

Thermal stability of solid and aqueous solutions of humic acid

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Abstract

The effects of temperature on the stability of a soil humic acid were studied in the present work. Solid samples of Gohy-573 humic acid (HA) and dissolved ones in aqueous solution (pH 6.0, 0.1 mol L⁻¹ NaClO₄) were investigated in order to understand the impact of temperature on the chemical properties of the material. The methods applied to solid samples in the present investigation were thermogravimetric analysis (TGA), temperature-programmed desorption coupled with mass spectrometry (TPD–MS), and in situ diffuse reflectance infrared Fourier transformed spectroscopy (in situ DRIFTS). Humic acid samples were studied in the 25–800 °C range, with focus on thermal/chemical processes up to 250 °C. The reversibility of the changes observed was investigated by cyclic changes to specified temperature ranges (40–110 °C). All measurements were conducted under inert-gas atmosphere in order to avoid samples combustion at increased temperatures. Aqueous solutions were analyzed by UV–vis absorption spectroscopy after storage at temperatures up to 95 °C, and storage times up to 1 week. For temperatures below 100 °C experiments on solid and aqueous samples have shown results which were consistent to each other. The amount of water desorbed is temperature dependent and up to 70 °C this process was totally reversible. Above 70 °C an irreversible loss of water was also observed, which according to UV–vis spectroscopy corresponds to water produced by condensation leading to more condensed polyaromatic structures. The water released up to 110 °C was about 7 wt% of the total mass of the dried humic acid, where less than 50% corresponded to reversibly adsorbed water. At higher temperatures (>110 °C), gradual decomposition resulting in the formation of carbon dioxide (110–240 °C), and carbon monoxide (140–240 °C) takes place. Hence, thermal treatment of Gohy-573 humic acid above 70 °C results in irreversible structural changes, that could affect chemical properties (e.g., complex formation) of the material.

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1. Introduction

The distribution and fate of heavy metal pollutants in aqueous solutions is strongly influenced by the presence of natural organic material, especially humic acids. The environmental significance of humic acids derives from the fact that these colloidal species are soluble and provide strong complexing groups (e.g., carboxylic and phenolic hydroxyls), so they can serve as carriers of toxic metals, by forming complexes that are stable and, therefore, could affect significantly the bioavailability and mobility of metals in soils, sediments, and aquatic systems. Nevertheless, depending on the filtration and sorption procedures of the aquifer system concerned, humic acids can cause either an enhancement of migration or retention. For the quantification

of each of these processes, a basic knowledge of the nature of humic acids and their complexation behaviour is indispensable [1].

Thermal analysis methods have been used extensively in the characterisation of organic material (e.g., humic substances) because they are simple and they do not need any special sample pre-treatment, providing information on the thermal behaviour and structural properties of humic substances [2–4]. The latter is true especially if spectroscopic methods such as FTIR [4,5], ¹³C-NMR [6], and mass spectrometry [7] are combined with the thermal methods. Investigations regarding the impact of temperature on the thermal stability of humic substances are of particular interest, since thermal pre-treatment has a strong impact on their water-content, structure, stability, microbial degradability, and solubility. The thermal behaviour of a humic substance also depends on its origin, type (e.g., fulvic or humic acid) and structural characteristics (e.g., protonated, complexed, adsorbed, etc.) [8–11].

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Humic substances of different origin and types vary in the overall composition, however, with a typical atom composition of $\text{CO}_{0.5}\text{H}$ (with minor contribution from S and N) [1]. Due to the relatively high oxygen content, oxidation products can also be formed under anaerobic conditions (exclusion of external oxygen). Published results show a wide spectrum of processes taking place upon thermal treatment of humic acid. Basic structural characteristics of humic acid remain intact up to 250°C , and the mass loss (about 15 wt%) is attributed to removal of water contained in the organic material [12]. Kucerik et al. [13] ascribed the mass loss observed at 110 and 210°C to the removal of physically and chemically adsorbed water, respectively. The mass loss at 210°C is associated also with partial decomposition of aliphatic groups and evaporation of small organic molecules [13,14]. Decarboxylation of the material and extensive decomposition of aliphatic structures starts above 300°C [2,15]. Furthermore, the mass loss up to 300°C is attributed to deterioration of alcoholic, phenolic, and amino groups [8,13]. In the $300\text{--}500^\circ\text{C}$ range, decomposition of aromatic structures takes place, whereas at 700°C condensation processes take place [15]. The latter processes result in increased aromaticity of the organic material [6]. Moreover, thermal studies have shown that: (a) humic acids are more stable than precursor molecules, such as lignin and cellulose, (b) protonated humic acid is less stable than the corresponding salt form, and (c) complexation of humic acids with metal ions (particularly heavy metal ions) favors thermal decomposition of the material [8–10].

