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# Role of Humic Substances in 'Green' and Sustainable Electronics: Current Status, Scope, and Future

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## ABSTRACT

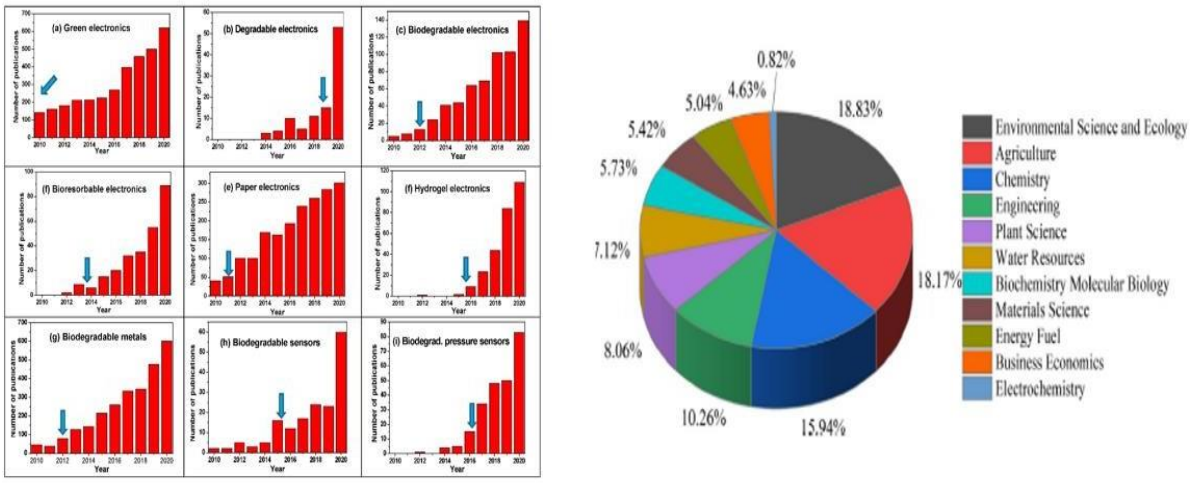
Finding sustainable solutions for the present global energy needs compels us to look after renewable energy resources. Conventional electronic technologies utilizing these resources offer obvious disadvantages such as low biocompatibility and biodegradability. Materials possessing biocompatibility, biodegradability, and low toxicity with increased performance are sought after by researchers in the field of organic electronics. The recent emergence of "Green electronics" indicates this shift in the field. The potential of many biomaterials for organic electronics applications has been realized fairly thoroughly. Out of these Humic Substances forming a significant part of biomass are relatively unexplored for applications in electronic devices. A large literature exists which explains their chemical, biological and geological

properties with applications in the field of agriculture and bio-medicine. However, research on their potential for electronic device applications has been comparatively low. Some of the recent investigations on humic substances, particularly on humic acids, reveal them to be a suitable candidate for the fabrication of a variety of electronic devices (Batteries, Supercapacitors, Solar Cells etc.). Easy availability, low-cost production, and environmental friendliness further add to their suitability. In the present review, we have discussed various important aspects of humic substances (chemical, electrical and optical) and attemptedto put forth the role these substances could play in electronic device making. A survey of pastresearch work on humic substances-based electronic devices is also presented. Furthermore, from a futuristic viewpoint, potential areas of investigation (e. g., Ferroelectricity, Supramolecular electronics etc.) have been touched upon.

## 1 Introduction

The development of sustainable technologies stands as a global challenge for humanity. Fast-paced depletion of non-renewable resources and pollution caused by these present a serious threat the world over. The worldwide dependency on renewable energy resources has increased in the past few decades [1]. Alternatives such as hydrogen fuel are already under intensive investigation and hold great promise for clean energy production [2]. ‘Green’ electronics and the use of bio-derived materials in the fabrication of electronic devices have emerged as a completely new domain for exploring sustainable alternatives, which promises not only better biocompatibility but also help tackle the problem of E-waste. Several biomaterials (e. g., wood, biomass, plants, paper etc.) and derivatives based on them have captured the attention of researchers for their use in electronic devices like Organic solar cells, Organic field effect transistors, and Biosensors etc. [3, 4]. Their Low toxicity, abundance, biodegradability, high mechanical flexibility, and efficient electrochemical properties make them a preferred choice over their traditional counterparts. Among these biomaterials, the potential of Humic

substances (HS) for applications in electronics has been relatively underexplored. The number of publications where biomaterials are used in the fabrication of electronic devices has seen an exponential rise in the last decade (Fig. 1 (a)). On the other hand, the fraction of research devoted to humic substances for material sciences applications has been comparatively low (Fig. 1 (b)) [5].




(a) (b)

Fig. 1 (a) number of publications on 'Green' electronics in decade 2010-2020 (adapted from [4]) (b) Applications of Humic acid in different fields from 2012 to 2021 (adapted from [5])

### 1.1 Humic substances and their formation

Humic substances (HS) are the result of the decomposition of dead plants and animals, which takes place over centuries of time interval. The major sources of HS include soil, brown coal, lake sediments, shales, city solid waste, and water [6]. HS make-up 60-80% of Soil Organic Matter (SOM) (Fig. 2), 50-80% of Dissolved Organic matter (DOM) in water, and 25% of

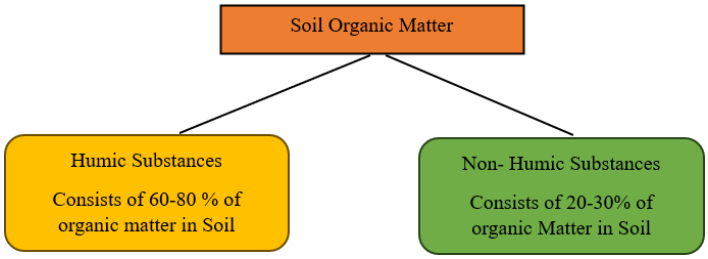



Fig 2. Content of HS in SOM

dissolved organic matter in groundwater [7]. These substances contain 1/4$^{th}$ of the total organic carbon content available on earth and provide characteristic brown/ black color to the soil's surface. They have a significant influence on the various physical, chemical, and microbiological activities related to the soil. Humic substances have highly heterogeneous structure, non-stoichiometric composition, and possess large molecular weight (1KDa- 1000 KDa) [8,9].

The Earliest recorded attempts in isolation of humic substances belong to Franz Karl Achard (1786) and Jon Jacob Berzelius (1806). Achard extracted HS from peat and soil through alkaline treatment, while Berzelius extracted from an aqueous system. Since those times the question How exactly these humic substances are formed? has not been answered satisfactorily by soil scientists. Various major theories were proposed in the 20$^{th}$ Century for determination of the exact pathway for the formation of humic substances (Fig. 3). Microbial-based theories emphasized the role of soil microbes in the generation of HS. Theories predicated on lignin as a direct source for HS assert two possible routes: First via hydrolysis of lignin, followed by oxidation (leading to polyphenols, quinone) and condensation, Second propounds formation of Lignin-protein complex and making them responsible for forming HS core. Autolysis theory


Fig. 3 Theories of Formation of HS

states that dead plants and tissues of microbes undergo enzyme autolysis and lead to HS, Sugar-amide condensation theory takes into account that sugars and amide on condensation form glucosylamine/ glycocyamine which on polymerization produces HS [loc. cit.].

HS are generally considered to be supramolecular structures, pH of the environment has significant influence on the structure of HS, Due to the bulky nature of these substances, precise identification of chemical structure has been a difficult task for researchers. At best we have proposed structures for these substances. However, in the last decade, new investigations on the chemical structure of humic substances have suggested that these substances are comparatively small molecules, but disguise themselves as large supramolecular entities [10]. Humic substances are usually described as a class of 3 compounds: Humic Acid, Fulvic acid, and Humin.

Humic acid (HA): This acid refers to that part of the soil that is insoluble in water, but at higher pH values it can dissolve. These are made of compounds that precipitate from the aqueous medium at highly acidic conditions. They are biopolymers that are heavily functionalized and comprise carbon in large quantities.

Fulvic acid (FA): This refers to the part of the soil that is completely soluble in the water at all pH conditions. Once humic acid is removed from the soil via acidification, this acid remains in the solution.

Humin: This is an insoluble part of the soil, which does not dissolve both in alkali and acids, even at a neutral pH range they are insoluble [11].

**1.2 Extraction methodologies for Humic substances**

Humic substances are obtained from diverse sources like soil, compost, brown coal, and city solid waste. There are different methods available for the isolation of humic substances, Methods such as oxidation after alkaline extraction, oxidation using nitric acid, KOH-Hydrothermal process, alkaline extraction followed by acidic precipitation and member

separation, the method used by the **I**nternational **H**umic **S**ubstance **S**ociety (IHSS) are used for humic acid isolation.

Fulvic acid has been isolated using alkali-soluble acid precipitation, chemical degradation, ultrasound, and microwave-aided extraction.

