



Hymato Products Ltd.

The harmony of the elements

Introduction to humic substances

**Written by:
Dr János Csicsor**

**member of the
International Humic Substance Society**

THE PROBLEM

Researchers often face insolvable problems when trying to join the sustainable development and environmental efforts along with globalization challenges.

The so called civilization diseases of human being (immune system problems, stress, allergy, obesity, acidity etc.) are caused mostly by micronutrient deficiency.

THE APPROACH

Complexes of humic and fulvic acids and micronutrients give a natural solution to the problems of people who try to satisfy the challenges of the technical civilization.

The medical and curative effects of humic substances have been known for thousands of years.

Modern science develop and understand these molecules and call them frequently „natural antiviral molecules” or „alternative antibiotics”.

THE SOLUTION

Our company is engaged in research and production of natural humic substances based pioneer products that are restoring the natural living standards. We are offering several humic acid, fulvic acid and hylatomelanic acid based products, as active ingredients for formulators of medicines, food supplements or cosmetics and we also offer ready to use products for dealers.

Table of content:

1. HUMIC SUBSTANCES IN NATURE
 - 1.1. Humification
 - 1.2. Coal formation
 - 1.3. Humic acid sources in nature
 - 1.4. Regularly used phrases related to humic acids
2. STRUCTURE OF HUMIC SUBSTANCES
3. CHEMICAL REACTIONS OF HUMIC SUBSTANCES
 - 3.1. Water solubility
 - 3.2. Metal complexes
 - 3.3. Biological availability
 - 3.3. Chemical bonds with organic and inorganic molecules
4. APPLICATION OF HUMIC SUBSTANCES

**Do not hesitate to contact us for more information.
www.hymato.hu**

1. HUMIC SUBSTANCES IN NATURE

Humic substances are the biological-chemical-geological decomposition products of the living plant origin matter on the Earth. The biggest part of the terrestrial organic matter (biomass) are Humic Substances. Humus (soil-peat-coal) is the most relevant decomposition product of living matter so Humus is the most important media for the reproduction of the continental biomass.

The positive effects of Humic Substances in Medical and Agricultural applications related to their Humic Acid content. Humic Acid molecules form a well defined chemical structure and are the intermediate product of decay of the living matter.

The decomposition process of the terrestrial biomass can be divided into two parts that are Humification and Coal Formation. During Humification the so called Recent Humic Substances while during Coal Formation the Fossile Humic Substances are forming.

The precursor molecules of Humic Acid during humification are the ligneous plant residues which are transforming under chemical-biological aerob and anaerob oxidation-reduction processes.

The formation of humic acids in humification processes needs geological times, that is thousands of years.

1.1. HUMIFICATION

In the first step of decomposition of the organic matter a chemical-biological aerob-anaerob oxidation starts. In this phase the biomass is under water surface. In this dynamic balanced process the basic compounds of Humic Substances are forming from the aromatic compounds like lignins, tannins, flavonoids, glycosides etc. - and their derivatives. Other parts of the residues - proteins, cellulose - leave the biomass as NH_3 , CO_2 , H_2S , CH_4 , H_2O . The hydrocarbon and protein compounds decompose quite fast during the Humification process and their derivatives bond weakly to Humic Substances. The main precursor molecules of Humic Acids are the lignin compounds.

The natural waxes and resins cannot decompose and become part of the insoluble Humin matter. Further in the Humification pathway the aromatic molecules transform to oxiquinon-hydroxi-carboxyl structures and undergo a polymerization and micella formation process.

The analysis of Humus compounds show different easily decomposing hydrocarbons, proteins and nitrogen containing molecules. It does not mean of course that all of them are Humic Substances. That is why it is so important to make difference between the terms HUMUS and HUMIC ACID.

Summarizing we can say that in the first phase of Humification the big molecules decompose into smaller so called building blocks while in the second phase they reorganize as Humic Substances.

