
| HA | 7.39 ± 0.08 |

Leaching of HS from coal as function of contact time with solution and its pH, checked by measuring absorbance in solution at 254 nm, is documented by Figure 4. In agreement with solubility of HA in neutral and alkaline solution, leaching increases with pH. It is much higher for oxihumulite than for coal samples. Oxidation for 200 h increases significantly leaching of HS, but yet it remains much lower than in case of oxihumulite. Checked by weighing dried samples after separation from solution, weight losses were about 3 and 13 % for J200 and M, respectively. Extraction decreased leaching of HS.

Figure 4: Leaching of HS from the samples checked by spectrophotometry

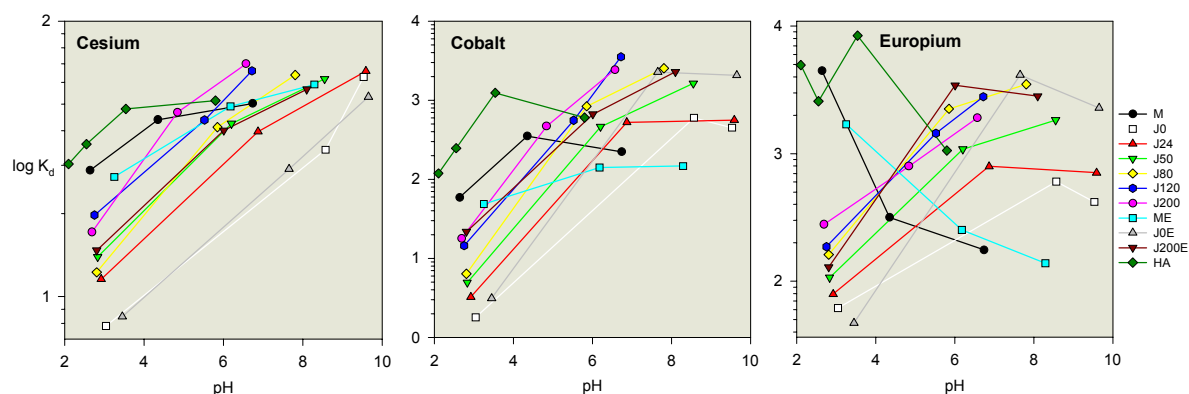


Sorption of Cs, Co and Eu. Activities (cpm, counts per minute) in solution were used to calculate distribution coefficient K_d defined by the equation

$$K_d = A_i / C_i$$

where A_i is concentration of adsorbate (radionuclide) on the solid at equilibrium (cpm./g), C_i is concentration of total dissolved adsorbate remaining in solution at equilibrium (cpm./mL). K_d values (Figure 5) increasing in the order Cs<Co<Eu reflect increasing charge of cation and ability of coordination-covalent binding to HS sites. Oxidation of coal increased K_d 's with no improving after 80 h oxidation. Generally, K_d 's increase with pH due to dissociation of the binding sites. K_d 's of Eu (and with Co, to a certain extent) with oxihumulite and HA, in alkaline region also with other samples, decrease with pH due to formation of soluble HS complexes leached to solution. Effect of extraction is negligible except for non-oxidized coal (J0 vs. JOE) with Eu and Co, whose sorption in neutral and alkaline region is enhanced, probably owing to suppressed leaching of HS.

Figure 5: Sorption of Cs, Co and Eu on the samples – K_d values vs. pH



Summary and Conclusions

As a source of naturally immobilized humic substances, low-rank coal (lignite) is a promising material to be used as a low-cost sorbent of toxic metals and radionuclides. It can be artificially oxidized to increase content of oxygen functionalities, carboxyl and phenolic groups. Oxidation on air at 140 °C for 80 hours is sufficient to obtain material with content of the functional groups similar to that of the naturally oxidized coal, oxihumulite. Despite similar (or even higher) content of oxygen functionalities, sorption ability for Cs, Co and Eu of the oxidized lignite is lower in acidic solution than in case of oxihumulite, probably due to a worse accessibility of the binding sites for the cations (7). In neutral and

alkaline region, sorption properties of oxihumolite deteriorate due to leaching of the originally in situ immobilized HS into solution, while for the artificially oxidized lignite with relatively low leaching of HS, sorption increases with pH until mildly alkaline region. Extraction of bitumen expected to ensure a better accessibility of the binding sites was accompanied with decrease in content of the oxygen groups, thus has brought a negligible effect. However, it enhanced immobilization of HS within coal matrix improving its sorption ability in neutral and alkaline solutions.

Acknowledgement

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