Some of the Methods for extracting Humin include Absorption of Minerals of soil using HF/HCl followed by alkali extraction of HA and FA, alkali extraction of HA and FA which is followed by humic extraction with solvents like DMSO, MIBK (methylisobutylketone), alkali extraction of HA and FA which is followed by HF/HCl absorption of the mineral component of soil, resin techniques, chromatographic techniques, ultra-filtration, and capillary electrophoresis [12-19].

### 1.3 Techniques of Characterization

The humic substances are usually characterized by UV-visible Spectroscopy, FTIR Spectroscopy, Raman spectroscopy, Mass spectrometry (MALDI-MS, LC-MS, GC-MS, ESI-MS), $^{1}$H-NMR, 2D-NMR (NOESY, ROESY, COSY, HMBC, HSQC), Solid State CP-MAS $^{13}$C NMR, Thermogravimetric Analysis (TGA) and Electron Paramagnetic Resonance (EPR), SEM, TEM, and chromatographic techniques (TLC, HPLC, Preparative TLC, Column, GPC), X-ray crystallography. The UV-visible technique is used for the identification of Conjugation, and Chromophores available in the species. FTIR is used for the determination of functional groups in the species, and other techniques such as Mass spectrometry, $^{1}$H-NMR, 2D NMR, SEM, TEM, and X-ray crystallography help in the determination of chemical structure in much greater detail. In addition, techniques such as Cyclic voltammetry (CV), Impedance spectroscopy, and dielectric spectroscopy are used for investigating redox activity, interface resistive behavior, and relaxation time [20-21].

### 1.4 The Chemical structure of humic substances

Humic substances, that is, Humic, Fulvic acids and Humin have large macromolecular structures consisting of a large number of different functional groups.

Investigations on the elemental composition of HA show that around 50% C, 35% O, 5% H and the rest of N and S constitute this large biopolymer. Humic acid contains quinone, enolic, phenolic, carboxylic acid, and ether along with sugars and peptides [22]. Among all other functional groups, carboxylic and phenolic groups are available in large numbers in HA. We can divide the structure of HA into two parts, Hydrophilic and Hydrophobic parts, Former contains OH, COOH groups, while the latter contains aromatic rings and aliphatic chains. The quinone groups act as electron acceptor groups, while the phenol groups show electron-donating behavior. Both groups make HA a redox species and contribute towards its electrochemical activity. Various Structures of HA have been proposed by different researchers in the last 50 years, some of them are shown in **(SI-I to IV)**. Recently, our research group has isolated a completely novel HA from the soil of Gwal Pahari, Haryana, India having a structure consisting of two cyclopentane ring systems connected via tetra-substituted $sp^3$ carbon atom [23] **(SI-V)**.

Fulvic acids elemental composition comprises C (44-49 %), O (44-49 %), H (3.5-5%) N (2-4%), and the rest S. The chemical structure consists of a large number of functional groups, such as carbonyl groups, hydroxyl groups, carboxyl groups, phenolic carboxyl groups, semiquinonyl groups and three benzene ring substituents. Predominantly carboxyl and phenolic hydroxyl groups are present in FA structure [24].

### 1.5 Electrical Properties of Humic substances

Humic substances contain redox active species, which makes them susceptible to efficient electron transport properties. HA has been extensively researched for its electron transport

properties, Bradley et al. reported the electron acceptor behavior of HA facilitates theoxidation of organic pollutants [25]. The phenolic moieties are correlated with the electron donating behavior of HA and quinone moieties are correlated with the electron acceptor behavior [26].

In the ESR Spectra of Humic Substances, the value of pectroscopic splitting constant "g" is found to be between 2.0037 and 2.0048, which is characteristic of humic substances and demonstrates semiquinones as major organic radicals. Hence, it shows quinone moieties to be responsible for the electron-accepting behavior [27]. Proper adjustments in the ESR spectrometer help reveal the hyperfine structure in their ESR spectra (Fig. 4) [28].

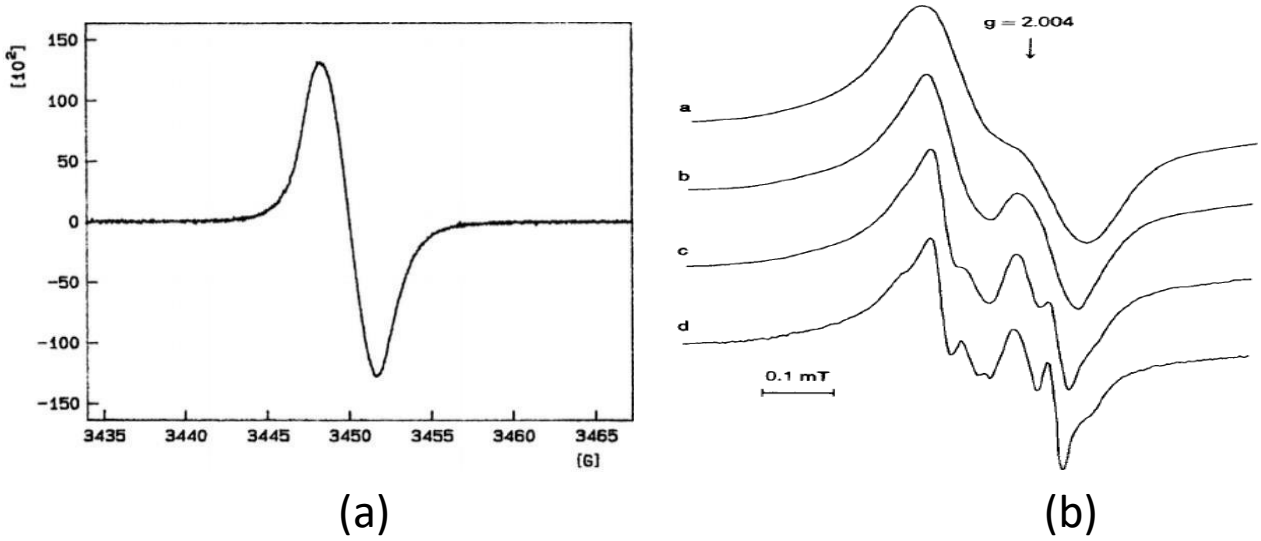



Fig.4 (a) ESR spectra of Humic substances (adapted from [27]) (b) Hyperfine splitting in ESR of humic substances (adapted from [28])

Aeschbacher et al. have performed measurements on the Electron Donating Capacity (EDC) of various humic substances. EDC is defined as the number of moles of electron donated by a mass of HS, Suwanee River Humic Acid (SRHA) with 2,2′-azino-bis (3-ethylbenzthiazoline-

6-sulphonic acid) (ABTS) exhibited strong oxidative peaks. In this work, HS correlated with titrated phenol identifies phenolic moieties to be major electron-donating groups (Fig. 5) [29].

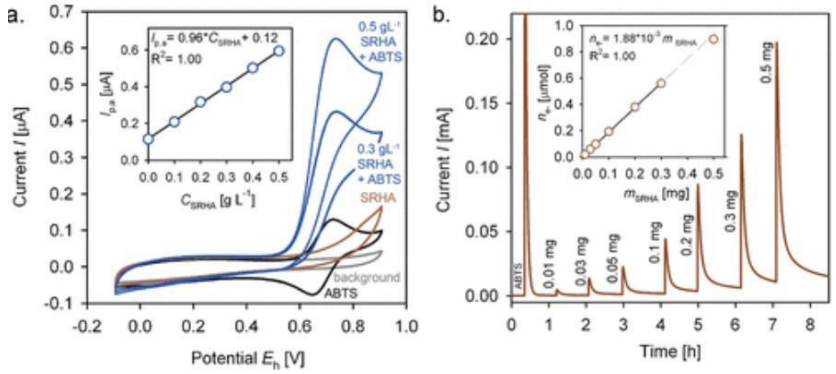



Fig. 5 Cyclic voltammetry studies on SRHA (adapted from [29])

Recently, some researchers have paid attention to the resistance offered by HS which has a direct impact on the electrical conductivity. Yuan et al. have investigated the impedance at the interface of HS adlayers on electrode and electroactive biofilms (EABs), their electron transfer resistances have been determined using the Nyquist plot [30]. Vekariya et al. have recorded the impedance response of HA used in the fabrication of a device, Charge injection mechanism were studied using an impedance plot, Tafel plot was used in the determination of rates of reaction occurring at the anode and cathode (Fig. 6) [31].

