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HUMIC ACIDS: PROPERTIES, STRUCTURE, AND APPLICATION

Abstract: *Humic substances (HSs) are a diverse class of natural compounds with no fixed chemical composition, formed from plant and microbial residues through the action of environmental factors and living organisms over many years. Despite extensive research spanning two centuries, the complex and variable nature of HSs' structure remains a subject of scientific inquiry. These substances, notably humic acids, fulvic acids, and humin, play crucial roles in ecological and environmental processes due to their abundant functional groups and resilience to biodegradation. This review explores the intricate structure and properties of HSs, their classification, and their occurrence in nature. It highlights the different models proposed to describe the structural fragments of humic acids, emphasizing their aromatic cores and diverse functional groups. The variability in the molecular weight distribution of HSs, attributed to their polydisperse nature, is also discussed, along with methods used for their determination, such as exclusion chromatography. Furthermore, the elemental and functional compositions of humic acids are examined, detailing their acid-base properties and capacity for heavy metal complexation. The synthesis of HSs from natural sources, such as soil, peat, coal, and artificial processes, is covered, showcasing methods like alkaline extraction and hydrothermal treatment. Recent advancements in artificial humification, including oxidative ammonolysis and Fenton reagent-based oxidation, are reviewed for their potential in producing environmentally friendly humic materials from lignin and waste biomass. The study concludes by underscoring the environmental significance and practical applications of HSs, particularly in agriculture, soil conditioning, and environmental remediation. The diverse properties and synthesis methods of HSs make them promising candidates for sustainable material production and environmental management. Humic acids are versatile compounds beneficial for human health due to their potent antioxidant properties, immune-modulating effects, and support for gastrointestinal health and detoxification. Structurally diverse, they feature groups like carboxyl, phenolic hydroxyl, quinones, ketonic carbonyls, amino, and sulfhydryl, contributing to their stability and amphiphilic nature. In pharmaceutical* *applications, they show promise for drug delivery, antioxidant therapies, wound healing, antimicrobial actions, and biofilm disruption, underlining their biocompatibility and safety.*

Key words: *humic acid, humic substances, metal humic complexes, polymer materials, electrochemical properties, synthesis of humic acid, structure of humic acid.*

Introduction. Humic substances are a class of natural polyfunctional compounds, which have no permanent chemical composition and are formed from plant and microbial residues as a result of many years of action by living organisms in combination with environmental factors [1,2]. Despite two centuries of research, the structure of humic substances remains elusive due to their intricate and ever-changing composition over time. This variability is attributed to the stochastic nature of humification processes, which operate based on the principle of natural selection favoring stable structures [3,4]. To date, scientists have agreed that humic substances are complex heterogeneous mixtures of polydisperse materials of variable composition, which are resistant to biodegradation. Important components involved in the humification process are plant lignin and products of its transformation, polysaccharides, melanin, cutin, proteins, nucleic acids, and lipids [5]. We hypothesize that humic substances could become an environmentally friendly material for producing metal nanoparticles, thanks to their incredible properties.

Structure and properties of humic substances. *Classification, structure, origin, and occurrence in nature.* There exists a widely accepted classification of humic substances [6], which is based on their solubility in solvents of varying natures. According to this classification, there are fulvic acids, a subset of humic substances soluble across all pH ranges; humic acids, another subset soluble in alkaline and neutral conditions but precipitates when the pH drops below 2; and humin, an insoluble and irretrievable residue. It's important to highlight that humic and fulvic acids, collectively referred to as humic acids, are the most mobile and reactive components of humic substances, actively engaging in chemical processes within ecosystems [7]. In certain instances, humic and fulvic acids are not separated; however, humic acids predominantly constitute the humic acid fraction and, due to their propensity to transfer to the solid phase, are subject to more thorough investigation. Since no specific humic acid molecule exists, various models of hypothetical structural fragments of humic acid molecules are created based on the accumulated NMR, IR, and other spectroscopy data, as well as complex chemical analysis [8-10]. A prevailing aspect in many models is the existence of two main components: a core structure (comprising an aromatic carbon skeleton adorned with functional groups, notably carboxyl, hydroxyl, and methoxyl groups), and a disordered outer region, encompassing polysaccharide-polypeptide and other fragments [9-17]. The prevailing model for the hypothetical humic acid molecule is the fragment model, as proposed by Kleinhempel [19], which effectively portrays the intricate and varied nature of its constituent structures.

Humic substances play vital roles in supporting life within the biosphere, owing to their abundance of diverse functional groups and the strong stability of structures developed through natural selection processes. The accumulative function is the accumulation of chemical elements, the transport function is the formation of geochemical flows of various substances, the regulatory function is the influence on the aggregate of metabolic processes in natural bodies, and the protective function is the binding of toxicants [20]. The main sources of humic substances are river water (up to 20 mg/l), swamp water (up to 300 mg/l), soil (1-12%), peat (up to 40%), and brown coal (up to 85%). ee is one of the richest sources of humic substances [21]. The global reserves of lignite are enormous [22]. However, lignite is poorly suited for use as a fuel because of its low calorific value and its tendency to spontaneously combust during transport. The production of humic acids and humic-containing products from lignite is a good alternative to its energy use and belongs to the field of deep processing of hydrocarbons, aimed at the comprehensive use of coal and increasing the added value of coal products [23].

Macromolecular structure and molecular weight distribution of HSs. Determining the molecular mass of humic fractions is a key issue in studying humic substances. Reviews have highlighted significant discrepancies between the values obtained by various methods, with differences reaching several orders of magnitude [19, 21, 24-26]. Humic acids' relative molecular mass ranges from a few hundred to several hundred thousand Daltons. These discrepancies have sparked debates about the nature of humic substances (HSs).

Traditionally, Kononova's concept, proposed in 1961, viewed HSs as polymer systems. According to this model, different humic fractions, isolated based on solubility, are part of a heterogeneous mixture with molecular masses ranging from hundreds to hundreds of thousands of

Daltons, showing continuity in chemical properties [7, 27, 28]. This idea was later replaced by the micellar arrangement concept [29], which suggested that HSs are clusters of short molecules linked by hydrophobic and hydrogen bonds, accounting for their large apparent size. However, this theory was criticized for being based on low pH conditions that distorted fractionation results [30].

