1. Humic Substances
Humic substances are long chains of numerous stable carbons that have physical, chemical, and biological effects on the soil, related to agricultural activity. They are one of the main sources of N, P, and S for plants, they influence the mobility of non-ionic organic compounds such as pesticides and pollutants, removing them from aqueous solutions, they retain nutrients due to their cation exchange properties [1].

According to Huelva (2013) [2], Humic Substances (HS) are very complex macromolecules. These have different functional groups that allow them to act as polyelectrolytes of weak acids and be sites of reaction with different chemical agents; It is accepted that this consideration is valid for each of its fractions where Humic Acids (HA) are also included as one of its components. Most of these reaction sites are attributed to the presence of oxygen in the OH functional groups of alcohols, phenols, carboxyl, and others, being those of carboxyl and phenolic groups the ones with the greatest interaction and quantity.

For Seguel et al., 2020 [1] and Janoš, 2003 [3], Humic substances are made up of three parts. These are Humins, Humic Acids, and Fulvic Acids, the last two can be separated in different pH media, Fulvic Acids, for example, are solubilized in pH acidic medium, while Humic Acids are soluble in alkaline mediums and humins are insoluble at all pH values.
2. Humic acids
These are macromolecules that are formed from organic, fossil, and plant residues through microbial decomposition carried out mainly by fungi, they can be found in peat, leonardite, and compost [4,5].

According to Noboa (2019) [6], he defines humic and fulvic acids as complex organic molecules formed by the decomposition of organic matter. These directly influence the fertility of the soil, while contributing significantly to its stability, affecting the absorption of nutrients and as a direct consequence, optimal growth, and development of the plant.

However, Mosquera (2007), states that humic acids are complex aromatic macromolecules with amino-acids, amino-sugars, peptides, and aliphatic compounds that are involved in the bonds between aromatic groups. The hypothetical structure for humic acids contains free and bonded phenolic groups, quinone structures, nitrogen and oxygen as bridges, and carboxylic acid groups at various locations on the aromatic rings (3); In addition, they are molecules in which the presence of aromatic rings of the di and trihydroxybenzene type is observed and nitrogen as a structural component that indicates the presence of carbohydrate and protein residues.

Other authors argue that AH are mixtures of carbohydrates, proteins, and lipids from both plants and microbial origin, together with partial degradations of lignin and tannins, and with microbial materials such as melanins, or are pseudo structures defined as hypothetical molecular constitutions with elements, structures and functional groups similar and consistent with some or all of the observed properties of a given mixture, which are not molecular structures, nor are they average structures or an average structural model [7-9].

Finally, Pantoja et al. [10], identifies humic acids as “A fraction of humic substances, made up of aromatic and polyaromatic nuclei, linked through aliphatic chains. These have a diversity of functional groups, which allow them to exercise various functions in the soil-plant relationship”.

3. Importance of humic acids
humic acids such as fulvic acids are of great importance in crops since they prevent the soil from compacting; They help to transfer nutrients from the soil to the plant, increase the water retention capacity, increase the speed of seed germination and stimulate the proliferation of the microflora present in the soil, increasing the soil's moisture retention capacity. In general, it is estimated that humic acids can retain water in a proportion of twenty times its weight. They increase the cationic and anionic exchange capacity of the soil and thus its capacity to provide nutrients to the crop, as well as its storage in the soil [11-12].

HA promote development and plant growth in crops of agronomic interest [13-15].

It has been shown that there is a relationship between the chemical properties and functions of humic acids and the changes in biological activity that are manifested in the growth of the plant that occurs after the chemical modification of humic acids [2,16].

According to Solórzano [4], 2019; Rodriguez [5], The water absorption capacity of humic acids is due to their large branched structure by aliphatic side chains of amino acids, peptides, and aliphatic acids, where this corresponds to around 65%, the remainder corresponds to structures with an aromatic character; These facilitate the rotation of cations in the medium due to their cation exchange capacity and ease of chelation.

