



Published in final edited form as:

Yang, F., & Antonietti, M. (2020). The sleeping giant: a polymer view on humic matter in synthesis and applications. *Progress in Polymer Science*, 100: 101182. doi:10.1016/j.progpolymsci.2019.101182.

The sleeping Giant: A Polymer View on Humic Matter in Synthesis and Applications

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The sleeping Giant: A Polymer View on Humic Matter in Synthesis and Applications

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Abstract:

Humic Acid is a natural polymer with high functionality which is omnipresent in Nature, but was up to now hardly considered as an object of polymer synthesis. We review the known structural properties of natural humic acids which are remarkably uniform, independent of source and origin and environment. We then present its simple retrosynthesis in the lab based on a hydrothermal polycondensation process. The for a polymer very unusual properties of Humic Acid, such as pH and redox buffering, strong ion binding, but also its ability to bind and carry both hydrophobic and very hydrophilic molecules make artificial humic acid also an exciting choice as a functional polymer for technical purposes.

Key Words: Natural Polymer, Humic Acid, Ion binding, redox, polyamphiphile

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List of abbreviations

A-FA	Artificial Fulvic Acid
A-HA	Artificial Humic Acid
ESI	Electron Spray Ionization
GC	Gas Chromatography
HTH	Hydrothermal Humification
HTC	Hydrothermal Carbonization
MS	Mass Spectroscopy
N-HA	Natural Humic Acid
NMR	Nuclear Magnetic Resonance
SOM	Soil Organic Matter
XPS	X-ray Photoelectron Spectroscopy

1. Introduction

If we have to list common natural polymers, 95 % of us will oversee the most nearby, but also the by far most omnipresent species: it is the humin/humic acid fraction in soil, a partly soluble, partly cross-linked polymer compound. The scale and importance of this “sleeping giant” is unimaginable large: humic matter accounts for up to 80% of the total organic matter in soil, playing a key role in soil fertility, but also the global carbon cycle [1]. Soil organic matter in fact contains significantly more carbon than even the combination of vegetation and the atmosphere and is a long-lasting, accumulated product of the degradation of land vegetation. Carbohydrates, but also lignin and lipids are the key monomers which are converted and condensed into the more persistent part of soil organic matter (SOM).

Photosynthesis immobilizes more than 220 billion metric tons of CO₂ per year world-wide [2], but only a small amount of this immobilized carbon ends up in SOM, as old plant matter is mostly metabolized and degraded, with little remainders are left via humification reactions to form the soil carbon pool. Nevertheless, this remainder piled up over geological timescales to very large amounts. Together with its tight relative, kerogen [3], it contains an estimated 10¹⁶ tons of carbon, exceeding the total organic content of current living matter by a factor of 10,000 [4]. To illustrate this number again: the annual world crude oil production is another factor 200 smaller, i.e. “only” 4 Gt (4*10⁹ t/a). Talking about humins as a polymer thereby has a significant scale and importance: is by far larger than all human chemistry activities, but as a “sleeping giant” hidden in the ground.

Humic substances are organic compounds that are included as a minority component (2-8 wt%) in topsoils, but at higher concentrations also found in peat and brown coal. The analysis of humic matter is as old as chemistry as such, and the notation “humic acid” comes from the fact that strong bases dissolve significant parts of the black-brown polymer, while reprecipitation

occurs after back-acidification, which is the typical behavior of a hydrophobic, weak polyelectrolyte. The name “fulvic acids” describes the more hydrophilic part which stays dissolved even after acidification and at higher ionic strength [5]. There are also larger parts of humic matter staying undissolved, the so-called humin, but it is very similar chemical character (see below) brings the simplification that this is only the more hydrophobic or cross-linked part of the same, chemically broad material.

To make it clear: humic matter is well explored in geochemistry, agriculture, and soil biology, it is just that to our opinion a polymer perspective on this relevant class of materials is missing. This goes up to a pure chemical lab-synthesis of humics, their chemical modification, and their valorization as an advanced polymer material, i.e. it is about taking humic acids out of the classical soil context and apply them in modern fields of functional polymers. These all are the tasks of the current review.

Humic acid as traditionally isolated is a condensate complex mixture of monomers that contain acidic carboxyl and phenolate groups so that the mixture behaves functionally as an anionic polyamphiphile. Modern analytics however starts to shed light on the inner molecular construction principles, and for instance modern tools of solid-state NMR [6, 7] have remarkably improved our picture of chemical architecture. In addition, the modern tools of metabolite analysis were also applied to humus, and the resulting so-called “Humeomics” allowed identification of many of the molecular architectures by advanced spectroscopic, mass spectroscopical and chromatographic methods [8]. We therefore feel confident that the knowledge is mature enough to be reused by materials chemistry.