Thermogravimetric analysis (TGA) and DSC studies focusing on temperatures below 100°C were also reported in the literature. In general, these investigations indicate small changes in the humic acid structure in the $40\text{--}80^\circ\text{C}$ range, which were described as glass transition processes [16–20]. The changes occurred at lower temperatures are generally attributed to the removal of different types of water molecules contained in the organic material. Three different types of water molecules are described, namely, freezable “bulk” water, physisorbed, and chemisorbed water [21,22]. According to these studies, removal of “bulk” water and physisorbed water are reversible processes, while removal of chemisorbed water is an irreversible process and results in structural changes. The release of chemisorbed water becomes predominant for temperatures above 60°C . However, these changes are also ascribed as gradual melting of residual lipids contained in the organic material [23].

The present investigation deals with the effect of temperature on the structural stability of humic acids, and in particular, the amounts and types of water released, structural changes in the residue, and also with the question if comparable processes take place in aqueous solutions compared to those in solid samples. The present studies focus on the temperature range below 250°C . For this purpose, TGA, in situ diffuse reflectance infrared Fourier transformed spectroscopy (in situ DRIFTS) and temperature-programmed desorption coupled with mass spectrometry (TPD–MS) techniques were used on solid protonated humic acid samples. Furthermore, corresponding investigations were conducted in aqueous humic acid solutions in the $25\text{--}90^\circ\text{C}$ range by means of UV–vis spectroscopy. A key question that

is addressed in the present work is the reversible desorption of water versus irreversible structural decomposition, including the comparability of processes in solid samples and samples in aqueous solution. Irreversible structural decomposition of humic acid is expected to affect its chemical properties.

2. Experimental

The soil humic acid Gohy-573 (HA) extracted from Gorleben groundwaters was used in all of the studies conducted in this work. The groundwater was isolated from 140 m depth in the Gorleben aquifer system. The humic acid originates from microbiologically mediated conversion of Miocene brown coal sand under simultaneous reduction of sulfates dissolving from the underlying Gorleben salt dome. The Gorleben salt formation has been selected as final repository for highly radioactive nuclear waste [1]. The humic acid from the Gorleben groundwater is isolated by precipitation after acidification with HCl to pH 1. The humic acid thus isolated is dissolved in 0.1 mol L^{-1} NaOH with addition of 0.2 g NaF per g humic acid and left over night. The F^- ion was introduced to dissolve silicate impurities. After duplicate purification cycles, i.e. precipitation (pH 1), dissolution (0.1 mol L^{-1} NaOH), and precipitation, the humic acid precipitates are washed with 0.1 mol L^{-1} HCl until no Na^+ ion is detected in the supernatant. Finally, the protonated product was freeze-dried. Details on origin, preparation, and characteristic properties of the humic acid samples used in the present work can be found elsewhere [1]. Gohy-573 (HA) was selected because this is an extensively characterized humic acid, particularly with respect to radionuclide migration in the geosphere. A single batch of humic acid was used and each measurement was performed in duplicate.

2.1. TPD–MS

Quantification of water, carbon dioxide, and carbon monoxide released from humic acid upon temperature elevation up to 240°C under He inert-gas atmosphere was performed by temperature-programmed desorption coupled with mass spectrometry. A custom designed gas flow-system was used [24]. Helium gas was used as a carrier in all MS experiments. Mass spectrometry was used for determination of the effluent gas composition resulting upon variation of the sample temperature under He flow [24]. The amount of humic acid sample used for the above experiments was 0.15 g. The flow rate of the carrier (He) was 30 mL min^{-1} , and the temperature of the solid sample was increased from 25 to 240°C using a heating rate of $15^\circ\text{C min}^{-1}$. Chemical analysis of the gas effluent stream was performed with an on line quadrupole mass spectrometer (Omnistar, Balzers) equipped with a fast response inlet capillary/leak valve (SVI 050, Balzers) and data acquisition systems. The gaseous responses obtained by mass spectrometry were calibrated against standard mixtures. The mass numbers (m/z) 15, 28, 44, and 46 were used for NH_3 , CO, CO_2 , and NO_2 , respectively. Before any measurements were taken, the humic solid samples were pre-treated in He flow for 30 min at 25°C .

