

Humic Acids – Are They Natural Products?*

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Alkaline cleavage of soil organic matter was studied by following the changes in absorbance at 250–270 nm, but particularly using differential pulse polarography. The measurement of peak currents obtained by the latter technique allowed to follow changes in concentration of CH₃O- and HO-substituted benzaldehydes as well as of α,β -unsaturated ketones with time directly in the suspension of soil. Kinetics of the cleavage of the organic materials from soil and in particular its pH-dependence, were similar to that of cleavage of lignin, but different from those obtained with samples of humic acids. Based on this comparison and on discussion of chemical processes taking place during procedures used for isolation of humic acids from soils and waters, it is strongly indicated that humic acids are man-made macromolecular species rather than natural products.

INTRODUCTION

The term »soil organic matter« (SOM)¹ is used to describe all organic material present in soil.² These materials result from decomposition of plants and living organisms, including microbes. This decomposition can occur in varying degrees. The transformation of original plants and living organisms and their products is called humification.³ The relatively stable product of humification is humus, which over some periods of time does undergo very slowly further decomposition. The timings of individual steps of such transformations differs considerably – from days and weeks to months. Humus must also undergo another – very slow – transformation, which can take place over periods of years. To follow such slow processes, involving most probably microorganisms, is difficult, but it must take place. The rate of final decomposition of humus must be comparable or faster than its

formation,⁴ as otherwise all continents would long be covered by a layer of humus.⁵ The rate of individual processes may depend on conditions, such as humidity, pH, temperature, presence of microbes and air as well as inorganic components, that can either act as catalysts or produce solid surfaces, where adsorption of reactive species can occur. The role of conditions can be illustrated on related formation of manure, which in piles can take months, but occurs much faster when mechanical aeration is used.

For the present discussion decomposition of living organisms and the fate of their products will be left aside and the attention restricted to the fate of materials originating from plants – from trees and bushes to grasses. The genesis of components of humus is still a widely open question. One obstacle in achieving the solution of this problem lies back in history. In 1826 Sprengel⁶ (based on observation of the influence of alkaline solution

* Dedicated to the memory of the late Professor Marko Branica.

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on peat by Aachard⁷ in 1786) proposed fractionation of SOM which was based on differences in solubility under varying conditions in aqueous media. In a procedure, still most frequently used for fractionation of SOM, the soil is treated with a strongly alkaline solution, typically between 0.1 and 2.0 M NaOH. The part of SOM, that remains insoluble in such alkaline solution, is called humin and this fraction remains practically insoluble over the entire pH-range. The soluble fraction is acidified to pH < 4, usually to pH = 1 or 2. This results in a formation of solid material, denoted as humic acids. The fraction remaining in the solution under such conditions is called »fulvic acids.«

In other approaches using less drastic conditions, the soil is extracted by an organic solvent, by solvent mixtures or concentrated salt solutions. Macromolecular species, which may not be related to humic acids are then obtained by acidification of the extract.

Soil in wooded or cultivated areas will contain pieces of more or less rotted wood or rotted straw, (which consist predominantly of lignin), pieces of plants and grasses and products of their decomposition, which can proceed to various degree. High molecular weight species present will consist of polysaccharides and natural polymers, such as lignins, tannins and similar materials. But present will be also products of microbial activity, which may include lower m.w. polymers, resulting from the cleavage of the large, often three-dimensional ones, as well as various low molecular weight compounds. When such a mixture is exposed to strongly alkaline solutions, numerous chemical reactions, including depolymerization and repolymerization can occur. The part of the lignin, which is soluble in alkaline media (possibly segments less cross-linked than the insoluble humin), yields on alkaline cleavage a mixture of reactive species, such as aromatic aldehydes and α,β -unsaturated carbonyl compounds.⁸ The low molecular weight organic compounds and some oligomers present in the mixture can undergo a variety of reactions, starting as Michael additions, aldolisations, Cannizzaro reactions and host of other reactions, which in some cases may result in re-polymerization, yielding new oligomers and low molecular weight polymers. As the alkaline treatment is usually carried out in the access of air, an oxidation favored by the high pH, takes place, in which for example present aldehydes yield carboxylic acids. Liberated phenolic compounds may also undergo base catalyzed polymerization. The alkaline cleavage of carbohydrates can result in formation of enediols – powerful reducing agents – as well as products of Malaprade conversions. Some of the products present in the mixture can undergo reactions with nucleophiles, such as compounds bearing amino and/or thiol groups resulting from decomposition of proteins.

Once this complex mixture is formed – often under not well-defined conditions, such as time of contact or temperature – it is acidified. The change in pH results in acid catalyzed reactions and some of them result in formation of macromolecular species. Slightly soluble fraction is separated and the mixture of low molecular weight organic compounds and possible some oligomers that remains dissolved at pH = 1 or 2 is denoted »fulvic acids.« The undissolved fraction, containing higher molecular weight species of limited solubility, are »humic acids.« These macromolecular species nevertheless differ in their properties from parent polymers, present before placing the soil into alkaline solutions. The natural larger molecular weight polymers present in soil, exemplified by lignin, are over a period of hours stable at pH < 8, whereas the macromolecular species known as humic acids, undergo cleavage already at pH > 5.