Supporting the high-molecular-mass structure of HSs is their origin from the biological processing of lignin, polyphenols, cellulose, and amino acids. Subsequent research led to the modern theory of supramolecular structure [31], proposing that HSs should be studied as molecular ensembles. This method determines average physicochemical characteristics, including molecular weight distribution, from which the average molecular weight is calculated [26]. The specific average molecular weight type depends on how the molecular weight distribution is averaged.

Table 1 – Approaches to averaging the distribution of molecular weights in polymers

Number average molar mass (M_n)	Mass average molar mass (M_w)	Viscosity average molar mass (M_v)
$\overline{M_n} = \frac{\sum n_i * M_i}{\sum n_i}$	$\overline{M_w} = \frac{\sum n_i * M_i^2}{\sum n_i * M_i}$	$\overline{M_v} = \frac{\sum n_i * M_i^3}{\sum n_i * M_i^2}$

Monodisperse polymeric systems show consistent average molecular weights across all methods, while polydisperse systems typically follow the inequality: Mv > Mw > Mn. This inequality allows the estimation of a polymer's polydispersity index (Mw/Mn) (Table 1). Various methods for determining the molecular weight of humic acids include light scattering, chromatography, ultracentrifugation, viscometry, and colligative property-based methods, each with its pros and cons [32, 33]. Techniques based on colligative properties, like cryoscopy and ebullioscopy, are less practical due to their sensitivity to low molecular weight impurities, a common characteristic of humic substances. Ultrafiltration is also complicated by interactions between humic acids and membranes [34]. Chromatographic methods, especially exclusion (gel permeation) chromatography, are the most commonly used for studying the molecular weight distribution of humic acids [35,36]. This method determines molecular mass distribution based on the size effect: smaller molecules penetrate the stationary phase pores more easily, resulting in longer retention times, while larger molecules pass through more quickly. It's important to note that exclusion chromatography measures molecular size distribution rather than molecular weight distribution, a significant distinction given the complex, flexible nature of humic acid molecules.

The effective size of humic acid molecules depends not only on their molar mass and shape but also on factors like concentration, pH, and ionic strength of the mobile phase [19]. Exclusion chromatography is complicated by the active nature of humic acids, including Coulomb interactions and specific adsorption [1]. Proper selection of gel and eluent can minimize these issues [24, 25, 37, 38]. Discrepancies in molecular weight distribution often arise from the choice of comparison samples [39,40]. Because humic substances have unique structures, suitable comparison compounds with known molecular masses are not available. Instead, polydextrans or polystyrene sulfonic acids are commonly used [7, 41]. It's crucial to consider the conditions under which molecular weight distribution curves are obtained when comparing average molecular weights [42]. Thus, humic acids, as polydisperse heteropolymers, are best characterized by exclusion chromatography for determining their molecular weights.

The elemental composition of humic acids. The elemental composition of humic acids is generally understood as the composition of the organic part, not including ash and water. The main elements present in humic substances in comparable quantities are carbon, hydrogen, oxygen, and, in smaller quantities, nitrogen. In many cases, sulfur is found [2, 42]. The ratio of these elements in humic acids essentially depends on their origin and varies not only for humic acids of different types of sources (for example, soil or lignite), but also from the place and history of formation [43, 44]. Thus, the aromatic carbon content in soil humic acids varies, increases with an increasing degree of humification [44], and reaches a maximum of 70% of total carbon [41,45,46]. The authors [47] suggested the use of the element ratios in humic acids as indicators in assessing the natural environment of different periods of paleographic history because they correspond to landscape conditions and even to the quantitative characteristics of the climatic indicators of the time of their formation [48, 49]. The elemental composition of different fractions of humic substances of the same source is also different.

The functional composition of humic acids. Acid-base properties. Buffer characteristics. The functional groups occupy a special place among the structural fragments of humic acids, as they are mainly responsible for the reactivity of humic molecules.

Among the oxygen-containing groups, the carboxyl, alcohol, and hydroxyl groups stand out as the most prevalent and influential. Specifically, within aromatic structures, phenolic and carboxyl groups play crucial roles in determining humic acids' capacity to form complexes with heavy metals [45,50]. Additionally, the quinone and semiquinone groups enable humic acids to engage in reactions via a free-radical mechanism. Nitrogen-containing groups within humic acids encompass heterocycles, amino acids, and aliphatic amines, all of which play a role in influencing the complexation behavior of heavy metals. Understanding the quantitative distribution of these main functional groups is essential for elucidating and predicting the chemical behavior of humic acids and their interactions with heavy metals. Potentiometric titration is a common method used to obtain this information [48, 51]. Due to humic acids' low solubility in water, reverse titration – where the sample is first dissolved in alkali – is necessary rather than direct titration. The acidic functional groups in humic acids predominantly fall into three categories [52]. At pH 2.0, the carboxylic groups of hydrocarbon chains are titrated, at pH 6.5, the carboxylic groups at the aromatic ring, and pH 10-11, the phenolic hydroxyls. The detection of 3 equivalence points makes it possible to calculate the number of groups of interest [23, 53, 54].

Synthesis of HSs. HSs are originated from naturally decaying biomass. The main products of HS are humic acids, fulvic acids, and humins. HS are extracted from natural origins (e.g., coals, lignite, forest, and river sediments). There are lots of recent developments in obtaining artificial humic substances by humification from waste biomass, lignin, and non-lignin biomass.

Synthesis of HAs from natural substances. Humic acids are complex organic compounds that are naturally present in soil, peat, coal, and other organic materials [55-63]. They play a crucial role in soil fertility, nutrient cycling, and environmental processes. While humic acids can be extracted from various natural sources, their synthesis involves complex biochemical and geochemical processes. Here's a general overview of how humic acids can be synthesized from different natural sources:

Coal:

– Humic acids can be derived from coal through a series of chemical and thermal processes.
– Coal is typically treated with alkalis or acids under controlled conditions to break down its organic components.
– The resulting mixture undergoes oxidation and hydrolysis reactions to release humic substances, including humic acids.
– These humic acids can then be separated, purified, and characterized for various applications, such as soil conditioning, agriculture, and environmental remediation.