2.2. DRIFTS

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of humic acid, water, and carbon dioxide released from humic acid was performed upon temperature elevation (up to 200 °C). The DRIFTS spectra were obtained using a Perkin-Elmer GX II FTIR spectrophotometer at a resolution of 1 cm⁻¹, using a high-temperature/high-pressure temperature controllable DRIFTS cell (Spectra. Tech.) equipped with ZnSe IR windows. About 30 mg of humic acid sample in powder form were used for each experiment. The experiments were carried out under pure Ar gas atmosphere with a flow rate of 50 mL min⁻¹. Spectra were collected after thermal pre-treatment at the appropriate temperature for 30 min and before the experiment to be followed. For FTIR single-beam background subtraction, the spectrum of the background was also taken in pure argon flow at each temperature. FTIR spectra were collected at the rate of 1 scan s⁻¹ at 1 cm⁻¹ resolution in the 800–3000 cm⁻¹ range and 40 spectra were collected and averaged. All spectra were analyzed using the instrument's Spectrum for Windows[®] software provided.

2.3. TGA

Thermogravimetric measurements were performed under inert-gas (nitrogen) atmosphere using a Shimadzu Thermogravimetric Analyzer (TGA 50). About 20 mg of humic acid solid sample in powder form was used for each experiment and the heating rate used was 5 °C min⁻¹. Four different types of TGA measurements have been performed: (a) temperature increase up to 800 °C with a constant heating rate of 5 °C min⁻¹, (b) stepwise increase of the temperature from 80 to 130 °C with thermal treatment of the sample for 0.5 h at each temperature (e.g., 80, 90, 100, 110, 120, and 130 °C), (c) temperature increase up to 110 °C and thermal treatment of the sample for 5 h at this temperature, and (d) humic acid samples (in duplicate) were thermally treated at different temperatures (40, 50, 60, 70, 80, 90, 100, and 110 °C) and were then kept for 24 h in parallel under inert-gas and normal atmospheric conditions. After 24 h the samples were weighted under inert-gas or normal atmospheric conditions to investigate cyclic temperature changes.

2.4. UV-vis

UV-vis spectroscopy was conducted with solutions of 12 mg L⁻¹ humic acid at pH 6 (10⁻³ mol L⁻¹ MES buffer) in 0.1 M NaClO₄. Solutions were kept in water bath for storage at different temperatures (e.g., 25, 60, 80, and 95 °C, ±0.1 °C). For comparability, measurements were performed after cooling down the sample to room temperature.

3. Results and discussion

The present results are discussed in the order of mass loss of solid humic acid and reversibility (TGA), chemical analysis of what is lost from the solid samples (TPD-MS), the structure of what is left after thermal treatment of the solid samples (in situ

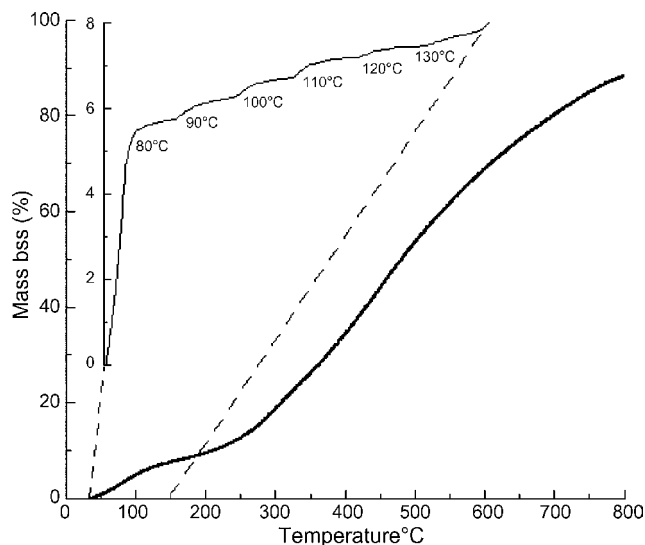


Fig. 1. Thermogravimetric analysis of Gohy-573(HA) under nitrogen inert-gas atmosphere. The temperature was increased up to 800 °C with a constant heating rate of 5 °C min⁻¹. The inserted graph shows the loss in mass as a function of the stepwise increase of the temperature from 30 to 130 °C with thermal treatment of the sample for 0.5 h at each temperature.