To prove the above working hypothesis, the cleavage of authentic lignin samples – both of natural origin (rotted wood) and commercial – was carried out under mildly alkaline conditions (pH = 8–11) at 25 °C. Under such conditions kinetics of the cleavage and formation of aromatic aldehydes and α,β -unsaturated ketones was followed. The kinetics of this cleavage was compared with cleavage, obtained under identical conditions, for different types of soils and for humic acids, obtained from soils by above described procedure as well as for commercial samples.

EXPERIMENTAL

Instrumentation

The dc current voltage curves and differential pulse polarographic (DPP) curves were recorded using a Sargent-Welch Mark 4001 polarograph with a controlled drop time of 1 s. DPP curves were recorded using an excitation signal $\Delta e = 50$ mV and a controlled drop time (1 s). The dropping mercury electrode used had $m = 3.01$ mg s⁻¹ and $t_1 = 2.9$ s at $h = 73.5$ cm in a 0.1 mol dm⁻³ KCl at 0.0 V (SCE). The curves were recorded with $h = 56$ cm. Polarographic studies were conducted in a Kalousek cell using a saturated calomel electrode separated by a liquid junction as a reference.

pH measurements were carried out with a PHM 84 Research pH meter (Radiometer) with a G202B glass electrode and a K422 saturated calomel electrode, both from Radiometer. UV absorption spectra were recorded with a Perkin-Elmer spectrophotometer Mark 559.

Chemicals and Solutions

Vanillin (4-hydroxy-3-methoxybenzaldehyde) (99 %), syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) (98 %), isovanillin (3-hydroxy-4-methoxybenzaldehyde) (99 %), 4-hydroxybenzaldehyde (98 %), *trans*-cinnamaldehyde (*trans*-3-phenyl-2-propenal) (99 %), and humic acid, sodium salt

were all obtained from Aldrich Chemical Company and used without further treatment.

Chemicals used for preparation of buffers were analytical or reagent grade and used as supplied. Acetate buffers were prepared by mixing solutions of acetic acid and sodium acetate in varying proportions, keeping the total analytical concentration of acetic acid 0.2 mol dm^{-3} . To prepare phosphate buffers pH = 3, 6–8, and 10.5–12, solutions of phosphoric acid, potassium dihydrogen phosphate, dipotassium hydrogen phosphate and sodium phosphate were mixed in varying proportions, keeping the total analytical concentration of phosphate 0.2 mol dm^{-3} . Another set of buffers was prepared using potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium phosphate and potassium chloride. In this series, pH = 6.6, 7.6, 10.0, and 11.1 were prepared with the concentration of HPO_4^{2-} kept at 0.1 mol dm^{-3} and ionic strength 0.5 mol dm^{-3} .

Borate buffers pH = 8 to 10 were prepared by titrating a solution of boric acid with sodium hydroxide keeping the total concentration of boric acid 0.2 mol dm^{-3} . Potassium chloride was added to keep the ionic strength 0.5 mol dm^{-3} . All solutions were purged with nitrogen for at least 2 minutes before recording the current voltage curves.

Preparation of Lignin Samples

The natural materials were ground with a mortar and pestle and passed through a screen with 0.14 cm openings before being washed with distilled water.

The first natural material came from the Clarkson University campus and was gathered from a rotten maple log. The material was of a light brown color, resembling indulin ATR-CK1, but still had some of the structure of the original wood. It was brittle and crumbled when pressed by fingers. It was dried before grinding. 91 g of this material were dispersed in 1 L of distilled water for two days, filtered and dried.

The second natural material was obtained from a rotten stump in the Manistee National Forest in Michigan and was similar in appearance to the first rotwood lignin. One portion was used directly after grinding and screening. For preparation of a second specimen, 57 g of the natural material were dispersed for 4–5 days in 1 L of distilled water, filtered and dried.

A third natural material was obtained from a rotten aspen log from Postwood Park, Hannawa Falls, NY. After grinding and screening, 26 g of the powdery material was dispersed in 1.5 L of distilled water, filtered and dried.

Samples of soil, identified as Swanton sandy loam and as silty loam by the Cooperative Extension of Cornell University at Canton, NY, were dried and passed through a 35 opening/inch sieve before use.

One commercial and three natural lignins (described above) were used in this study. Indulin ATR-CK1 from Westvaco was prepared from precipitated softwood kraft lignin by heat coalescence and spraying: C_9 formula, $\text{C}_9\text{H}_{8.40}\text{O}_{2.39}\text{S}_{0.09}(\text{OCH}_3)_{0.79}$ (64.5 % C, 5.82 % H, 27.7 % O, 1.6 % S); $M_r = 180$; pH = 3.68; ash 1.65 %; acetone solu-

bility 68.8 %; carboxylic acid content 0.42 mol kg^{-1} ; methoxy group content 4.50 mol kg^{-1} ; phenolic hydroxide content 4.2 mol kg^{-1} . The surface area is about $100 \text{ m}^2 \text{ g}^{-1}$ (BET). This material (177 g) was washed twice with 1.5 L of distilled water and dried. This material was sieved with a 120 opening/inch screen before use.

