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Humic Acids: Overview and prospective with especial emphasis on lignite derived

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Abstract

Humic acid is organically derived organo-chemical which is multi-structural, multi-functional, ubiquitous whose demand to enhance soil quality is very low compared to bulky manures. There are various sources of humic acid whose composition and characteristics varies accordingly source, place, time etc. The global demand of organic produce increases 21% annually whereas in Indian sub-continent as well India increases thirty-six and 51% respectively. The bulky application of organic manure is the major constraint in terms of availability and applicability of input with improved technology. Thus, organic manure though with best nutritional qualities should be ruled out for production in larger areas as it is quite tedious along with high input cost per unit production.

The overview under the presentation is made for the humic acids derived from Lignite coal which is high in hydro-carbon and sulphur compared to other sources (compost, peat, forest land, agricultural land, river and lakes) high in nitrogen and oxygen. Calorimetrically, humic acids obtained from the lignite coal is yellow, black and brown colored which is extracted conventionally for the humic acids (via alkali followed by acid treatment). Chemical characterization of the lignite coal derived humic acids shows high E2:E3, E3:E5, E4:E6 with major carboxylic, hydroxylic, phenolic, alcoholic, methoxylic functional groups and high surface area to chelate and complexates with the metals to from organo-metallic. Application of humic acid in the soil had been reported to increase aggregate stability (i.e., higher the doze of humic acid higher the size of aggregate revealed to be stable). Chemically, less buffering with high available nutrient and biologically the increase of aerobic bacteria compared to anaerobic has been reported. The nutrient content along with yield also stated to increase with a common myth that humic acid is acting as a bridge between soil surface and desorbing behavior of element esp. phosphorous. Thus, Lignite coal derived humic acid are highly aromatic to improve soil health, reduces loss of nutrient in agricultural crop production.

Keywords: Lignite coal, Humic Acid, chelate and complexates

Introduction

In the current scenario due to continuous non-judicious use of agro-chemicals, a heavy deterioration in the soil health had been reported, thereby functional use of bio-chemical or bio-stimulants increased to enhance environmentally sustainable potential for agricultural production (Singh et al., 2019a)^[51]. Many bio-stimulants originated from various sectors of agriculture, livestock, mining, rivers & lakes, waste material highlights its use and enhance the economy of the produce by lowering input cost (Singh et al., 2019b)^[52]. The statement was reported by several scientist across the globe with the common myth of hydrophobicity, hydrophilicity, chelation, and complexation. However, its extent varies with the source of origin (i.e., number of aromatic and aliphatic compounds). Total seven sources had been taken to review the extent of aromaticity (Table - 1) and found that humic acid derived from lignite coal suits the high resemblance of aromaticity. The underlying high impact of humic acid on the soil health is strongly related to the presence of different functional groups (Spark et al., 1997) ^[54]. In hydroponic or green house like assays due to absence of local control results sharp behavior however, when applied on the field condition it ruled behavioral changes viz – soil, climate, field management etc (Heinze et al., 2016)^[31]. Keeping the view in mind, the review is made with the major emphasis on following points:

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- 1. Sources and chemical composition of humic acid
- 2. Spectroscopic features of humic acid
- 3. Extraction of humic acid
- 4. Application and utilization of humic acid for different crop production
- 5. The mechanism of humic acid effects on the plant growth (Physiological aspects)
- 6. Impact of physico-chemical and biological properties on soil

Sources and chemical composition of Humic Acids

Humic acid is resistant fraction corresponds to passive pools of the soil organic matter which takes atleast two million years to turn to final product (F. J. Stevenson, 1994)^[55]. It is ubiquitous and present in all organic sources buried over a period (Schmidt & Noack, 2000)^[47]. They are found in compost, peat river & lakes, forest land etc. whose chemical parameters varies due to difference in the substrate (Thorn & Cox, 2009)^[56]. The decomposed product corresponds into various pool of the same nutrient. whose proportion varies by several factors depending upon place, time, parent input source, physio-chemical and biological properties of the place where the formation of humic acid initiates etc. (Thorn *et al.*, 1989)^[57].

The organic substances when are substrated under anaerobic condition, its decomposition and compression led formation of peaty sediments and finally converted into lignite (Del Rio *et al.*, 1994)^[19]. Furthermore, decomposition and compression of lignite results bituminous followed by anorthite (Fuller *et al.*, 2018)^[28].