Soil:

– Humic acids naturally form in soil through the decomposition of organic matter, such as plant and animal residues.
– Microorganisms play a crucial role in the transformation of organic materials into humic substances.
– During decomposition, complex organic molecules are broken down into simpler compounds, which undergo further polymerization and condensation reactions to form humic acids.
– Humification, the process by which organic matter is converted into humic substances, is influenced by temperature, pH, moisture, and microbial activity.
– Humic acids in soil contribute to soil structure, water retention, nutrient availability, and cation exchange capacity.

Peat:

– Peat, a type of organic soil formed from partially decomposed plant material, is rich in humic substances, including humic acids.
– Humic acids in peat are derived from the decomposition and transformation of plant residues over thousands of years.
– Peat extraction involves harvesting and processing peat bogs to obtain humic-rich materials.
– Humic acids extracted from peat are used in agriculture, horticulture, water treatment, and other applications for their soil conditioning and environmental benefits.

Other Sources:

– Humic acids can also be found in lignite, leonardite, and other organic-rich materials.

– Extraction methods vary depending on the source material and intended applications.
– Chemical, physical, and biological processes may be employed to isolate and concentrate humic acids from these sources.

Chemical techniques for extracting humic acids encompass various methods, with alkaline extraction being the predominant approach. This method entails treating natural substances with a solution containing potassium or sodium alkali, followed by precipitation using hydrochloric acid or sulfuric acid solution. A crucial aspect of this technique involves subjecting the alkaline extract to heat during neutralization to enhance the coagulation of humic acid particles effectively (Figure 1). Additionally, physical activation methods, like ultrasonic treatment or extraction under elevated pressure, are employed to enhance the efficiency of alkaline extraction from raw materials. Humic substances consist of three main high molecular compounds respectively HA, HMA, and FA [64, 65].

A simple reaction for extracting humic substances from natural substances is as follows

$$\text{N} + \text{NaOH} \rightarrow \text{HA-COONa} + \text{ГМҚ-COONa} + \text{FA-COONa}$$

N – any substance containing humic compounds
HA – humic acid radical
HMA – radical of himatomelanic acid
FA – radical of fulvic acid

If acid is added to the resulting alkaline extract at a pH of 1-2, humic and hematomelinic acid will precipitate, and fulva will remain in the acidic solution:

$$\text{HA-COONa} + \text{HMA-COONa} + \text{FA-COONa} + \text{HCl} \rightarrow \text{NaCl} + \text{HA-COOH} + \text{HMA-COOH} + \text{FA-COOH}$$

The precipitates of HM and HMA are easily separated, and after drying, they are obtained as black or dark brown powder [65].

Artificial humification. The humification of waste biomass and non-lignin materials involves various chemical processes and conditions aimed at yielding HA, FA, and humins. For instance, the process can include two-stage hydrothermal (HT) treatment, alkaline HT treatment, and neutral HT treatment [66-73]. These processes can yield significant HA, with conditions such as high temperature and specific pH levels affecting the yield. The preferred temperature for the humification process can significantly impact the yield of HSs. Studies have shown that increasing the temperature can lead to an increase in the formation of substances. For instance, in the HT treatment of broccoli stem, elevating the temperature from 184 to 220 degrees resulted in a higher yield of HA [72]. The temperature of the HT treatment of waste biomass, such as wheat straw and sugarcane exocarp, food wastes has been reported to influence the yield of HA. Therefore, it's evident that temperature plays a crucial role in the humification process, affecting the yield of HSs. The yield from the direct alkali hydrothermal treatment process is relatively low (1.8–2.3%), potentially obstructing the production of hydroxymethylfurfural aldehyde (HMF) in environments with high alkalinity (Table 2) [69, 71, 74]. Additionally, the neutral HT treatment of waste biomass under specific conditions has been reported to generate a considerable yield of HA, which can have applications in soil enrichment, fertilizer production, wastewater treatment, water decontamination, and even medicines. The transformation of waste biomass toxic complex chemical reactions can have implications for environmental sustainability and resource management.

The artificial humification can be carried out by the direct oxidation (DO) and oxidative ammonolysis (OA) process of lignin. The process of alkaline wet oxidation for lignin necessitates elevated temperatures (125-320 °C) and pressures (up to 2 MPa), with air or oxygen present [75]**.** Recent methods for transforming technical lignin into materials resembling humic substances can be broadly categorized into three approaches: alkaline aerobic oxidation (AAO) of technical lignin, alkaline oxidative digestion (AOD) of lignocellulosic biomass using hydrogen peroxide, and Fenton reagent-based oxidation of lignin with hydrogen peroxide (Figure 2). Figure 2① presents a diagrammatic representation of the synthesis of artificial lignohumate (ALH) from technical lignin through the AAO method [76]. During this procedure, lignin is dissolved in an alkaline medium like KOH or NaOH, which catalyzes to activation of the phenolic OH groups within the lignin, followed by oxidation using air/oxygen or hydrogen peroxide. Post-reaction, the resultant product is ready for use in its liquid or solid state. Nonetheless, ALH produced via NaOH may require dialysis to remove excess sodium ions that could potentially increase soil salinity and adversely affect plant growth when used as a fertilizer [76].