Preparation of Humic Acid Samples

The sodium humate was obtained from Aldrich Chemical Company and was technical quality, containing approximately 50–60 % actual humic acid. It was prepared from brown coal and contained chelated metal ions, had a molecular weight range from 2 000 to 50 000, contained 15–25 % moisture and an additional 15–25 % ash.

A portion of the sodium humate (5.5 g) was dissolved in water (200 mL) and precipitated at pH = 2.00 with HCl. The precipitate was separated by centrifugation, rinsed, centrifuged again and dialyzed (Cellophane tubing, Fisher Scientific) against distilled water. After several days of dialysis, the material was dried, ground with a mortar and pestle, and passed through a 120 opening/inch sieve.

Humic acids were also obtained from both rotwood and commercial lignins and from soil (Swanton Sandy loam). Samples of each material were placed in 1.0 M NaOH and stirred under nitrogen for several hours. The resulting solutions were filtered, acidified with HCl to pH = 2, the resulting precipitate washed several times with distilled water, and dialyzed against distilled water for several days before drying, grinding and sieving.

Alkaline Cleavage of Lignins, Humic Acids and Soils

To follow the kinetics of cleavage reactions as a function of pH, 0.1 g of the studied material was suspended in 15 mL of the selected buffer in a polarographic cell. The buffer was purged with nitrogen for at least 2 minutes before the addition of the organic material and the DPP base line recorded. After the introduction of the organic material, the DPP curves were recorded at selected time intervals. Periodically some nitrogen was introduced to stir the solution. Occasionally, the particles adhering at the top of the cell were rinsed down using some of the solution. The current at infinite time was estimated and the natural logarithms of the difference between the peak current at infinite time and at a given time were plotted as a function of time. The rate constants at different pH values were obtained from the linear portions of these plots.

Identification of Reduction Peaks

Appropriate amounts of lignin or humic acid were dispersed in 0.2 M phosphate buffer, pH = 11 and kept for 40 minutes under nitrogen. An aliquot was transferred to the electrolytic cell and a DPP curve recorded. Samples of vanillin, isovanillin, and syringaldehyde were added and increasing peaks were identified on the DPP curves.

RESULTS AND DISCUSSION

To demonstrate the relationships between lignins, soil organic material and humic acids, samples of the studied materials were dispersed in alkaline solutions and changes in composition were followed with time using spectrophotometry and polarography. The suspensions of lignins, soils and humic acids in buffered solution were turbid due to the presence of solid and colloidal particles. This situation resulted in considerable limitation of the application of spectrophotometry. Due to a strong background, resulting in turbid samples, predominantly from light-scattering, the absorption spectra did not manifest any well-defined absorption bands (Figure 1). It was, nevertheless, possible to measure the change in absorbance in the range between 250 and 270 nm to follow the kinetics of dissolving benzenoid substances, bearing conjugated side-chains.

Differential pulse polarography, on the other hand, proved to be a suitable method for following the kinetics of the alkaline cleavage of studied materials. Under conditions used the slightly soluble and colloidal materials present in the turbid samples proved not to affect the re-

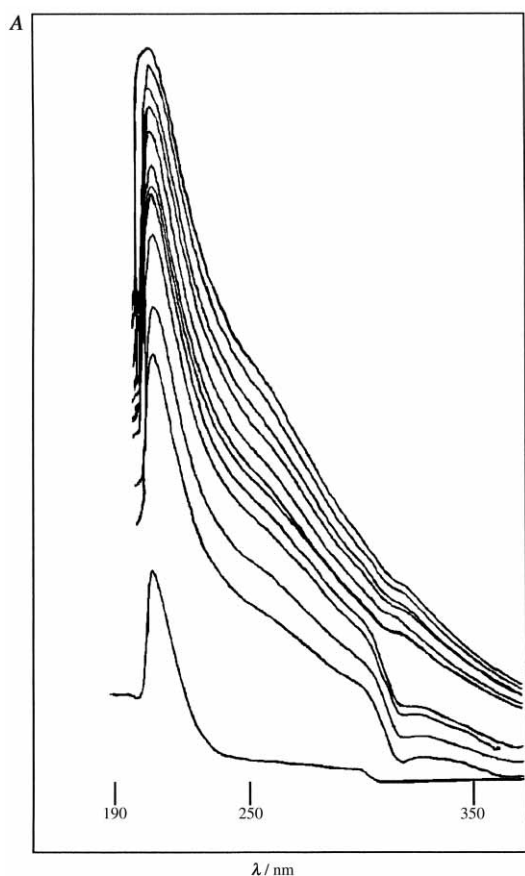


Figure 1. Alkaline cleavage of organic materials from Swanton sandy loam. 0.5 g of soil suspended in 25 mL of phosphate buffer, pH = 10.5. Reaction quenched by adjusting the pH to 8.0 and spectra recorded after filtering. Time of quenching from bottom curve up: 0; 1.0; 1.23; 2.13; 3.18; 4.19; 5.17; 9.50; 14.0; 19.95 and 23.0 min.

corded current-voltage curves. It is indicated that the insoluble materials are sufficiently hydrophilic so that are not strongly adsorbed at the dropping mercury electrode.⁹ Neither the peak shape nor the peak current is affected by the presence of the solid and colloidal material.

