minerals

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Supplementary Material

S.1. Description of ^{1}H-NMR and IR.

1. Spectra of HmA

^{1}H-NMR and IR analyses of potassium (HmK) and ammonium (HmA) humates were performed at the Nazarbayev University Core Facilities laboratories (Kazakhstan) using a JEOL ECA-500 MHz NMR spectrometer and a Nicolet iS 10 FTIR spectrometer, respectively. ^{1}H-NMR spectra were recorded from samples in D_2O (15.68 mg/mL). The NMR spectra were recorded with a one-pulse sequence, a 45° pulse angle, a 3 s relaxation delay, and a sweep width of 5 kHz. To suppress the resonance of water, gated irradiation was applied between acquisitions. A total of 2048 scans were required to obtain a satisfactory signal-to-noise ratio of ^{1}H-NMR spectra. ^{1}H chemical shifts were referenced to residual protons of D_2O (4.79 ppm [62]).

The ^{1}H-NMR spectrum of HmA in D_2O is shown in Figure S1 and is almost identical to the ^{1}H-NMR spectrum of HmK in D_2O (shown in the paper, Section 3.1.2., Figure 7). Similarly, it can be divided into four regions. First, an intense and broad proton region from 5.25 ppm to 9.50 ppm was observed, which corresponds to the extensive polyaromatic structure (aromatic CH resonances), overlapping with the NH resonances from aromatic carboxamide functionalities ArC(O)N*H*R (7.75–9.00 ppm) and CH resonances of alkene groups $R_2C{=}CR\mathit{H}$ (at approx. 5.50–6.75 ppm). The second broad proton region from approx. 3.00 ppm to approx. 4.25 ppm shows the presence of carbohydrates (H-sugar-like), CH protons of esters $RCO_2C\mathit{H}R_2$, and alcohol/ether $R_2C\mathit{H}$-OR/H resonances. The third broad proton region from approx. 1.87 ppm to approx. 3.00 ppm shows the presence of acetate and acetoacetate resonances (α-CH_3 groups; 1.87–2.25 ppm), as well as aliphatic CH resonances in alkylamines/*N*-alkyla mides, ketones, and Ar$C\mathit{H}R_2$ derivatives (2.00–2.78 ppm). Finally, the broad region from approx. 0.50 ppm to approx. 1.60 ppm shows the resonances of aliphatic CH, CH_2 (1.15–1.60 ppm), and CH_3 (0.85 ppm) groups. Analogously to HmK, carboxylic and phenolic OH protons as well as amide/amine/ammonium NH protons of HmA are not evident in the ^{1}H-NMR spectrum due to extensive hydrogen bonding (D_2O was used as a solvent), resulting in significant broadening of the OH and NH resonances.

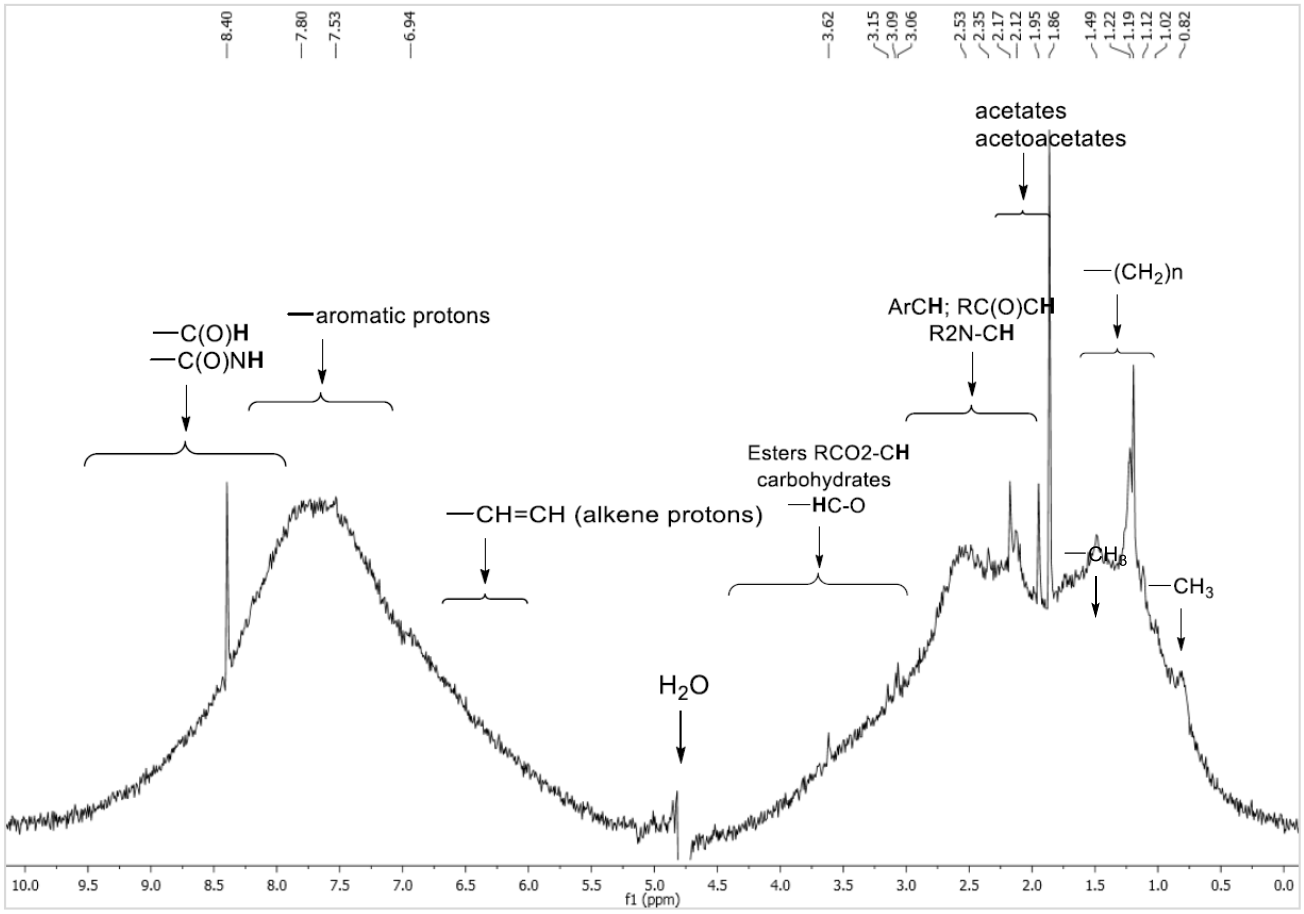


Figure S1. ^{1}H-NMR spectrum of ammonium humate (HmA) in D_2O.