4. Methodology for Humic acid extraction
For the extraction of humic acids, separation is carried out in an alkaline medium where the humic acids are precipitated. For this extraction, many times some type of oxidation is carried out that increases the original amount of HA found in the carbonaceous matrix, this can be carried out through various types of oxidizing agents, even starting from different raw materials. Next, we will look at some of the many ways that can be used to extract humic acids.

Vasquez et al. (2019) [17], uses a factorial type experimental design, with a $2^2 \times 3$ arrangement, testing two levels of time (3h and 6h), three levels of concentration, 30, 40, and 50% of oxidizing agent ($H_2O_2$) and two levels of particle size, 0.25mm (60 mesh) and 0.125mm (120 mesh). For sample preparation,
the coal from the Cerrejón mine, located in the department of La Guajira (Colombia), was crushed in a ball mill (Pulvex brand) and sieved to two particle sizes, using sieves with mesh number 60 and 120. Demineralization and solvent removal was carried out according to the procedure suggested by Anillo-Correa et al. [18]. Aqueous Oxidation was performed according to [18]. In the characterization of the materials, the carbon and humic acid samples were characterized by infrared spectrometry (FTIR). Proximal studies, in accordance with ASTM (2012) standards, to determine the percentage of moisture, volatile matter (% MV), ash, percentage of fixed carbon (% CF) and the % CF / MV ratio.

Santana [19], shows different methods for the extraction of humic substances, one of them is through the determination of humic substances in sediments by focused ultrasound and ultraviolet-visible spectroscopy. The development of a new and rapid methodology to determine the amount of humic substances (HSs) present in sediment samples is deeply optimized with this method. Emphasis is placed on alkaline extraction because traditional methods required high volumes and long extraction times. The extraction of liquids-solids by focused ultrasound (FUSLE) is carried out, followed by the separation of SHs in acidic media. The determination of it using visible ultraviolet spectroscopy turned out to be a very suitable analytical procedure to accelerate the extraction of HSs, specifically humic acid (HA) and fulvic acid (AF). All the variables that affect the extraction process (sodium hydroxide concentration and volume, ultrasound power, cycles, and time) were selected using the analysis of variance and the multivariate design. The optimal values of these variables are the power of continuous application of the (FUSLE), 95% (10 cycles), and 15 mL of NaOH 1 mol/ L-1. p.12 [20]

Santana refers to Susic (2016) [21], to classify humic acid extraction methodologies and achieves to classify them according to the type of extractant and material to be extracted into three types, mild, medium, and strong extractants, see table 1.

The methodology proposed by Anillo et al (2013) [18] was the following: For oxidation with air, 50g of sample and an airflow of 100 mL/min were used in a porcelain reactor with a fluidized bed. This process was carried out at temperatures of 180, 200, and 220 °C. The oxidation in an aqueous medium was carried out with hydrogen peroxide (Merck) and with nitric acid (Merck). For oxidation with hydrogen peroxide, 5 g of air-oxidized carbon, 30 mL of a 30% (v/v) solution of H₂O₂ and 15 mL of concentrated acetic acid (Merck 99-100%) were added to an Erlenmeyer flask. This system was heated to 60 °C and kept under continuous stirring for 6 and 12 h. oxidation with Nitric acid was carried out by mixing 5 g of oxidized carbon with air with 30 mL of HNO₃ at 30% (m/v). This system was heated to 60 °C and kept under continuous stirring for 6 and 12 h. For the extraction of humic acids from oxidized coals, 100 mL of NaOH (0.1 M) (Sigma-Aldrich) were added to 5 g of these materials, maintaining this system for 1 h under continuous stirring. Subsequently, the solution was filtered under vacuum and 100 mL of HCl (0.1 M) (Merck) were added to the filtrate to precipitate humic acids. This system was kept at rest for 24 h and was subsequently centrifuged at 3600 rpm for 10 min. The colloid obtained after centrifugation was washed with portions of ethanol and finally dried at 100 °C for 1 h to be subjected to different analyzes. The oxidation process in aqueous solution was carried out in triplicate in the case of the two oxidizing agents, not being observed standard deviations greater than 1.3% in any of the cases.