Recording of current-voltage curves in dispersions of lignins and soils in buffers, pH = 8–12, as a function of time resulted in an increase of a peak at about -1.6 V (Figure 2). By spiking the studied solutions with vanillin, syringaldehyde and isovanillin it was possible to attribute this peak to the reduction of the formyl (CHO) group in methoxy- and hydroxy-substituted benzaldehydes. In solutions of pure buffers in the same pH-range the peaks of these three aldehydes can be separated, but in the presence of colloidal materials among the cleavage products their peaks overlap. The peak current at -1.6 V is thus a measure of the total concentration of benzaldehydes, bearing in *m*- and *p*-positions OH and OCH₃ groups.

The increase of the peak of benzaldehydes at -1.6 V is accompanied by an increase of a broader, step-like peak at about -1.3 V (Figure 2). By a comparison with reduction peaks of *trans*-cinnamaldehyde and chalcone at several pH-values this peak was identified as corresponding to a hydrogenation of the C=C bond in an α,β -unsaturated carbonyl compound.

For a given sample of lignin or of soil, the dependence of the peak current at -1.6 V, obtained by differential pulse polarography (DPP), on time in a chosen buffer, resembles the time-dependence of the absorbance at 250 nm (Figure 3). The parallel time dependence of the absorbance at 250 nm and of the DPP peak currents at -1.6 V indicates that the change in absorption spectra is predominantly due to a change in concentration of compounds with an ArCH=O grouping. Nevertheless, the spectral data do not allow to exclude formation of other aromatic species, *e.g.*, phenolates or benzoic acid derivatives, in parallel reactions. As thus the polarographic data are more selective and the current peaks obtained by DPP can be measured with greater accuracy, and as the changes in peak currents at -1.6 V correspond to concentration changes of a single type of cleavage products, DPP became the analytical method of choice in further kinetics studies. Full advantages could have been taken of the possibility to follow the kinetics directly, *in situ*.

Various lignins undergo in buffers of pH = 8 to 12 at 25 °C a cleavage resulting in formation of benzaldehydes substituted in *meta*- and *para*-positions by OH and OCH₃ groups.⁸ This cleavage follows, at a given pH, kinetics first order in the benzaldehyde formed. The rate constant (k_{obs}) of this reaction increases with increasing pH. In suspensions of soil the increase in peak current at -1.6 V obtained by DPP follows a pattern closely resem-

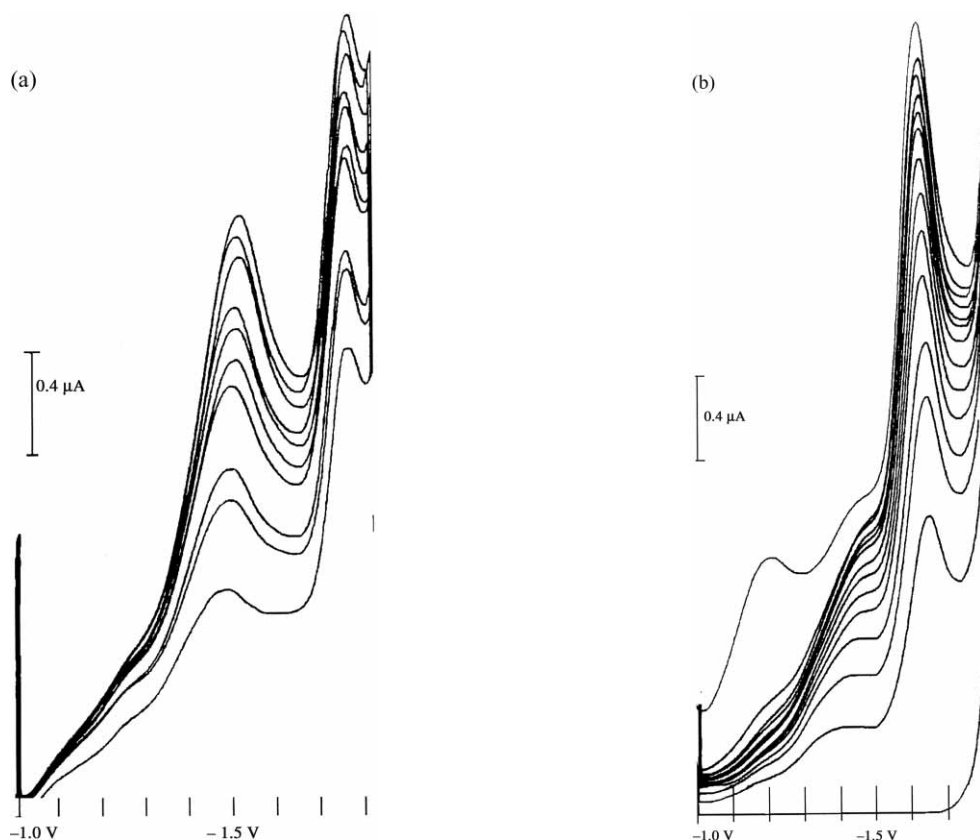


Figure 2. Alkaline cleavage of organic materials from (a) Canton silty loam and (b) Manistee National Forest rotwood lignin. 0.5 g of soil or lignin was suspended in 15 mL phosphate buffer, pH = 10.6. Reaction followed directly in suspension by recording current-voltage curves using differential pulse polarography after following times after mixing: For (a) 0.5; 3.0; 5.0; 8.0; 11.0; 14.0; 20; 30; 40 and 60 min; for (b) 0.4; 2.2; 4.0; 6.3; 8.0; 11.0; 15.0; 20; 24; 32; 50; 65 min and 22 hours. Times increase from bottom up. Potential range -1.0 V to -1.8 V (SCE), $t_1 = 3.1$ s.