DRIFTS), and finally the impact of thermal treatment on humic acid in aqueous solutions (UV-vis spectroscopy).

3.1. Thermogravimetric analysis (TGA)

Fig. 1 shows the mass loss (wt%) of solid humic acid under inert N₂ gas as a function of temperature. At about 250 °C, there is a sharp rise in mass loss which reaches almost the value of 90% at 800 °C. Most interesting is the region where a plateau is obtained (around 140 °C up to 240 °C). The mass loss at 80 °C is about 5.5 wt%. Increase of the temperature in steps of 10 °C leads to additional mass loss of the order of 0.3 wt%. The response to a temperature increase of 10 °C resulted in an initial relatively rapid mass loss, followed by a flattening of the mass loss curve. The different temperature steps between 80 and 130 °C correspond to different degrees of mass loss, which can be ascribed to water molecules adsorbed at different structures/characteristic groups of the humic acid requiring a certain temperature for their desorption or even the decomposition of certain structures/characteristic groups of the material [25]. The absence of a defined and constant temperature for water desorption and the gradual mass loss observed in this study is described in the literature as glass transition process [16–20] or even as the gradual melting of residual lipids contained in the organic matter [23]. In Fig. 2 this time-dependent response is shown in more detail for a temperature elevation to 110 °C. Steady state is achieved after about 5 h with a fading out mass loss between 1 and 5 h of about 0.3 wt%. The question that arises at this point is to which extent the mass losses are reversible or associated with irreversible decomposition processes.

In order to investigate the reversibility of the mass loss behaviour, cyclic temperature changes were conducted. Humic acid samples treated thermally under nitrogen inert-gas atmosphere at different temperatures (from 40 to 110 °C) were

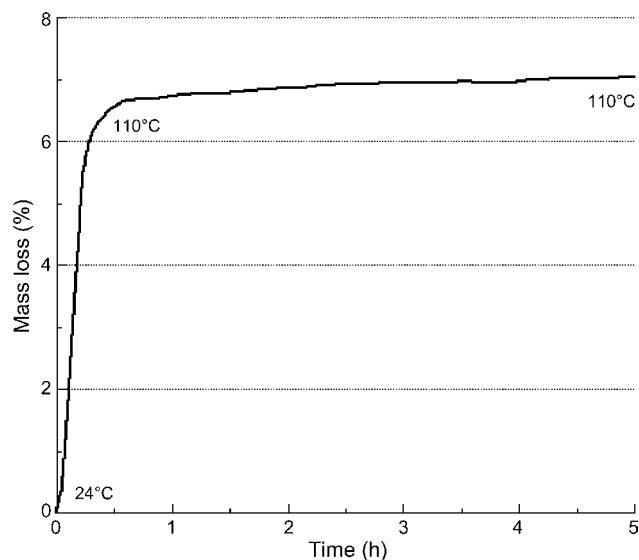


Fig. 2. Thermogravimetric analysis of Gohy-573(HA) at constant temperature of $T = 110^{\circ}\text{C}$ and under nitrogen inert-gas atmosphere.

afterwards left in parallel under nitrogen gas atmosphere and normal atmospheric conditions and the change in weight was determined after 24 h storage. The results for such investigations within the temperature range between 40 and 110°C are presented in Fig. 3. In contrast to samples kept under inert-gas atmosphere, samples under normal atmospheric conditions adsorb water from the environment, indicating a reversible water loss. This process is quantitative for samples treated up to 70°C . However, above 80°C a significant irreversible mass loss was found that increases with increasing temperature. The quantitative re-adsorption of water in samples treated up to 70°C is a strong indication that the reversible mass loss is associated only to water molecules. However, the irreversible mass loss could be related to water release of chemisorbed water molecules and water molecules produced by condensation or to decarboxylation processes as well. The question of which material is lost at