1.2. COAL FORMATION

When the biomass deposits are overlaid with inorganic-soil mineral layers than the coal formation starts. The temperature and pressure are increasing. In this anaerobe phase the biological activity practically stops and dehydration ($-\text{H}_2\text{O}$) decarboxylation ($-\text{COOH}$) and dehydrogenation processes are the main chemical reactions. The polymer molecules condensed by C-O-C bonds transform to C-C aromatic (antracen) bonds.

During these processes the carbon content of compounds changes as follows:

Wood	50%	Peat:	55-60%	Lignite:	65-70%
Black coal:	80-90%	Antracit:	80-98%	Graphite:	100%

The Coal Formation process may turn back or may stop under exceptional geological conditions. This happens when the coal deposits go up to the earth's surface or air and water move into the deposit layers (earth-quake etc.). These kind of coal is the so called reoxidized coal.

Regarding Humic Acid based products these reoxidized –conserved- coal layers can be considered the best quality raw materials. These oxidized (reoxidized) coal deposits are named as leonardite in the international literature (after Leonard geologist professor). At the same time it must be mentioned that there are only some leonardite deposits in the World. One of the best is in Hungary.

1.3. HUMIC ACID SOURCES IN NATURE

There are many sources of Humic Substances in Nature.

SOIL: The commonly known continuously renewing Humus source. The Humic Acid content of the upper 20-30 cm soil layers are generally 1-5 %.

WATERS: Natural ground waters generally contain certain amount of Humic Substances especially Fulvic Acids. The yellowish brown color of waters are coming from Humic Substances dissolved from soil and other organic sources.

ORGANIC MANURE Used to be applied instead of fertilizers with good efficiency in the former times. Humic Acid content is 5-15 %. The modern animal farm management technologies made the quality unsuitable for direct fertilizing – chemical, pesticide and medicine residues, toxic heavy metals, non humified organic residues.

COMPOSTS A popular form of Humus production. The bio-humus and humus names of composts are misleading because the Humic Acid content is not exceeding a good quality soil.

SAPROPELS Humic Acid containing organic matter on the bottom of some rivers and lakes as the decomposition product of plants and some microorganisms, planktons, algae in waters. Humic Acid content is about 10-20 %.

PEAT The first step of humification process in nature. Humic Acid content is about 10-50 %. As raw material has great importance related to some balneological applications - medical, thermal waters - where the medical effects are related mainly to their Humic Substance content.

LIGNITE, BROWN COAL In the normal coal formation process lignites contain 20-40% Humic Acids while brown coals contain 10-30 % Humic Acid.

LEONARDITE Under certain exceptional geological conditions Humic Acids may be conserved in highly oxidized form. The Humic Acid content of these leonardite deposits can be 50-80%. These are the economically extractable Humic Acid sources. It must be emphasised that these leonardite deposits are free of any contaminates and pollutants. Leonardite can be considered as an almost “sterile” raw material for Humic Acid extraction.

1.4. REGULARLY USED PHRASES RELATED TO HUMIC ACIDS

The international literature uses several phrases related to humus and organic matter and humic acids. These terms are not always used consequently. We define below the most frequently used terms:

HUMUS: The organic matter in soil containing humic acids and non humified organic residues.

HUMIC SUBSTANCES: Collecting name of humic acid, fulvic acid, humin matter and hymatomelanic acid. Completely humified organic matter. Soluble in alkaline (Na^+ , K^+ , NH_4^+) solutions.

HUMIC ACIDS (plural): Collecting name of humic acid and fulvic acid. Alkaline extractable fraction of Humic Substances.

FULVIC ACID: The smallest molecular weight fraction of Humic Substances. Soluble in alkaline and also in acidic solutions (pH=2-14)

HYMATOMELANIC ACID: This fraction of Humic Substances is soluble in alcohol.

HUMATES: Different salts (Fe-humate or K-humate etc.) of Humic Acids

FULVATES: Different salts (Zn-fulvate or Na-fulvate etc.) of Fulvic Acids

HUMIN: Overhumified fraction of Humic Substances. This fraction is not soluble even in alkaline liquids.