bling that obtained in the same buffer of pH = 10.0 in a suspension of a rotwood lignin (Figure 4). In both cases the cleavage follows kinetics that is first order in the formed benzaldehyde derivative (Figure 5). The first order rate constant (k_{obs}) obtained from $\log i = f(t)$ plots (Fig-

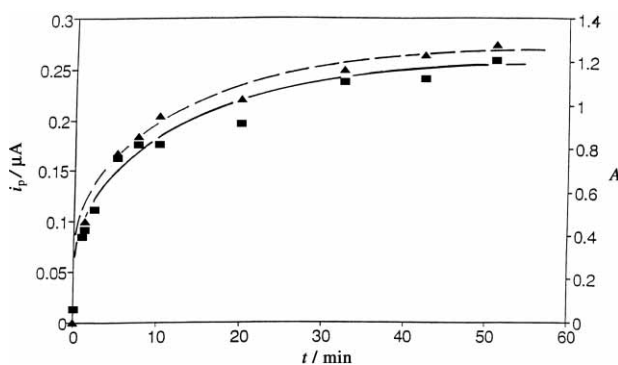


Figure 3. Alkaline cleavage of organic materials from Canton silty loam. Comparison of time dependence of absorbance at 250 nm (■) and peak currents, i_p (▲). Reaction carried out in a borate buffer, pH = 10: Current-voltage curves recorded directly in the suspension, spectra recorded after quenching to pH = 8 and filtration.

ure 5) for suspensions both of a lignin and of soil increases with increasing pH (Figure 6). The plot of the rate constant k_{obs} as a function of pH has a shape of a part of a dissociation curve of an acid with $\text{p}K_a$ -value about 11 (Figure 7). Such shape of the pH-dependence of k_{obs} excludes the possibility that depolymerization-cleavage is initiated by a nucleophilic attack of OH^- ions. Rather it indicates that the initial step is a rapidly established acid-base equilibrium with $\text{p}K_a$ about 11, which precedes the rate-determining step of the depolymerization. A possible candidate in a lignin molecule is a phenolic hydroxy group. Thus it seems necessary to convert a phenol into a phenolate to initiate the depolymerization. Alternatively, the initiating reaction may be addition of hydroxide ions to formyl groups, forming a geminal diol anion. This reaction has also $\text{p}K_a$ value of about 12. Thus the kinetics and in particular the shape of the dependence of k_{obs} on pH indicate that alkali induced changes in lignin and changes in SOMs from soil follow a very similar pattern.

On the other hand, the behavior of all humic acid specimens – the one obtained from soil using the procedure described in Experimental as well as the one pre-

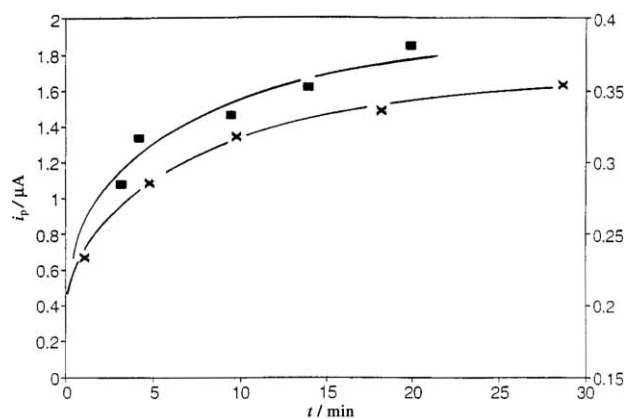


Figure 4. Comparison of alkaline cleavage of the soil organic material with alkaline cleavage of rotwood lignin in phosphate buffer, pH = 10.5. Peak currents, i_p , obtained by differential pulse polarography as a function of time. Curves obtained in a suspension of 0.1 g of rotwood lignin from Clarkson maple (x) and left hand current axis) in 15 mL buffer and 0.5 g of Swanton sandy loam in 25 mL buffer (right hand scale and ■).

