



SUPPLEMENTARY MATERIAL TO

Deashing and desulfurization of subbituminous coal from the East field (Bogovina Basin, Serbia) – Insights from chemical leaching

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Low temperature ashing (LTA) process and X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was used for determination of the qualitative composition of the minerals in the samples' ashes before and after the leaching treatments. Prior to XRD, all samples were subjected to low temperature ashing (LTA) process.¹ The method is favorable for isolating the MM from coal, as unaltered, as possible. Dried and weighted initial coal sample and solid residues obtained by chemical leaching (~3 g) were burnt at 370 °C in the air atmosphere for 3 h using the Nabertherm L3/11/B 410 pre-heating furnace. The samples were gradually heated to 200 °C with the heating rate of 3 °C min⁻¹ followed by the heating rate of 10 °C min⁻¹ up to the final temperature of 370 °C.

The XRD analysis was performed using a “Philips” X-ray diffractometer, type PW-1710, with graphite monochromator and a scintillation counter. The intensities of diffracted CuK α X-ray radiation ($\lambda = 1.54178 \text{ \AA}$) were measured at room temperature. Samples were recorded in 2θ range from 4 to 65° in 0.02° intervals for duration of 1 s. The working voltage was 40 kV and working current was 30 mA. The slits for directing the primary and diffracted beam were fixed at 1° and 0.1 mm.

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Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared (FTIR) analysis of initial and treated coal samples was performed on a Thermo Fisher Scientific Nicolet IS-50. Recording was done by ATR (Attenuated Total Reflectance) technique in the range from 4000 to 450 cm^{-1} , and 32 scans at resolution 4.

XRD results

XRD has been done on all samples, however due to their congruence for same reagent independently on concentration and temperature, those corresponding to optimal leaching conditions, marked by bolded text in Table II, are shown here). LTA of Bogovina coal dominates by amorphous matter, whereas other constituents are quartz (Q), olivine (O), calcite (C) anhydrite (A), mica (M) and unidentified phase (U) (Fig. S-1). Amorphous matter also dominates in LTA of HCl and HNO_3 leached solid residues. As expected, treatment with both inorganic acids resulted in removal of calcite, anhydrite and mica,² as well as unidentified phase (Fig. S-1). Scarce distribution of minerals in leached solid residues, represented mostly by resistant quartz, is consistent with efficient deashing (~ 80 %; Table II). In addition to quartz, the solid residues obtained by HCl treatment contain low amount of olivine (Fig. S-1), which is also relatively prone to acidic dissolution resulted from ion-exchange reaction between $\text{Mg}^{2+}/\text{Fe}^{2+}$ and H^+ .³ The solid residue obtained by HNO_3 treatment does not contain even olivine, probably due to the possible oxidation of Fe^{2+} from fayalite to Fe^{3+} , associated with common dissolution by ion-exchange reaction mentioned above. The very low amount of plagioclase (P) in this solid residue can be attributed to the presence of this mineral in initial coal sample rather than its formation during chemical leaching (Fig. S-1). However, due to the extremely low content of plagioclase in comparison to other minerals it is not identified in other samples, with exception of HNO_3 leaching residue from which other minerals were almost fully removed. The presence of plagioclase in leached solid residue after leaching with HNO_3 can be attributed to greater resistance of feldspar mineral groups against acidic treatment than other silicates with exception of quartz.^{2,4}

FTIR results

The main changes in FTIR spectra of coal OM after treatment with 15 vol.% HCl at 60 °C or 15 vol.% HNO_3 at the same temperature are expressed by decrease of amount of unsaturated comparing to saturated hydrocarbons moieties that is reflected by lowering of intensity of C=C stretching (around 1600 cm^{-1}) in relation to peaks around 2900 cm^{-1} , representing C–H stretching in saturated aliphatic chains. Acid treated samples contain less O–H bending peaks around 1400 cm^{-1} , whereas C–O stretching peaks and aliphatic C–H bending vibrations about 1050 cm^{-1} become more prominent in leached solid residues (Fig. S-2). In

the case of HNO₃ treatment, the increase of peak abundance in the latter area in partly can be attributed to the S=O stretching resulted from oxidation of organic bounded sulfur.