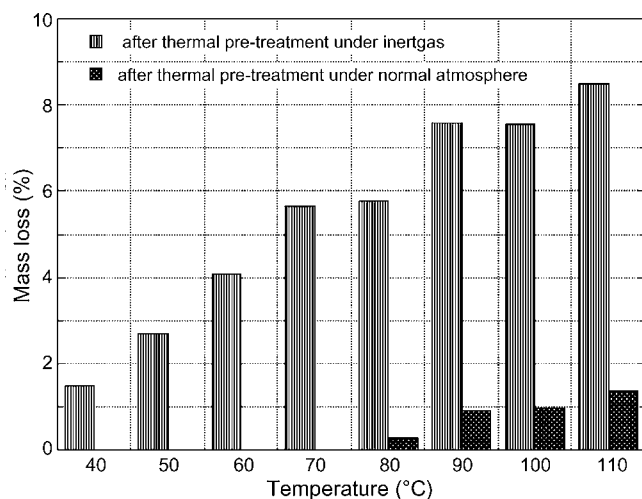


Fig. 3. Loss in mass (wt%) of humic acid Gohy-573(HA) sample at different temperatures (grey bars) and “non-reversible” mass loss (wt%) after subsequent contact with normal atmospheric conditions (black bars).

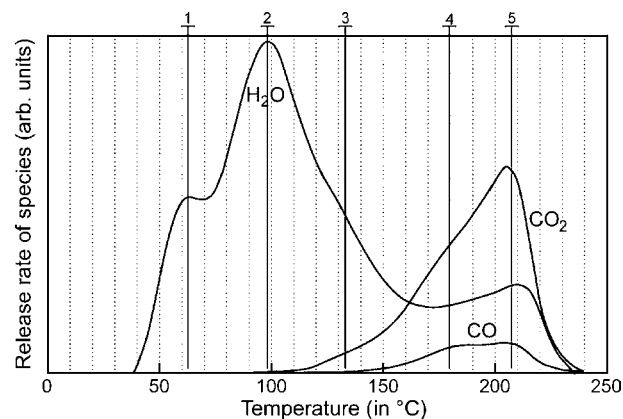


Fig. 4. Release of water, carbon dioxide and carbon monoxide monitored by mass spectrometry upon thermal treatment of Gohy-573(HA) under helium inert-gas atmosphere.

different temperatures, and how this relates to any reversible versus irreversible contributions was further investigated by means of temperature-programmed desorption with mass spectrometry.

3.2. Temperature-programmed desorption with mass spectrometry (TPD–MS)

Fig. 4 presents the rate of release of water, carbon dioxide, and carbon monoxide from solid humic acid as a function of the temperature of the solid. Five different process steps are observed. The first step is the loss of water peaking around 60°C . As the temperature was increased, a second stronger peak which also corresponds to the loss of water appears at around 100°C . Above 100°C , carbon dioxide is released in three steps. The first release takes place up to about 150°C , while the next two steps coincide with the release of carbon monoxide with peaks appearing at around 180 and 205°C . The oxygen to carbon atom ratio in humic acid is around 1:2. This allows the formation of considerable amounts of carbon monoxide and dioxide in the absence of external oxygen source, as observed in the present TPD–MS experiments conducted under helium inert-gas.

By combining the above-mentioned results with the TGA ones, it appears as if the first peak observed in Fig. 4 is associated with reversible loss of water, whereas the subsequent steps are associated with irreversible decomposition processes. Furthermore, the mass spectrum clearly shows that decarboxylation of the humic acid starts above 100°C and that this is a parallel process to water release, up to about 250°C . This findings are complementary to previous investigations [12–15], which ascribe the mass loss up to 250°C to water release and consider that basic structural characteristics of humic acids remain intact up to 250°C and decarboxylation of the material starts above 300°C .