The IR spectrum of HmA is similar to that of HmK (Figure 8, Section 3.1.2 of the paper) and is shown in Figure S2. Analogously to the spectrum for HmK, the following bands can be observed in the IR spectrum of HmA: 3500–3000 cm^{-1} (OH of phenols, carboxylic acids, and water, as well as NH of amines and carboxamides), approx. 2900 cm^{-1} (which refers to asymmetric and symmetric features of the methylene CH_2 group, typical for aliphatic and undeformed cyclic hydrocarbons), 2883 cm^{-1} and 2827 cm^{-1} (both correspond to the aliphatic C-H bond), 1560 cm^{-1} (which can be attributed to asymmetric vibrations of the carboxylate ion -COO^{-}, as well as stretching vibrations of the carboxamide -C=O group; a shoulder towards higher wavenumbers may be due to double-bond stretching, for example, -C=C- and -C=N-), 1475 cm^{-1} and 1361 cm^{-1} (which could correspond to combinations of O-H bending, CH_2 and CH_3 deformations, C-H alkene bending, C-N stretching vibrations of carboxamide, and symmetric stretching vibrations of -COO^{-} carboxylate ion), 1200 cm^{-1} (C-O stretching vibrations), 1031 cm^{-1} and 1007 cm^{-1} (C-O stretching vibrations in polysaccharides or polysaccharide-like substances), 909 cm^{-1} and 882 cm^{-1} (C-N/C-C stretching vibrations), 756 cm^{-1} (out-of-plane bending vibrations of aromatic C-H), and 526 cm^{-1} and 471 cm^{-1} (out-of-plane bending vibrations of aromatic groups). The observed features are consistent with the general structural description of humates and humic substances [61].

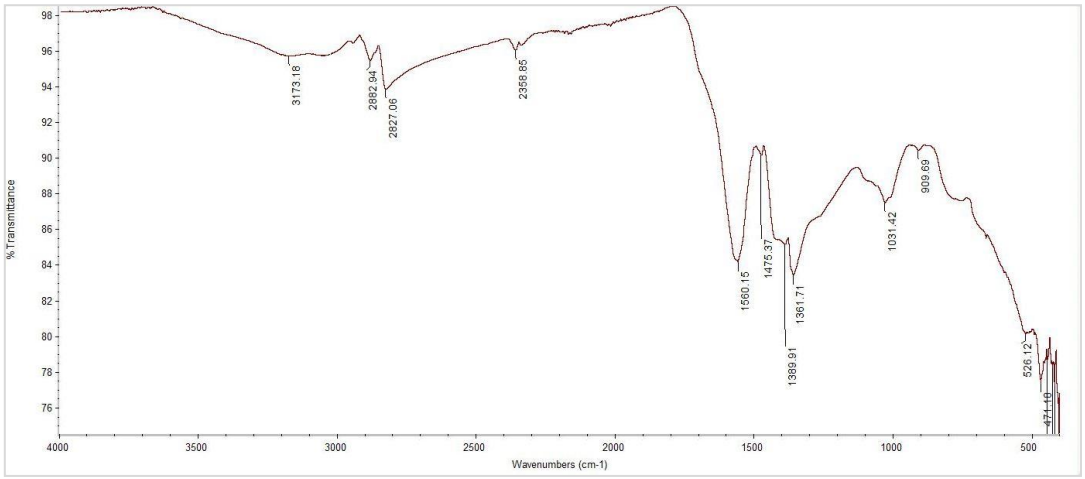
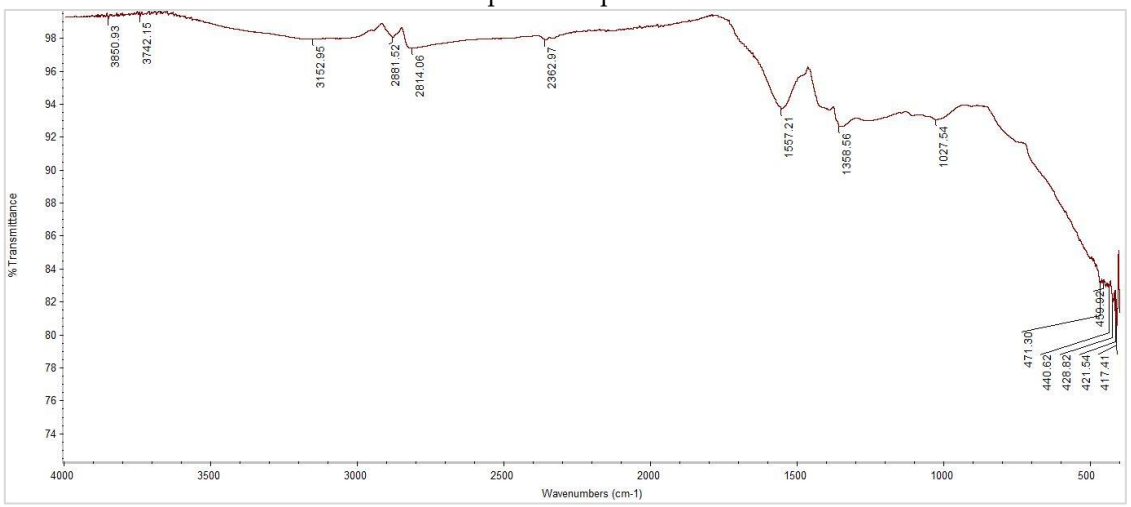