2. Natural Huminogenesis and Chemical Retrosynthesis

Huminogenesis describes the organic and biological cascades towards organic humic matter and is thereby a subdomain of pedogenesis. Careful observation of natural processes can teach

us some general rules being valid towards the formation of soil humic substances and can be used to create a potential “synthetic lab approach” to humic matter. To our deep satisfaction, the average properties of extracted humic substances from different sources depend in a certain range on the biomass they are made of and the region with its special microbiome and climate, but are in spite of the remarkably similar and resistant to further biodegradation [4]. This allows for the hope that we talk about only one class of then defined organic polymers. As a typical copolymer, humic acids always contain organic acids (from the alkaline or anaerobic digestion of carbohydrates), phenolic groups (from lignin), and beside minor residues of amino acids, a significant fraction of hydrocarbons, coming from waxes and (cross-linked) fatty acids. The three major components vary in a certain range, but are contained in all samples we ever analyzed. Fulvic acids are –as mentioned, more polar, and to a large extent only low molecular weight organic (poly)acids, thereby free of lignin and hydrocarbon fragments. Insoluble humins show just gradually different composition and for instance very similar pyrolysis-MS data. i.e. they are presumably cross-linked polymers or the more hydrophobic tail created by one and the same process.

The formation of humic substances in Nature is nevertheless from a physico-chemical perspective rather badly understood. SOM contains humic substances as the main constituents (up to 75%) of SOM [9], the remainder being lower molecular weight organic compounds including *mono*-, *di*-, and *tri*-hydroxy acids, fatty acids, dicarboxylic acids, linear alcohols, phenolic acids, terpenoids, carbohydrates and aminoacids [10]. This mixture is the result from this biomass degradation through biological, physical and chemical transformation processes, and the components are even able to form complexes with soil minerals that can be stable up to thousands of years [11]. The primary chemical theories for humin formation were threefold: there is one based on lignin [12], a second is the polyphenol theory, and the sugar-amine

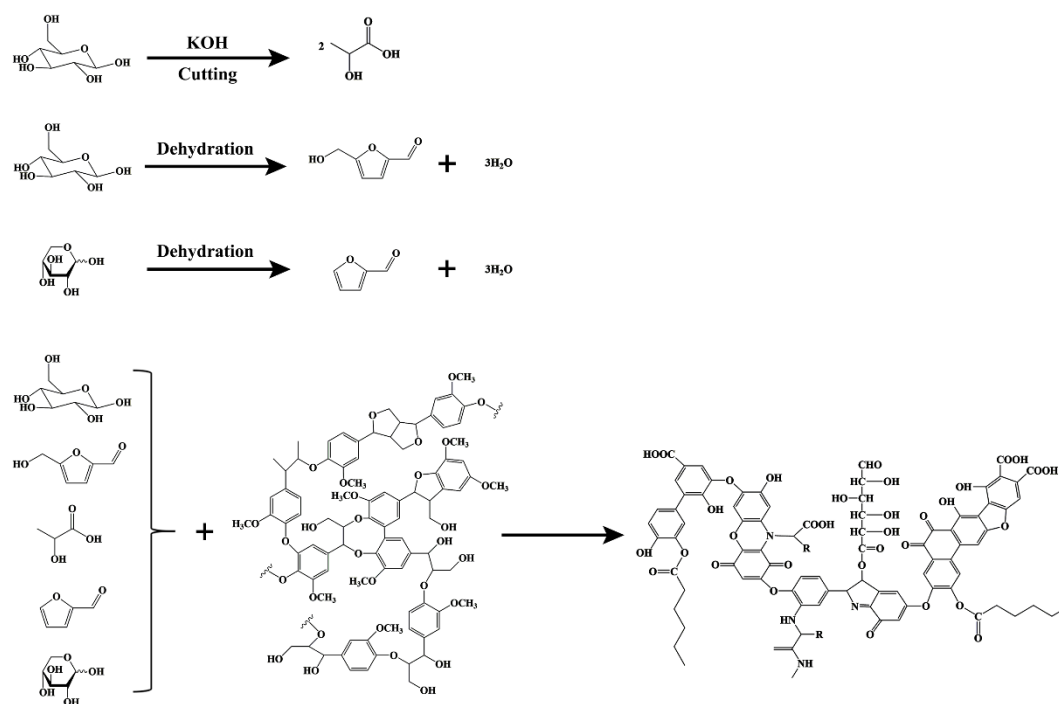
condensation model [13, 14]. All three meanwhile turned out to be insufficient to describe the experimental observations [15].

Careful observation of natural processes gives extra evidence towards the formation of soil humic substances. The formation of humic substances under natural conditions requires many years and involves biological and abiotic reactions. As an example, the formation of humic substances found in the deep peat of papyrus and sphagnum may last for up to 15000 years [16]. Black soil is usually found in zones with four distinct seasons and phases of rather humid soils in the warm period, while the soil can be deeply frozen in winter. Both conditions retard biological processes and promote the role of chemistry. This causes a slower metabolization of dead leaves and plant residues by microbial activity, thus resulting in the build-up of a humus layer. Peatlands as carbon-rich ecosystems store one-third of the soil carbon but cover just three percent of the land surface of the earth [17]. Peatlands are found again mostly in moderate climatic regions, and the decomposition of organic matter under waterlogged non-aerobic conditions with low pH and low oxygen availability [18] is something that inspires chemical processing.