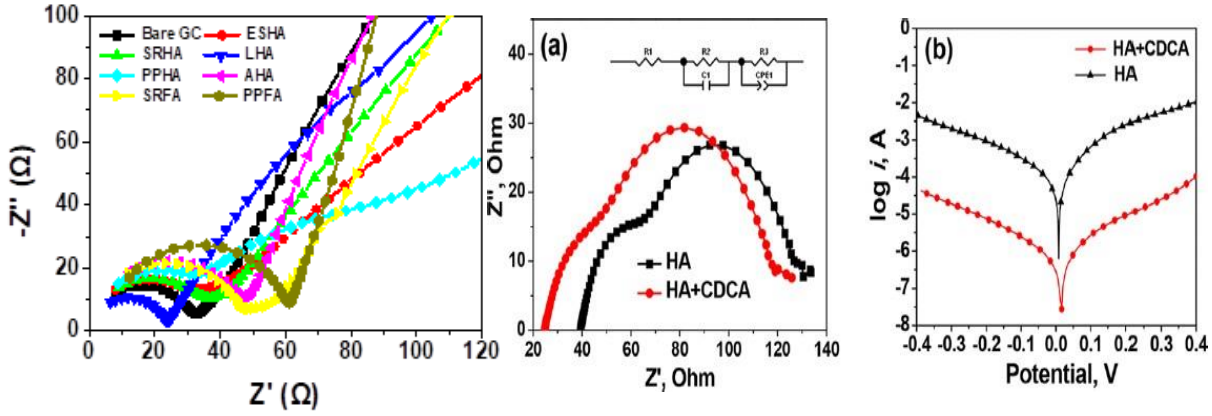



Fig. 6 Impedance and Tafel Plot of Humic Substances (adapted from [30] and [31])

### 1.6 Optical Properties of humic substances

The optical properties of humic substances such as absorbance, transmittance, and reflectivity etc. can be investigated using UV-visible spectroscopy and FT-IR spectroscopy. The decrease in absorption with increasing wavelength and red shifting of emission spectra on increasing the excitation wavelength are some of the well-studied behaviours of humic substances [32]. A satisfactory mechanism that can explain this behaviour is currently not available in literature, very little has been understood concerning what molecular mechanism permits such spectral properties. The absorption of radiation shown in the UV range is expected to occur due to the presence of multiple bonds and unshared electron pairs in the HA molecule. The usual chromophores which are present in HA are -C=C- and -C=O groups [33]. Absorption peaks of HA lies in the interval 200-300 nm [34,35]. The UV-visible spectra exhibited by fulvic acid is similar to HA.

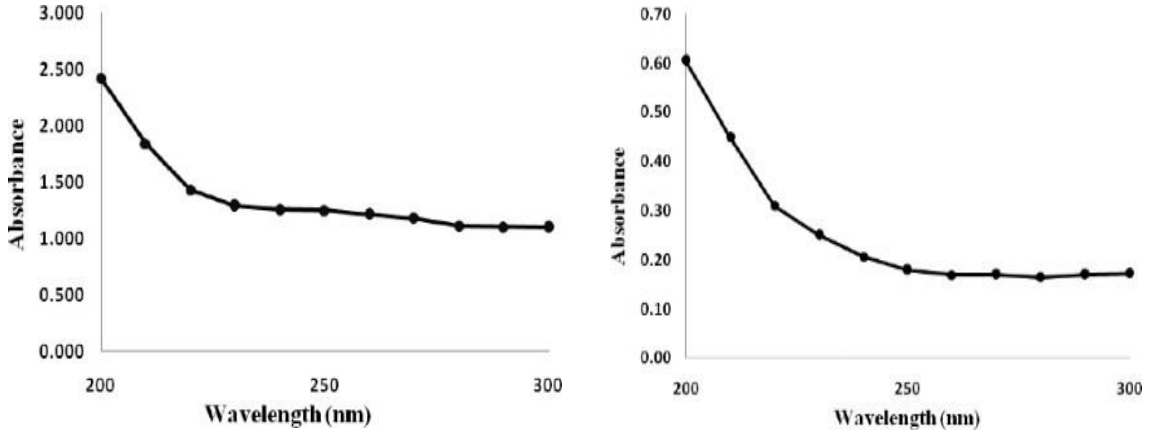



Fig. 7 UV-vis of HA and FA (adapted from [33])

In the FT-IR studies on humic acids, the peaks obtained in the wavenumber region (3400 $cm^{-1}$ - 2900 $cm^{-1}$) are correlated with the stretching of hydroxyl groups and the presence of aliphatic species. Another major broad absorption band ranging from (1700 $cm^{-1}$ – 1000 $cm^{-1}$), shows the presence of -C=O, -C-O- stretching vibrations in phenol, ether, and alcohol groups. These

peaks also indicate the existence of strong hydrogen bonding and a large number of carboxylic acid groups (Fig. 8) [36].

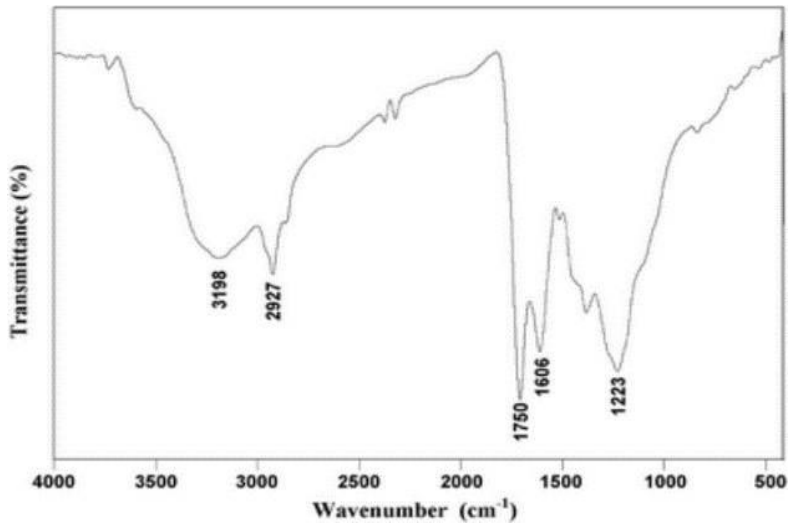



Fig. 8 FT-IR of HA (adapted from [36])

For FA, a broad peak in the region (3400 $cm^{-1}$ – 3000 $cm^{-1}$) is attributed to stretching vibration of the -O-H bond. Broad interval from (1700 $cm^{-1}$ - 1000 $cm^{-1}$) have many peaks which are assigned to -C-O and O-H vibrations of the carboxyl group, which points towards the heavy presence of carboxyl groups in the FA structure (Fig. 9) [37].

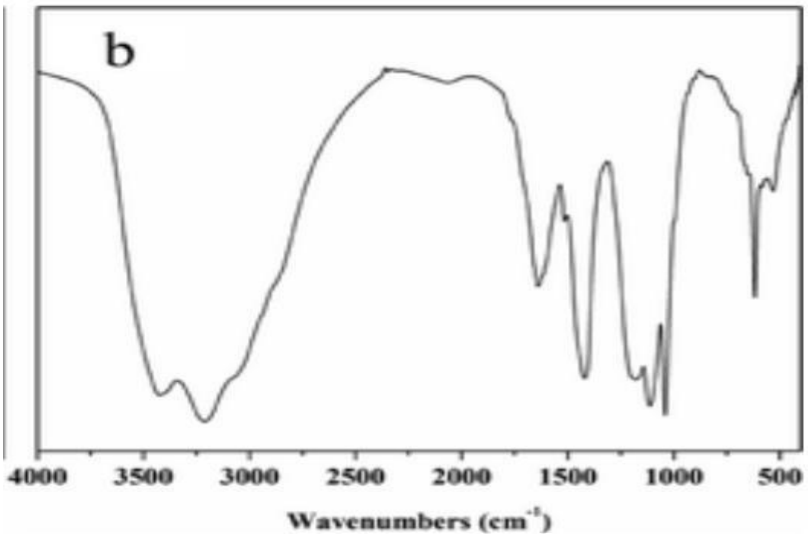



Fig. 9 FT-IR of FA (adapted from [37])

Fig. 10 illustrates the excitation spectra of different Humic acids and excitation wavelength dependence with emission maxima and quantum yield for SRHA and different humic substances. For all HA, $\lambda_{max}$ in excitation spectra corresponds to a peak at 490 nm, and another shoulder peak was observed at 390 nm. The intensity and position of these peaks were found to vary slightly in different pH conditions.

The emission spectra of HS (Fig. 11) reveal broad fluorescence maxima usually observed for HS [38]. Investigations carried out in recent decades report that the optical properties of HS (For ex: Excitation and Emission wavelengths) are related to the structural properties of these substances such as intramolecular charge transfer interactions between acceptors and donors [39].