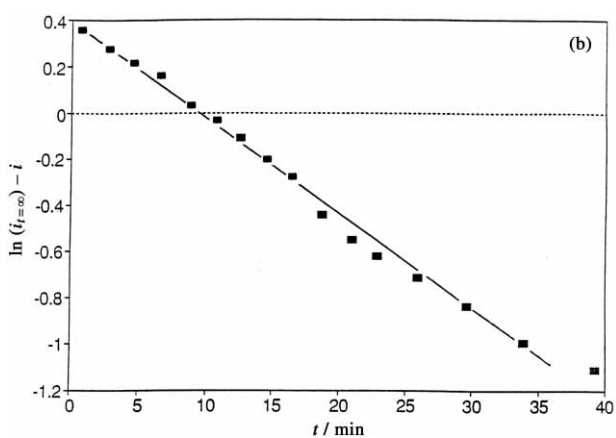
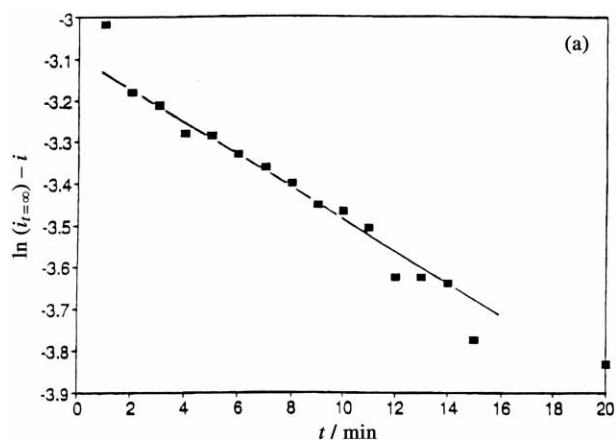


Figure 5. Comparison of alkaline cleavage of soil organic material with alkaline cleavage of rotwood lignin in a borate buffer of pH = 10. First order kinetic plots, $\log(i_\infty - i) = f(t)$ for: (a) cleavage of soil organic matter: 0.4 g silty loam dispersed in 15 ml borate buffer, pH = 8.0; (b) 0.5 g rotwood lignin from Clarkson maple in a borate buffer, pH = 10.0.

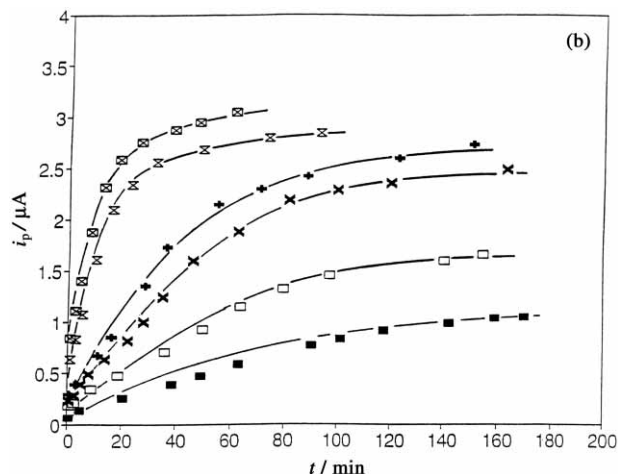
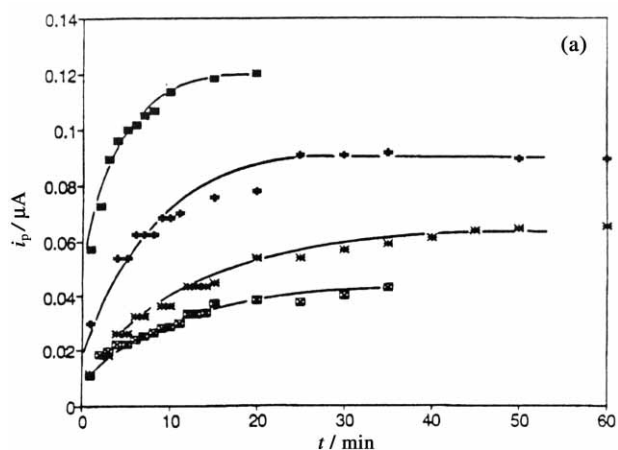


Figure 6. Comparison of alkaline cleavage of soil organic material with alkaline cleavage of a lignin. Effect of pH on the increase of peak current i_p obtained by differential pulse polarography with time. (a) cleavage of soil organic matter: 0.4 g silty loam dispersed in following buffers: phosphate buffer, pH = 8.0 (⊠); borate buffer, pH = 9.0 (x); borate buffer, pH = 10.0 (+); phosphate, buffer pH = 10.0 (■); (b) cleavage of rotwood lignin from Clarkson maple: 0.1 g lignin dispersed in following buffers: phosphate, pH = 7.4 (■); borate, pH = 8.3 (□); borate, pH = 8.7 (x); borate, pH = 9.0 (+); borate pH 10 (⊠) and phosphate, pH = 10.3 (⊠).

pared from natural and commercial kraft lignins, which all were similar – were different from behaviors of lignins and SOMs. The humic acid specimens became well soluble at pH > 3, whereas lignins remain insoluble at least up to pH = 7.5. The cleavage of humic acids producing benzaldehyde derivatives takes place already at pH > 5 whereas of lignins and SOMs only at pH > 8. The kinetics of the cleavage was as above followed by the increase in concentration of soluble benzaldehyde derivatives, which at lower pH-values used, occurred at –1.3 V to –1.4 V. The plots of dependence of peak currents obtained by DPP on time of the contact with the buffer used were similar for all humic acids investigated. The shape of these plots (Figure 8) were, nevertheless,