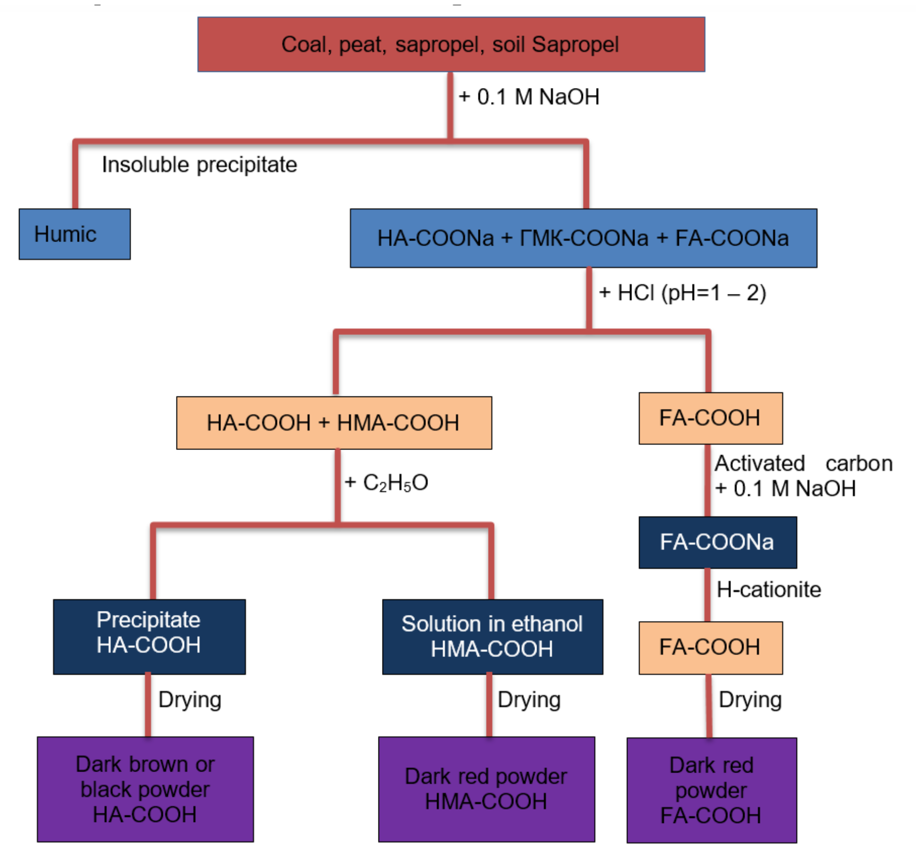

Figure 1 – Schematic synthesis diagram of humic Acids from natural substances

Table 2 – The transformation of biomass and non-lignin materials utilizing alternative techniques to create humic substances

Raw material	Chemical processes	Conditions	Yield	Refs.
Corn stalk	Two-stage Hydrothermal	180 °C, 4 h, pH 1 180 °C, 4 h, pH 13	HA-28.7%	[66]
Wheat straw	Hydrothermal	220 °C, 4 h	HA-30.2%	[71]
Broccoli stem	Hydrothermal	204–220 °C, 10 min	HS-198 g/kg HA-50.7 g/kg FA-28 g/kg	[72]
Sugarcane exocarp	Hydrothermal	200 °C, 1 h	HA-14.85%	[69]
Cabbage leaf	Alkali- Hydrothermal	KOH (25%), NH4OH (20%), 195 °C, 4 h	Not available	[70]
Glucose, saw dust, tulip tree leaves	Alkali-Hydrothermal	KOH	HA-1.8%	[67]
Food wastes (rice, meat, cabbage, potatoes)	Hydrothermal	215 °C, 1 h	HA-43.5	[74]
Fermented Furfural	Alkali dissolution and acidification	KOH (8%) 70 °C, 2.5 h	HA-49%	[68]
Carbohydrates monomer	Hydrothermal	([BMIM]Cl) (10 g) $CrCl_3$ (0.74 g) 110 °C, 4 h	HA-56.6%	[81]

In an alternative approach, lignocellulosic biomass is subjected to alkaline oxidation digestion to produce water-soluble lignin, which is then utilized for generating HS-like materials. A schematic representation of this procedure is illustrated in Figure 2③ [77-79]. This method involves the biomass undergoing digestion in an alkaline environment, typically with KOH or NaOH, in the presence of an oxidizing agent such as hydrogen peroxide. Following digestion, insoluble cellulosic fibers are filtered out, and the filtrate is acidified to separate hemicelluloses/sugars from lignin. The separated lignin is then suspended in water and neutralized to yield water-soluble fractions known as lignohumates. The oxidative mechanism acting on lignin in this process is expected to mirror that of alkaline aerobic oxidation. The AOD process offers several advantages, including the direct utilization of biomass, operation at low temperatures (around 50 °C, overnight), and the generation of cellulose fibers as secondary products. Additionally, the acidification step facilitates the production of monomeric toxic phenolic compounds, also referred to as phytotoxic chemicals [77,78,80].

A novel approach has been devised for oxidizing lignin, such as kraft lignin, utilizing hydrogen peroxide with a Fenton reagent catalyst at ambient temperature (Figure 2②) [82]. Here, lignin is combined with a hydrogen peroxide solution, followed by oxidation at room temperature in the presence of iron (II) sulfate heptahydrate. After the oxidation reaction, the solution undergoes centrifugation and multiple washes with deionized water to eliminate residual chemicals and harmful phenolic compounds. The resulting solid residue, oxidized lignin, is then freeze-dried for subsequent use as lignohumate. Fenton reagent-based lignin depolymerization, a broad oxidation method, transforms lignin into HA-like substances with iron-based inorganics enhancing the oxygen-to-carbon (O/C) ratio and adding functional groups like quinones. The process's efficiency depends on lignin's structure and the hydrogen peroxide to iron (II) sulfate ratio [82, 83]. However, it may produce phytotoxic phenolic compounds [83], necessitating post-process separation for a clean product.

Artificial humification can be achieved through the OA process of lignin, which allows the incorporation of a significant amount of nitrogen into the humified lignin in various forms. In soil, organic matter like HS requires nitrogen for efficient biodegradation. Research indicates that a carbon-to-nitrogen ratio below 20 facilitates biological degradation [84], while a value higher than 25 may hinder the process. Natural humification can also be simulated by reacting technical lignin with ammonium hydroxide or ammonia solution, thereby increasing the C/N ratio and enhancing crop productivity [85]. Figure 3 illustrates the preparation of nitrogen-enriched lignohumates (N-ALHs) using the oxidative ammonolysis process [86-88]. In this, lignin is suspended in different concentrations of NH_4OH solution. The reaction occurs within temperature ranges of 130–150 °C and can be treated with or without oxidants (such as air or oxygen). After the reaction, the water-soluble and insoluble components are separated and can be utilized as different grades of fertilizers [84].