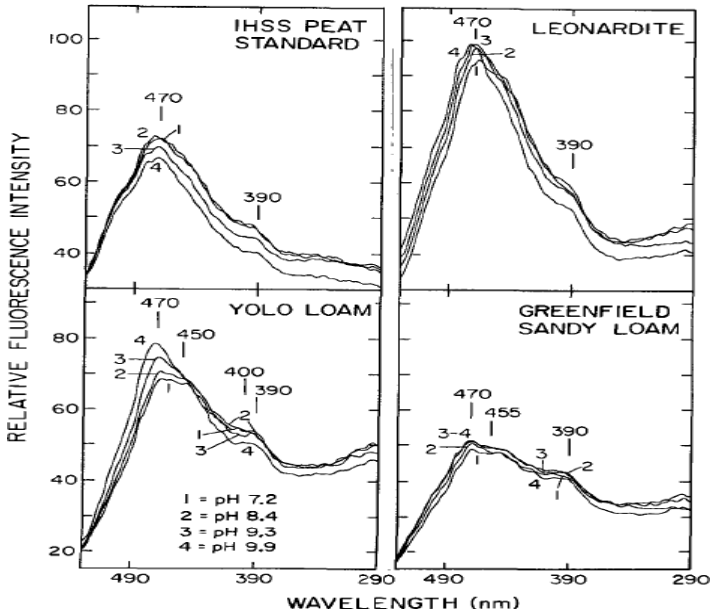



Fig. 10 Fluorescence excitation Spectra of Humic Substances (adapted from [38])

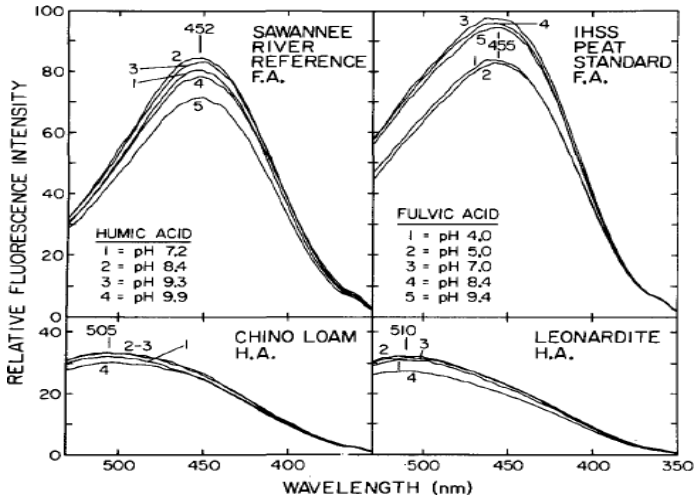



Fig. 11 Fluorescence emission spectra of HS (adapted from [38])

Optical Methods like Raman spectroscopy reveal the disordered graphite-like structure of humic substances. There are 2 bands observed at 1386 $cm^{-1}$ and 1602 $cm^{-1}$ respectively. The former is assigned with in-plane c-c phonons at the M point of the Brillouin Zone referred to as D-band, while the latter is assigned with zone-center $E_{2g}$ mode of graphite referred to as G-band (Fig. 12) [40]. In acidic conditions, these substances show more amorphous conformations. When neutralized, their Raman Spectra resemble the spectra of typical graphite-like carbons [41].

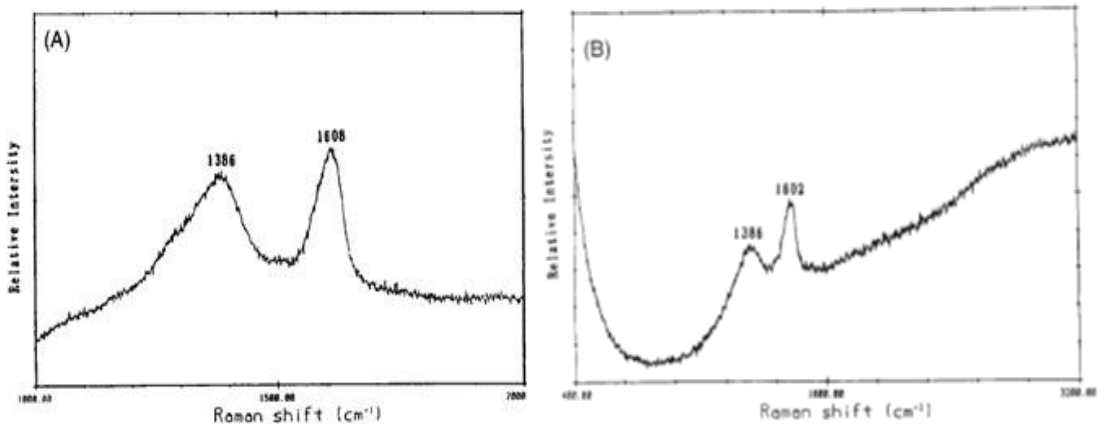



Fig. 12 Raman Spectra of Humic Substances (adapted from [40])

### 1.7 Potential Applications of humic substances

Just in recent decades, there has been a proliferation in using humic substances for the fabrication of electro-chemical devices. Since it is well understood that HS exhibits impressive redox activity and can act as a source for deriving large amounts of carbon. This has led to important applications i.e., fabrication of working and counter electrode in batteries and supercapacitors. Metal complexation activity (Binding with heavy metals such as Fe (III), Pb (II), Cu (II), Mn (II), Cd (II), Zn (II) etc.), is another front where HS has been used significantly as a sensor for detection of contaminants. Despite these efforts, in our view, HS has much to offer in the field of electronic device fabrication and the number of fundamental investigations which are required to exploit the full potential of these substances has been minimal. For instance, properties such as electronic conductivity, dielectric response, Mechanical Flexibility, Ferroelectricity, Magnetization etc. have not been explored in greater detail. With the development of many novel spectroscopic techniques, there is bound to be significant progress in understanding the chemical structure and physical properties of these substances, which will put into light many new unexplored aspects of these substances and will guide towards novel applications.

In the coming sections, existing applications in various electronic devices of humic substances have been discussed. The focus has been on the enumeration of less well-known applications of HS. In addition, attention is turned to whether HS could exhibit some of the interesting effects that are found to be present in other organic materials.

## 2 Existing applications of Humic substances in electronic device fabrication

### 2.1 Batteries

In recent decades, researchers have started paying attention to the usage of organic compounds as electrode material in lithium and sodium-ion batteries. In comparison to inorganic materials, investigations have shown that organic materials perform well in storage and rate performance. Hitherto, much of the work has been done on the preparation of cathode using organic materials, but progress on the development of anode has been comparatively slow. Among organic materials, naturally derived humic acids can act as a promising material in the development of anodes. The sheet-like porous structure of HA permits easy mass transportation and makes participation in redox reactions efficient. The abundance of functional groups in HA leads to much better ion storage performance which can directly be used in charge storage applications [42].

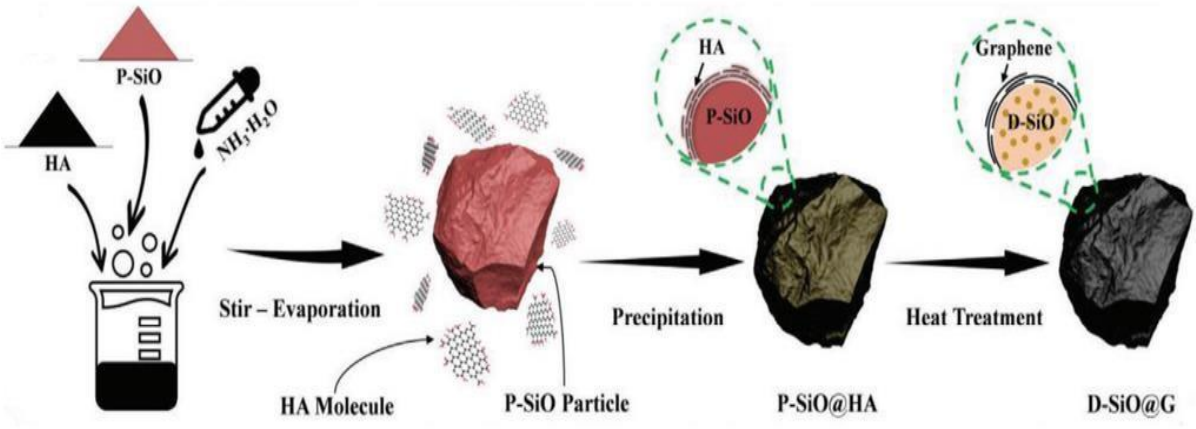



Fig. 13 Preparation of Graphene Coated Pristine SiO (adapted from [43])

Xu et al. have synthesized anodes for lithium-ion batteries using graphene coated silicon monoxide. The graphene for this work was derived from Humic acid. They took 2 g of pure SiO and 0.5 g of HA (which was extracted and purified from North Dakota lignite). The mixture was subjected to heating, stirring, grinding and sintering. Finally, the composite of SiO-coated graphene was obtained [43].

Zhang et al. prepared an N(Nitrogen)-doped hierarchical porous composite (NHPC) using residue that is left after the extraction of humic acid from lignite. They used this residue to prepare NHPC via chemical activation and NHPC is utilized in fabricating anode for lithium/ sodium batteries. The complete production of NHPC was environmentally friendly, which further adds to the utility of this work [44].

Zhao et al. prepared an anode for sodium battery using Polyacrylonitrile/Humic acid composite carbon fibres. Anode displayed good cyclic stability, rate capability and storage capacity [45].