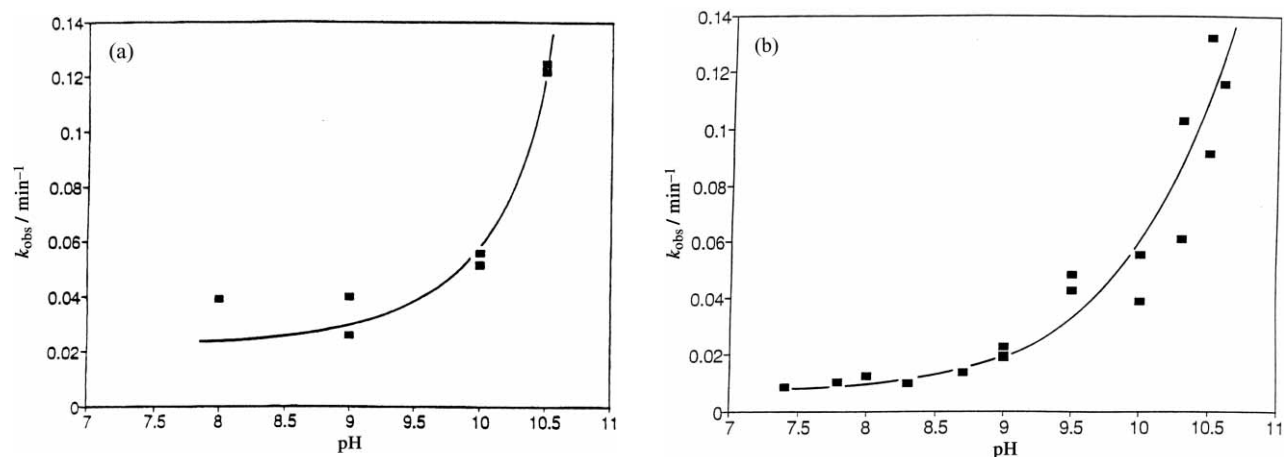


Figure 7. Comparison of alkaline cleavage of soil organic material with alkaline cleavage of rotwood lignin. Dependences of first order rate constants of the cleavage on pH: (a) rate constants for Swanton sandy loam; (b) rate constants for lignin from rotten aspen log from Postwood Park, Hannawa Falls, NY.

completely different from patterns observed for soils and lignins (Figure 6).

The cleavage of humic acids takes place in two steps: In the first step a reaction occurs, which at pH higher than about 7.5 is fast and practically completed in less than 2 minutes. The yield of this fast reaction, as indicated by current extrapolated to $t = 0$, does not seem to change much with increasing pH (Figure 8). The slower cleavage of humic acids was still much faster than the cleavage observed in suspension of soils and lignins. The conversion of a humic acid was – at pH 7 – practically complete within 5 minutes. For lignins and SOMs – even at pH = 11 – the reaction needed at least 30 min to reach completion. Also the pH-dependence has shown a different pattern: The rate of the slower reaction in the cleavage of humic acids decreased with increasing pH, whereas just the opposite was observed for cleavages of

lignins and SOMs. Similar difference was observed also for the maximum yields. Whereas for humic acids the maximum yield decreased with increasing pH, for lignins and SOMs the yields of aromatic aldehydes increased with increasing pH (Figures 6 and 8). The rates and yields of cleavage have been shown to be independent of the size of particles of sodium humate (Figure 9), indicating that the rate of dissolution is not the limiting factor of the rate of cleavage.

Even when our experiments were restricted to comparison of alkaline cleavages of SOMs with those of lignins, some comments can be added dealing with separation of humic acids from soils using extraction and with processes involved in isolation of humic acids from waters.

When organic solvents are used to separate humic acids from soils, small fragments of lignin, possibly containing some oligomers, are extracted into organic phase.