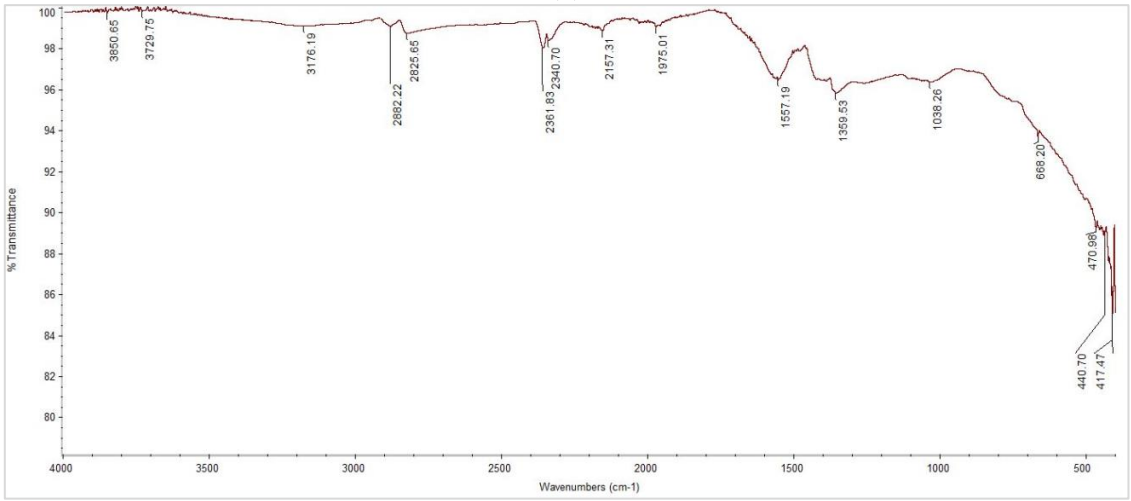
Figure S2. IR spectrum of ammonium humate (HmA).

2. Spectra of HASs after CO_2 absorption

The results of IR and NMR spectroscopy for HmA and HmK samples after CO_2 absorption tests are presented. For clarity and better comparison, the spectra of HmA and HmK before CO_2 absorption are presented.



(**a**)



(**b**)

Figure S3. (**A**) IR spectra of HmA (obtained from 30% solution in H_2O) in Nujol before (**A**) and after (**B**) CO_2 absorption at 25 °C.

The IR spectrum of HmA obtained from 30% solution in H_2O is shown in Figure S3 and is analogous to the spectrum of HmA from 100% solution. After CO_2 absorption by 30% solution of HmA at 25°C, the IR spectrum of the solid residue remained practically unchanged. Only very weak bands appeared at 2157 and 1975 cm^{-1}, which can correspond to $–COO^-$ vibrations in amino acid fragments ($R_2C=NH^+$- salts can also occur in this region) that may appear as a group of bands; however, this assignment is rather tentative due to very weak intensity of the bands).

Figure S4 shows ^{1}H-NMR spectra for HmA from its 30% solution in H_2O before and after CO_2 absorption at 25°C. The initial spectrum of humate, before the addition of CO_2, is similar to the spectrum of 100% HmA (please see Figure S1) and is consistent with the literature data [63]. After the saturation of 30% solution of HmA with CO_2, several noticeable changes in the ^{1}H-NMR spectrum of the solid residue obtained from this solution were detected. Thus, the spectrum revealed the presence of a broad resonance at 4.61 ppm, which may correspond to protons of alkene groups, as well as Ar-CH(R)-O- groups and protons of cyclic organic carbonates (possibly also substituted with aromatic groups); OR groups of esters can also give resonances in this region. In addition, the resonance at 2.24 ppm increased noticeably, which may correspond to acetate and acetoacetate resonances (α-CH_3 groups; 1.87–2.25 ppm), as well as aliphatic CH resonances of alkylamines/*N*-alkylamides, ketones, and $ArCHR_2$ derivatives. Unexpectedly, after treatment with CO_2, the proportion of aliphatic protons in the sample seems to increase significantly, resulting in a series of intense resonances at 0.50–1.50 ppm. Notably, since the NMR analysis was performed in D_2O, the protons of carboxylic groups are most likely not visible due to the extensive hydrogen bonding in the system.