In addition, the processes to convert dead biomass into organic products must be seen in the frame of an intimate association with soil minerals, and here we mostly must consider pH and redox properties. Independent of the involved mineral components, a near neutral pH is an important characteristic of black soil. Obviously, the organic decomposition cascades in presence of minerals are “self-neutralizing”, i.e., both rather acidic and alkaline starting products generate organic counter-products prompting their neutralization.

Inspired by these facts, our group recently presented the first technical synthesis of humic acids. This “hydrothermal humification” (HTH, see ref [19]) is based on the hydrothermal condensation of still wet biomass under exclusion of oxygen and at autogenous pressure. When for instance runned at 200 °C and 16 bar, HTH can be considered a mild chemical engineering

process simulating natural humification, but with an acceleration factor of up to 10^9 . In addition, as an abiotic process, hydrothermal processing is free of metabolization and usually achieves excellent carbon yields, i.e. the majority of the carbon bound in biomass ends up in the humified product. This procedure is thereby very different from flame processes, where a major part of the biomass carbon is oxidized and released as greenhouse gases (CO_2 and CO) [20, 21]. Previous hydrothermal recipes gave hydrochar [22], but to generate the hydrophilic, acidic character of SOM, a previously unexpected modification was developed. Artificial fulvic acid (A-FA, from carbohydrates only) and humic acid (A-HA, from lignocellulosic biomass) are successfully synthesized through one-step hydrothermal technology with crude biomass using the principle of “auto-neutralization” discussed above. The reaction started with appropriately alkaline solutions, which then stimulate formation of exactly the corresponding amount of carboxylate groups in a first auto-neutralization step. After some time, the created acids turn the overall reaction solution into weakly acidic; then the conversion of carbohydrates switches from retro aldol splitting to dehydration to form the reactive monomer species, furan derivatives such as hydroxymethylfurfural, which then condense together with the organic acids to a covalent humic polymer condensate [19]. Lignin turned out to be important coreactant to bring the mandatory phenolic sites to the product, and their amount in the A-HA exactly follows the included lignin content, i.e. lignin rich biomasses also give phenol rich HAs. These condensation steps are summarized in Scheme 1:



Scheme. 1: Condensation scheme reflecting the artificial humification process. Taken with permission from ref [19].

Fatty acids, which come from microbial lipids, as well as Amadori-like amino acid condensates complete the monomer diversity, they are however only minority co-structures in the final product mimicking the N-HA.

For a possible expansion of composition space and the synthesis of specialty polymers based on humins beyond Nature, the increase of these entities however points to a possible polymer chemistry. A higher load of unsaturated fats for instance improves hydrophobicity, lowers glass transition and promotes plasticity of the material (up to thermoplastic films), while waste more protein increases nitrogen heterocycle content and secondary interactions with polar organic compounds for a possible delivery and detoxification discussed below. The fact that N-HAs are restricted to lower contents of these units is most presumably microbiology: these “monomers” are too important food sources and simply metabolized whenever possible.

3. Analysis

3.1. Polymer analysis of a traditional humic polymer

The structure of humins is thereby complex and varies in a certain range, according to the origin. Most researchers believe that humus is a polymer with polyphenol and quinone as aromatic core, in which the functional rim contains carboxyl, phenolic, carbonyl, sugar, peptide fragments and other components. The subentities are connected by various bridge bonds, such as -O-, -CH₂-, =CH-, -NH -, -S-S-, etc. The chemical structure of humins is thereby a random polycondensate with a conjugated, aromatic backbone [23, 24].

The acidity of humus mainly comes from the dissociation of hydroxyl and phenolic groups in the molecular structure. The pK_A distribution is polymer-like rather broad, but contains two peaks related to activated organic carboxylic acids (e.g. as lactid acid, pK_A=3.8) and substituted phenols (e.g. cresol, pK_A=10.3). Under acidic conditions, humus in water forms a huge aggregate through the physical and chemical effects of hydrogen bonds, π bonds and van der Waals forces, presenting a porous and loose sponge structure with a large specific surface and colloidal properties. Most of the physicochemical properties of humus are the manifestation of colloidal properties rather than determined by the covalent linkages between the different monomers. The overall structure will behave rather as a complex supramolecular polymer, with properties and their secondary structure depending on pH, concentration, and other physicochemical conditions. Especially, it will responsibly react towards changes of those parameters, re-adjusting the supramolecular structure in response to these triggers.

Molecular weight determination in such situations is notoriously difficult, and ultrafiltration [25], gel-electrophoresis [26], and high performance Size Exclusion Chromatography [27] have been applied, and a mixture of low molecular weight oligomers with a polymer with apparent molecular weights of 20000-200000 g/mol seems to be typical.