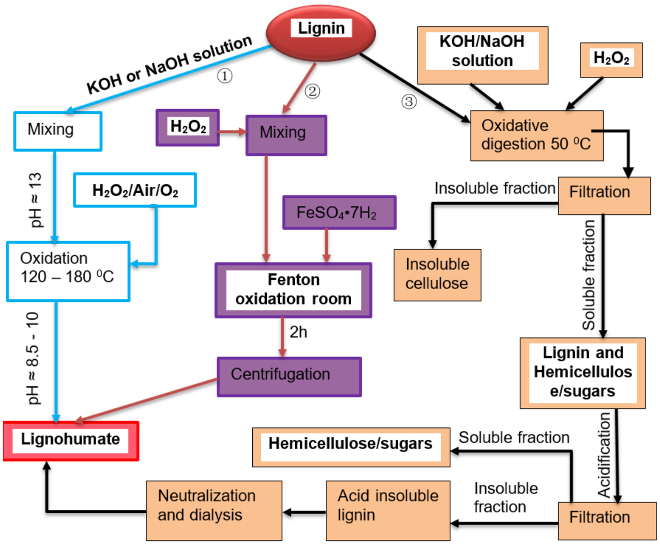

Figure 2 – A schematic flow diagram of the various direct oxidation for lignohumate production from lignin

The complexing properties of humic acids. Humic acids, known for their complex structure and versatility, also function as ligands in metal complexes, confirming their role in soil coordination structures [89]]. Research focuses on heavy metal contamination, metal-humic complex formation, and interactions with herbicides and hydrocarbons. Humic acids form stable water-soluble salts with monovalent cations (NH4+, Na+, K+, etc.) and less soluble complexes with divalent/trivalent cations (Ca2+, Al3+, etc.), influenced by pH [90]. Their functional groups (carboxyl, hydroxyl, amine, etc.) enable coordination bonds with metals [91].

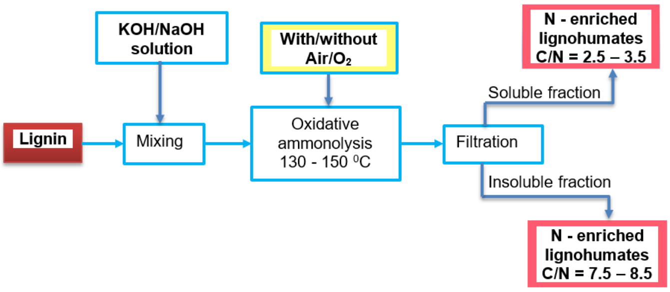

Figure 3 – A schema of the process of oxidative ammonolysis to produce nitrogen-enriched lignohumate from lignin

Recent studies highlight the importance of organic compounds in soil, including humic substances formed from biomass decomposition. Humic-like substances, produced via hydrothermal carbonization, show similar metal complexation properties as natural humics [92]. For example, humic acids strongly bind copper ions, influenced by their functional groups and structural characteristics [93]. The complexation with iron cations occurs notably on the aromatic side groups [94].

Experimental studies show dissolved organic substances form complexes with Al^{3+}, Fe^{3+}, and Cu^{2+} in surface waters, with significant contributions from humic acids [95]. Metal-humic complexes exhibit high stability; for instance, fulvic acids form strong complexes with Fe (III) and Al (III) at different pH levels. Stability varies among metals, with Cu^{2+} and Pb^{2+} complexes being more stable than those with Cd^{2+}.

Humic substances can be grouped by their metal ion binding:

1. Humates and fulvates with alkali/alkaline earth metals.
2. Covalent bonds with polyvalent cations.
3. Coordination complexes with transition metals.

Sorption efficiency decreases in the order: $Fe^{3+} > Al^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$, reflecting solubility trends. Thus, humic acids play a crucial role in forming stable metal complexes in various environmental contexts.

Electrochemical properties of humic substances. Humic substances form metal-humic complexes, enabling electrochemical studies and enhancing analytical methods due to their high sensitivity. Combining electrochemical and molecular analysis assesses changes in humic substances' composition and redox properties during sorption processes, crucial since most humic substances in soil and groundwater are sorbed, not dissolved [94]. These studies help understand biogeochemical processes involving electron transport and the adsorption and redox properties of active soil components, like iron-containing minerals.

In oxygen-rich environments, minerals, natural organic matter, and divalent manganese (Mn(II)) coexist, influencing the reactivity of organic substances and manganese toward metals and pollutants. The interaction of Mn(II) with humic acids and iron oxides (like goethite) affects adsorption and oxidation processes, particularly at pH 5-8, altering the formation and composition of Mn(II) oxidation products [96]. Humic acids, modified for various applications, show initiating properties for oxygen electroreduction at pH >7 and inhibitory properties at pH ≤7 [97]. Increasing humic acid in a solution accelerates metal reduction on the cathode, reducing metal complex accumulation on the electrode. Cyclic voltammetry studies indicate that electrodes modified with humic acid are highly sensitive and effectively accumulate copper ions.

The formation of carboxylates at pH 4.5 is faster than at pH 3, increasing voltammetry sensitivity in the pH range of 3-4.5. At pH <7, the rate of complexation decreases. With more humic acid on the electrode surface, the sensitivity increases, aiding the detection of metal ions from various media. Electrode potentials of humic compounds range from +0.15V to +0.70V, depending on their origin: 0.79V for peat-derived humic substances, 0.78V for soil-derived, and 0.50V for fulvic acids. Oxidation of humic substances produces oxygen-containing functional groups like carboxyl, hydroxyl, and aldehyde [98].

Amphiphilic character and functional groups. Humic substances (HSs) are a varied mixture of intricate molecules with differing structures and chemical compositions. Typically characterized by aromatic rings, aliphatic chains, O-, N-, and S-containing functional groups, as well as nonpolar segments, these compounds display amphiphilicity due to the presence of both polar and non-polar fragments [99,100]. This dual nature enables them to demonstrate hydrophobic and hydrophilic properties, facilitating interactions with a wide range of polar and non-polar substances, essential for their varied biological and environmental roles.