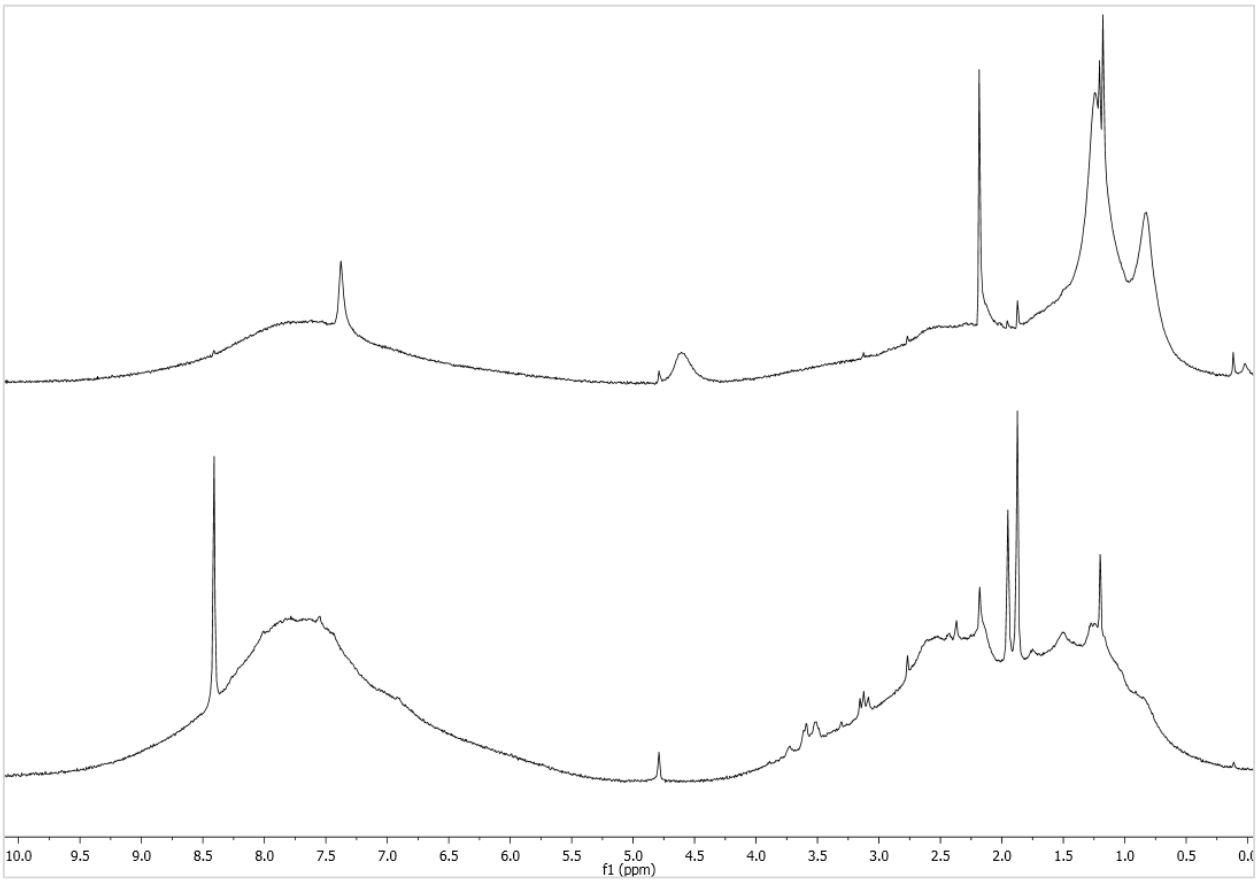
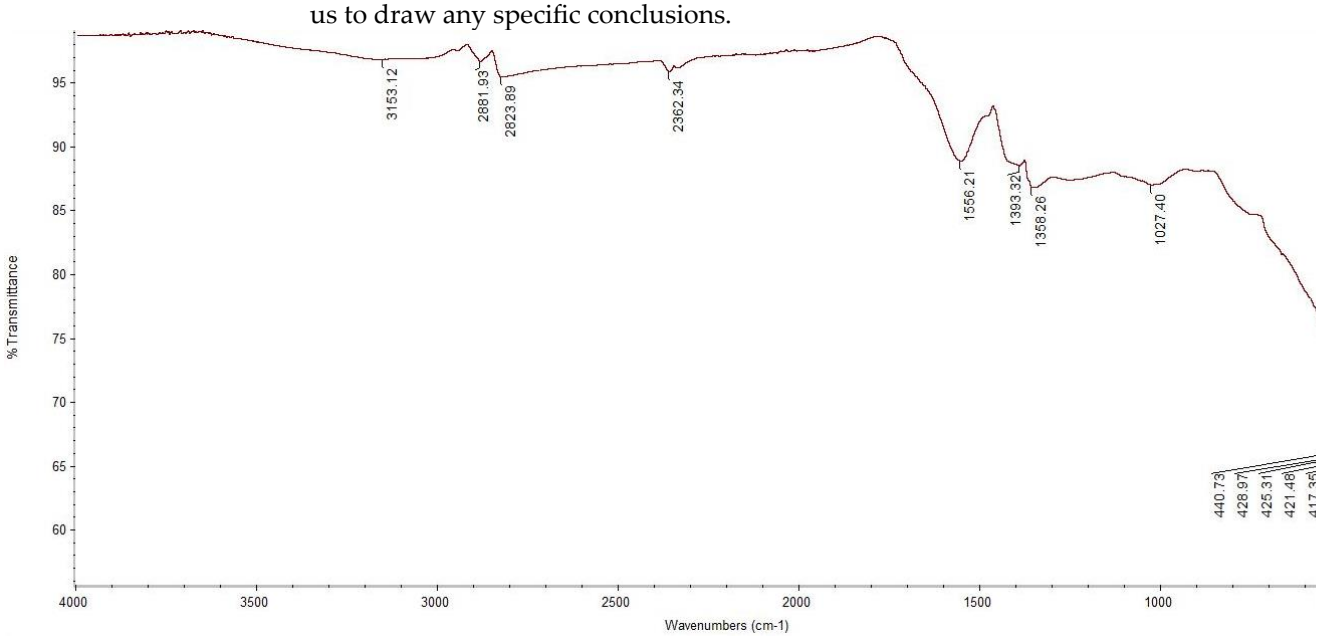
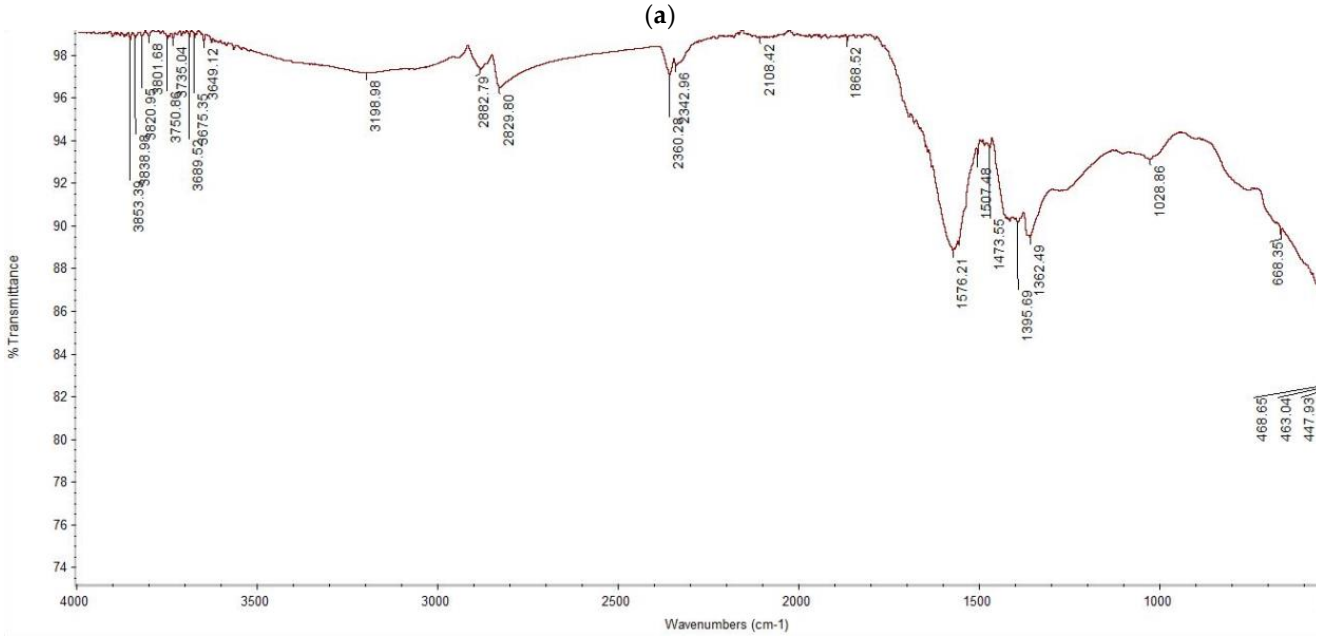


Figure S4. Comparison of ^{1}H-NMR spectra (in D_2O) for 30% AmH before CO_2 absorption (bottom) and after CO_2 absorption at 25 °C (top).