3.2. Structural Analysis of Humic Matter

Humic polymers are thereby typical amphiphilic organic polyelectrolytes, for natural extracts with some inorganic counterions and mineral clusters included. This represents over all communities a complicated problem for structural analysis. From only speculating about the occurring “black magic” in earlier years, the progress in solid-state characterization experienced in the last years is remarkable. We especially want to highlight the “Humeomics” approach, where the tools of metabolomics are applied to analyze the “humusic pentagram” [28]. Idea is to apply different physical and chemical separation techniques (e.g. ester or ether hydrolysis) to split and separate the broadly distributed polymer distribution in more defined entities. GC coupled to ESI-Orbitrap MS enable the molecular characterization of extracts in large diversity maps. The history and the potential of this technique in humus research is nicely reviewed [25] so that we can stay away from further details-

Solid state NMR and Pyrolysis-MS are, compared to that, rather classical techniques for black soil analysis. Fig. 2 shows from practical work the comparison of extracted natural humic acids with synthetic humic acids in typical solid-state ^{13}C -spectra:

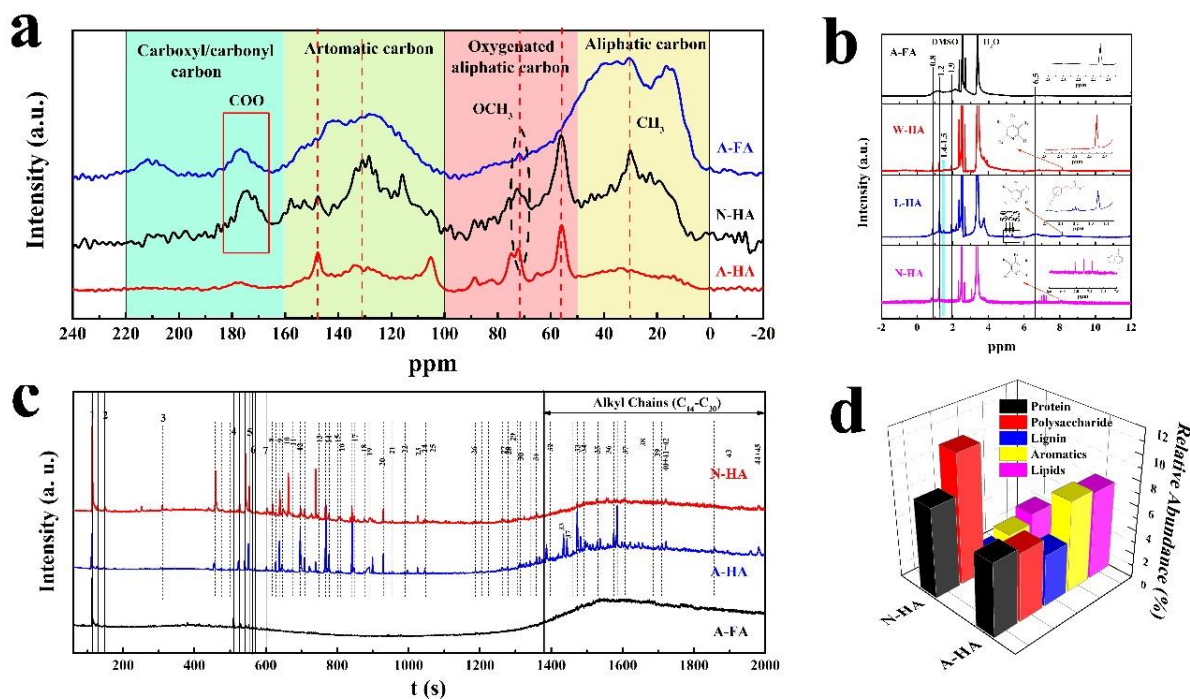


Fig. 2: (a) Solid-state ^{13}C -NMR spectra from artificial and natural humic substances; (b) Liquid state ^1H -NMR spectra of A-FA derived from glucose, A-HA derived from corewood powders and tulip tree fruit stands, and natural humic acid extracted from black soil; (c) Chromatographic patterns obtained by the pyrolysis of comparative curves of natural-, artificial humic acid and artificial fulvic acid; (d) Relative abundance of compounds of protein-based, lignin-derived, carbohydrate-derived and aliphatics in the pyrograms of A-HA and N-HA samples [19].

The differentiation between highly oxidized carbon (160-240 ppm), aromatic carbons (100-160 ppm), oxygenated aliphatic carbons (50-100 ppm), and pure aliphatic carbons (0-50 ppm) is in general straightforward and allows a non-quantitative assignment of the different structural elements to the polymer structure. Interestingly, on the base of such experiments the similarity of humic acids can be systematized. NMR can be directly complemented by (also non quantitative) pyrolysis MS data. The diverse peaks (easily more than 50 major, identifiable peaks) constitute some type of “fingerprint” and are usually chemically attributed to be typical for polysaccharide, protein, lipid, or lignin origin, i.e. the polymer chemist can relate the structure to the different monomers, essentially giving similar results as the solid-state NMR

spectra. The “aromatic” fraction in both NMR and pyrolysis-MS makes it clear in this example case that the condensation of primary components towards the polymer also progresses along with cross-aromatization, i.e. we find conjugated entities not contained in the primary starting products.

