Chapter

Dry Cowdung Powder - Novel Unearthed Humus: Sustains Water-Food-Energy Nexus

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Abstract

Water-Food-Energy (WFE) Nexus regulates biosphere and irrespective of alphabetical or chronological order, it must have synergy for the sustainability of life. Population, Pollution and current Pandemic- COVID has made it vivid to entire scientific community that unless we strengthen this trio, our progressive humanity is sure to collapse. Humic Substances (HS), the originator of the life has promising utilization in almost every sectors of life, reinforcing WFE Nexus. This chapter dedicates to novel unearthed HS, Dry Cowdung Powder (DCP) and its unique contribution in sustaining the triangle of life, WFE. DCP has been employed as humiresin for bioremediation of wastewater containing heavy metals and radionuclides. The known candidate for Biorhexistasy, DCP increases soil fertility, minimizes erosion and acidification. It is also extensively explored as biofuel, green and clean source of energy. 'Nothing of Nature is a Waste' and 'Waste is a Commodity' aptly describes DCP, the sustainer of WFE Nexus.

Keywords: Sustainability, Dry Cowdung Powder, Unearthed Humus, Humiresin, Biorhexistasy, Biofuel

1. Introduction

The biosphere or Earth's layer of Living Matter harbors living organisms that interact with each other as well as with the soil, water, and air. The necessity of the entire living biota is based on Water-Food-Energy (WFE) Nexus, exceptionally governed by our Mother Nature. In the past few centuries, rapid industrialization has overexploited pristine ecosystems and led to a steady decline in the nutrient quality of ecosystems, flora, and fauna. The plume of population and pollution has created a 'water-food hungry scenario' but the 21st century socio-political race has created 'energy hungry' attitude too. The high rate of resource consumption has posed an unintended and negative impact not only on the entire ecosystem but also on global geopolitical harmony. Almost every nation has gobbled up their own abundance of natural resources due to utilitarian attitude and drive of being energy independent. This has compromised the holistic functioning of the environment and given rise to deprived soils and declining fauna.

Present resource crisis is so all-prevailing that, both developed as well as developing countries have come to the common conclusion of Sustainability through Socio-Scientific Integrity for the smooth survival of todays and tomorrows.

Nonetheless, current pandemic Covid-19 has sparked SOS to refurbish the global policies of governance and accelerate scientific eclecticism towards sustaining the WFE Nexus by participating in Sustainable Ecosystem Management (SEM). The philosophy of SEM is pegged on adaptive management and holistic consideration of ecological resources. It is environmentally sensitive, ecosystem, and eco-regional based [1]. It emphasizes on balancing long-term sustainability of ecosystems with human needs and moves beyond compartmentalized focus on some species and regions, to holistic management of natural resources amidst hindrances of rising resource of demand, population increase, and climate variability [2, 3].

The aim of this study is to evaluate, equate and exercise the application of novel humiresin- unearthed, ecology-economy friendly, zero-waste prototype Dry Cowdung Powder (DCP) towards sustaining WFE Nexus and ecosystem.

2. WFE Nexus: humic substances

2.1 Sustainability through humic substance fecundity

Sustainability is not the futuristic projection of survival but is the continuous mechanism of proliferation just like the evolution of life. The evolutionary journey from the prebiotic world to today's most complex homochiral D-sugars, L-amino acids organisms; we sapiens, are the product of spatial characteristics and elemental selectivity of Humic Substances (HS), the originator of life! [4] The first organic machinery in proplanetary disk, HS is approximately four billion years old and is the bridge which connects no-life to life [5]. The Miller's experiments gave the first proof of HS as the placenta of evolution and this theory has been supported by many researchers [6, 7]. Owing to its universal properties, HS are popularly known as 'the black gold of the earth' by farmers and 'the black box' by soil analysts [8].

Soil is an ecosystem as a whole and acts as a modifier of planet Earth's atmosphere. The organic matter present in it originates mainly from plant metabolites with the onset of senescence and humification. Humic Substances are defined as a heterogeneous mixture of morphologically changed degradation products of biomolecules which on humification give rise to a family of amorphous, polyelectrolytic, polydisperse and colloidal compounds [9]. HS are universally recognized as chemically, biologically, and physically active due to the typical composition, macromolecular structure, polyfuntionality, surface properties, and presence of multiple reactive sites, variable size-shapes, and intrinsic porosity [10]. Operationally, HSs are usually extracted at high pH and classified into three categories based on their solubility: acid-soluble Fulvic acid (FA), acid-insoluble Humic acid (HA), and base-insoluble Humins with the average properties and a large assembly of components with diverse structure and molecular weight [11].

Humic substances exhibit exceptional characteristics for soil conditioning. HS have shown to contain auxin-like activities [12] and hence they are successfully used in agronomy, environmental, industrial, medicinal, and pharmaceutical fields [13, 14]. Besides providing nutrients and aeration to the soil, they interact and bind with toxic heavy metals, radionuclides, pesticides, industrial dyes, and other xenobiotics that may be present as pollutants in the ecosystem, thus acting as natural sieves. HS mimics geochemical barrier and hence potentially can be used as a filling material for barrier walls to prevent transport and bioavailability of heavy metals in soil [15]. HS can significantly reduce the acute toxicity of metals and bioavailability of metals. It plays a crucial role in the inactivation of pesticides, heavy metals, and other polluting agents. The various studies on HS, have confirmed a great potential for an application in aerobic and anaerobic wastewater treatment as well as in bioremediation [16]. Study of HS has proven to be a robust approach in resolving environmental issues and developing meaningful paths for modification steps [17]. HS provides insights into pollutant mobility, behavior, and fate, and allows better understanding of natural mitigation phenomena and potential impact on the environment [18].

Our global scientific community has univocal conscience on how amazing and myriad utilization of HS have been fructified in almost every sectors of life since the inception of life. Being ubiquitous in both terrestrial and aquatic niche, HS is considered to play a crucial role in sustaining the ecosystem.

2.2 Managing nexus through humus and waste

Entire ecosystem is governed by many layers and sectors, inter and intra connected, independent yet mutually operating native ecosystems. The concept of WFE Nexus is very much like the vertices of an equilateral tripod, regulating the survival of life. Irrespective of its alphabetical or chronological order, there is a need to govern and manage inter and intra disciplinary synergy to ensure fundamental and survival rights of clean air, food, and water to our future generations. Governing the Nexus is probably one of the grand challenges of current time, as quoted by Jeremy Allouche et.al, explicitly explaining the reason for complexity in the management of so called 'nirvana concept' of nexus [19]. Author's justification on 'Nexus or Nexuses?' indicates that holistic, comprehensive, and integrated implementation of the scientific aptitude is required to achieve the goal of global sustainability. Nexuses, is a conceptual approach that does not hold rigidly to a single sector or a paradigm or set of assumptions. Instead, it appeals upon multiple scientific theories or principles to gain complementary insights according to geography and climate of the sector. It does not appreciate the 'silo' concept or 'two at once' methodology to address the sustainability issues, but focuses on simultaneous operating approach.

A review by A. Hamidov and K. Helming [20] rationalizes that to improve cross-sectoral coordination in support of sustainable development, WFE nexus has become an important concept in natural resource management. On the same note, Zhang et al. [21] suggests, shifting the focus to WFE nexus is valuable but downplaying their interrelations can have adverse consequences on the entire biota. Hence, there is a need for the balanced approach with 'no-regrets' solution as studied by Konadu et al. [22].