In contrast to 30% HmA, both IR (Figure S5) and ^{1}H-NMR spectra (Figure S6) of 50% HmA before and after CO_2 absorption were found to be identical, which does not allow us to draw any specific conclusions.



(**a**)



(**b**)

Figure S5. IR spectra of HmA (obtained from 50% solution in H_2O) in Nujol before (**A**) and after (**B**) CO_2 absorption at 25 °C.

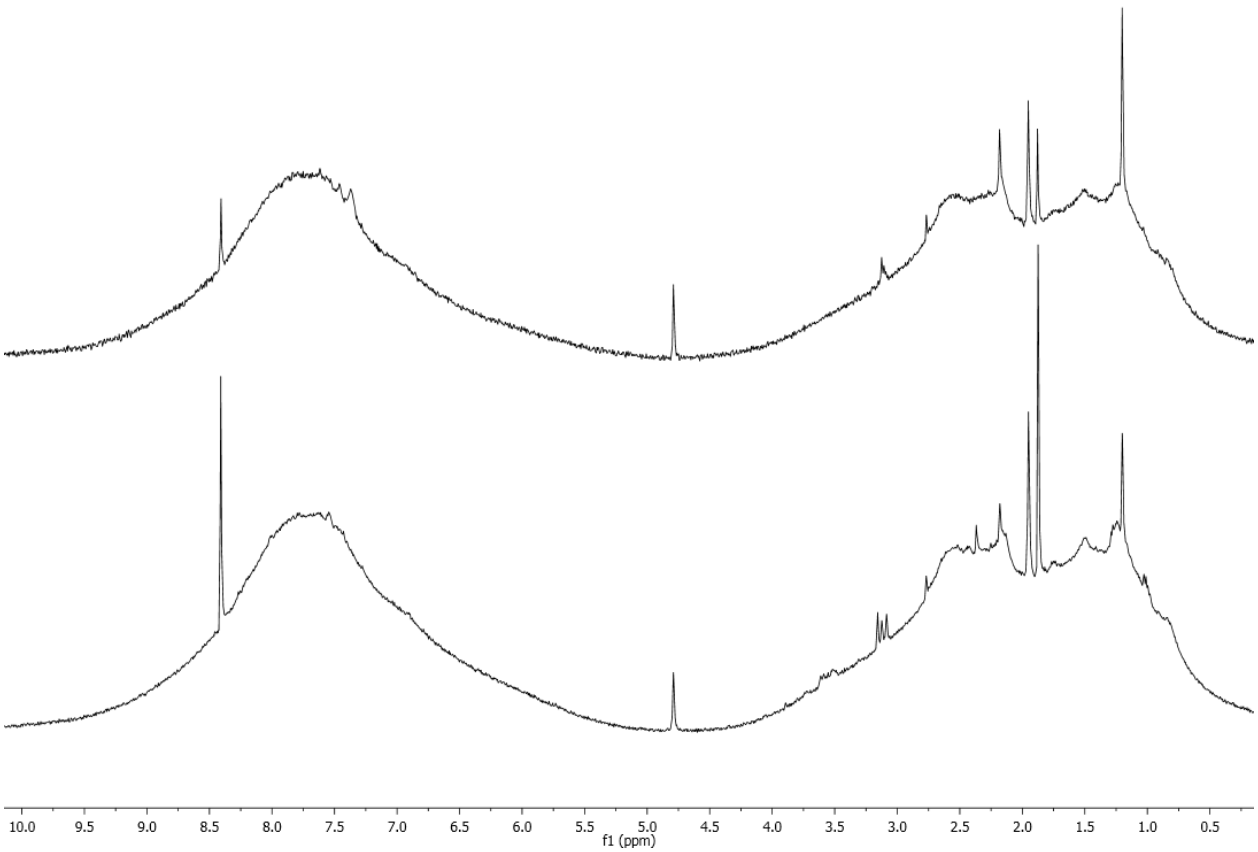
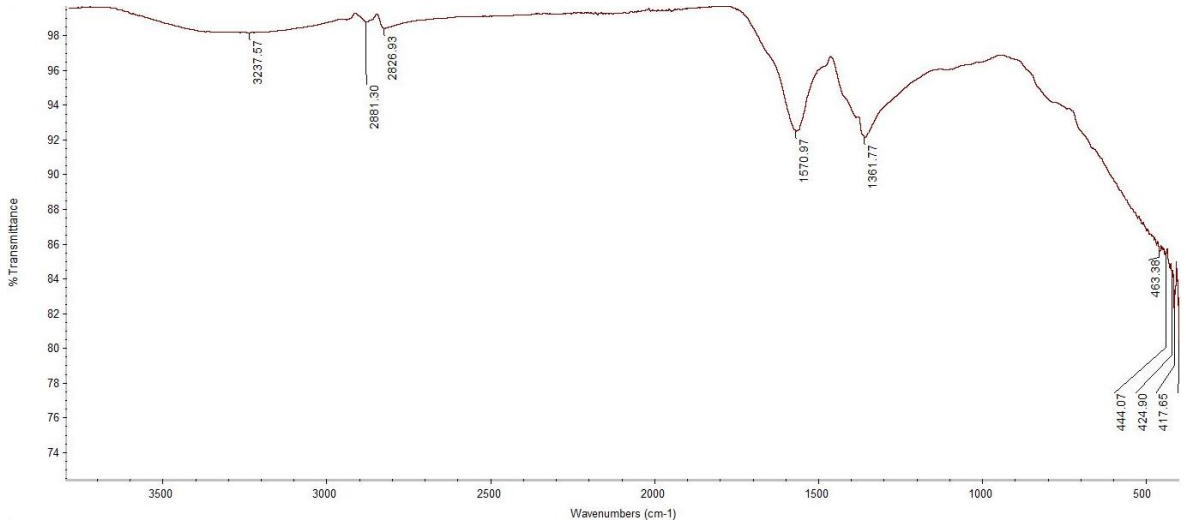
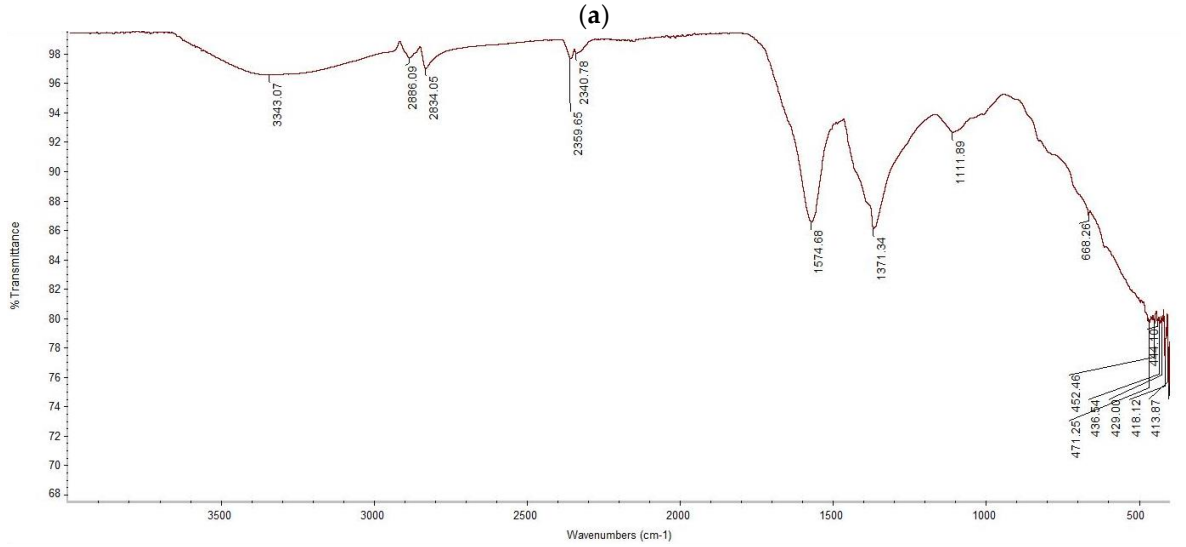