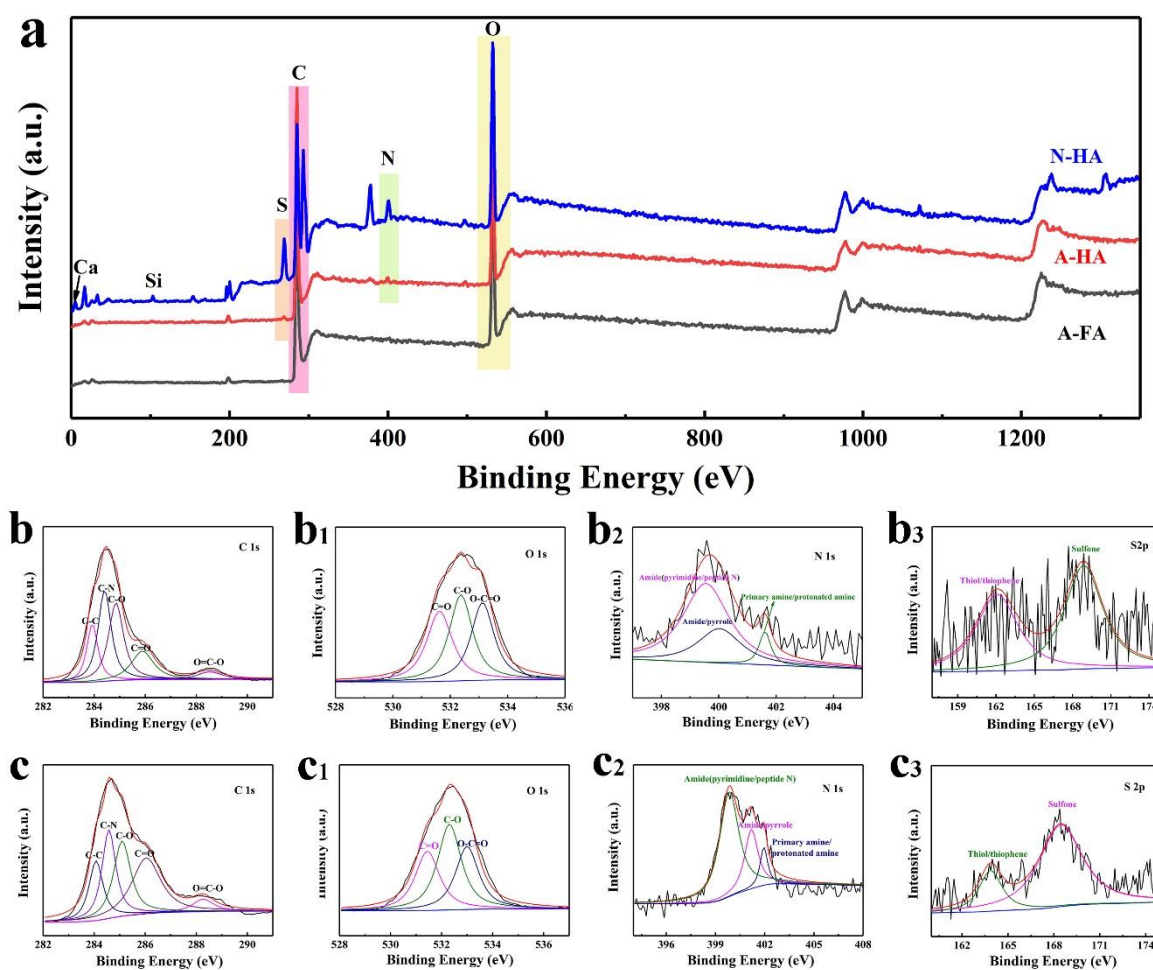


Fig. 3: XPS full survey of the artificial- and natural humic substances (a); High-resolution XPS scan of the C 1s (b), O 1s (b₁), N 1s (b₂) and S 2p (b₃) for A-HA sample; High-resolution XPS scan of the C 1s (c), O 1s (c₁), N 1s (c₂) and S 2p (c₃) for N-HA sample [19].

XPS is another of those solid-state tools which allows us not only to quantify the element composition at the surface of the material, but also gives from fine structure peak analysis detailed information about the binding environments of each element. Fig. 3 is considered as a

teaching example from actual work to delineate the typical analytical progress and arguments. Intention of this XPS comparison of natural extracted humic acid and a synthetically hydrothermally condensed humic acid is the deconvolution of the spectra into single atom-atom binding motifs, i.e. we get a picture of all the bonds present in the polymer and their relative probability. The samples are practically indistinguishable, except a higher nitrogen and sulfur content of the natural humic acids (corresponding monomers not added to the synthetic material). This is for us a good indication how close accelerated synthetic processes nowadays already match with natural, extracted product.

In solid-state NMR, Schmidt-Rohr and coworkers really drove this technique to quantify elemental composition as well as functional groups of a broad range of extracted humic acids [6]. Aromatic carbons and oxygen bound carbons made up more than 60 %, i.e. were significantly underestimated in the standard NMR experiments, and especially the carboxylates were found to be a factor 2 higher than before. The authors also compared the quantitative spectra with a variety of structure models, and partial agreement was obtained at most. Nevertheless, HA turned out to be rather uniform, independent of sourcing, and supported our view that a general model for humic acids is possible as its formation follows always similar chemistry. In further work, the same group determined the amount of methylene-based aliphatic domains in humic acids and was able to show that they bind hydrophobic organic model contaminants [7].