NOM: Natural Organic Matter

2. STRUCTURE OF HUMIC SUBSTANCES

During the natural formation of Humic Substances the Humic Acid molecules can be found in different chemical environment (metals, bitumens, waxes, proteins, carbohydrates etc.) At the same time it must be emphasized that apart of these disturbing molecules there exist chemically clean Humic Acid molecule. Chemically characterized and defined Humic Acid can be extracted independently of their source.

The Humic Substances (Fulvic Acid, Humic Acid, Humic Matter) are practically build up from the same building blocks. The difference between Humic and Fulvic Acids is the degree of polymerization that is their molecular weight. The literature contains many extremely different molecular weight values about the same Humic Acids because authors do not define what they mean Humic Acid. The molecular weight of Humic Substances is changing continuously in nature we cannot draw a strict line between Humic and Fulvic acid molecules.

According to the theoretical model of Humic Acid all the chemical, biological reactions can successfully be interpreted.

3. CHEMICAL REACTIONS OF HUMIC SUBSTANCES

3.1. WATER SOLUBILITY

Only Fulvic Acid is water soluble. The bigger the molecular weight the worse is the water solubility. The interpretation of this fact can be understood from the model structure: as the polymerization degree is higher the specific number (meqv/g) of hydrophil groups - active sites - decreases in the molecule.

In alkaline solution (K, Na, NH₄) the lactone ring opens causing the well known solubility of Humic Acids. In acidic media the dissociation of carboxyl and hydroxyl groups are pressed back and the lactone ring is closed so the molecule is precipitating.

3.2. METAL COMPLEXES

The polyvalent cations make Humic Acid insoluble in water. These cations may bound together several building units like a bridge. The forming big complexes become insoluble in water.

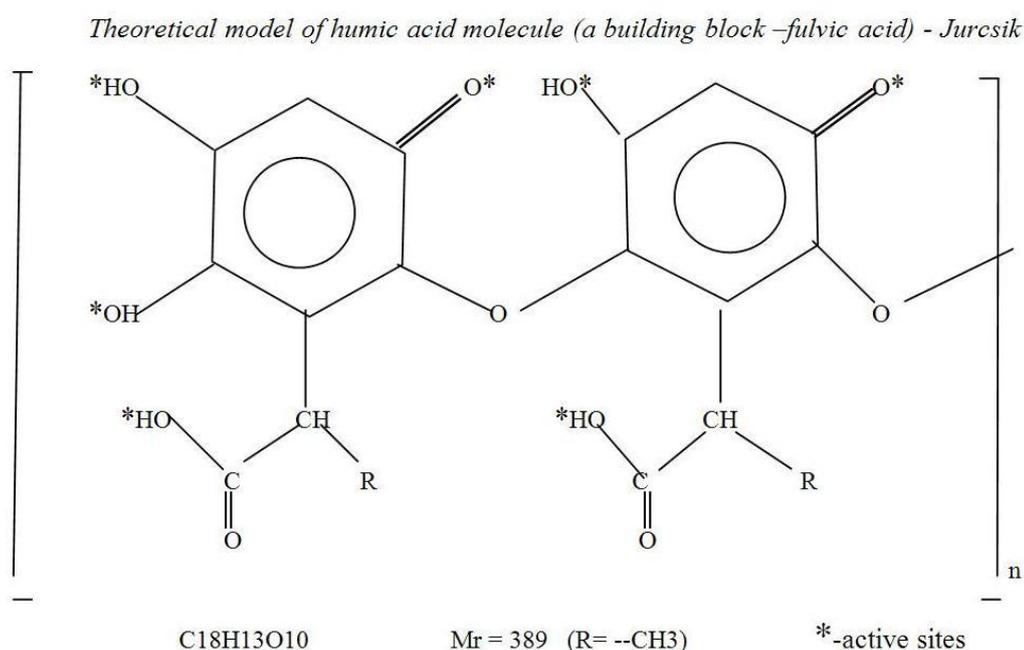
3.3. BIOLOGICAL ACTIVITY

The biological activity of Humic Substances is known for a long time which is coming from the following facts - also well interpreted by the model:

Humic Substances have an electron and active oxygen transfer capability. These molecules are able to take part in the cell respiration chain processes:



The electron and oxygen transfer capability is connected to the quinon-semi quinon structure. The simplified process is the following:



The strict prove of this mechanism cannot be the aim of this short description but it must mentioned that many analytical and biological tests were carried out which proved this theory.