Figure S6. Comparison of ^{1}H-NMR spectra (in D_2O) for 50% HmA before CO_2 absorption (bottom) and after CO_2 absorption at 25 °C (top).

The IR spectrum of HmK (30%) is shown in Figure S7 (very similar to the spectrum of HmA; see Figure S3A) and indicates the presence of OH groups of phenols, carboxylic acids, water, and NH of amines and carboxamides (3500–3000 cm^{-1}). The band at 1571 cm^{-1} can be attributed to the asymmetric vibration of the -COO^- carboxylate ion, as well as to the stretching vibrations of the carboxamide carbonyl group (a shift towards higher wavenumbers may be due to stretching of the double bond, for example, -C=C- and -C=N-). Other bands were seen at 1475–1359 cm^{-1} (stretching vibrations of carboxamide C-N and symmetric stretching vibrations of the -COO^- carboxylate ion), 1200 cm^{-1} (stretching vibrations of C-O), and 1028 cm^{-1} and 1007 cm^{-1} (stretching vibrations of C-O in polysaccharides or polysaccharide-like substances). After CO_2 absorption, the IR spectrum of the solid residue obtained from the solution was found to be identical to the original spectrum. However, the band at 1112 cm^{-1} became somewhat more intense, which may indicate changes in the polysaccharide structure. This range may refer to the C-O stretching vibrations, to the vibrations of ethers, ketals, acetals, and C-O-C vibrations of simple cyclic ethers. In addition, the weak band at about 1055 cm^{-1} could be related to symmetric C(=O)-O- vibrations (asymmetric C(=O)-O- vibrations are found at about 1250 cm^{-1}) and C-O stretching vibrations, and O-H deformation vibrations can be also observed in the selected region (1040–1150 cm^{-1}). All this may tentatively indicate the formation of new –C(=O)O^-groups.



(**a**)



(**b**)

Figure S7. IR spectra of HmK (obtained from 30% solution in H_2O) in Nujol before (**A**) and after (**B**) CO_2 absorption at 25 °C.

Figure S8 shows the ^{1}H-NMR spectra for HmK (30%) before and after absorption of CO_2 at 25°C. The spectra before and after absorption of CO_2 are almost identical. Some slight changes in the spectrum after CO_2 absorption could be seen from 1.80 to 3.00 ppm, which may correspond to some rearrangements in the acetate and acetoacetate, alkylamine and *N*-alkylamide, keto-, and $ArCHR_2$ functionalities. As in the case of 30% HmA, a broad (though not very intense) resonance appears at 4.67 ppm, which may correspond to the protons of alkene groups as well as Ar-CH(R)-O- groups and protons of cyclic organic carbonates (possibly also substituted by aromatic groups); OR groups of esters can also give resonances in this region. The rest remains without any visible changes.