Hua et al. have developed a metal-organic-framework (MOF) predicated on humic acids as anode materials for lithium-ion battery applications. They have synthesized HA-Co-BPDC MOF, where ‘Co’ and ‘BPDC’ stands for Cobalt ion and Biphenyl-4-4′-dicarboxylic acid. MOFs are known to exhibit large surface area, highly porous structure, and tunability which makes them suitable for such applications. Despite these advantages, these frameworks show poor conductivity and cycling stability. In HA-Co-BPDC MOF, the contribution from each component provides a highly porous structure, improved conductivity, and a large number of active sites for ion storage. The synthesized framework is predicted to display a fast charging-discharging process at high current density which is of great utility in electronic applications [46].

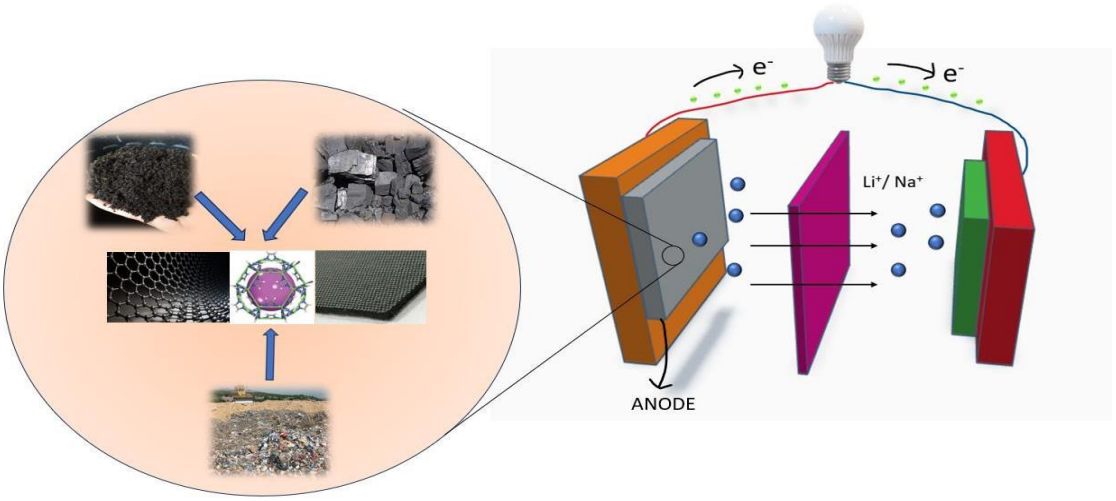



Fig. 14 Carbon-based materials from HS for applications in batteries

### 2.2 Supercapacitors

Supercapacitors are the result of the evolution in battery technology. These electrochemical devices add up the advantages of both conventional capacitors and batteries. They exhibit much greater stability, higher value of energy and power density, and allow fast charging [47]. A supercapacitor is made up of three elements: two electrodes, an electrolyte, and a porous membrane as a separator. When a potential is applied to the electrodes, charge transfer takes place and it forms an “electric-double layer” on the electrode-electrolyte interface, this is equivalent to connecting two capacitors in a series connection, which enhances the total capacitance of the system.

Carbon-based electrodes have been one of the most widely used electrodes for the fabrication of supercapacitors [48]. Examples of these electrodes include graphene, carbon nano-tubes, activated carbon fibres, and carbon aerogels. As humic substances are large repositories of carbon content, they have been used for the synthesis of many carbon-based materials which have applications in a variety of energy storage devices. Dong et al. have reported that carbon-based dots are available in large quantities in humic substances. These carbon dots are graphene- oxide nanosheets with very small sizes (almost like dots), These dots exhibit impressive electrical and optical properties and provide a large number of surface states. These dots can have applications in fields such as Bio-imaging, Bio-medicine, Sensors, and Optoelectronics [49]. Yin et al. have synthesized micro and mesoporous electrodes which can have applications in the fabrication of supercapacitors. They mixed Humic acid with KOH (acting as activating agent), Ground the mixture and performed heating in a tubular furnace at 800$^{o}$ C, after washing the product with 2M HCl, HA-derived activated carbon was obtained, which was further used for the preparation of the electrode [50].

A group of researchers from China has utilized humic acids for making porous carbon electrodes, which enhanced the performance of the device. They prepared an Oxygen-rich hierarchical porous carbon electrode via activation of humic acid using manganese nitrate-assisted KOH [51]. This electrode showed a high value of specific capacitance (304 F $g^{-1}$ at 0.057 A $g^{-1}$), remarkable cycling stability and energy density (30 W-h $Kg^{-1}$ at a power density of 43.6 W $Kg^{-1}$).


Fig. 15 Carbon electrodes from HS for Supercapacitors

| HS used | Application | Performance | Reference |
|---|---|---|---|
| HA from North Dakota Lignite | HA precipitated on SiO particles and coated with graphene | Current density of 2 A $g^{-1}$ and 5 A $g^{-1}$, ICE of 78.2 % | [43] |
| HA extraction from Lignite from China | Nitrogen-doped Hierarchical porous carbon (NHPC) anode from HA | In Li ion battery, Specific capacity at $700^0$ C is 508 mAh/g. In Na ion battery, at $700^0$C specific capacity at 320mAh/g | [44] |
| HA from Beijing Zimingyuanyi Co., Ltd | HA based carbon nano fibres as anode material in Na ion battery | Current density of 1 A $g^{-1}$, Cycling stability of 249.6 mAh g-1 | [45] |
| HA from Aladdin Biochemical Technology Co. Ltd. | HA based MOF, HA-Co- BPDC | High Specific capacity of 315/ 242 mAh $g^{-1}$ | [46] |
| HA from Tianjing guangfu chemical Co. Ltd. | HA-derived Activated carbons for supercapacitor | Specific capacitance 350 $Fg^{-1}$, Good Cycling stability | [50] |
| HA from Yunnan (China) | HA-based Graphene nanosheets | Energy density 6.47 $Wh.Kg^{-1}$, Power density 2250 $W.Kg^{-1}$ | [52] |

Table 1: Source of HS and their performances in Batteries and Supercapacitors

Xing et al. have synthesized nanosheets of graphene using humic acid through carbonization conjoined with oxidation-exfoliation-thermal reduction. These graphene sheets show high porosity and specific surface area, the meso-porosity and uniform oxygen-containing functional groups in the graphene structure provide an unobstructed pathway for the propagation of electrolyte material, which enables efficient conductivity in the structure, hence useful for applications in electronic devices. They used these HA-derived graphene sheets for the fabrication of electrodes for supercapacitors, electrodes exhibited remarkable specific capacitance 272 $Fg^{-1}$ at 50 $mAg^{-1}$ value of current density in aqueous electrolyte. In addition to this, electrodes demonstrated an impressive rate capability and cyclic performance [52].

A similar work was carried out by Shulga et al. They prepared a composite of humic acid and graphene oxide and obtained two materials out of it. One material was obtained by carbonization of HA-GO composite and the other was obtained via reduction of HA-GO composite with hydrazine hydrate. The porous materials obtained can be used in a variety of applications [53].

**2.3 Dye-sensitized solar cells (DSSCs)**

DSSCs are third-generation photovoltaics and offer an alternative to traditional Silicon-based solar cells. They are most suitable for indoor and diffused light condition applications. In the recent past, Humic-based substances have been used as photosensitizers for DSSCs fabrication (Fig. 16). Vekariya et al. fabricated a DSSC using Humic acid with PCE (Photoconversion efficiency) of 1.4% under 1 Sun illumination. Further on adding Co-adsorbent CDCA (Chenodeoxycholic acid) with HA resulted in PCE of 2.4 %. The PCE obtained for HA was much better compared to other natural photosensitizers such as those obtained from vegetables and flowers [loc. cit.]. Di et al. have used the HA- Ni complex as a source for deriving a new

carbon matrix incorporated with Ni. The HA-Ni complex was pyrolyzed to obtain the desired material. Electrochemical measurement shows increased reducing capacity of the Ni incorporated carbon matrix towards Triiodide electrolyte. Thus, the obtained material was used at the Counter electrode and yielded PCE of 7.04% which is comparable to PCE provided by standard Pt-based counter electrode. This study opens the possibility of low-cost manufacturing of counter electrodes for DSSCs [54].