Resources produce waste and it is undoubtedly inseparable from any sector of life, omnipresent both inside and outside of our existence. Globally, hulk of waste is directly or indirectly connected to production of humus and hence HS plays a very important role in Waste Management (WM). WM [23] is the collection, transport, processing, monitoring, and recycling or disposal of the waste material. It is based on waste hierarchy [24] of reduce, reuse, and recycle coined with re-think. The effective implementation and maintenance of stipulated laws requires legions of regulators. It offers an efficient means of managing waste that fits ideally with the needs of large population centers, while providing a source of alternative and renewable energy [25]. Waste-to-Energy (WTE) is a philosophy of energy production using the waste and its role in enhancing all interconnected nexuses, is gaining high importance in every nation [26, 27]. 'Nothing of Nature is a Waste' and 'Waste is Green Commodity' aptly describes DCP and our research on its application proves its pivotal role in sustaining the Nexus.

2.3 Unearthed humus DCP- zero waste prototype

The pedosphere or soil body is rich in organic matter, soil fauna, minerals, water, gases, that together support life. It comprises of weathered rocks from the lithosphere, trapped air pockets from the atmosphere, moisture from the hydrosphere, along with decomposing matter from the biosphere, and is thus known as an interface between these subsystems. Besides purifying water in terrestrial systems, soils process decaying matter from the biosphere and recycle nutrients back into the food chain. The pedosphere thus interconnects with other spheres and regulates life processes.

Humus, the organic matter in soil, permits better aeration, enhances the absorption, releases nutrients, and makes the soil less susceptible to leaching and erosion, thus the agent of soil's vitality. Soils contain more organic carbon than the atmosphere and vegetation combined; therefore, mineralization of soil organic matter and release of carbon versus humification processes, could greatly affect carbon capture and stabilization, and consequently the global climate change. Carbon sequestration and storage in soils provide an important means of reducing greenhouse gases in the atmosphere to mitigate predicted climate changes [28].

The aforementioned qualities of HS make it a very powerful tool not only in sustenance of WFE Nexus but its essential role in mitigation of climate change. This draws our attention towards requirement of highly appropriate method for the Selection of HS products as there are enormous variety of HS available globally. The quality and composition of any mined or extracted Humates or HS depends on many different factors as HS are essentially time and climate dependent.

Under ideal conditions, the turnover time of organic carbon added in form of HS each year from plant and animal residues into the soil, averages approximately 30 years [29]. Due to this time constraint in production of fresh humus, we face many challenges ovulated due to multiple sites and over digging of soils. Also, soil humus development is highly affected by seasonal change, litter type and time, hot or cold climate and freeze–thaw cycle [30]. Studies by Dou et al. have explained that freeze–thaw cycles can even destroy the structure of newly formed humus [31]. Nonetheless, a good HS material can be destroyed by improper mining or processing. Hence the mining and the extraction of HS must be meticulously processed as any error or shift in parameters may change their physicochemical properties.

Thus, it is fundamentally important to extract them with minimal change into its original structure [32]. The physical process of removing the ores or materials from the ground is disruptive to the environment and alarming questions regarding the statutory norms for safety are overwhelming. Also, the pre and post process for concentration of raw material and final product is time consuming and makes an essential call for the higher degree of purification. This leads to the generation of many undesirable chemical steps, adding to cost of actual extraction process as well as stress on environmental safety.

To solve this complicated situation, we bring the concept of Unearthed Humus, DCP – clean, economical, and essentially inert to any climatic condition, due to its generation in to the biotic environment of cow's rumen. It is with least contaminants as the process of Humification takes place during the period of 1 month of Sun drying, hence conditioning of any type is not required thanks to its biological matrix. These qualities of DCP projects the Zero Waste concept of Waste Management, boosting Green Chemistry principles. Zero Waste Management is the holistic concept of waste management which recognizes waste as a resource produced during the interim phase of the process of resource consumption [33]. The prime objective of this protocol is based on the sustainable avoidance and management of waste and resources. This makes us very positive to conclude that Unearthed DCP is the Zero Waste Prototype in comparison with all the HSs used at present.

2.4 Green solution to soil pollution: DCP- agrarian booster

Soil is a heavenly resource, a living, breathing and ever-changing dynamic ecosystem. The theory of Biorhexistasy, describes two crucial climatic phases of soil i.e., Biostasy, period of soil formation and Rhexistasy, periods of soil erosion [34]. The theory emphasizes on the role of climatic conditions that initiate pedogenesis and subsequent soil retrogression. For example, moist climates promote the chemical deterioration of rocks, leading to formation of soils and improvement in vegetation, which reflects the period of biostasy. On the other hand, dry climates and winds bring about displacement of soils and mechanical disintegration of exposed rocks, leading to the unfavorable period of rhexistasy or soil erosion and degradation. The two stages occur in cyclic form and control soil quality and vegetation. Extended periods of rhexistasy lead to ever-increasing soil degradation.

Thus, due to soil erosion, salination, and extreme acidification, large portions of arable land lose their fertility. The scale of this agrarian distress can be improved by the addition of HA, which promotes root growth and induces salt tolerance in plants, thus reversing the adverse effects of salt stress [35].

For economizing the addition of HA into soils, DCP can be used since it is freely available and inexpensive. Addition of DCP initiates the biotransformation of saline soils and enhances their humus content. Due to the rich microbial biota and chemically inert properties, DCP has been utilized as a soil conditioner and fertilizer since ancient times. Thus, we reiterate that DCP is soil's Green ambrosia and one of the best contenders for soil replenishing and rejuvenation.

2.5 Waste to green energy: DCP- biofuel

As any other non-conventional and renewable green source of energy, DCP has been explored as biofuel and proves to be pseudo shale, boosting renewable energy sector. Feng et al. have developed a high-performance anode from carbonized cow dung for bio-electrochemical systems [36]. Kumar et al. found that in the generation of electricity, natural cow dung was found more suitable as it generated 150.9 mV Open Circuit Voltage (OCV) [37]. There is a review by Gupta et al., focusing on recent findings on cow dung harnessed for biofuel production and management of environmental pollutants and its usage in different areas such as medicine, agriculture, and industry [38].

2.6 Wastewater remediation: DCP - Humiresin

The research work of Bagla et al., has examined and justified an innovative and concrete role of DCP in the bioremediation of toxic metal pollutants and hazardous radionuclides from the pool of various effluents using Radiotracer technique. Notable heavy metal pollutants like trivalent and hexavalent chromium, cadmium [39], mercury [40], silver [41], zinc [42] have been eliminated from aqueous systems using DCP as a biosorbent. Similarly, radionuclides commonly found in radioactive waste - ^{60}Co, ^{90}Sr and ^{137}Cs [43, 44], have been removed from simulated systems of reactor and reprocessing waste.

Being freely and easily available DCP has an edge over processed natural adsorbent considering their cost, time, and energy efficiency. Also, DCP does not impart any foul odor to treated water, nor does it lead to increase in biomass, unlike other natural adsorbents. DCP used for heavy metal adsorption can be subjected to standard desorption and re-adsorption cycles and finally the spent DCP can be employed as a landfill material in deteriorated soils. Because of its strong chelating properties, any residual metallic ions are well-bonded to DCP and do not leach out under normal environmental conditions.

This study concludes that DCP is affordable and adaptable due to its Combo nature and its acceptability lies in its working mechanism based on HSAB concept of sorption [45]. DCP has a great potential in the field of water decontamination, industrial water treatment and in abatement of water pollution.

3. Dry cowdung powder - DCP: The best of waste

DCP is naturally available bioorganic, complex, polymorphic humified fecal matter of cow and is enriched with minerals, carbohydrates, fats, proteins, bile pigments, aliphatic - aromatic species such as HA, FA, Ulmic acid and Humus etc. Many functional groups such as carboxyl, phenols, quinols, amide, enhance its biosorption properties.