Humic acid is organically derived macromolecules whose skeleton chemical composition relies mainly on carbon (C),

hydrogen (H), oxygen (O), nitrogen (N), sulphur (S) and phosphorous (P) (Chefetz et al., 2002)^[13]. Of these CHONS analyzer analyzes total carbon, hydrogen, nitrogen, oxygen and sulphur however, total phosphorous were determined by usual analytical technique (Fadeeva et al., 2008; R. A. Bowman, 1988) ^[25, 9]. Several observations relies that lignite coal derived humic acid is rich in C, H and S compared to other sources (viz – peat, compost, river & lakes, organic and acidic forest and maize land soils) which is high in nitrogen and oxygen (Table - 1). Total carbon picturizes aromatic: aliphatic ratio which is discussed in NMR spectroscopy (Mullen et al., 2009)^[40]. Total hydrogen is the total acidity of magnitude nearly 6 meq/gm is expected to be derived from the carboxylic acid and phenolic group (M. Schnitzer, 1977) ^[49]. Total nitrogen estimates nitrogen mineralization rate by C : N ratio (Total Carbon : Total Nitrogen) which ranges 52.9 -65.6 (>30:1) (Bengtsson et al., 2003) ^[7]. Thus, humic acid can be derived in the soil for the long time with certain amount of functional groups hence, can be either used as adsorbent or chelator and complexator (Tsutsuki & Kuwatsuka, 1978)^[58]. Lignite coal is formed at high temperature and high pressure un anaerobic condition of buried organism (Yao et al., 2010) ^[66]. However, the other sources of humic acid acquainted with the tillage practice and have optimum microbial activities. That's why, nitrogen, phosphorous and sulphur are relatively high in other sources compared to lignite derived. The chemical characterization involves the degree of condensation, homo-hetero cyclic, functional group attached with surface etc. Depending upon the molecular weight of the humic acid (2.0 - 1300 kDa), the structural and chemical composition of humic acid varies (Van Stempvoort and Lesage, 2002) [60].

					1		
Materials used	% C	% H	% N	% O	% S	%Ash	Researchers
Lignite coal (a)	54.45	5.17	0.83	24.04	2.35 [HS]		Be´atrice Allard (2006) ^[3]
Lignite coal (b)	68.79	5.29	1.10	23.64	1.18		Souz and Braganc (2017) ^[18]
Lignite coal (c)	66.8	6.0	1.3	26.0	-na-		Schulten and Schnitzer (1993) ^[49]
Range	54.45-68.79	5.17-6.0	0.83-1.3	23.64-26	1.8-2.35		
Peats	52.3	4.7	0.75	42	-na-	3.5	Gondar et al., (2005) ^[29]
River and lakes	43.7-53.7	4.1-5.8	3.5-6.2	31.1-37.1	-na-	1.2-13	Mengchang et al., (2008) [39]
Organic Forest lands	54.65	4.92	2.3	37.4	0.37		Be´atrice Allard (2006) ^[3]
Acidic Forest lands	52.9-58.9	3.9-5.7	3.8-5.8	-na-	0.9-5.98 [HS]	-na-	LO´ PEZ` et al., (2008) [36]
Agricultural lands (Maize)	53.69	5.04	3.13	37.5	0.28		Be´atrice Allard (2006) ^[3] ;
Range	43.7-58.9	3.9-5.8	0.75-5.8	31.1-37.1	0.28-5.98		Paola et al., (2005)

Table 1: Various sources of Humic Acid with its specification

Chemical composition of humic acid Functional group

The cyclic nature (homo-hetro), aromatic nature and certain functional group of any organic compound is mainly characterized by the specific absorbance of the dissoluted solution under UV or *Viz* range in UV-*Viz* spectroscopy (Akarshini *et al.*, 2013). UV-*Viz* spectra work on the principle of electronic transition from its bonding molecular orbital to anti-bonding molecular orbital (σ to σ^* , n to σ^* , π to π^* and n to π^*) (C.N.R. Rao, 1967). Aromaticity and homo-hetero

cyclic character can be observed from SUVA254, E4:E6 and E2:E3 ratio whereas phenol, quinonoid or lignin and other humified material by E270:400 and E280: 470 ratio. The brief description of these indices is presented in the table – 2. Data inferred from table-2 depicts the UV-*VIZ* characterization of humic acid obtained from various sources ruled over lignite coal derived by E4:E6 and E2:E3 ratio compared to other sources which have high E270:400, E250:472, E280:665 due to higher concentration of hydrocarbons in its elemental composition.