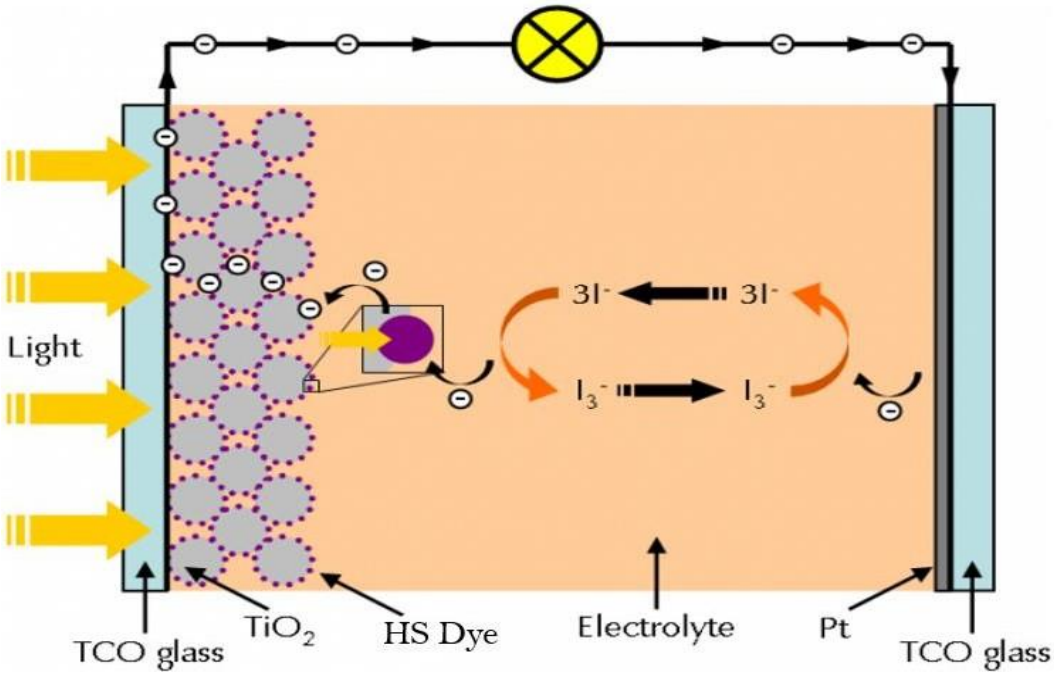



Fig. 16 DSSC with HS as a Photosensitizer

**2.4 In Perovskite solar cells**

The use of lead in perovskite solar cells has been one of the major disadvantages which hinders their possibilities of commercialization in the near future. Some researchers have found out that humic acid can act as a remediator for this toxicity issue, The coating of humic acid on the perovskite nanoparticle surface prevents the release of $Pb^{+2}$ ions from the active sites of the nanoparticle surface. Humic acid forms a complex with the $Pb^{+2}$ ions and thus leads to a reduction in toxicity due to the $Pb^{+2}$ ions [55].

### 2.5 Biosensors

The biosensors make use of biological molecules coupled with a Physico-chemical systems which detects and helps in recording the result of interaction between biological molecules and external analyte (which is under study) (Fig. 17). It has been reported that humic substances show affinity towards Biomolecules (For Ex: with Single-Stranded DNA), Such phenomena have been utilized for their applications in Biosensors [56]. Preethika et al. has fabricated a FAD (Flavin adenine dinucleotide) immobilized HA/HNT (Halloysite nanotube dispersed in Humic acid solution) based hydrogen peroxide detecting biosensor. This biosensor exhibited impressive electrocatalytic activity for the detection of $H_2O_2$ [57]. Salvador Alegret et al. has fabricated a potentiometric sensor based on humic substances. In this work humic acid was employed as material for sensing purposes, they studied its response to Copper (II) ions [58]. Crespilho et al. have introduced Humic acid in nanostructured polymeric films with the help of the Layer-by-layer technique, Alternate HA layer and PAH (Poly (allylamine hydrochloride)) layers were formed. The films formed displayed good electroactivity which enables them to be used as biosensors for the detection of pesticides [59]. In a study done in 2004 by Masson et al, for the fabrication of a surface plasmon resonance (SPR) biosensor, 9 polymers were used, among these one of the polymer was humic acid. The Humic-based SPRbiosensor showed much better performance compared to the traditional polymer CM-dextran used in the fabrication of SPR biosensors [60]. Dubas et al have synthesized silver nanoparticles by reduction of silver nitrate in the presence of Humic acids. These HA-based silver nanoparticles can act as a sensor for the detection of herbicide, they show a change in colour from yellow to purple after they come in contact with increasing concentration of herbicide [61]. Galeska et al. have developed multilayer films of humic acids that can act as asemipermeable membrane for application in glucose biosensors. These films are expected to exhibit impressive stability after their implantation in the sensor [62].

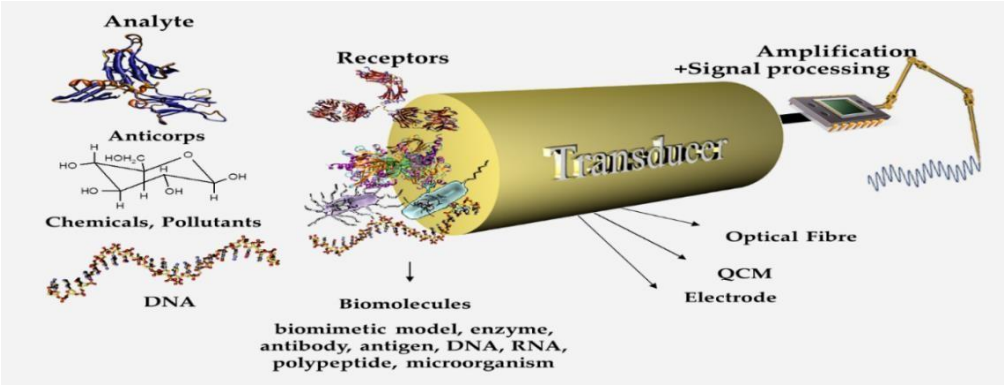



Fig. 17 HS as bio-receptors in biosensors

| HS used | Application | Performance | Reference |
|---|---|---|---|
| HA sodium salt from Sigma Aldrich | HA used for making Halloysite nanotube (HNT) | Successfully detected $H_2O_2$ | [57] |
| HA from Spain | Incorporated PVC membrane with HA for Sensing application | Detection of Cu (II) ions with a response time of 30 Sec | [58] |
| HA from Brazil | HA incorporated into nano PAH films | Able to detect PCP with detection limit 1.6 X $10^{-9}$ mol $L^{-1}$ | [59] |
| HA from sigma Aldrich | HA-based SPR sensor | Antibody shift 3.2 nm, MG shift 0.041 nm | [60] |
| HA from Sigma Aldrich | Silver nano particles from HA for sensing | With increasing Herbicide Conc. Change in colour of Ag nanoparticles solution | [61] |
| HA from Sigma Aldrich | HA films for Glucose sensor | Diffusion coefficient 5 X $10^{-8}$ $cm^2/s$ | [62] |

Table 2: Biosensors based on HS and their performances

### 2.6 Piezoelectric sensors

Zvyagin et al. have used humic acids in the formation of gas-sensitive layers which are used in piezoelectric resonance gravimetric sensors. These HA-based gas-sensitive layer have much great greater stability compared to conventionally used layers, which were usually predicated on Pyridoxine Hydrochloride or ascorbic acid [63].

### 2.7 Humic Substances based Polymers for Microelectronics

Lebedev et al. have developed conductive hybrid biopolymer nanocomposites which are based on humic substances and polyactid which can have applications in micro and nanoelectronics [64]. Filicito et al. have conducted a photophysical study on Humin. Through various characterization techniques, they have put forth a polymeric furan-rich structure for Humin which is connected with short aliphatic chains and ether and/ or acetal functional groups which leads to a highly oxygenated structure that can possibly be like conjugated system such as Polyacetylenes. This conjugated system allows for the possibility of application in a wide range of electronic devices (organic photovoltaics, organic light emitting devices, and organic FET etc.) [65].

### 2.8 Humidity sensors

Duraia et al. have synthesized a nanocomposite consisting of Humic acid nanosheets over which $SnO_2$ nanoparticles are distributed. This nanocomposite was studied using different characterization techniques, as a material for humidity sensing applications. It showed a fast response along with rapid recovery time. The presence of a large number of hydrophilic functional groups in the HA structure makes possible the sensing application, with the increase in the content of relative humidity, the resistance of humic acid-based sensor was found to be decreasing [66].