The total characterization of DCP has been carried out for its physical, chemical as well as microbiological properties. DCP was provided by Keshav Shrushti, Research Centre on Cow products (Thane, India). Fresh cow dung was collected by efficient workers and due safety measures were taken to avoid any toxic and heavy metal contamination during collection. Cow dung is basically the feed residues digested by symbiotic bacteria residing within the animal rumen. The net effect of digestion in the rumen is the conversion of dietary materials to a mixture of fatty acids (mainly acetic, butyric and propionic acids), gases (primarily CO_2 and CH_4 which are voided by eructation) and microbial biomass [46]. The innate existence of different microbes, beetles and other dung related arthropods bring about humification of the organic matter present in cow dung [47].

There are different pigments and lipids in cow dung which are related to its color and typical odor. The bile pigment biliverdin is mainly present in cow dung (herbivore) giving it its green color. Also, bile salts give dung its emulsifying properties by which it confers hydrophilic coat to the droplets, otherwise of its hydrophobic nature [48]. It is also flourished with number of microorganisms as well as some classes of Arthropods. To ascertain passive biosorption by dead microbes, it is necessary to have an overall account of microbiological consortium of fresh dung.

Cow dung consists of approximately 60 species of bacteria, including species from the following genera - Bacillus, Actinomycetes, Corynebacterium, Pseudomonas, Cellulomonas, Flavobacterium, Lactobacillus, Serratia, and Alcaligens [49, 50]. It also includes *Escherichia coli* and Staphyloccocus aureus along with roughly 100 species of protozoa and yeasts including Saccharomyces and Candida spp. Cow dung also contains certain fungi like Trichoderma and Aspergillus spp. Due to the profusion of diverse micro flora, it has considerable potential for biodegradation and biotransformation [51].

The presence of petroleum utilizing microbes is indicative of high percentage of Hydrocarbon in the environment and cow dung too has a great abundance of this microbiota [52]. The presence of these microbes is also dependent on the geographical and environmental milieu. This microbial consortium enables cow dung with considerable potentials for biodegradation and biotransformation of oil - petroleum products and other pollutants as well as it further contributes to plant production and in many biogeochemical processes [53].

In order to select any new material for a process, the material should fulfill the theory of 3A's, which stand for affordability, acceptability, and adaptability. DCP is affordable due to its free availability and its supply is not hampered by climatic conditions. Most of every HS available requires pretreatments or conditioning for optimal results, unlike DCP, hence it is more time, energy and cost efficient and hence has an edge over other HS. DCP is acceptable owing to its biological matrix, full of microbe's nutrients and least contaminated by any pollutant or contaminants, thanks to its production in perfectly inert or biological niche of rumen. Its adaptability is learned by its combo nature and heterogeneous functionality due to presence of numerous organic and inorganic ligands. These descriptions with its present global application emboss that DCP is the ultimate *Best of Waste*.

4. Physical and chemical characterization of DCP

4.1 Physical characterization

4.1.1 Proximate analysis

The total characterizations of DCP for its physical and chemical properties have been designed. The physical characterization has been carried out by proximate analysis **Table 1** as per the standard procedure given by American Public Health Association (APHA). The elemental, structural, morphological analysis, and thermal stability of DCP has been conducted at Sophisticated Analytical Instrument Facility- Indian Institute of Technology (SAIF- IIT), Mumbai. Physical parameters such as moisture content, ash content, mesh size, fiber content, etc. have been evaluated. Biochemical analysis of DCP for its amino acid, carbohydrate and other contents has been carried out by Radial Chromatography.

4.1.2 The elemental composition by XRF and CHNSO Analyzer

The DCP has been characterized using XRF technology for its quantitative as well as qualitative elemental composition as shown in **Table 2.** For the complete elemental composition, complimentary to XRF technique, C, H, N, S, (O), has also been obtained, **Table 3** shows the same.

Sr. No.	Physio-chemical parameters	Value	Sr. No.	Physio-chemical parameters	Value
1.	Color and Odor	Brownish, Humus smell	9.	Crude fiber content	13.25%
2.	Texture/ Appearance	Powdered	10.	Total Nitrogen content	7.10%
3.	Mesh size	100	11.	Thermal stability	Stable till 150°C
4.	Solubility	Sparingly soluble in water except soluble sugars	12.	Acid-Alkali resistance	Quite high
5.	Moisture content	10–11% & 8.93%	13.	pH	7.14
6.	Ash content	25.07%	14.	Conductance (mmhos/cm)	2.92
7.	Potash content (kg/ ha)	525.00	15.	% Organic carbon	0.60
8.	Total Carbohydrate content	37.13%	16.	Humus content (kg/ha)	35.84

Table 1.
Proximate analysis of DCP.

Element	%
Na	0.946
Mg	2.853
Al	1.684
Si	22.691
P	3.883
K	3.343
Ca	2.360
Ti	0.329
Mn	0.115
Fe	2.419
Cl	1.56
Cr	0.014

Table 2.
Elemental composition of dry cow dung by XRF.

Element %	Component
3.104	Nitrogen
37.367	Carbon
5.142	Hydrogen
3.432	Sulfur
29.654	Oxygen

Table 3.
C,H,N,S,O analysis of DCP.

4.1.3 Scanning electron microscopy (SEM)

The SEM patterns **Figure 1(a-i)**, shows that DCP has some fibrous structure with some holes and small openings on the surface. Also, the surface of DCP is heterogeneous, rough, porous and with dentations. It shows the presence of cell debris of some prokaryotic cells. The holes and openings on DCP increase the contact area and facilitate the pore diffusion during adsorption. SEM study of DCP also affirms the theory of metal ion diffusion into porous biomass**.** According to this theory, metal ions can either be present on the surface of the biomass or can permeate into the expanded pores, which make desorption of metal ions difficult [54].

4.1.4 Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA)

For the verification of DCP to be thermally stable, *Thermal Gravimetric Analysis* (TGA) as well as *Differential Thermal Analysis* (DTA) have been carried out. **Figure 2** for TGA reveals that, the moisture content of DCP is 8.928% and it is quite stable till 230°C. After 350°C, the weight loss of DCP is about 50%. This can be attributed to simple process such as drying, or from more complex chemical reactions that liberate gasses, such as structural water release, structural decomposition, carbonate decomposition, sulfur oxidation, and fluoride oxidation. Thus, it can be concluded that DCP is thermally stable.