According to the International Society of Humic Substances (2008), the methodology used for the extraction of humic acid is based on two methods, which are based on two fundamental stages, first the extraction of humic substances using NaOH as extractants, which is recommended by IHSS, (2008) and Santi, (2000) [22] or KOH (Rocha et al., [23]) and then the separation of humic and fulvic acids from the acidification of humic substances with diluted HCl or H₂SO₄. The best extraction percentages are obtained with NaOH and HCl.
| Extractant | Fundaments | References |
|------------|------------|------------|
| NaOH       | It is the most used procedure for the extraction of humic substances of commercial type, due to its high percentage of extraction (80%). | Hemati et al., 2012; Scaglia et al., 2016; Lukyanov et al., 2016; Fuentes et al., 2016; Asing et al., 2009 |
| KOH        | These extractants produce minimal alterations in the matter organic. In some cases they are used together with alkaline products to increase their effectiveness. | |
| Na₄P₂O₇, EDTA | One way to increase effectiveness is to mix these reagents with other products, such as urea at high concentrations. Obviously, although the alterations that occur in the extracted organic matter are minor, the effectiveness shown by these products is much lower. | Fuentes et al., 2016; Asing et al., 2009 |
| EDTA, acetylacetone, cupferron and various types of organic solvents such as tetrahydrofuran | | |
| Formic Acid (HCOOH) | It is obtained from 55% extraction of organic matter in mineral soils, up to 80% in compost. Formic acid extraction is the most efficient for where most organic substances are partially humified. | Ramos, 2000 |

### 4.1. Methodology used in our research

The Carbon sample from the Cerrejón mine (Guajira - Colombia) was provided by Professor Yazmin Agamez Pertuz from the National University of Colombia. This was crushed and sieved to a particle size between 1mm and 150µm corresponding to mesh size # 18 and # 100 respectively.

#### 4.1.1. Oxidation

For the oxidation in an aqueous medium, two different oxidizing agents were used, hydrogen peroxide (H₂O₂) at 30% (v/v) and nitric acid (HNO₃) at 30% (v/v). The oxidation time was 10 hours.

For oxidation with hydrogen peroxide, 5 g of carbon (C10), 15 mL of glacial acetic acid, and 30 mL of hydrogen peroxide at 30% (v/v) were added in a 100mL flat-bottom balloon in a proportion of 1:2, this system was immersed in a water bath on a heating plate with magnetic stirring. The system was heated to 60 °C and kept under constant stirring for 10 h.

For oxidation with nitric acid, 5 g of carbon (C10), 15 mL of glacial acetic acid, and 30 mL of nitric acid at 30% (v/v) were added in a proportion of 1:2, this system was immersed in a water bath on a heating plate with magnetic stirring. The system was heated to 60 °C and kept under constant stirring for 10 h.
4.1.2. Extraction of humic acid. For the extraction of humic acids, sodium hydroxide (NaOH) was used.

For the extraction of the oxidized humic acids with hydrogen peroxide, 100 mL of NaOH (0.1 M) were added, maintaining this system for 1 hour under continuous stirring and heating at 60°C. Subsequently, the solution was filtered under vacuum and 100 mL of HCl (0.1 M) were added to the filtrate to precipitate humic acids. This system was kept at rest for 24 hours well covered to avoid contact with air, then it was filtered under vacuum again and the precipitate obtained was washed with portions of distilled water and 2 portions of 5 mL of ethanol and the humic acid obtained was dried at a temperature of 100 °C for 1 h. finally, it was subjected to different analyzes for its respective characterization.

For the extraction of the oxidized humic acids with nitric acid, 100 mL of NaOH (0.1 M) were added, maintaining this system for 1 hour under continuous stirring and heating at 60°C. Subsequently, the solution was filtered under vacuum and 100 mL of HCl (0.1 M) were added to the filtrate to precipitate humic acids. This system was kept at rest for 24 hours well covered to avoid contact with air, then it was filtered under vacuum again and the precipitate obtained was washed with portions of distilled water and 2 portions of 5 mL of ethanol and the humic acid obtained was dried at a temperature of 100 °C for 1 h, finally it was subjected to different analyzes for its respective characterization.