The question arising is whether the water release and the decarboxylation process can also be monitored by structural changes of the remaining substance following thermal treatment of the solid humic acid. To answer this question humic acid sample were investigated by diffuse reflectance infrared Fourier

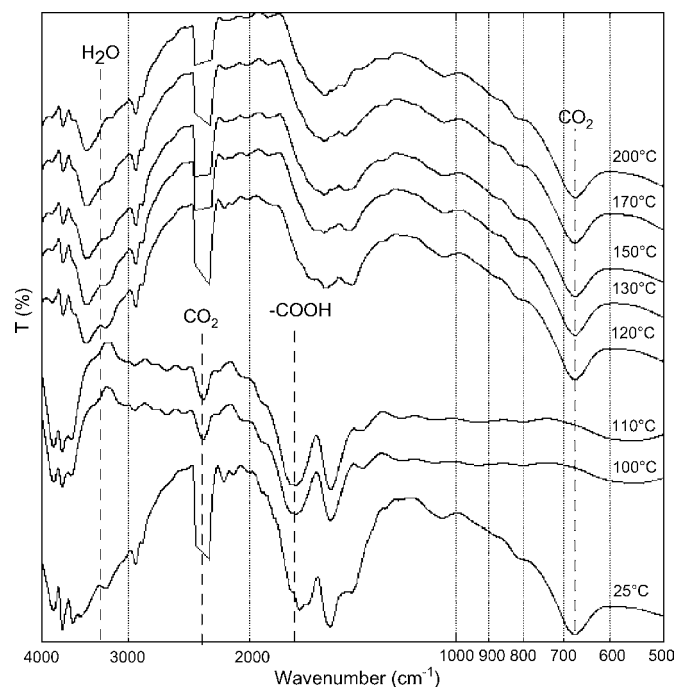


Fig. 5. In situ DRIFTS spectra at different temperatures of Gohy-573(HA) under argon inert-gas atmosphere. Dotted vertical lines show water, carbon dioxide and carboxylic groups, the former two also present in the inert-gas in the measurement chamber, after release from the humic acid.

transformed spectroscopy at different temperatures under inert-gas atmosphere.

3.3. Diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS)

Fig. 5 compares the in situ DRIFTS spectra obtained after heating the humic acid sample from room temperature to 100 and stepwise to 200 °C. The spectrum obtained at room temperature shows the typical characteristics of humic acid (e.g., the OH-stretching at 3450 cm^{-1} , the methylene bands C–H at 2920 and 2850 cm^{-1} , the C=O stretching vibrations due to carboxylic groups at 1720 cm^{-1} , the 1620 cm^{-1} band due to C=C bonds conjugated with C=O and COO^- groups). In addition, carbon dioxide is observed to be remaining in the sample holder. This carbon dioxide is not flushed out of the chamber with the argon gas because it is adsorbed on the silica used as filling material within the sample holder of the DRIFTS cell used. Desorption of the adsorbed carbon dioxide starts when the sample holder is heated and the carbon dioxide is flushed out almost completely by the carrier gas flowing in the chamber (spectra at 100 and 110 °C). With respect to the humic acid, the main difference obtained at 100 and 110 °C as compared to the spectrum obtained at room temperature, is the loss of water (IR band around 3200 cm^{-1}). At higher temperatures, the bands of COOH (around 1720 and 3600 cm^{-1}) were significantly decreased. At the same time, carbon dioxide gas appears in the sample holder, indicating carbon dioxide production caused only by the decarboxylation/decomposition of the thermally treated humic acid. The latter results are in harmony with the ones shown in Fig. 4,

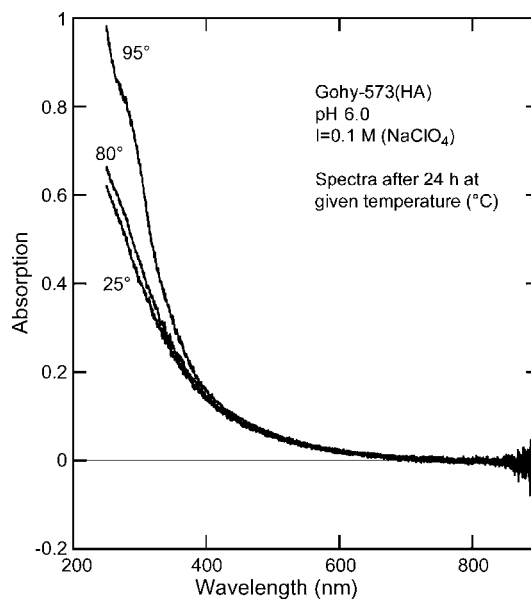


Fig. 6. UV/vis spectra of Gohy-573(HA) solution after storage at different temperatures for 24 h.

namely that the key process up to about 100 °C is the loss of water, followed by the release of carbon monoxide and dioxide, e.g., decarboxylation at higher temperatures.