Amphiphilic Nature. Humic acids derived from soils of varying origins exhibit differences in their amphiphilic component proportions. When examining humus acid preparations through hydrophobic interaction chromatography, a higher concentration of hydrophobic compounds is observed in humic acids from quasigley chernozem compared to those from brown soil, as well as compared to fulvic acids from brown soil. The elevated hydrophilic characteristics of humic substances (HSs) suggest increased mobility within the soil profile and a greater capacity to dissolve minerals [101]. Conversely, hydrophobic HSs tend to remain fixed in their formation location, contributing to the accumulative properties of the soil profile. The amphiphilic attributes of HSs appear to play a significant role in fulfilling these functions during the development of soil humus profiles. Additionally, humic acids from brown soil display higher hydrophilicity, attributed to the prevalence of side groups within their molecular structures, in contrast to those from quasigley chernozem, which contain numerous hydrophobic aromatic structures.

Functional groups. Humic acid is very acidic mainly because of carboxyl and phenolic-hydroxyl groups. Its overall acidity can vary widely, from 1 mol/kg to over 14 mol/kg. Additionally, humic acid contains other functional groups such as quinone and ketonic carbonyl, as well as amino and sulfhydryl groups [102-107]. Carboxylic acids (-COOH) are plentiful in humic acids, imparting acidity. They can ionize in water, influencing pH and facilitating metal ion chelation. Phenolic hydroxyls (-OH) are also present in humic acids, contributing to their antioxidant properties by donating hydrogen atoms to neutralize free radicals and reduce oxidative stress. Quinones and ketones participate in redox reactions and electron transfers within humic acids. They enhance electron accepting capacity, crucial in environmental chemistry and potential biological interactions. Aromatic rings in humic acids bolster their stability and structure. These rings also facilitate interactions with other aromatics and form complexes with metals and other molecules. Aliphatic chains within humic acids create hydrophobic regions, contributing to their amphiphilic nature and interactions with non-polar substances. Esters and ether linkages within humic acids enhance overall stability and solubility characteristics [108, 109].

Scope of application of humic substances. With the development of electronic manufacturing, a great deal of electricity and electronic devices have been produced. The main component of these devices is printed circuit boards, which are heterogeneous and complex. The remnants of printed circuit boards often contain a polymer, an inert oxide, and a metal. In particular, the presence of copper in the board is much greater than the amount of copper in the metal mines. Besides, the printed circuit boards have polymer and inert oxide retardants. If handled improperly, they can lead to numerous environmental problems as well as resource recovery [110].

HA is a macromolecular organic compound formed by the biodegradation of biopolymers and is widely distributed in soil, air, and other media. HA in general can bind to all components of the environment, as well as affect the microorganisms that pollute the environment, slowing their spread. The hydroxyl and carboxyl groups contained in humic acid can be used to localize on mineral surfaces through electrostatic adsorption and organic complexation to promote the release of metals from the solid phase to the liquid phase [111]. Humic acid is re-oxidized, it can be reused as an electron acceptor to act as an electron shuttle. Based on these interactions, humic acid has the potential to influence microbial activity in biocommunication processes [5]. The above properties are considered in the research work [6]. The main purpose of the research work is to study the effect of HA on the biological leaching of copper ions from an unwanted computer motherboard. HA has been used as an additive. The experiment has shown that under the following optimum conditions the process of biological leaching of copper proceeds at a rate of 100%: pH = 1,53 and the content of HA = 0,31 g/L. The research findings suggest of biological leaching and SEM analysis, HA not only increases the percentage of copper leaching but also reduces the leaching time.

As mentioned in some literature sources, HA can be used for biological leaching of other minerals (for example, hematite, chalcopyrite, etc.) [112] Thus, we can conclude that HA is a valuable, inexpensive, and available additive, which is now found in many adsorbents.

Multifunctionalities of humic acids on human health. Humic acids exhibit multifunctional properties that can benefit human health across various areas.

Antioxidant Properties. Humic acids have been studied for their antioxidant capabilities. They scavenge free radicals, which are implicated in various diseases including cancer and cardiovascular disorders. The pharmacological activity of natural substances often hinges significantly on their antioxidant properties. This is because virtually all living organisms, from the simplest to the most complex multicellular structures (with few exceptions among obligate anaerobes), rely on the absorption and utilization of molecular oxygen in the mitochondrial respiratory chain. HSs have demonstrated antioxidant activity by effectively reducing levels of stable free radicals such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) and ABTS•+. This capability is comparable to that of standard reference compounds like dihydroquercetin and trolox. Moreover, HS exhibit a strong ability to inhibit free radicals like O^{2-}• (superoxide anion) and HO• (hydroxyl radical) in experimental models, akin to well-established antioxidants such as ascorbic acid and mannitol [113]. These antioxidative effects are likely attributable to the abundant presence of phenolic and quinoid groups, along with semiquinone-type radicals within their molecular structure [114-118]. Additionally, oxidized phenolic groups forming phenoxyl radicals may also contribute to the antioxidant potential of HSs [119].

Immunomodulatory effects. Humic acids have been studied for their potential immunomodulatory effects [120-122], which refers to their ability to regulate and modulate the immune response in the body. Researchers suggested that humic acids may have anti-inflammatory effects [123-125], immune system regulation [126, 127] and wound healing [128] immunomodulatory properties. Humic acids have displayed anti-inflammatory characteristics in certain research studies. By diminishing inflammation, they could potentially regulate the immune response and lower the likelihood of inflammatory ailments. Their capacity to modulate the immune system has also been under scrutiny, with the possibility of augmenting immune reactions against pathogens and preventing excessive immune responses in conditions like autoimmune disorders. Additionally, investigations have been conducted on humic acids' ability to promote tissue repair and regeneration, which may indirectly contribute to supporting the immune system's function. While existing studies indicate these immunomodulatory effects of humic acids, further research is necessary to comprehensively grasp the underlying mechanisms and explore their potential applications in human health.

Gastrointestinal health. Humic acids have been examined for their potential advantages in promoting gastrointestinal health [129, 130], although ongoing research is still developing in this field. Various aspects of how humic acids can influence gastrointestinal health include their impact on gut microbiota [131], gut barrier function [132], and detoxification [133]. They have been studied for their ability to alter the balance and variety of gut microbiota, crucial for digestive health and overall well-being. This promotion of a healthy gut microbiome by humic acids may contribute to improved digestive function. Additionally, research suggests that humic acids may aid in upholding the integrity of the gut barrier, essential for preventing the entry of harmful substances into the bloodstream and facilitating proper nutrient absorption. Known for their capacity to bind to toxins and heavy metals, humic acids may help eliminate harmful substances from the gastrointestinal tract, thereby enhancing overall gut health. While research continues to explore the potential gastrointestinal benefits of humic acids, it's essential to recognize that individual responses can vary. To receive personalized recommendations and guidance on integrating humic acids into a gut health-focused wellness routine, consulting healthcare professionals or experts in gastrointestinal health is advisable.