4. Applications

Obviously, such a highly functional polymer covering amphiphilic properties, ion binding and polyelectrolyte properties, optical properties as well as (phenol-based) redox properties is of high interest for a diversity of applications, both in the classical soil context as also in

technology to replace functional polymers by this cheap, omni-available, sustainable, and environmental benign substitute.

4.1. Agricultural usage

This is the oldest and most common application, and we just shortly repeat some obvious aspects to be complete in this review. Adding animal or plant residues (“composting”) for soil amendment is presumably as old as farming as such [29]. Early believe was that plants can “eat” the ingredients of plant matter as such, while Justus Liebig reduced the practical use to the contained elements P, N, and K as such. Other literature pointed out that humic substances promote plant growth beyond that, and that metabolites included in SOM can serve as phytohormones [30]. As it is also known that plants can absorb and translocate systemic insecticides, molecular uptake of organic fragments of humic matter is rather probable [29]. Most importantly, SOM and the complexes with inorganic minerals bind water, retain nutrients in soils and thereby make up land quality [31]. Therefore, the addition of extracted and as generated humic substances to weaker crop fields has gained popularity in agricultural practice due to the potential reduction of irrigation and fertilizer.

The actual picture of the positive effects of humic acid and fulvic acid on soil fertility and remediation is multi-faceted and includes physico-chemical aspects as wettability, textural aspects, and water and ion binding capacity. They can be summarized as follows:

(1) Improving the physical and chemical properties of the soil, increasing fertilizer utilization rate, and then enhancing the soil fertility. The main manifestation is that the surface functional groups react with soil minerals to change soil structure properly and increase soil permeability, thus activating soil nutrient elements and enhancing enzymatic promotion. In addition, humic acid oxygen-containing functional groups indirectly improve the mineralization of organic matter, enhance and increase soil activity [32].

(2) Promoting crop growth and improving crop quality. It can stimulate the division and growth of root cells, increase the number of roots and lengthen the length of roots, so that crops can absorb more water and nutrients [33].

(3) Rehabilitating soil by physical and chemical adsorption, precipitation and redox buffering. Fixation of heavy metals and degradation of organic pollutants occurring in parallel. Ion exchange, complexation and surface adsorption can reduce toxicity of heavy metals, and decompose organic pollutants by adsorption and redox processes [34, 35].

(4) The high-molecular-weight humic materials, humic acid, alter the physical characteristics of the soil, while the low-molecular-weight humic substances, fulvic acid, are involved in chemical reactions in the soil that in turn influence plants' metabolic process [36]. The large amount of organic acids contained in humic acid and fulvic acid in the soil is considered to be one of the most important substrates for microorganisms [37]. However, when the addition of humic acid is excessive, it will cause harm. Since humic acid contains a large amount of soluble substances, excessive humic acid will create a high osmotic pressure, have a certain inhibitory effect on growth and reproduction. Excessive acidic pH will inhibit the proliferation of microorganisms such as actinomycetes. This in turn reduces the abundance of microorganisms and the activity of enzymes in the soil.

(5) Humic acid binds the dispersed soil particles together, so that the probability of the soil forming agglomerate structure becomes larger, thereby increasing soil aeration and water permeability [38]. The active groups in humic acid can strongly adsorb to particles and exchange soil mineral composition [39], thereby reducing the concentration of chlorides, nitrates, etc., decreasing soil salinity and improving fertilizer utilization [40].

To summarize in simple words, we can quote work that stated phenomenologically that "humic acids increased plant growth" with "relatively large responses at low application rates" [41].

There is an effect of humic matter beyond simple addition of valuable molecules and elements, found already at dose levels typical for functional polymers in technical formulations. Such a view makes a much straighter synthesis of humic matter by a polymer-like synthesis process for agriculture, but also other technical uses a valuable challenge.

4.2. Ion binding and environmental remediation

Carboxylate and phenolate groups give the humic acids the ability to bind ions either via Coulombic forces (for Na^+ , K^+ , or Mg^{2+} , Ca^{2+} , Fe^{2+}), metal chelation (all *d*-elements, especially Fe^{3+}), and surface adsorption (e.g. phosphate). Solubility in water, but also ion binding capacity indicate the presence of many binding sites along the conjugated backbone, so binding occurs in a polyelectrolyte- or chelate type fashion. Binding site densities vary, but are for a typical alkali-soluble humic acid fraction 1 carboxylate and 1 phenolate per 600 mass units. Ion binding is important for keeping fertilizer minerals in the topsoil and avoiding their rinsing to ground water, but also to immobilize heavy metals, thus lowering their uptake or bioavailability.

The heavy-metal binding abilities of humic acids have been exploited to develop remediation technologies for removing heavy metals from waste water. Brown et al. already reviewed the use of peat for metal removal [42]. This approach is very cheap, environmental benign, and the peat can be recycled by leaching the ions with acid. Optimal ion binding is obtained at slightly acidic pH (5.5-6.5), which underlines the role carboxylates and phenols, not phenolates, in this process. In this article, also first trials for pelletizing are described, essentially creating polymer ion exchange resin beads from peat.