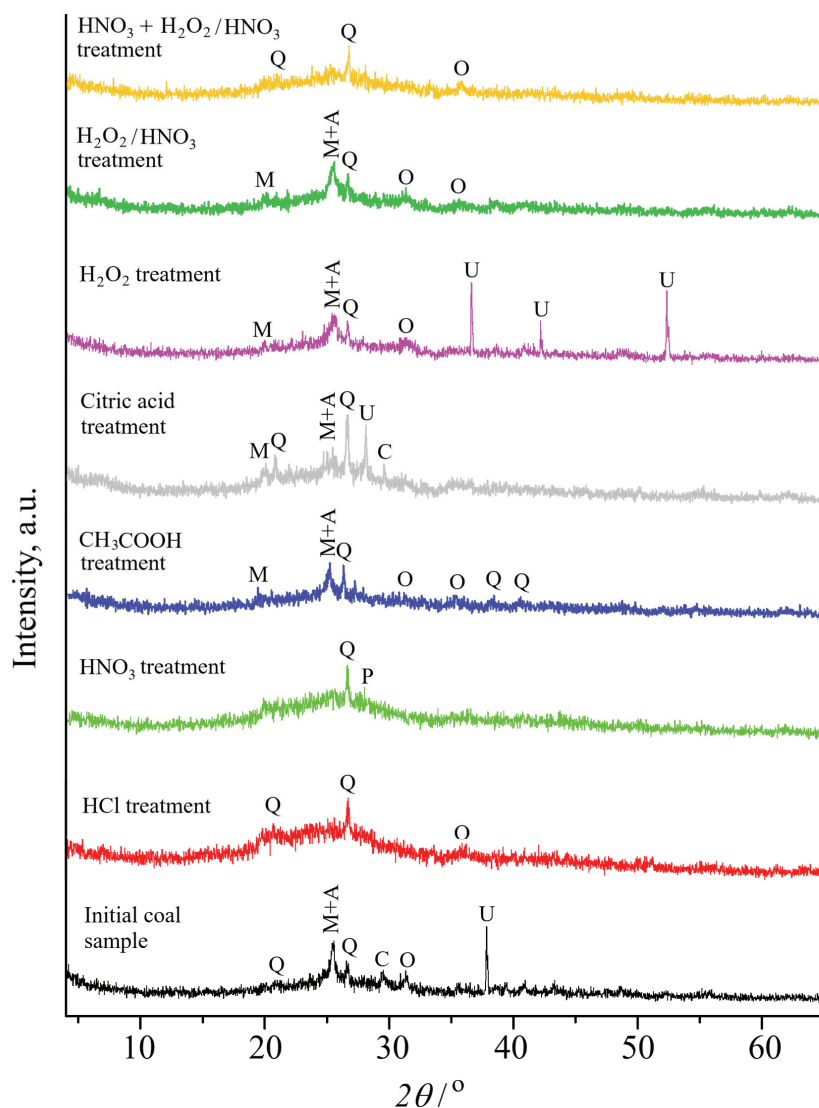


Fig. S-1. XRD spectra of LTA of initial coal sample and solid residues obtained by chemical leaching with: HCl, HNO₃, CH₃COOH, citric acid, H₂O₂, H₂O₂/HNO₃ mixture, pH 2 and HNO₃, followed by H₂O₂/HNO₃ mixture, pH 2 in two-step leaching process; legend: Q – quartz; O – olivine; C – calcite; A – anhydrite; M – mica; U – unidentified phase; P – plagioclase; note: the results for optimal concentrations and temperatures (marked by bolded text in Table II) are provided.