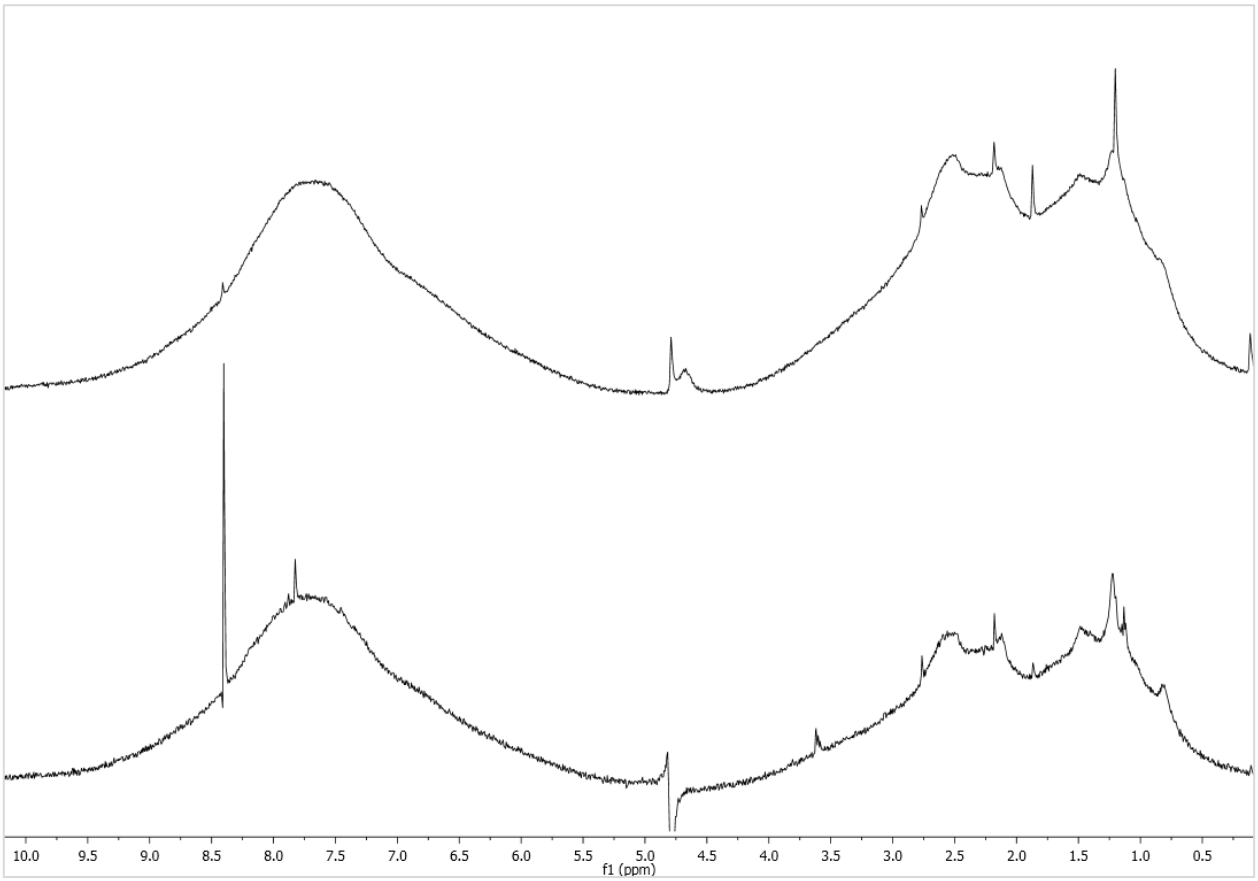
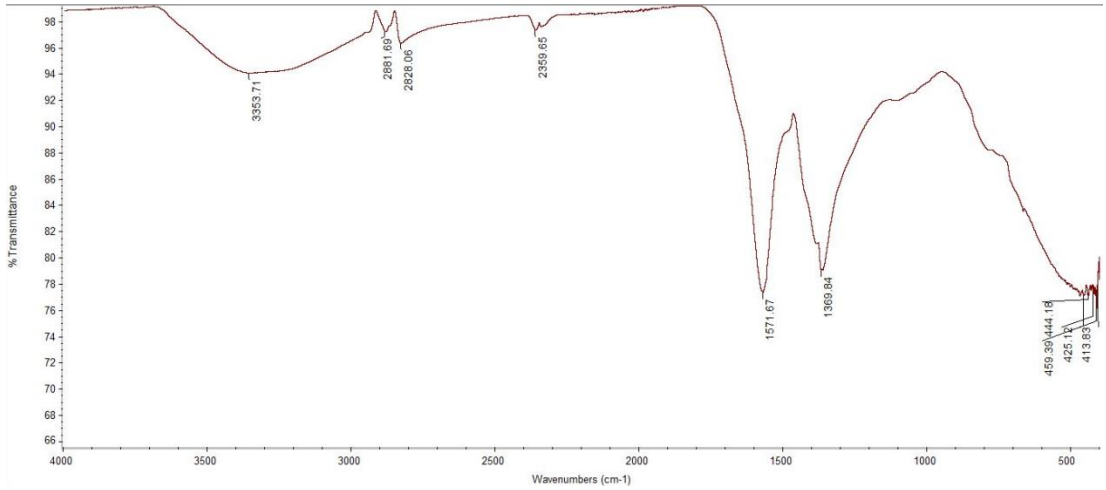
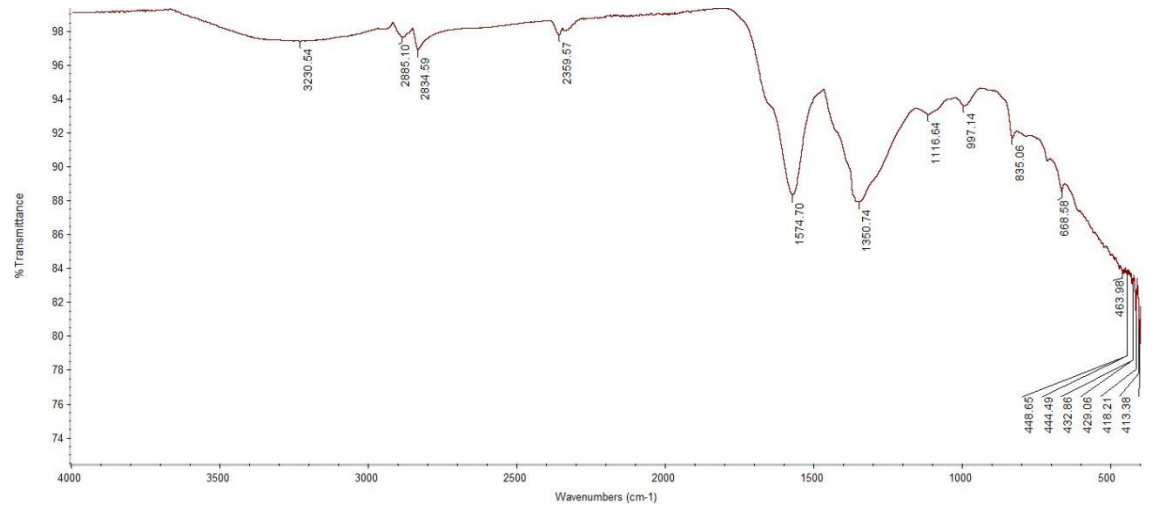