Novel technological developments. Humic acids have gained attention in the pharmaceutical field due to their diverse chemical properties and potential therapeutic applications [134]. novel technological perspectives have as following: first, humic acids can be utilized as carriers or excipients in drug delivery systems [135]. Their amphiphilic nature allows them to interact with both hydrophilic and hydrophobic drugs, improving their solubility and bioavailability. Encapsulation techniques using humic acids can protect drugs from degradation and enhance targeted delivery to specific tissues or cells [136]. Second, the antioxidant properties of humic acids, attributed to phenolic hydroxyl groups, make them promising candidates for developing anti-inflammatory and antioxidant therapies [116-118]. They can scavenge free radicals and reduce oxidative stress, potentially mitigating inflammation-related diseases such as arthritis and inflammatory bowel diseases [121, 122]. Third, humic acids' ability to chelate metals can be harnessed for detoxification purposes. They can bind to toxic heavy metals and facilitate their excretion from the body, which is beneficial in treating heavy metal poisoning and environmental detoxification [133, 137]. Forth, Studies suggest that humic acids possess wound healing properties by promoting cell proliferation, angiogenesis, and collagen synthesis. Incorporating humic acids into wound dressings or topical formulations could accelerate wound closure and improve tissue regeneration [128]. Fifth, humic acids have demonstrated antimicrobial and antiviral activities against a wide range of pathogens [138, 139]. They can disrupt microbial cell membranes, inhibit viral replication, and enhance immune responses. This makes them potential candidates for developing novel antimicrobial agents or adjuvants for vaccines. Sixth, humic acids are generally biocompatible and non-toxic, which is advantageous for pharmaceutical applications [140, 141]. They have been used traditionally in folk medicine and are considered safe for human consumption at appropriate doses. Latest, humic acids have shown promise in disrupting bacterial biofilms [142, 143], which are implicated in chronic infections and antibiotic resistance. Incorporating humic acids into therapies aimed at biofilm eradication could enhance treatment efficacy.

Conclusion. Humic acid is a high molecular weight heterogeneous compound, which is one of the main components of soils and many aquatic objects. Humic substances are widely used in various fields of human life: they are part of fertilizers, which are the basis for plant growth, are used in industry as sorbents for the purification of water and various levels of toxic solutions, in medicine as radioprotectants and active additives. It is also possible to obtain sensory electrodes sensitive to various organic and inorganic compounds utilizing metal-humic complexes. Such electrodes help to solve many problems in the fields of analytical chemistry, electrochemistry, medicine and simplify some processes. The peculiarity of humic acid in the manufacture of such electrodes is its economic efficiency, affordability, and versatility. One of the most important issues in the study of such compounds is the study of their structure and composition. Despite much research, there is still much debate on this topic. Future research should focus on elucidating the detailed mechanisms of humic acid interactions at the molecular level, optimizing extraction and synthesis techniques, and expanding their applications in various fields to fully exploit their environmental and economic potential. The functionalities of humic acids arise from their amphiphilic character and the diverse array of functional groups present in their complex molecular structure. Exploring humic acids in pharmaceutical applications involves leveraging their unique chemical properties for drug delivery, antioxidant therapy, metal detoxification, wound healing, antimicrobial activities, and biofilm disruption. Further research and development are needed to fully exploit their potential and optimize their use in clinical settings.

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ГУМИН ҚЫШҚЫЛДАРЫ: ҚАСИЕТТЕРІ, ҚҰРЫЛЫСЫ ЖӘНЕ ҚОЛДАНЫЛУЫ

Гуминді заттар – көптеген жылдар бойы қоршаған орта факторлары мен тірі организмдердің әсерінен өсімдік және микробтық қалдықтардан түзілетін, тұрақты химиялық құрамы жоқ табиғи қосылыстардың алуан түрлі класы. Екі ғасырға созылған ауқымды зерттеулерге қарамастан, HS құрылымының күрделі және өзгермелі сипаты ғылыми зерттеу нысаны болып қала береді. Бұл заттар, атап айтқанда гумин қышқылдары, фульвоқышқылдары және гумин функционалдық топтары және биодеградацияға төзімділігі арқасында экологиялық және экологиялық процестерде шешуші рөл атқарады. Бұл шолу HS-тің күрделі құрылымы мен қасиеттерін, олардың жіктелуін және табиғатта кездесетінін зерттейді. Ол гумин қышқылдарының құрылымдық фрагменттерін сипаттау үшін ұсынылған әртүрлі үлгілерді бөліп көрсетеді, олардың хош иісті өзектері мен әртүрлі функционалдық топтарын атап көрсетеді. Сондай-ақ олардың полидисперстік табиғатына жататын HS молекулалық массасының таралуының өзгермелілігі және оларды анықтау үшін қолданылатын әдістермен, мысалы, алып тастау хроматографиясы талқыланады. Сонымен қатар, гумин қышқылдарының элементтік және функционалдық құрамы зерттеліп, олардың қышқылдық-негіздік қасиеттері мен ауыр металдарды құрау қабілеті егжей-тегжейлі қарастырылады. Топырақ, шымтезек, көмір және жасанды процестер сияқты табиғи көздерден HS синтезі сілтілі экстракция және гидротермиялық өңдеу сияқты әдістерді көрсетеді. Тотығу аммонолизін және фентон реагентіне негізделген тотығуды қоса алғанда, жасанды гумификациядағы соңғы жетістіктер лигнин мен қалдықтар биомассасынан экологиялық таза гуминді материалдарды өндірудегі әлеуеті үшін қарастырылады. Зерттеу қоршаған ортаның маңыздылығын және HS-ның практикалық қолданылуын атап өтумен аяқталады, әсіресе ауыл шаруашылығында, топырақты өңдеуде және қоршаған ортаны қалпына келтіруде. HS-дің әртүрлі қасиеттері мен синтез әдістері оларды тұрақты материалдық өндіріс пен қоршаған ортаны басқару үшін перспективалы үміткерлер етеді.