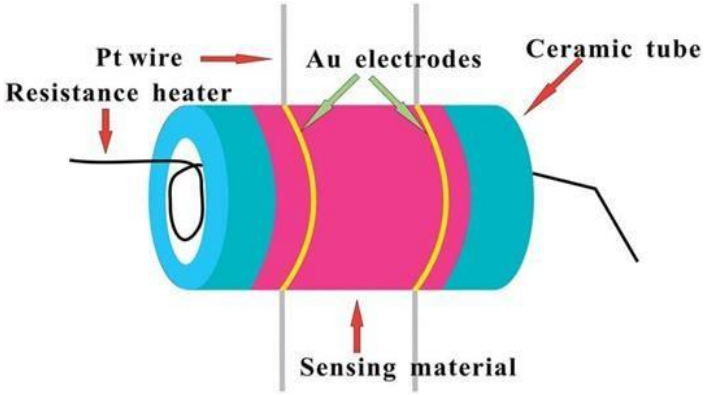



Fig. 18 Schematic of Humidity sensor

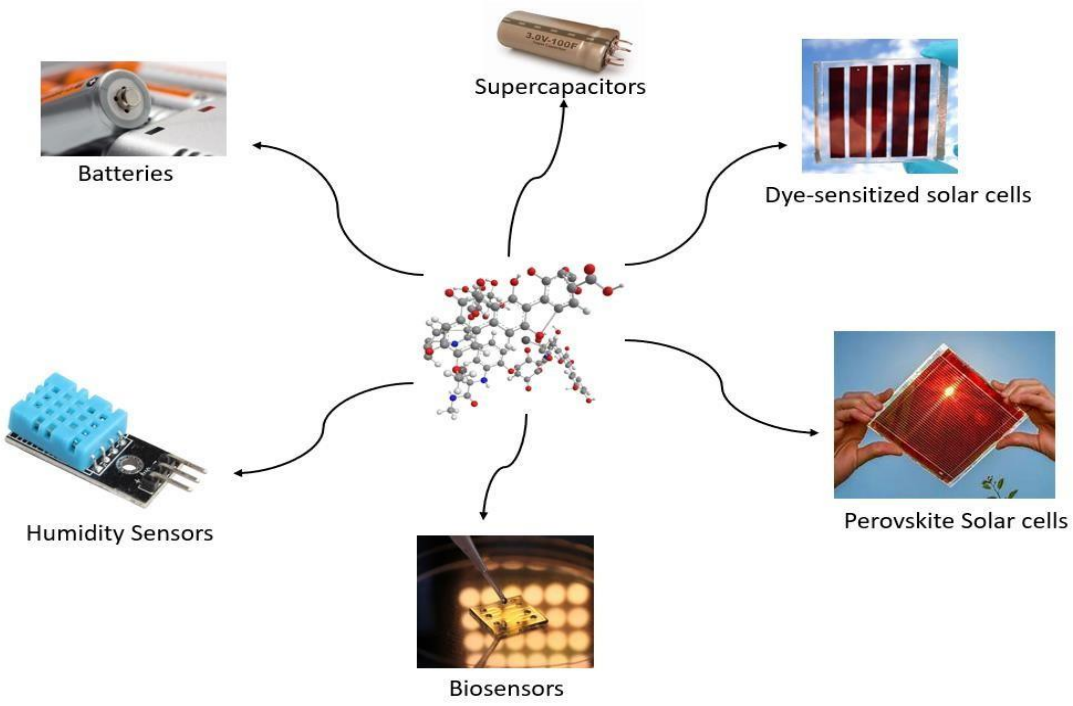



Fig. 19 Applications of HS in various devices

### 3. Future of humic substances for device technology

Humic substances have found successful applications in the fields of agriculture and biomedicine. Research on electro-chemical and photochemical properties of HS have been modest till recently, but now on an upsurge. This has led to applications of these substances in the fabrication of devices like batteries, supercapacitors etc. However, these substances being

polymeric macromolecular/ supramolecular species have not been completely explored in many of the interesting aspects that these species could potentially exhibit.

### 3.1 Ferroelectricity in Large Molecular Systems

Ferroelectric materials are known to possess permanent electric dipole moment even after the removal of the externally applied electric field. These materials have found various uses in sensors, data storage applications, and optoelectronics. Recent interest in organic ferroelectrics has opened up new possibilities for research in their design and applications and are expected to overcome some of the disadvantages of inorganic ferroelectrics such as their high toxicity etc. [67]. These materials show the well-known hysteresis curve, also called the P-E (polarization-electric field) loop, on the application of voltage. This curve displays various parameters (saturation polarization, remnant polarization, and coercive field) for any material (Fig. 20).

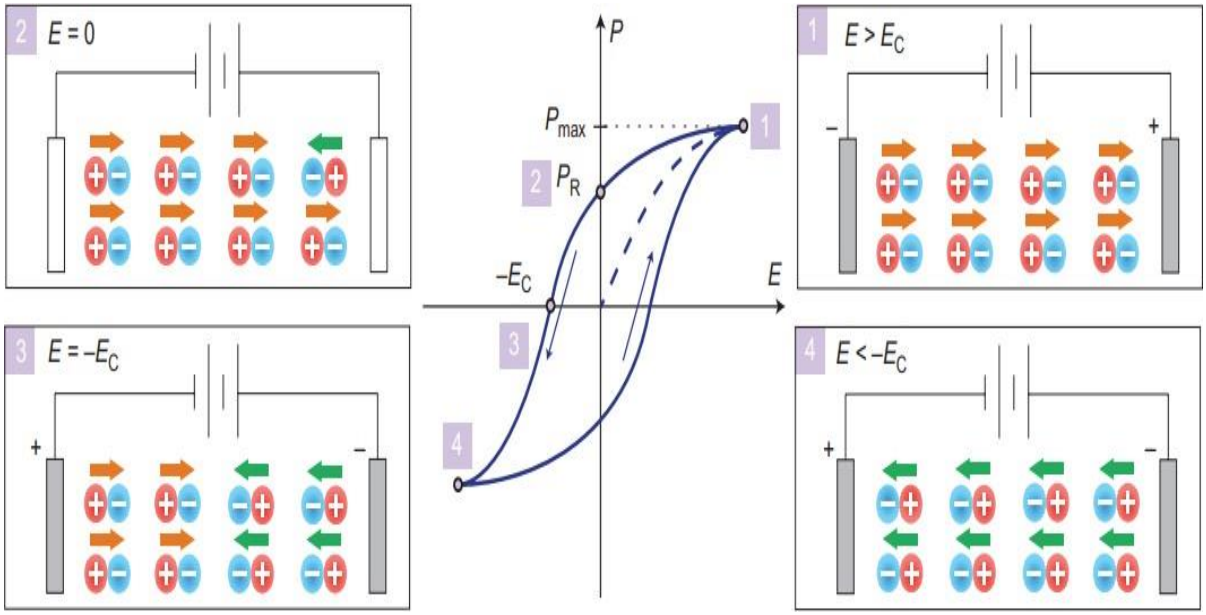



Fig. 20 Canonical hysteresis loop (adapted from [68])

Many crystalline polymers with some degree of polarity are known to exhibit ferroelectricity. Supramolecular assemblies have been shown to possess permanent electric polarization even after the removal of the applied electric field. This is due to the non-centrosymmetric nature and the presence of bistable dipoles in such structures (Fig. 21). We may consider the possibility of the same in supramolecular assemblies based on humic substances [68].

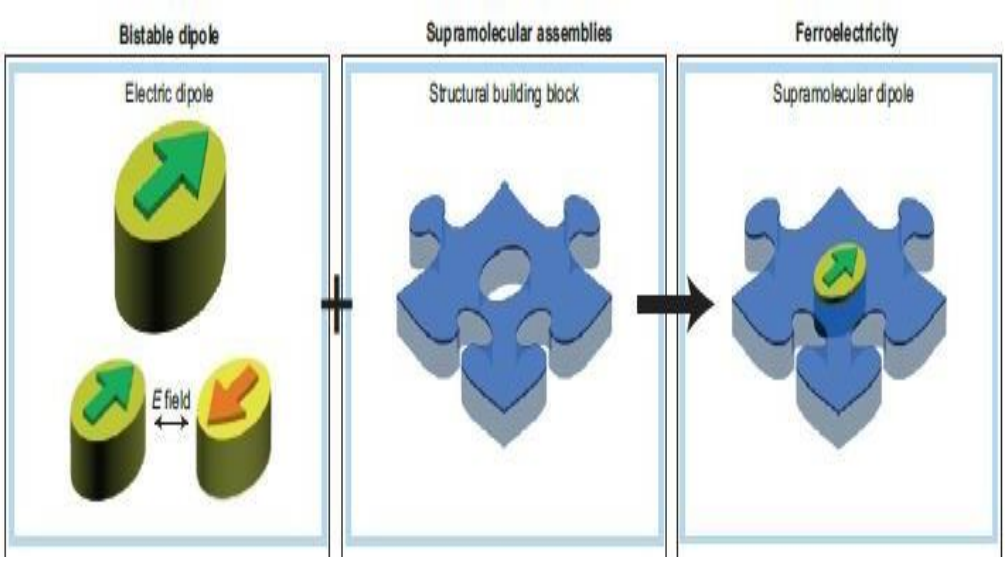



Fig. 21 Requirements for supramolecular ferroelectricity: ‘green’ and ‘orange’ arrows denote bistable electronic dipoles and non-centrosymmetric lattice respectively (adapted from [68]).

As far as we know, Hitherto, P-E loop (Electric polarization curve) investigations on humic-based substances have not been reported so far in the literature. We propose here that detailed computational studies could throw light on the ferroelectric behaviour of humic substances. The possibility of developing artificial humic acid gives further control in tuning various properties of these materials and could allow ferroelectric design. Piezoelectric and pyroelectric responses are yet another unexplored aspect [69].