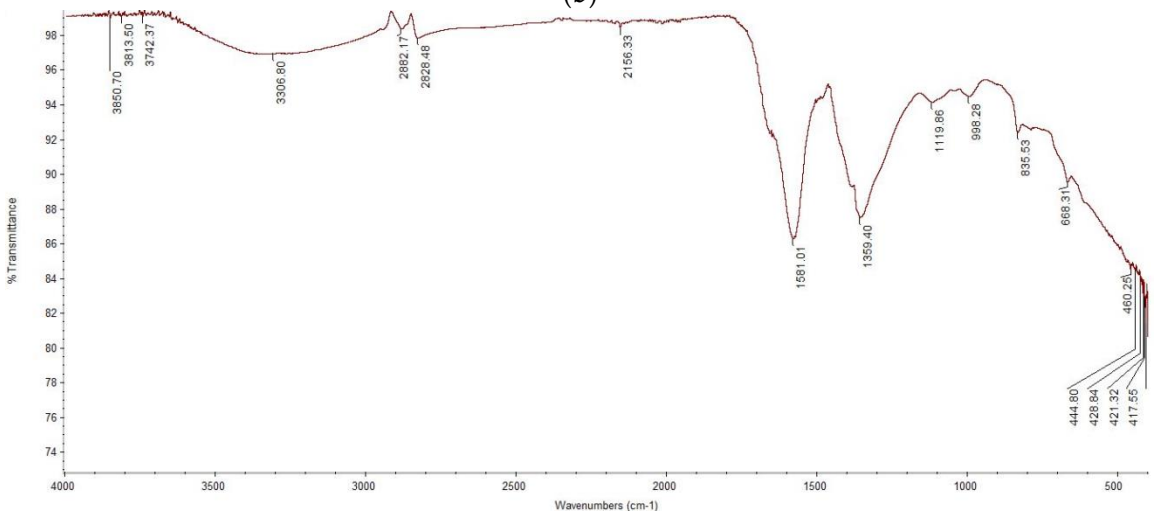
Figure S8. Comparison of ^{1}H-NMR spectra (in D_2O) for 30% HmK before CO_2 absorption (bottom) and after CO_2 absorption at 25 °C (top).



(**a**)



(**b**)



(**c**)

Figure S9. IR spectra of HmK (obtained from 50% solution in H_2O) in Nujol before (**A**) and after CO_2 absorption at 25 °C (**B**) and 40 °C (**C**).

The IR spectrum of potassium humate (HmK, 50%) shown in Figure S9 is identical to the spectrum obtained for HmK from a 30% solution. After treatment with CO_2, the result is very similar to a 30% solution. The bands at 1117–1120 cm^{-1} and 997–998 cm^{-1} also become more clearly visible, which may indicate changes in the polysaccharide structure (see the description of Figure S7).

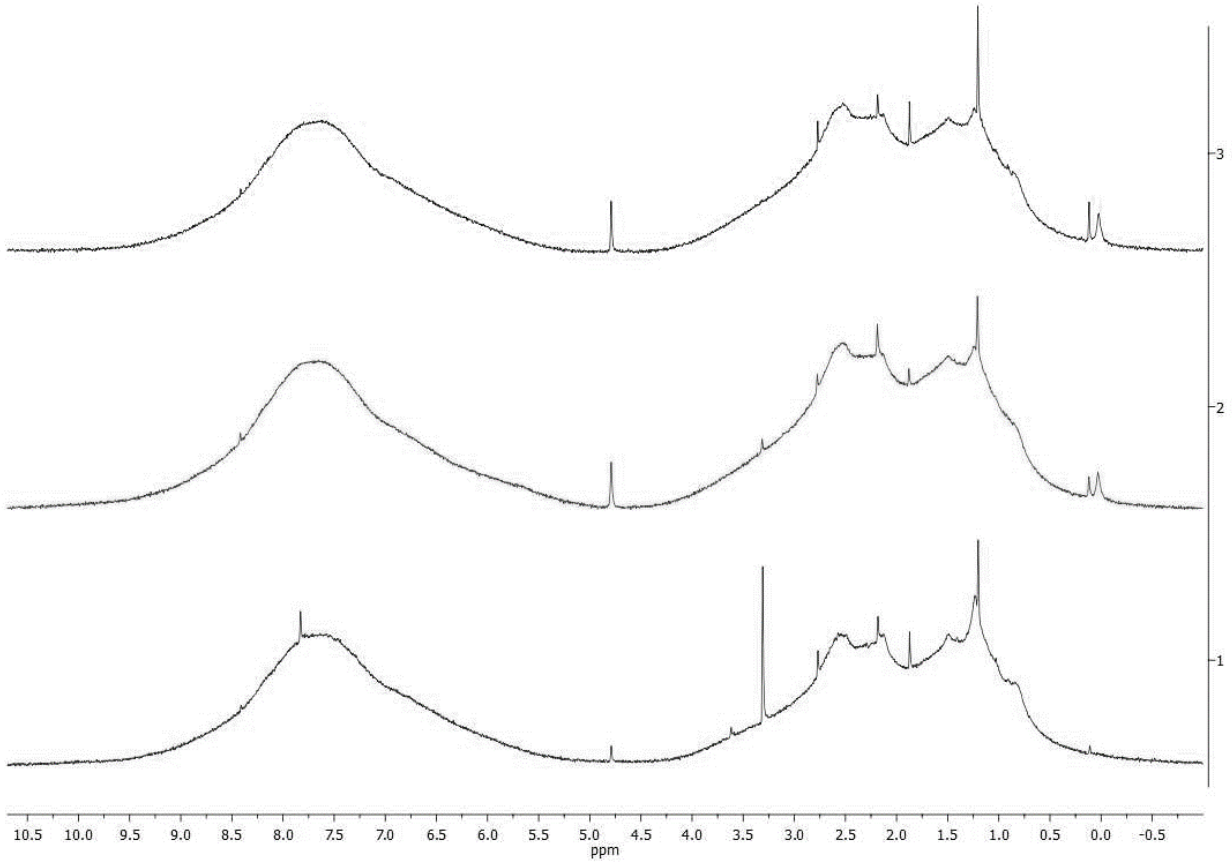


Figure S10. Comparison of ^{1}H-NMR spectra (in D_2O) for 50% HmK before CO_2 absorption (bottom) and after CO_2 absorption at 25 °C (middle) and at 40°C (top).

NMR spectra of potassium humate (50%) before and after absorption of CO_2 at 25°C and 40°C are shown in Fig. 10. Significant changes in the spectra of the CO_2 treatment field are not observed, with the exception of minor changes in the intensity of the signals. Although minor changes occur in the ester/carbohydrate region (the signal at 3.31 practically disappears), it is impossible to single out any very characteristic changes.