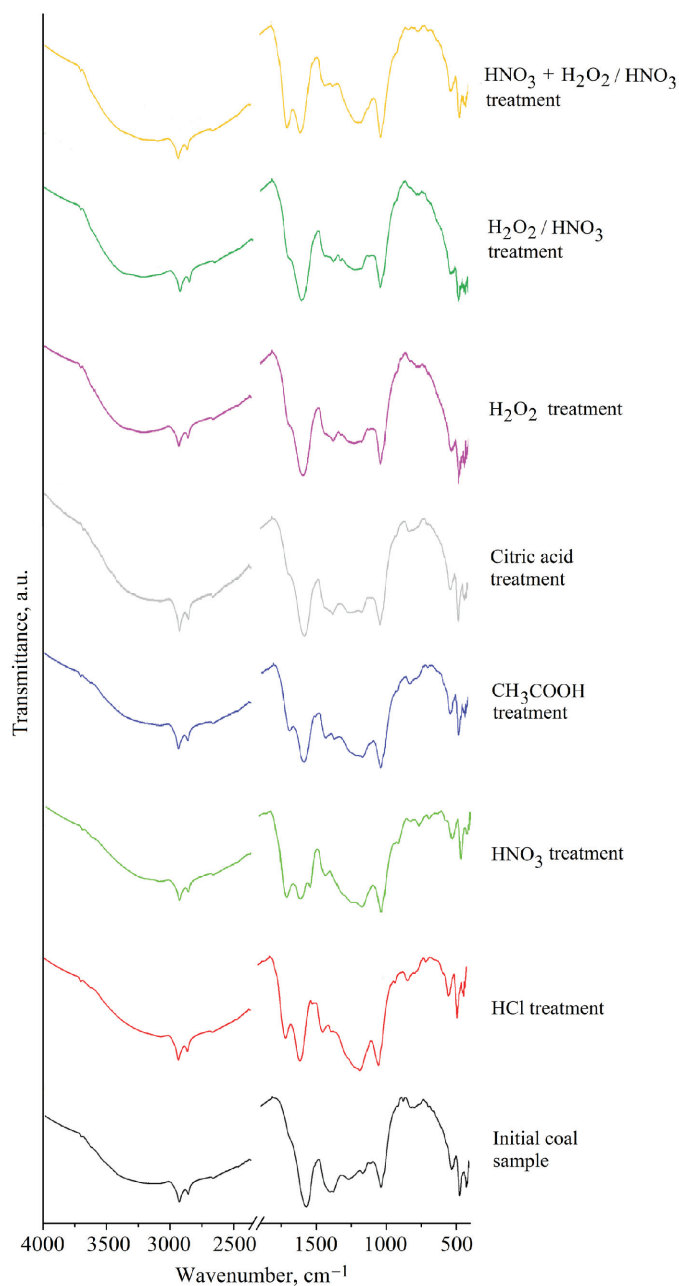


Fig. S-2. FTIR spectra of initial coal sample and solid residues obtained by chemical leaching with: HCl, HNO₃, CH₃COOH, citric acid, H₂O₂, H₂O₂/HNO₃ mixture, pH 2 and HNO₃, followed by H₂O₂/HNO₃ mixture, pH 2 in two-step leaching process; note: results for optimal concentrations and temperatures (bolded text in Table II) are provided.

Both acid leached residues have more intense peak at about 1720 cm^{-1} corresponding to C=O stretching (in carbonyl compounds and acids) in relation to C=C stretching (around 1600 cm^{-1}) than initial coal. This is particularly visible for HNO_3 leaching due to its oxidation properties. Interaction of HCl with coal OM is recorded by C-Cl stretching peak at around 820 cm^{-1} . Decrease in intensity of bands in area from 450 to 600 cm^{-1} that corresponds to mineral part of the coal is consistent with its partial removal. Despite mentioned changes, the FTIR spectra (Fig. S-2) show that there are not significant alterations of coal OM structure caused by inorganic acids treatments. The result is expected since kerogen is generally insoluble in conventional acids and bases water solutions and in accordance with literature data.⁵ Furthermore, kerogen is usually in close connection with MM⁶ that is primarily degraded/dissolved, protecting the significant alteration of the OM structure.

Coal leaching with organic acids

XRD diagrams in Fig. S-1 are consistent with low deashing efficiency of organic acids. They dominate by amorphous matter and indicate that only calcite and unidentified mineral phase are removed from the coal sample. Furthermore, it is obvious that after treatment with citric acid new unidentified mineral phase is formed, confirming the incorporation of this acid into coal MM.

The FTIR spectra of residues obtained by leaching with organic acids are almost identical to FTIR spectrum of initial coal, indicating that alterations of structure of coal OM by treatment with organic acids are less pronounced in comparison to inorganic acids leaching (Fig. S-2). The solely difference is noticed in the FTIR spectrum of CH_3COOH leached residue, that is reflected through a more intense peak at about 1720 cm^{-1} corresponding to C=O stretching (in carbonyl compounds and acids) in relation to C=C stretching (around 1600 cm^{-1}) than in initial coal.

Coal leaching with oxidizing reagents

Low efficiency of 35 vol.% H_2O_2 and 35 vol.% $\text{H}_2\text{O}_2/10\text{ vol.}\% \text{HNO}_3$ mixture (pH 2) in deashing (51–59 wt.% at optimal temperature, Table II) is also confirmed by XRD data that indicate prevalence amorphous matter and successful calcite removal, only, using aforementioned reagents. Furthermore it is obvious that 35 vol.% H_2O_2 treatment resulted in formation of new unidentified mineral phases (Fig. S-1). On the other hand, XRD diffractogram of the solid residue after the two-step leaching process is very similar to those obtained by 10 vol.% inorganic acids treatment, indicating the presence of amorphous matter (dominating), quartz and olivine (Fig. S-1).

The FTIR spectra of solid residues obtained by treatment with 35 vol.% H_2O_2 at $40\text{ }^\circ\text{C}$ and $\text{H}_2\text{O}_2/\text{HNO}_3$ mixture (pH 2) at $60\text{ }^\circ\text{C}$ are almost identical and generally similar to those of initial coal sample. The main difference is reflected

through a more intense peak at about 1720 cm^{-1} (representing C=O stretching in carbonyl compounds and acids), associated with less pronounced C=C stretching peak at 1600 cm^{-1} in relation to initial coal, resulting from oxidation properties of aforementioned reagents (Fig. S-2). The two-step leached solid residue (10 vol.% $\text{HNO}_3 + \text{H}_2\text{O}_2/\text{HNO}_3$ mixture at pH 2) has almost identical FTIR spectrum as residue obtained by 10 vol.% HNO_3 , indicating greater impact of HNO_3 on structure of coal OM in comparison to H_2O_2 (Fig. S-2).

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