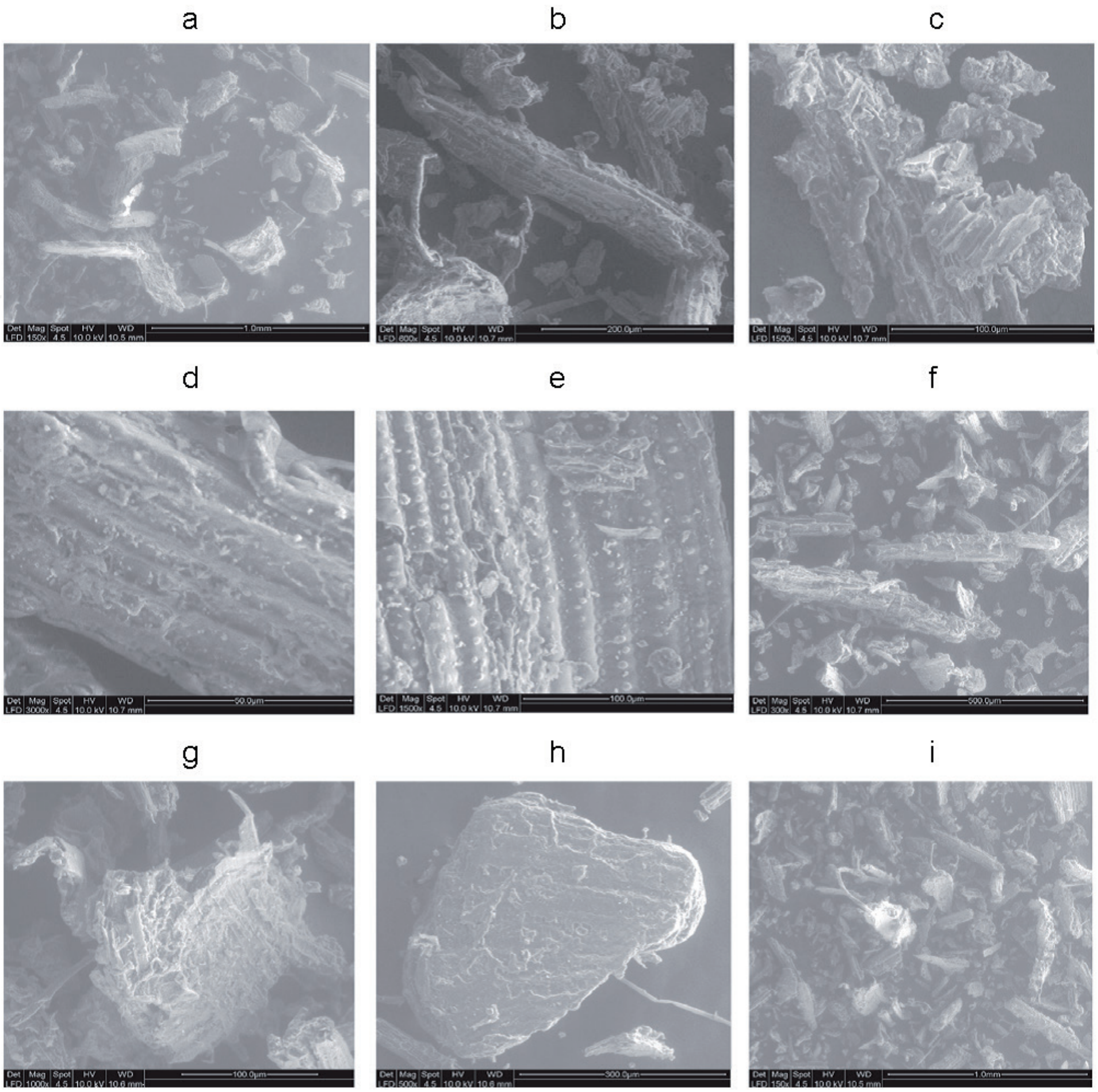

Figure 1.
SEM of DCP.

Figure 3 of DTA shows two endothermic peaks near the region of 48-50°C, which is a small peak and second at 230–270°C is a broad peak. It also describes two exothermic peaks, one smaller peak at 170–175°C and a broader peak from 300°C onwards. This study supports our observation that the biosorption of metal ions on DCP decreases on increasing the temperature. In case of DTA, the mean progression of the combustion profile and the limits of different temperature ranges delineating the phases of thermal decomposition of DCP using 2.311 mg, within a temperature range of 25–420°C with the heating rate of 10°C min^{-1} as can be seen in Graph 2. There are two endothermic and one exothermic peak on curve, corresponding to respective decomposition steps. The first step is in the temperature range between 39.09°C & 60°C and might correspond to the evaporation of water incorporated in or adsorbed onto DCP, being accompanied by a little loss in weight and is signified by first endothermic peak. A small exothermic peak is observed around at 180–185°C, it may be due to some crystallization process involved during heat transfer process [55].

The second endothermic peak is observed in the temperature range from around 214.88–265°C and is accompanied by some weight loss which may be due to loss of polar functional groups. The phenolic OH groups are eliminated between 250°C [56]. Around 280°C the decline in weight is seen which may be caused by decarboxylation and unsaturation [57]. The decomposition of carboxylic, phenolic,

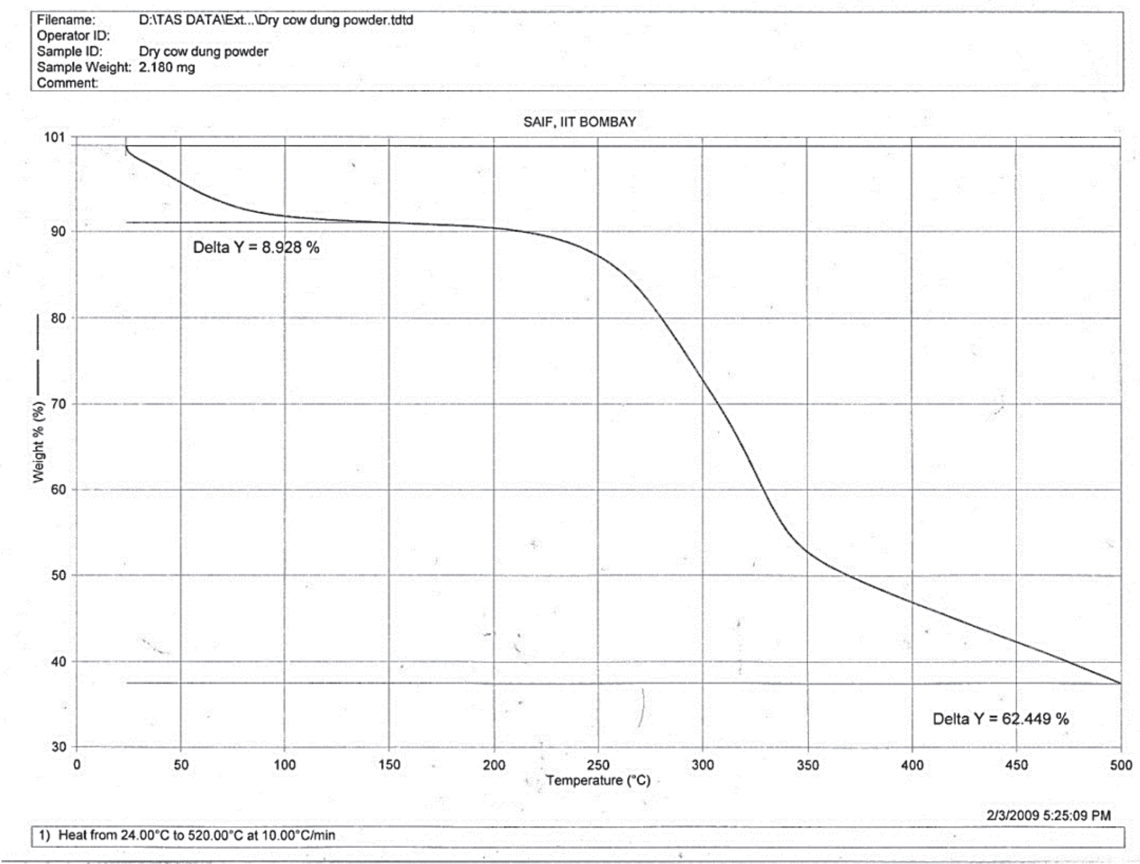

Figure 2.
Thermogravimetric analysis spectra of DCP.

carbonyl and alcoholic groups at higher temperatures have often been attributed to the thermal breakdown of aromatics. In the analytical conditions of TGA and DTA analysis (with a heating rate of 10°C min^{-1}) aromatic structures can be formed from cyclic structures [58].