The following facts are the most important regarding biological activity:

- a. HA speed up the cell respiration chain processes which indirectly speed up the processes in the citrate circle. The electron transfer capability of HA stimulate the whole metabolism where the HA molecules take part as catalysators. This is a general effect by which more energy becomes free in cells - not specific like hormones.
- b. The relevant chemical parameter in this process is the free electron concentration or spin concentration (not molecular weight or total acidity). Generally the bigger molecules have better biostimulant activity containing more delocalized free electrons. That is Fulvic Acid is not so effective as Humic Acid.
- c. Humic Acids have an optimal concentration in the biostimulation process. This concentration is different in different living organisms but an optimum always can be registered.

3.3. CHEMICAL BONDS WITH ORGANIC AND INORGANIC MOLECULES

The structure of Humic Substances predestine them to make bonds with almost every kind of chemical biochemical structures.

- a. **Inorganic cations** may bond to HA by ionic, complex, chelate and adsorption polar bonds. The acidic carboxyl, hydroxyl groups are the most important reaction partners but semiquinon and carbonyl groups may also react.
- b. **Inorganic anions** practically cannot bond directly to HA being negatively charged like HA. Nevertheless through metal bridges these molecules can be bond with very good efficiency to HA.
- c. **Organic compounds** the chemical bonds between organic compounds and HA depends on their structure (aromatic, aliphatic) on their charge (positive, negative) Based on the several experiments it can be stated that in almost every cases there are ways how to bond these molecules (xenobiotics, proteins, enzymes etc.) to Humic Substances.

4. APPLICATION OF HUMIC SUBSTANCES

The chemical structure, the biological activity and the natural origin of Humic Substances predestine them to become Substances having fast growing importance in the fields of:

Agriculture, Veterinary, Environmental Protection, Industrial Additives, Cosmetics and Pharmacy.

Upon request we send detailed application about these fields.

Literature:

1. **FUCHS, W.:** Die Chemie der Braunkohle, Berlin, 1931.
2. **POTONIE, R.:** Braunkohle, XXX. Leipzig, RECLAM, 1931.
3. **KREULEN, J.W.:** Grundzüge der Chemie und Systematic der Kohlen, Amsterdam, 1935.
4. **KONONOVA, M.M.:** Biochemistry of Humic Acid formation. Publication of the USSR Academie of Science, Institute of Soil Science, Moscow, 1948.
5. **SZÁDECZKY, E.:** Über Systematic und Umwandlungen der Kohlengemengteile, Acta echn. Hungarica, Budapest, 1948.
6. **SÁNDOR J., SMITH, R.H.:** Formation of Humus and its relation to coal. Bangham: progress in coal science, London, 1950.
7. **PRÁT, S.:** Humus, Praha, CSAV, 1961.
8. **STEVENSON F.J.:** Humus Chemistry, Genesis, Composition, Reactions, Wiley, New York, 1982.
9. **SEQUI, P., SCHNITZER, M.:** Humic Substances, Applications in Agriculture, REDA, Roma, 1986.
10. **CSICSOR, J.:** The Biostimulant effect of Different Humic Substance Fractions on Seed Germination, HS in the global environment, implications om human health, ELSEVIER, 1994.
11. **JURCSIK, I.:** Investigations in the mechanism of electron transmission and active oxygen generating humic acids supported by redoxindicators. HS in the global environment, ELSEVIER, 1994.