In order to study to which extent the reversible and irreversible structural changes observed also take place in aqueous solutions of humic acid, UV–vis spectroscopy was used to investigate aqueous humic acid samples after thermal treatment.

3.4. UV–vis of aqueous humic acid solutions

Fig. 6 shows UV–vis spectra of humic acid solutions after storage for 24 h at 80 and 95 °C in comparison with the spectrum stored at 25 °C. The spectra were recorded after lowering the temperature to 25 °C, allowing therefore a comparison of the samples and reversible re-hydration. After 24 h of storage at 60 °C, no change is observed (not shown). A slight change is seen after storage for 24 h at 80 °C. However, at 95 °C storage temperature the change becomes substantial. The impact of storage at 60 °C for longer storage times is shown in Fig. 7. A slight change in the spectra is seen upon storage at 60 °C for 1 week. This change is in comparable magnitude to that obtained after storage for 24 h at 80 °C. The substantial change observed after storage at 95 °C for 24 h is very comparable to the one obtained upon storage at 80 °C for 1 week.

The temperature dependent change in the UV–vis absorption spectra and in particular the molar absorption coefficient at e.g., 280 nm indicates the formation of more condensed polyaromatic structures caused by the thermally induced condensation of carboxylic and phenolic groups of the humic acid [26]. The above results show clearly that the changes observed between humic acid in aqueous solution and the solid humic acid samples are comparable, namely that reversible de-hydration/re-hydration takes place at temperatures corresponding to the loss of water with its maximum at 60 °C (see Figs. 3 and 4). On the contrary, at higher temperatures and extended times, irreversible changes are

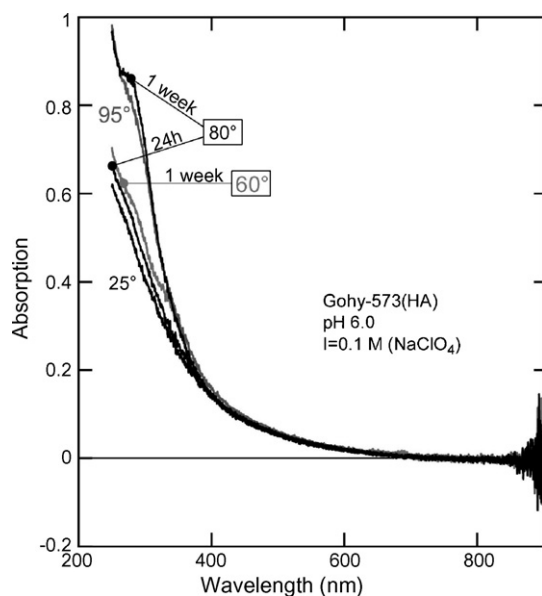


Fig. 7. UV/vis spectra of Gohy-573(HA) as given in Fig. 1 (24 h storage time). In addition, influence of 1 week storage time at 60 and 80 °C.

initiated at around 80 °C, through loss of water. The latter is most probably related to the release of chemisorbed water molecules or water molecules produced by condensation processes, which could occur among adjacent carboxylic and alcoholic groups of humic acids.

4. Conclusions

The results obtained from this study lead to the following conclusions:

- Reversible loss of water takes place at about 60 °C.
- Irreversible loss of water starts above 70 °C.
- Above 100 °C decomposition of HA takes place followed by release of carbon dioxide and above about 140 °C, carbon monoxide is also released.
- Humic acid dissolved in aqueous solution (pH 6.0, 0.1 mol L⁻¹ NaClO₄) shows similar responses to thermal treatment up to 95 °C. The corresponding UV–vis spectra indicate the formation of more condensed polyaromatic structures caused by the thermal treatment of the aqueous humic acid above 70 °C.

The results obtained in the present work have important implications for a number of topics, such as the stability of humic material in the vicinity of heat sources, such as disposed heat generating nuclear waste in the early phase after closure of such a repository. They also have important implications for studies on the complexation behavior of humic acid as a function of temperature. Thermodynamic evaluation of data where irreversible decomposition takes place would result in erroneous conclusions.

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