4.1.5 Electron spin resonance spectroscopy

The abundance and presence of unpaired electron and free radicals in the DCP has been assessed by ESR spectroscopy. The spectral information from **Figure 4** is not very vivid but explains that DCP contains some free radical biotic groups. The source of free radicals can be organic radicals of semi-quinine nature conjugated with extended aromatic systems or paramagnetic metal ions such as Fe, Mn and V [59]. Also, ESR data of IHSS samples do show free radical contents with g-values approximately around 2.000 and we have also obtained the g-value for DCP, around 2.000 in agreement with standard samples.

4.1.6 Fourier-transform infrared spectroscopy (FTIR)

As explained earlier the detailed information of various adsorptive functional groups of biosorbent is of great importance and DCP has been assayed for all the possible functionality present on it. There are various organic groups present on DCP such as carbohydrate, protein, lignin, cellulose etc. In case of carbohydrate, only carboxyl and sulphonate contribute majorly in the formation of metallic ligands. Similarly, in protein moiety the group such as carboxyl, sulphonate,

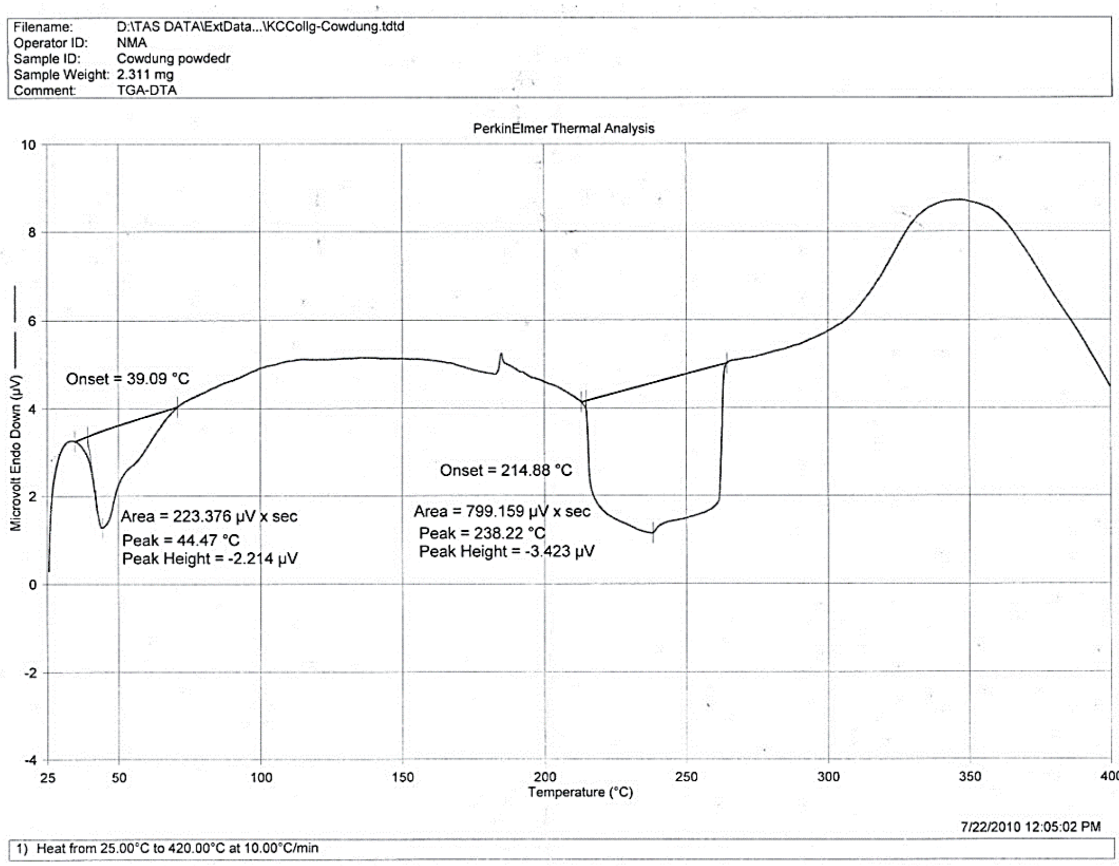

Figure 3.
Differential thermogravimetric analysis spectra of DCP.

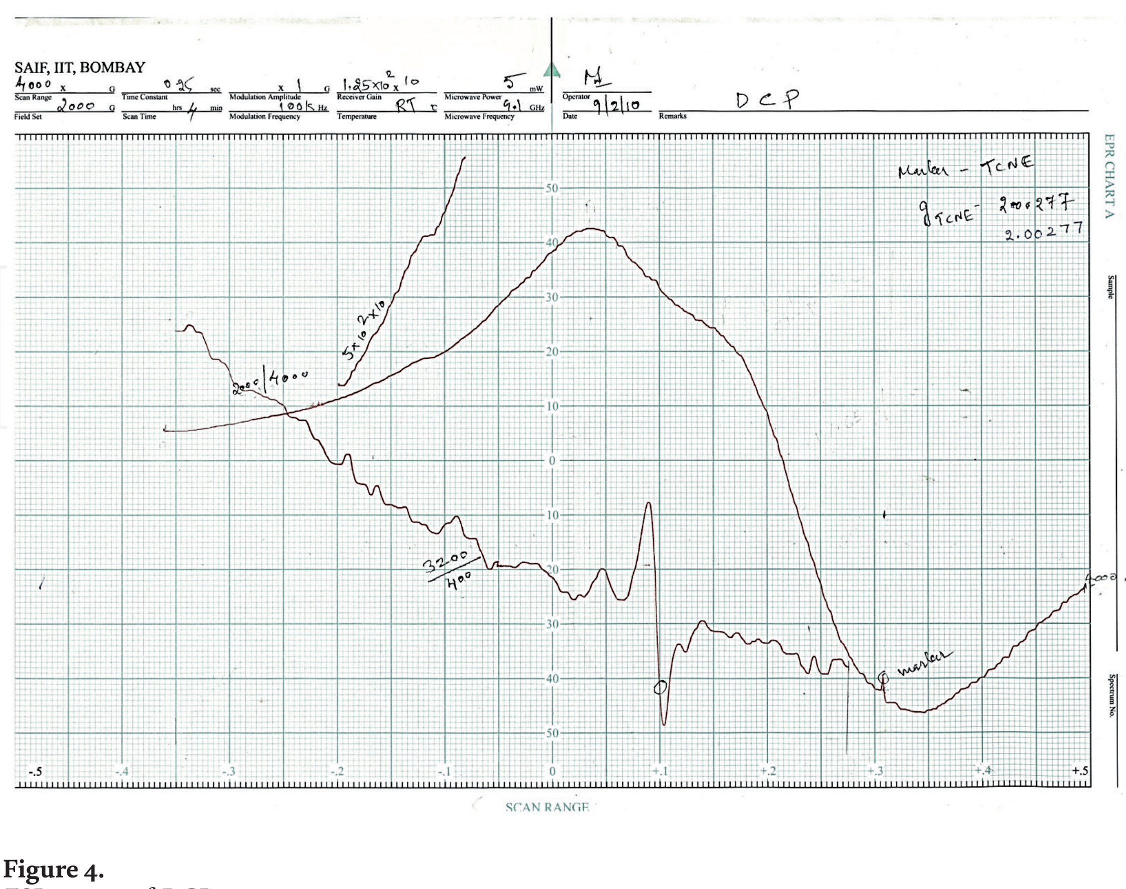

Figure 4.
ESR spectra of DCP.