Stability constants of diverse metal cations with humic acids were determined [43] and followed the sequence $\text{Cu} > \text{Fe} > \text{Pb} > \text{Ni} > \text{Co} > \text{Ca} > \text{Cd} > \text{Zn} > \text{Mn} > \text{Mg}$. The binding capacities were found to be rather high, and it was explicitly stated that “an organic ligand like humic acid may render almost all metals immobile, thereby helping in detoxication processes”. Considering the high

concentration of functional metal binding group and multidentate binding, this statement goes well with the confirmed polymer structures.

Gardea-Torresdey et al. [44] analyzed the binding of Cu^{2+} on diverse peat and peat moss fractions. The binding capacity at pH 4.0 could reach 28 mg/g, at high binding affinity and fast binding kinetics. There are in fact countless examinations like that, all reporting on fast, strong, and efficient ion binding by humic soils and isolated humic matter. Titirici et al. [45] synthesized a chemically “amplified” artificial humic acid from glucose and acrylic acid and found Pb^{2+} binding of up to 350 mg/g at pH 6.0. This clearly illustrated the potential of synthetic humin polymers with purpose optimized structures. All binding capacities can be translated, using structural models, into metal binding site densities, and values between 300-1000 mass units per carboxylate or phenolate are obtained.

Tang et al. [35] went one level higher and reviewed the synergies of dissolved humic/fulvic acids) and nanomaterials for ion binding and ion transport. Indeed, the interactions are complex, and in some cases a positive effect of nanoparticle immobilization, in some cases even ion mobilization was observed. In the current discussion of nanoparticles and their toxicology, we want to point to the fact that humic acids in favorable cases do bind and immobilize nanoparticles, while an excess of humic acid acts as a stabilizer and even increases aquatic availability. In terms of a forthcoming soil nanotechnology, Yurishcheva et al. [46] coated magnetic nanoparticles with humic acids. After capturing lead ions, the nanoparticles could then be separated from the dispersion using a magnet.

4.3. Uptake and activation of organic compounds/delivery

Humus can interact with organic pollutants in water via hydrophobic and secondary interactions, thus increasing the solubility of organic pollutants in water, reducing volatility, increasing the photolysis rate as well as changing of biological availability and affect the

toxicity of organic pollutants. Also, humic acids have an important influence on the morphology of organic pollutants, their migration, transformation, toxicity and biological effects [47, 48]. The research showed that the aromaticity of humins is one of the key factors to drive the interaction between organic pollutants and humus [49]. Fulvic acid with its lower molecular weight and higher carboxyl content than humic acid is less amphiphilic and thereby only has little adhesion to hydrophobic compounds, but it often shows high metal complexing ability. Humic acids on the other hand have pronounced hydrophobic and hydrophilic domains and form "micellar" aggregates in which organic hydrophobic molecules can internally adsorb.

The water solubility of organic molecules/ pollutants is one of the most important physical properties to control their transport and fate in aqueous systems, and dissolved humic acid and fulvic acid can improve the water solubility of molecules, due to the hydrophilic functional groups dissolving in water while the hydrophobic moieties complete the carrier system. In biomedical polymers, this is called a delivery system. Interestingly, with humic acids low concentrations of organic co-solutes do not produce significant solubility enhancement, regardless of the polarity of small organic co-solutes. The hydrophobic effect between phenolic moieties, water, and the solute can explain the enhancement of water solubility [50].

By adsorption, HA also has a direct effect on the toxicity of organic pollutants, as a reduced bioavailability results in lower toxicity. The degree of reduction depends on the binding constant onto the specific humic matter. The mechanism that humus can reduce the bioavailability works via suppression of molecular species, while the as formed polymer micelles have difficulties to bind to exoreceptors or to permeate the decorated cell membrane of organisms [51].

4.4. Redox Properties, Redox buffering

As we learned that humic acids are largely heteroaromatic or phenol based, a very pronounced redox activity similar to semiconducting polymers of is to be expected. This is of course of highest importance for a stable, pH and redox buffered soil medium, and indeed, the numbers of electrons (and protons) which can be stored in humic matter are high. Maurer et al. have applied electrochemical reduction of extracted humic matter (from a Gleysol in northern Switzerland) and quantifies an uptake of 0.54 mol protons/kg and 0.55 mol electrons/kg [52]. Even when compared to a synthetic electrochemically active polymers, these values (27.8 Ah/kg) are promisingly high, or on other words: humic acid has 15% of the storage capacity of a lithium ion battery material! It is a real surprise to a material chemist that such potential was not realized and optimized in detail before. The parental lignin is a redox-active compound too, and here, in optimized systems values of ca 80 Ah/kg were accessed [53]. It is thereby reasonable to assume that the redox activity of humic acids is mainly related to the phenolic sites brought in by the lignin fraction, which indeed accounts for about 30 % in most humic matter. Lignin rich humic acids are thereby also most redox active.