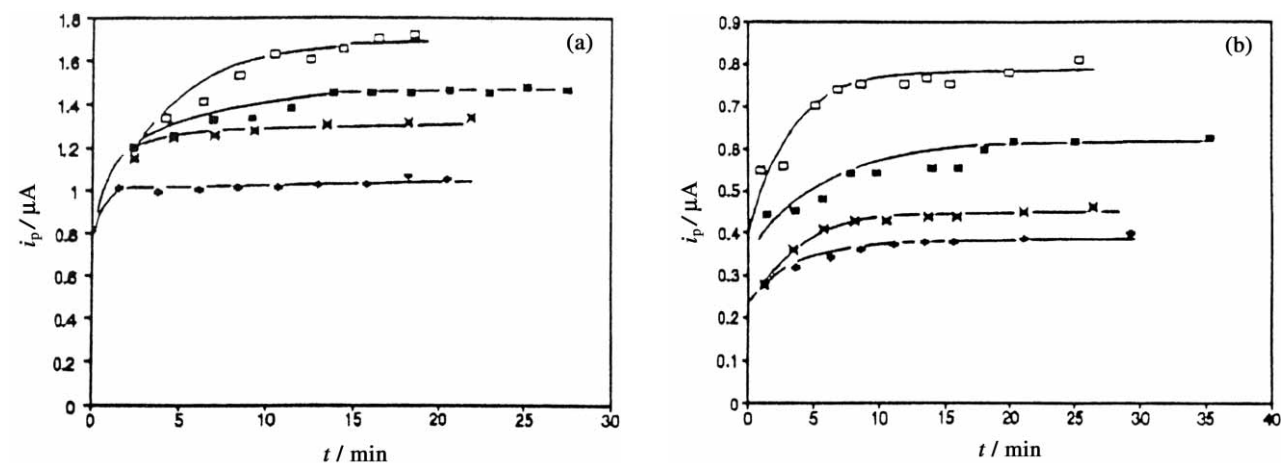


Figure 8. Comparison of dependence of alkaline cleavage of humic acid isolated from soil (a) and commercial sodium humate (b) on time. 0.02 g humic acid sample dispersed in 15 ml phosphate buffers, pH: 6.6 (□); 7.6 (■); 10.0 (x) and 11.1 (+). Currents measured at pH = 6.6 and 7.6 at -1.4 V; at pH = 10.0 and 11.1 at -1.46 V.

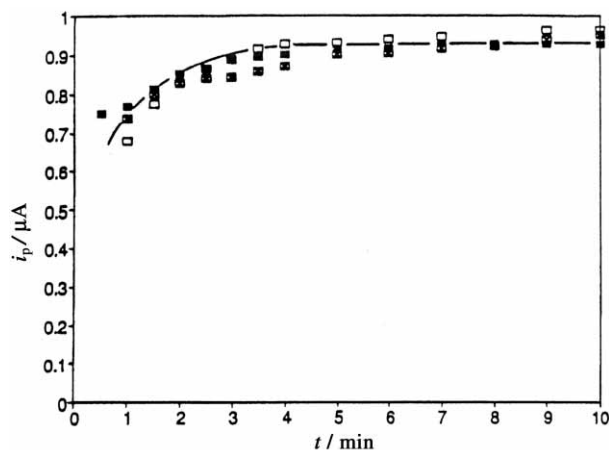


Fig. 9. Time-dependence of the alkaline cleavage of sodium humate is independent of particle size. 0.02 g of humate was dispersed in 15 mL borate buffer of pH = 9.0. No pretreatment of sample (\square); ground with mortar and pestle (\blacksquare); ground and sieved with 120 opening/inch screen (\boxtimes). Peak current recorded in the suspension.

The extract is acidified to pH = 1 or 2 and at this stage new polymers, denoted humic acids, are formed. Under these acidic conditions these polymers are slightly soluble and are isolated as humic acids.¹⁰ The unreacted low molecular weight compounds, that remain soluble, are fulvic acids.

Similar type of processes can take place in some procedures used to isolate aquatic humic acids. Thus in the procedure proposed by Thurman and Malcom¹¹ the soluble organic material is separated from particulate organic carbon and colloidal clays using a 0.45 μm silver membrane filter. By acidification to pH = 1.0 low molecular weight compounds and some oligomers present are polymerized and the resulting slightly soluble polymers are concentrated on a column of a XAD-8 resin. By washing the column with 0.1 M NaOH these polymers are solubilized. In the resulting mixture of low molecular weight organic substances another type of macromolecular species can be formed. By treatment with hydrochloric acid, when the pH is adjusted to 1.0, another conversion, possibly repolymerization takes place yielding slightly soluble humic acids. The sequence is once more repeated, dissolving humic acids in 0.1 M NaOH and reacidifying by passage through a cation exchange resin in H-form, resulting in another conversion, possibly repolymerization yielding humic acids.

CONCLUSIONS

A comparison of kinetics of alkaline cleavage of soil organic matter with kinetics of degradation of lignins and humic acids indicated that the properties of soil organic matter resemble closely that of lignin and are different from those of isolated humic acids. It can be concluded that lignin and its decomposition products form a considerable portion of the soil organic matter. Properties of macromolecular species known as humic acids differ from those of organic substances initially present in soil. Discussion of possible chemical reactions taking place in procedures commonly used in isolation of humic acid together with the above mentioned alkaline cleavage strongly indicate that humic acids are man-made macromolecular species rather than a natural product.

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SAŽETAK

Jesu li humusne kiseline prirodne tvorevine?

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Praćenjem promjena apsorpcije zračenja od 250 do 270 nm i diferencijalnom pulsnom polarografijom proučavano je u alkalnoj otopini cijepanje organske tvari izolirane iz tla. Mjerenje polarografskih vršnih struja omogućuje praćenje promjena koncentracija benzaldehida supstituiranih na CH₃O- i HO- skupinama i α,β -nezasićenih ketona u suspenziji zemlje. Kinetika cijepanja organskih tvari izoliranih iz tla, a posebno njena zavisnost o pH, slična je kinetici cijepanja lignina, ali se razlikuje od kinetike cijepanja humusnih kiselina. Na osnovu razlike u kinetici cijepanja, a uzimajući u obzir kemijske procese koji se odvijaju tijekom izolacije humusnih kiselina iz tla i vode, zaključuje se da postoje indikacije da su humusne kiseline umjetno stvoreni polimeri, a ne prirodne tvari.