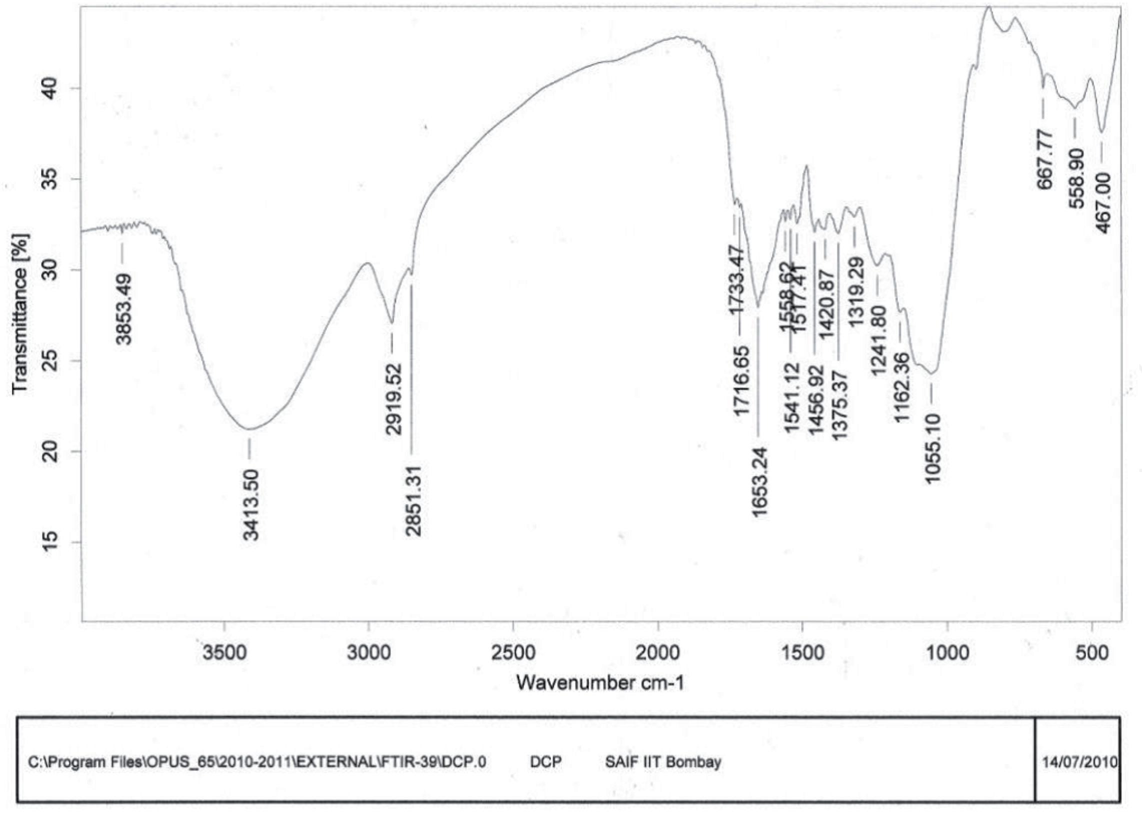

Figure 5.
FTIR spectra of DCP.

sulfhydryl, hydroxyl, phosphonate, thioester, secondary amine, imines participates in ligand formation [60] Lignin derivative contain an abundance of oxygen containing functional group such as phenolic, alcoholic and enolic structure which forms lignin- metal complexes. **Figure 5** and **Table 4** explains the same in brief. Also, the FTIR analysis of DCP after and before the metal ion adsorption has been carried out to confirm the biosorption process with the observed shifts in wavelength of functional group involved in biosorption.

4.2 Chemical assay

4.2.1 Extraction of humic acid from DCP

Literature survey confirms that till today HA has been extracted from the different Abiotic origin worldwide, but a successful pioneering research of extraction from a Biotic Animal origin DCP, has been carried out by authors, employing Green Chemistry Principles as described earlier. We have obtained 9–10% extraction of HA from DCP.

The following technique was devised for extracting HA from dry cow dung powder.

a. For the neutralization of dry cow dung powder, different series of alkali with concentrations ranging from 0.1 to 1.0 M of NaOH, KOH, Na_2CO_3, and $NaHCO_3$ were studied. With 0.1 M NaOH, the best results were obtained.

b. Acids such as HCl, HNO_3, and H_2SO_4 in the molarity range of 0.1–1.0 M were tested for the re-acidification process. With around 0.1 M HCl, the best results were obtained.

c. 15 mL of 0.1 M HCl is desirable for 100 mL of neutralized supernatant.

Functional groups	Compounds	DCP Signal (cm^{-1})
N-H	Amines	3413.50
-COOH	Carboxylic Acid O-H Stretch	2851.31 2919.52
C-H	Alkane	2851.31 2919.52
C=O & (RCOOR)	Esters & Lactones 6-membered and 5 - membered lactone	1733.47
C=O	Carboxylic acid, (C=O stretch)	1716.65 1733.47
C=OR	6-membered cyclic ketone	1716.65
C=C	Alkene	1653.24
C=C (Stretching Vibrations)	Nonconjugated	1653.24
	Conjugated	1558.62 1541.12
C-H (Bending Vibrations)	CH_2	1456.95 1420.87
	CH_3	1375.37 1319.29
C-Br or Inorganic Impurities	Alkyl halide stretch clay, minerals	558.90 667.77
$Si\text{-}CH_3$	Silicon functions	1241.80
C-O	Saturated secondary or cyclic tertiary amine	1055.10 1162.36
C-Cl	Chlorine	667.77
-Na	metal group	467.00

Table 4.
FTIR data of DCP.

The decantation procedure was used to remove hay and other light non-humic particles by mixing DCP (100mesh) with purified water and stirring for 20 minutes at room temperature. After filtering non-humic materials from cow dung, the resulting slurry was stirred with 0.1 M NaOH for 24 hours. After that, the whole mixture was allowed to settle before being purified. The soluble HA, FA, and other biological matter are found in the filtrate, while the residual contains Humins, Ulmic acid, and insoluble bio-organic matter. Since HA is insoluble at low pH, the filtrate was acidified by slowly applying 0.1 M HCl at room temperature (pH 1) with continuous stirring to mitigate the heat of neutralization and centrifuged for HA precipitation. Fulvic acid and other organic acids are found in centrifugate. To extract HA, the HA was carefully washed with double distilled water until it passed a chloride inspection and dried in an oven at 383 K. We were able to remove 9–10% of the content. FTIR and Raman spectroscopy were used to identify and characterize HA, which was then compared to standard HA from IHSS [61]. At Indian Institute of Technology, Mumbai, we obtained FTIR spectra on a Nicolet Instrument Corporation-USA model-MAGNA 500 with a specification scale of 4000 cm-1 to 50 cm-1. Raman spectra were obtained using a RENISHAW Laser Raman Spectrometer with 325, 514.5, and 785 nm laser excitation and a CCD detector with confocal microscope at the Gemological Institute of India in Mumbai.