The importance of such a redox capacity in natural and artificial humic acids and the materials systems built from such polymers (e.g. anticorrosive coatings) cannot be underestimated. We report just one case to illustrate the ecological importance. Kappler et al. [54] analyzed electron shuttling via humic acids in freshwater sediments of the lake Constance and found mostly Fe(III) in the aerobic top layers, where Fe(II) was dominant in the reductive, anaerobic lower layers. When analyzing the bacterial polytype, they found substantially larger populations of humic acid reducing than iron reducing bacteria, with HA based bacteria being even of the same order of magnitude than the fermenting bacteria. This of course underlines the central role of redox active humic acids in anoxic aquatic environments, acting as the major redox shuttle.

It is obvious that current measurements were practically exclusively done on non-optimized, natural humic fractions and only within the standard electrochemical window of aqueous systems. We believe that there is a world of electrochemistry and electrocatalysis to be discovered when extending this range in non-biological experiments.

4.5. From Ancient masonry to biomineralization and hybrid materials

Mudbricks, a mixture of straw with clay, were potentially introduced by the old Egyptians, but are still a standard building material around the world. The straw reinforces the bricks and create a much better composite material. Modern investigations have found that humic acids are formed and released and bind to the clay fraction, thus increasing the toughness and plasticity [55]. This ancient invention points to a potential use of artificial humic acids for improved construction materials, say to make elastic concrete [56]. We might therefore expect that humic acids can replace commercial fossil-based cementum flow additives, as also the related lignin does [57].

In fact, also in spite of the very strong metal ion binding properties, we expect humic acids to play a key role in crystal morphosynthesis and non-classical crystallization [58], then applicable also to mineralization and remineralization processes in soil.

4.6. Climate and land remediation

It was stated above that the carbon of humic matter by far exceeds all carbon contained in the biosphere and the atmosphere. Little changes of humic matter concentration in soil thereby have the potential to cure the (complete) climate problem (multiple times) while bringing improved agricultural fertility at the same time. The overall scale of easily available biomass (ca 10 Gt/a of waste biomass from industrial agriculture, solely), in combination with a synthetic, effective and decentral chemical humification process, allows us to speculate to use as-generated

artificial humic matter as an effective tool for land rehabilitation or even terraforming, while being CO₂ negative at the same time. This was already discussed in our previous publication [59]. Many of the challenges along such an “Apollo-project” are already solved or addressed: artificial humification processes are stable and comparably cheap. The carbon yield even based on waste biomass is very high, and first tests in agriculture indicate very positive influence on soil structure, water and ion binding capacities and the final agricultural fertility and productivity [60]. In our earlier work, we still found a slightly retarding influence on the soil mycorrhiza at acidic carbon loadings exceeding 10 wt% [61]. This problem has been apparently fixed by moving from HTC to HTH technology using the auto-pH neutralizing chemistry. On the other hand, influence on the soil microbiome, medium term stability in soil, as well as potential secondary solubilization issues of even natural nanomaterials and related health risks always must be carefully addressed.

Nevertheless, the general approach (of adding carbon materials to soil as a tool to address the climate change) has already reached the highest political level: the “4 per 1000” initiative (<https://www.4p1000.org/>, accessed 5.11.2019) is a significant action within the framework of the Lima-Paris Action Plan of the Paris climate convention 2015, considered to be able to treat indeed major parts of the complete CO₂ problem. Comparing the technologies discussed at those platforms with the current state of A-HA makes it to our opinion clear how far this field already has progressed, and how much polymer science is also needed in this urgent matter of survival.

5. Conclusion and Outlook

The yearly (natural) production of humic polymers with about 10 Gt/a is one order of magnitude lower than biomass productivity of Earth, but by far larger than any synthetic polymer under

consideration. Nevertheless, only little is known in the materials community about this polymer, in spite of the facts which soil scientists have found out throughout long analyses and observations. Humic acids bind water and ions and hydrophobic molecules, they are surface active and change and interact with minerals, they are very effective in pH and redox buffering and provide a stabilizing milieu for microbial and fungal activity, and so many more. Although humic polymers are obviously rather universal amphiphiles or all-rounders, also their specific properties are quite extraordinary, such as that their ion binding capacity is about 20 % of an (optimized) battery storage material.

The purpose of this article is however to go the step beyond: inspired by Nature, we can emulate humification by much faster and efficient chemical engineering processes and can come up with artificial humic acids (A-HA) or even “designer humic acids”, where we optimize wanted properties, such as amphiphilicity or redox capacity, and use such humin polymers for agroindustrial and industrial purposes. As such A-HAs can be made essentially from biomass waste, these polymers are cheap and sustainable and by definition even have a “negative carbon footprint”. i.e. they lower atmospheric CO₂. One ton of A-HA could compensate for our intercontinental flight, but brings soil fertility at the same time and is a lasting, sustainable effect on biomass productivity.

Co-polymerization with flexible monomers or esterification introduces plasticity, the influence of humic acids on crystal growth could access better control of mineralization, such as in concrete flow additives, and optimizing specific ion binding might bring new options in environmental remediation, when heavy metals or ionic nuclear isotopes are involved. This article can only be understood as a trend article pointing to the possibilities of these speciality polymers, as brought nearby by the natural originals.

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