### 3.2 Molecular Magnetism

The emerging field of Molecular magnetism investigates paramagnetic molecule-based materials for applications in fields of magneto-chemistry, biomedicine, electronics, spintronics

and quantum computing [70]. For any material to show magnetism, it should contain large number of unpaired electrons. The spins of these unpaired electrons interact and give rise to the resultant magnetism in the material [71]. The presence of free radicals in Humic substances imparts a paramagnetic nature to them [72]. The inclusion of magnetic transition metal ions, and rare earth ions is an approach to enhance the magnetism present in these substances. Aim will remain to increase the number of spin centres in these species such that local spin-spin interaction is favored and something akin to ferromagnetic coupling is achieved. Also, these substances are well-known to form supramolecular aggregates, Supramolecular entities possessing magnetism have been already known in the literature [73]. Is it possible that Humic substances can exhibit magnetism even in their supramolecular form?, Could we map out the ordering of spin centres in these substances? As discussed in the ferroelectricity section, here too there is a need for both computational and experimental studies which could assist in answering these questions.

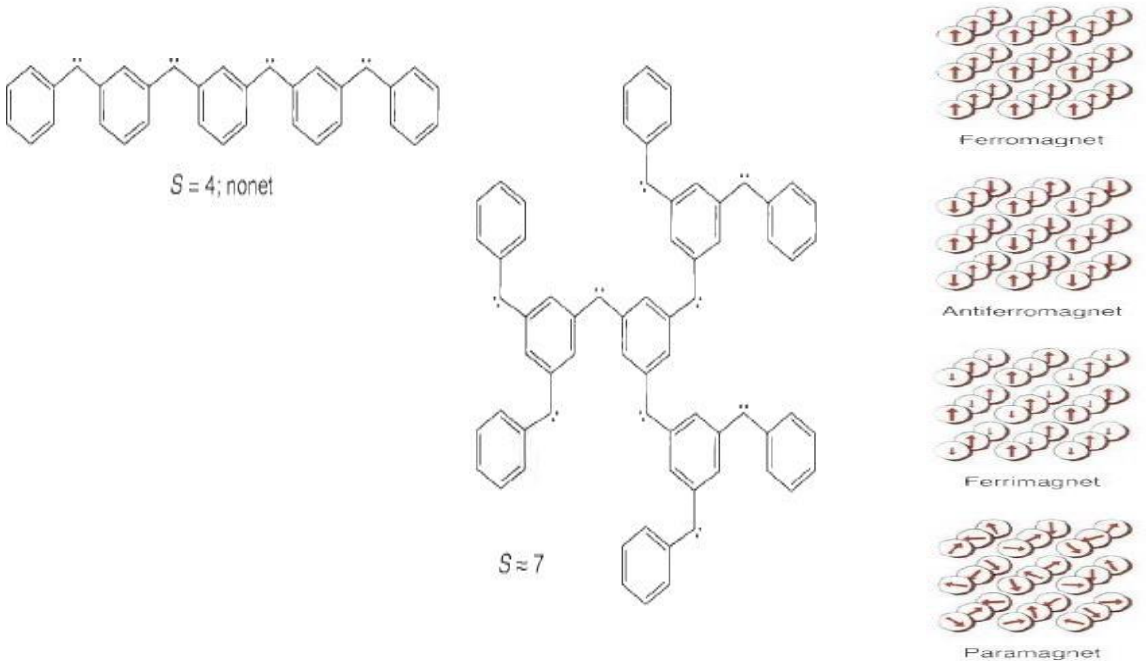



Fig. 22 High Spin tetracarbene and nonacarbene systems (adapted from [71])

A fairly recent study demonstrates the influence of magnetic field on humic acid bioactivity and reveals that the amount of carboxyl group in HA increases when the aqueous solution of

HA is subjected to a constant magnetic field [74]. Such a Phenomenon suggests possibilities of controlling the Electro-chemical activity of these substances using magnetic field.

### 3.3 Supramolecular Electronics

The charge transport property associated with non-covalent bonding has been a subject matter of major focus in the field of supramolecular electronics [75]. Humic substances can be understood as forming supramolecular aggregates in which each small molecule is connected to the other by weak interactions (Van der Waal, hydrogen bonding etc.). Hence, investigating how charge transport takes place in humic substances at the supramolecular level can be fruitful and may lead to significant results. Another aspect that relates to charge transport is bulk electrical conductivity and mobility of the supramolecular aggregates. Could these explorations

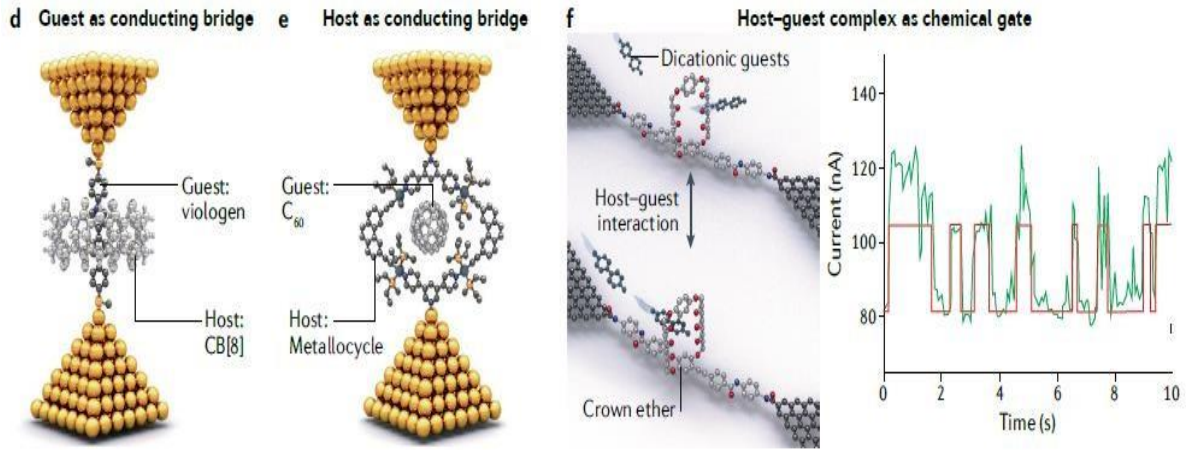



Fig. 23 Conduction mechanism in Supramolecular structures (adapted from [75])

lead to novel applications for humic substances in device making? Recently, Magnetoelectric coupling has been detected in some of the organic polymers due to spin-dipole interactions in them, which may lead to applications in flexible electronics, Could such magnetoelectric effects be existing in humic substances as well? [76].

### 3.4 Electro/ Magneto-optic and Chromism effects

The existence of polar domains in humic substances could lead to electro-optic effects, Macromolecules displaying such non-linear optical effects have been known by researchers, and they have even been used for waveguide applications [77]. Functionalization of humic substances with other non-linear optical materials can be a strategy for improving the presence of such effects in them. Humic acid and Humin-based conductive polymer-like materials have been discussed in previous sections, some reports have been there which describes the presence of magneto-optic effect in conjugated polymers [78].

Magnetoresistance in macromolecular systems is an important research area of organic spintronics. Green biodegradable materials possessing such effects are more desirable compared to inorganic materials with low biocompatibility [79]. Investigating magnetoresistive effects in humic substances is another interesting possibility. Many Devices predicated on electrochromism have been fabricated using supramolecular assemblies which show significant redox activity [80]. Humic substances as carriers of a large number of redox species could manifest electrochromic effects

From the above discussion, it is indicated that investigations on various functionalities of Humic substances could open a plethora of possibilities. Utilizing novel spectroscopic techniques, computational approaches, isolation and synthesis methodologies could bring a transformation in the way we understand humic substances and their significance. Wang et al. have suggested the use of high-resolution techniques (Scanning ion conductance microscopy, nano infrared spectrum generation) for probing the electro-chemical properties of Humic acid in much greater detail [loc. cit.]. In the same vein, we propose that in addition to the usage of novel techniques, well-known techniques such as P-E hysteresis loop, Vibrating sample magnetometry, SQUID magnetometry, Conductive atomic force Microscopy (C-AFM), Kelvin

Probe Force microscopy (KPFM), Tip Enhanced Raman Spectroscopy (TERS) etc. be utilized for much more detailed investigations in electronic and magnetic properties of these materials. This could help in bringing humic substances on par with other currently popular green materials (Cellulose, chitosan etc.) for organic electronics and will allow integration of one of the most abundant material available on planet earth in sustainable electronics.

## 4. Conclusions

Biomaterials have shown great promise in electronic applications, their low toxicity, biodegradability, and biocompatibility particularly make them advantageous. Humic substances forming a significant part of soil organic matter have largely remained underexplored in terms of their electronic and magnetic properties. Recently, humic substances with their ease of availability, substantial amount of carbon content, large number of redox-active species (leading to enhanced electrochemical activity), hydrophilicity, and greater responsiveness towards stimuli (chemical, biological etc.) have been utilized in the fabrication of various electrochemical devices (Batteries, supercapacitors) and Sensors etc. There is an effort to show that Humic substances have the potential to go much far beyond their traditionally existing applications in the agricultural, and biomedical territory. Further, as a prospect for humic substances research in the field of electronics, a few interesting novel phenomena are discussed briefly that these substances could potentially exhibit. We hope that the present work will provide better insights towards more innovative uses of humic substances in ‘Green’ electronic device technologies.

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## Conflict of Interest

The Authors declare no conflict of interest.

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