5. Applications

5.1. Bioactivity of humic acids.

5.1.1. First application. Huelva and Martínez and other members of the Agrarian University of Havana worked with humic acids obtained through vermicompost of bovine manure. The chemical modifications in the structure of the HA were analyzed to determine the structural changes through Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT) techniques and, through their spectra, the hydrophobicity (HI) and condensation (IC) indices of molecules were calculated [2].

Table 2. shows the content of C obtained by humic acids after the structural modification and the optical coefficient E4 / E6, where the observed values for C are values that are within the range of the values reported in the scientific literature and compared with other humic acids extracted with other methods and from other origins [24].

| humic substances | percent of C | E4 / E6 |
|------------------|--------------|---------|
| AH               | 56.53 b      | 5.25 b  |
| AH-Ac            | 60.75 a      | 4.93 c  |
| AH-Met           | 66.70 a      | 3.78 d  |
| AH-NH₃           | 55.65 b      | 6.54    |

The percentage of C was lower in the AH-NH₃ treated with Thionyl due to the formation of amides because the entering group is -NH₂, since a blockage is formed between the Thionyl chloride and the anhydride which creates a steric impediment for the molecule [2].,

5.1.2. Second application. In this case, the Federal Rural University of Rio de Janeiro in Brazil carried out studies on rice crops. This to measure the protection capacity of rice plants that were treated with humic acids against water stress. For this study, two different humic acids identified as AHC and AHB from Cuba and Brazil respectively were used, where according to the partial characterization of these materials, the only differences significant structural between the two different humic acids were
evidenced in the percentage of Carbon C% and oxygen O%, according to this, the rice plants with humic acids were subjected to water stress for 96 hours, where it was shown that those samples of rice plants that interacted with humic acids preserved the permeability of the membrane. This study was carried out because humic acids provide plants with the ability to adapt to abiotic stresses such as salinity, the presence of heavy metals at toxic levels, and water deficiencies [16].

5.1.3. Third application. In a study carried out at the University of Chile, positive and significant results were obtained in Haplohumult soil samples that were quite fragile due to constant and intensive agricultural use. Humic acid was used to test the water retention capacity, increase in porosity, increase of up to 24% in wheat yield, and among other factors. This study was carried out in the Araucanía Region of southern Chile, where it was determined that the use of humic acid contributed to a better wheat crop yield to more grains per ears and higher biomass production. In this study, 30 grams of humic acid were added in 20 liters of water, spreading them evenly all over the soil study, there were different types of soils, T0, T1, and T2, with T0 being an area of soil without humic acid, T1 the area of soil with humic acid and T2 a soil native to the study area, two soil samples were taken at different depths, the first from 0-10cm deep and the second from 30-40cm deep. Wilson and Valenzuela state in their study that the wheat root system is considerably formed in the first 10 cm and decreases considerably according to the depth of the soil [1, 25]

5.1.4. Fourth application. The Research Group of Organic Matter and Biostimulants of the Department of Chemistry of the Agrarian University of Havana, obtained an aqueous extract of HS from vermicompost of bovine manure, the biostimulation of different doses of the extract of vermicompost has been verified in crops of agronomic interest such as corn, lettuce, tomato and beans. The foliar application of these extracts in tomato plants promoted the biological development of the plants, as well as the agricultural productivity in indicators such as the mass of the fruit and the yield for two consecutive years. The physical-chemical characterization of these extracts has shown the presence of humic substances such as humic and fulvic acids, phytohormones, beneficial microorganisms, amino acids, and essential elements that could contribute to their biostimulant action [24, 26-29].

6. Conclusions. The extraction of humic acids is a good alternative for the remediation of eroded soils. In addition to being a low-cost practice, it also represents an alternative that does not leave polluting residues of the material where it is extracted. HA are capable of capturing contaminating materials in their matrix due to their great multi-substituted structure with -OH and -COOH groups, due to their great ionic affinity, which makes it a technique for improving soil quality as it contributes with ease nutrients to the soil and plants.

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