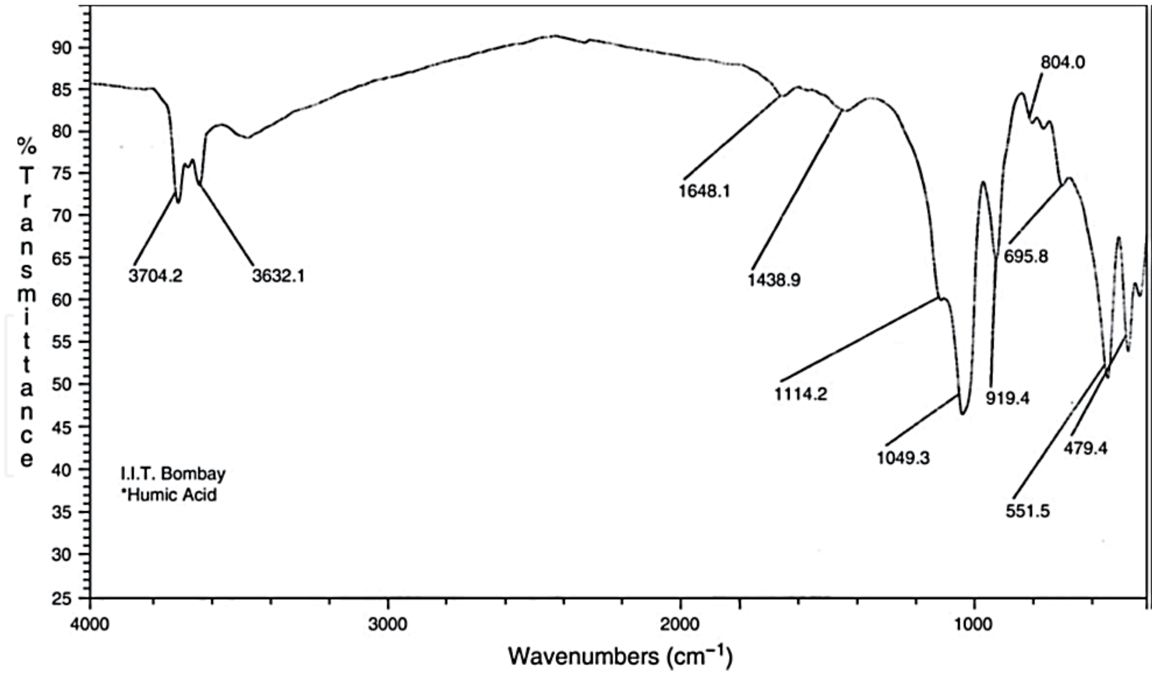

Figure 6.
FTIR spectra of standard HA.

4.2.2 Results and discussion

Two FTIR Spectrum were compared - Standard HA (**Figure 6**) from International Humic Substances Society (IHSS) and HA extracted from DCP (**Figure 7**). **Table 5** elucidates the absorption peaks and their corresponding bonds/functional groups. Certain shifts in absorption bands may be observed due to inter and intramolecular hydrogen bonding, varying degrees of conjugation, steric hinderances, physical factors and matrix effect. This is mainly because the extracted HA is from a biotic source (cow) and the standard HA has an abiotic origin.

At 3421.0 and 3422.8 cm^{-1}, we observed the band for N-H stretch of primary amine for the standard HA and extracted HA respectively. Whereas the N-H bend

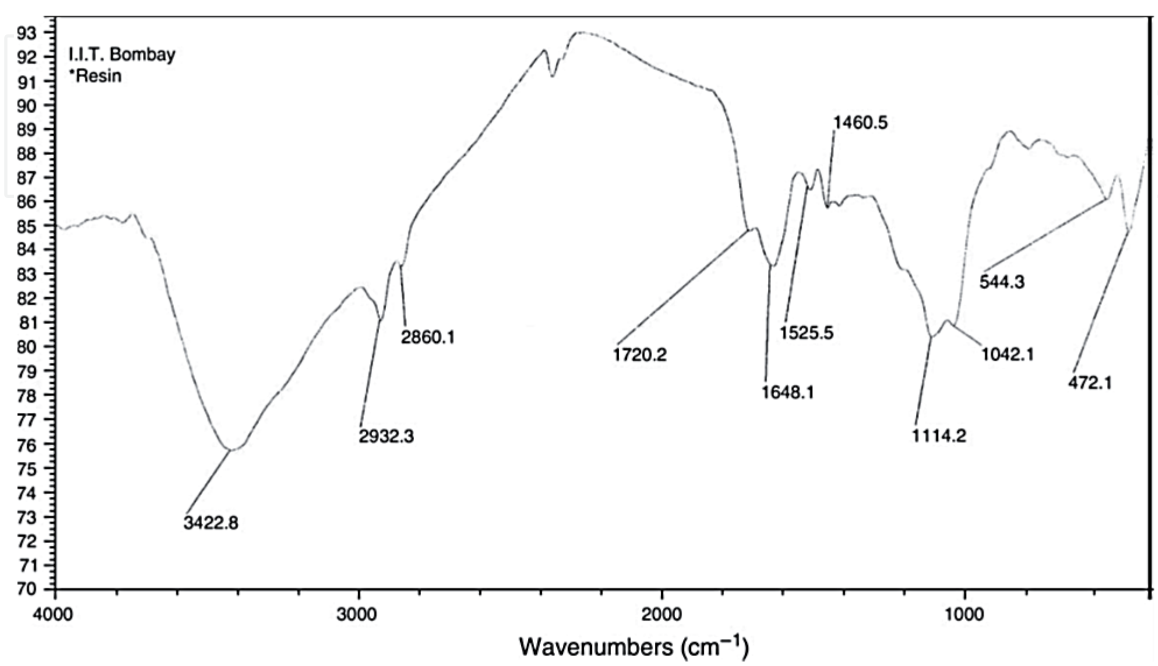

Figure 7.
FTIR spectra of extracted HA.

No.	Functional group	Compounds	Std HA IHSS (cm^{-1})	Ext. HA DCP (cm^{-1})
1.	N-H stretch	Aromatic Monomeric Alcohols, Phenols	3421.0	3422.8
2.	O-H	Carboxylic acid	—	2932.3 2860.1
3.	C=O	Carboxylic acid, Aldehydes, Esters, Ketones	—	1720.2
4.	N-H bend	Primary Amines	1648.1	1648.1
5.	C-N	Aryl or alkyl substituted tertiary amines	1114.2	1114.2
6.	C-O	Primary alcohols	1049.3	1042.1
7.	C-Cl	Chloroalkanes	551.5	544.3

Table 5.
FTIR data of HA.

was seen at 1648.1 cm^{-1}, in both the spectra. Both spectra showed identical bands at 1114.2 cm^{-1} for aryl or alkyl substituted tertiary amines. The band for primary alcohols (C-O) was observed at 1049.3 and 1042.1 cm^{-1} for the standard HA and extracted HA respectively. Similarly, the band for chloroalkanes was observed at 551.5 and 544.3 cm^{-1}, in the two spectra respectively. In the extracted HA, a band is seen at 1720.2 cm^{-1} which is very important as it describes the presence of lactones, which is also influenced by conjugation and ring size and standard HA does not show any band in this region. Thus, we confirm the matrix of extracted HA is from bovine species i.e., fecal residue of cow.