Түйін сөздер: *гумин қышқылы, гуминді заттар, металлогумин кешендері, полимерлі материалдар, электрохимиялық қасиеттер, гумин қышқылының синтезі, гумин қышқылының құрылымы.*

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ГУМИНОВЫЕ КИСЛОТЫ: СВОЙСТВА, СТРУКТУРА И ПРИМЕНЕНИЕ

Гуминовые вещества (ГВ) – это разнообразный класс природных соединений без фиксированного химического состава, образующихся из растительных и микробных остатков под действием факторов окружающей среды и живых организмов в течение многих лет. Несмотря на обширные исследования, продолжавшиеся два столетия, сложный и изменчивый характер *структуры ГВ остается предметом научных исследований. Эти вещества, особенно гуминовые кислоты, фульвокислоты и гумин, играют решающую роль в экологических и экологических процессах из-за их большого количества функциональных групп и устойчивости к биоразложению. В обзоре рассматриваются сложная структура и свойства ГВ, их классификация и распространение в природе. В нем освещаются различные модели, предложенные для описания структурных фрагментов гуминовых кислот, подчеркиваются их ароматические ядра и разнообразные функциональные группы. Обсуждается также изменчивость молекулярно-массового распределения ГВ, обусловленная их полидисперсной природой, а также методы их определения, такие как эксклюзионная хроматография. Кроме того, изучен элементный и функциональный состав гуминовых кислот, уточнены их кислотно-основные свойства и способность к комплексообразованию тяжелых металлов. Освещается синтез ГВ из природных источников, таких как почва, торф, уголь, а также искусственных процессов, демонстрируя такие методы, как щелочная экстракция и гидротермальная обработка. Последние достижения в области искусственной гумификации, включая окислительный аммонолиз и окисление на основе реагента Фентона, рассматриваются на предмет их потенциала в производстве экологически чистых гуминовых материалов из лигнина и биомассы отходов. В заключение исследования подчеркивается экологическая значимость и практическое применение ГВ, особенно в сельском хозяйстве, кондиционировании почвы и восстановлении окружающей среды. Разнообразные свойства и методы синтеза ГВ делают их перспективными кандидатами для устойчивого производства материалов и управления окружающей средой.*

Ключевые слова: *гуминовая кислота,* Гуминовые вещества, *металлогуминовые комплексы, полимерные материалы, электрохимические свойства, синтез гуминовой кислоты, структура гуминовой кислоты.*

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ТЕМІРҚҰРАМДАС ОКСИДТЕРДІҢ НАНОБӨЛШЕКТЕРІН АЛУ ӘДІСІ ЖӘНЕ ОЛАРДЫҢ ҚАСИЕТТЕРІН ЗЕРТТЕУ

***Аңдатпа:** Темірқұрамдас оксидтердің нанобөлшектерінің синтезі оларды әр түрлі технологиялық процестерде қолдану мүмкіндігі бар магниттік, каталитикалық және адсорбциялық сияқты бірегей физика-химиялық қасиеттеріне байланысты медицинада, электроникада, экология салаларында қызығушылық тудырады. Осыған байланысты, бұл мақалада темірқұрамдас оксидтердің нанобөлшектерін алу және олардың физика-химиялық қасиеттерін зерттеу нәтижелері келтірілген. Металл нанобөлшектерін алуда табиғи полимерлермен тұрақтандырудың маңызы зор екені белгілі. Сол себепті, бұл зерттеуде синтездеу калий гуматымен тұрақтандыру арқылы жоғары температурада жүргізіледі. Алынған темірқұрамдас нанобөлшектердің қасиеттерін зерттеу үшін рентгенфазалық талдау, трансмиссиялы электронды микроскопия, инфрақызыл спектроскопия әдістері қолданылады. Физика-химиялық зерттеу нәтижесінде синтезделген металл нанобөлшектерінің гетерогенділігі және монодисперстілігі анықталады. Синтезделген үлгілердің бөлшектерінің орташа өлшемі 8,3 нм құрады, ал кристалдық тордың параметрі 0,8426 нм болды. ИҚ-спектроскопия әдісімен зерттеу нәтижесі үлгілердің тотығуы туралы болжамды растайды. Сонымен қатар, дайындалған үлгілердің кристалдану дәрежесінің жоғары екені анықталады. Трансмиссиялық электронды микроскопия нәтижесінде нанобөлшектердің өлшемдері бойынша айырмашылық анықталмады. Зерттеу жұмысында қолданылған әдіспен темір нанобөлшектерінің синтезі процесінде таза темір оксиді түзілмейді. Зерттеу нәтижесінде алынған темірқұрамдас оксидтер нанобөлшектерінің бірегей қасиеттері қоғамның өмір сүру сапасын жақсартуға және тұрақты дамуына бағытталған инновациялық технологиялар мен шешімдерді құру үшін перспективалы болып табылады.*

***Түйін сөздер**. Темірқұрамдас оксид нанобөлшектері, калий гуматы, гематит, магнетит, маггемит, рентгенфазалық талдау, инфрақызыл спектроскопия.*

Кіріспе

Соңғы екі онжылдықта нанотехнология зерттеудің бірнеше салаларына үлкен үлес қосты және 21 ғасырдағы революциялық технологияның шлюзі болып саналады. Соңғы уақытта бұл технология ғылымның жаңа саласына, сонымен қатар жаңа наноөлшемді бөлшектер мен оларды қолданудың қуатты құралына айналды [1]. Нанотехнология ғылымы әртүрлі салаларда маңызды қолданбалы жаңа материалдарды жасау үшін атомдар мен молекулаларды басқаруды қамтиды [2]. Наноматериалдар оптикалық, электрлік, магниттік және каталитикалық қасиеттеріне байланысты көп назар аудартты. Белгілі болғандай, наноматериалдардың қасиеттері және олардың әлеуетті қолданылуы фаза, өлшем және морфология арқылы айтарлықтай әсер етеді. Осылайша, басқарылатын және жаңа