The absorption patterns are depicted in the Raman spectra of standard HA in **Figure 8** and extracted HA in **Figure 9**. **Table 6** lists the absorption bands and their descriptions. Absorption of (C=C) aromatic ring chain heavy vibration was visible at 1580 & 1600 cm^{-1}; ($C\text{-}NO_2$) asymmetric mild vibration at 1530–1590 cm^{-1}; (N=N) aliphatic mild vibration at 1550–1580 cm^{-1}; and (X-Metal-O) heavy vibration at 150–450 cm^{-1}. The presence of heavy metals such as iodine, selenium, and silicon is shown by a sharp small absorption band at 150–450 cm^{-1} in the spectra of standard HA. A spectrum of extracted HA is devoid of absorption band at that

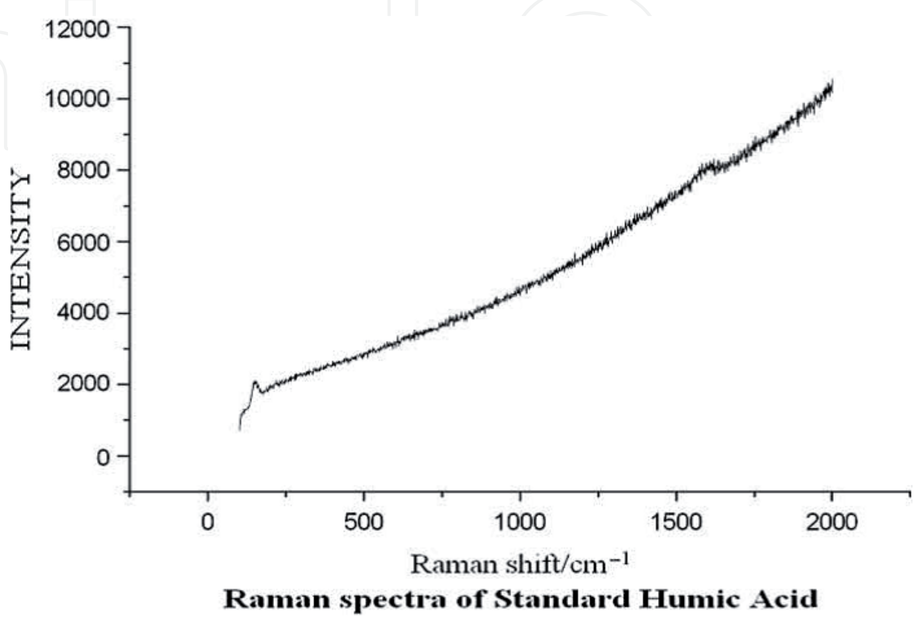

Figure 8.
Raman spectra of standard HA.

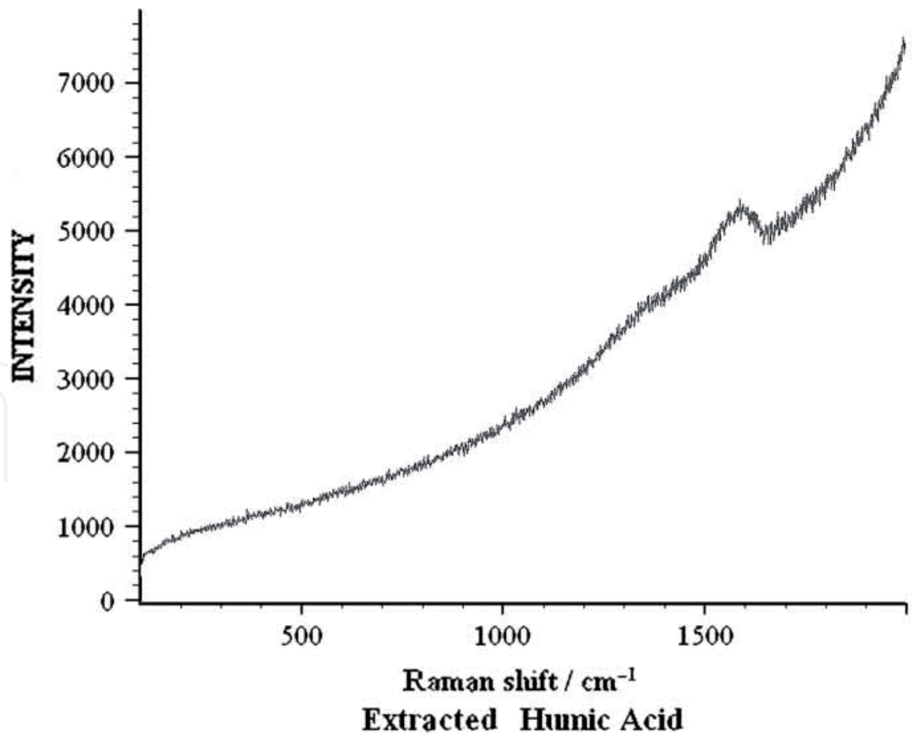

Figure 9.
Raman spectra of extracted HA.

No.	Functional group	Raman shift (cm^{-1})	Band type
1.	$C\text{-}NO_2$	1530–1590	Asymmetrical medium
2.	Aliphatic N=N	1550–1580	Medium
3.	C=N	1610–1680	Medium
4.	C=C	1500–1900	Strong
5.	C=O	1680–1820	Medium
6.	X-Metal-O	150–450	Medium

Table 6.
Raman spectral data of HA.

region which indicates the absence of any contamination of metal ion. This concludes that DCP does not induce any undesirable matrix effect.

4.3 SWOC analysis

SWOC analysis is a strategic planning technique for examining the Strengths, Weaknesses, Opportunities, and Challenges that any project may face. It entails defining the project's goal and determining the internal and external variables that will help or hinder the goal's achievement. Any research project's aim is to move from the lab to the real world. The SWOC analysis of DCP and its application as biosorbent is thoroughly scrutinized to know the feasibility of scaling up in industrial effluent and water treatment process.

4.3.1 Strengths

- DCP is a non-conventional, biodegradable, renewable and ever easy and freely available feedstock with minimum capital, thus lowering the need to regenerate the same from spent.

- The transport, storage and handling operations are very simple due to nonperishable nature of DCP.
- The HA extraction from DCP is also a *green process* wherein catalyst or any other auxiliary substances are not employed to add on to the cost, time, and chemicals, as compared to its other competitive methods presently dealt with.
- For the biosorption process, DCP is successfully employed without any pretreatment or modification process. Having porous and coarse nature settling is easy and hence it is efficient in decontamination.
- The disposal of DCP is easy as it can be sun dried and utilized as a landfill due to its minimum leaching nature.
- Being freely and easily available DCP has an edge over processed natural adsorbent considering their cost, time, and energy efficiency.

4.3.2 Weaknesses

- Biosorption mechanism of DCP still requires detailed studies due to its heterogeneous nature.
- Back extraction is difficult. Thus, research is required for stripping back of precious metals.

4.3.3 Opportunities

- Computer simulation will offer extremely powerful tools for designing.
- Metal recovery by different processes will prove Atom Economy.
- A need for R&D studies dealing more cogently with the molecular mechanisms, including such issues as binding sites, valence states, coordination chemistry, life cycle analysis and the speciation of metals in solution will surely optimize the Industrial Applications.

4.3.4 Challenges

- Direct Industrial Applications will be challenging.
- For a real application more research regarding direct impact of stability of partially or fully saturated DCP on nature is urgently needed.
- Eco-friendly Disposal Mechanism of DCP must be formulized for long term storage.

5. Conclusions

The Ancient Indian Epitome of Energy, DCP-unearthed ecofriendly resin has been scientifically studied to strongly echo its multispectral utility as a Humiresin, Green agrarian booster and Pseudo shale, sustaining WFE Nexus. The development of green and clean HA extraction process from DCP and its comparison with standard HA from IHSS holds great importance in the chapter. As our environmentalists and green chemists urge for *Reduce, Reuse, and Recycle* - the 3R's of Zero Waste Management theory, coined with Re-think, we can Re-balance the WFE Nexus and the sustainability of Life by employing DCP in various sectors as studied in this chapter. The utility of DCP will surely contribute to convert waste into wealth and refuse into resource, which is the ultimate goal of waste management strategy. This chapter tries to answer and express the great potential of DCP in the industry of Environmental Management, which can not only fix WFE Nexus but also the future and us.

Appendices and nomenclature

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