Table 2: Indices calculation and value for the chemical characterization of different humic acid

Indices	Measurement	Explanation	References		
SUVA254	Indices Value = $\frac{A_{254}}{C}$	It explains the aromaticity of the humic acid.	Kumke <i>et al.</i> , 2001 ^[34] ; Weishaar <i>et al.</i> , 2003 ^[64]		
E4:E6	Indices Value = $\frac{A_{465}}{A_{665}}$	It explains the degree of aromatic C condensation.	M. M. Kononova, 1966 ^[33] ; F. J. Stevenson, 1994 ^[55]		
E2:E3	$Indices Value = \frac{A_{250}}{A_{365}}$	It explains the correlation study with the molecular size and aromaticity.	Peuravuori and Pihlaja 1997 ^[44]		

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E280:E472	Indices Value = $\frac{A_{280}}{A_{472}}$	It reflects the lignin and other humified materials at the beginning of the humification.	Albrecht et al., 2011 ^[2]					
E270:E400	Indices Value = $\frac{A_{270}}{A_{400}}$	Characterize the phenol and other quinoids.	Uyguner and Bekbolet, 2005 ^[59]					
E280:E665	Indices Value = $\frac{A_{280}}{A_{665}}$	Correlation between humified and non-humified organic matter.	Zbytniewski and Buszewski 2005 ^[69]					
A is the absorbance of disso	A is the absorbance of dissolved or natural organic matter and C is the concentration of the solution in mg-C/L and number is the wavelength (nm) at which concentration is to be measured.							

Sample	E2:E3	E270/400	E280/472	E280/665	E4:E6	References
Lignite coal derived_1	2.4	3.2	5.8	31.9	5.8	Dong et al., (2009) [22], Chu-Fan Wang et al., (2017)
Lignite coal derived_2	2.6	3.4	6.3	36.5	6.2	Dong et al., (2008) ^[22] , Peuravuori et al., (2006) ^[44]
Lignite coal derived_3	2.9	3.8	6.6	42.1	6.7	Fong and Mohamed; (2006) ^[26] , Dick <i>et al.</i> , (2002) ^[20]
Peat_1	2.8	3.7	6.6	33.6	5.4	Francioso et al., (2002) ^[27]
Peat_2	3.0	3.9	7.0	34.1	5.1	Zykova <i>et al.</i> , (2018) ^[70]
Compost	3.0	3.9	7.0	34.1	5.1	Spaccinia and Piccolo; (2009) [53], Yuan et al., (2017) [69]

The clear picture of the functional group attached with the humic acid can be estimated from FTIR spectroscopy (He *et al.*, 2017). It principally depends upon the stretching of bond due to transition, rotation, and vibration. Every functional group have its own individual signature in the IR series whose resonance corresponds the maxima peak (Kim *et al.*, 2005)^[32]. FTIR spectra of humic acid of lignite coal reveals that it gives absorption maxima at 3400 cm⁻¹ (H- bonding, -OH), 1700 cm⁻¹ (carboxylic acids) and 1620 cm⁻¹ (aromatic carbon) (L.D.S. Yadav, 2013)^[65] (Table – 4). The other sources too connonates from above wave number with some other functional groups attached due to high nitrogen and oxygen content in its elemental part. These functional group creates stearic hindrance and results for the instability for the compound (Peuravuori *et al.*, 2006)^[44].

 Table 4: FTIR stretching of different functional groups in humic acids

Stretching wavelength(cm ⁻¹)	Functional group
3400	H bonded -OH stretching
2930	-CH Aliphatic
1720	Carboxylic acid
1620	Aromatic C=C conjugation with C=O

The indices of aromaticity can be obtained from the UV-VIZ spectroscopy however, the atoms involved in satisfying the Huckle rule is obtained from the NMR spectroscopy (McBeath et al., 2011) [38]. It is the key mark of stability of the organic compound (Boldyrev & Wang, 2016)^[8]. More the aromatic character more would be the stability and vice versa. NMR is the suit spectroscopical techniques for the determination of the aromatic and aliphatic atom by Iso-spin quantum number of nucleus (Pykett et al., 1982) [46]. Data obtained from NMR spectra revealed that humic acid derived from the lignite coal due to high hydrocarbon and sulphur are more aromatic in nature compared to other sources (F.J. Stevenson, 1994)^[55]. Carboxyl group have also been reported in high concentration (Chen et al., 2022) (Table - 4). Thus, higher oxygen in other sources might reveals heterocyclic oxygen as centered compound (M. Schnitzer, 1977)^[48]. Apart from aromatic character, NMR experienced the presence of quinonoid group which produces ROS (reacting oxygen species) through it reduction (Scott et al., 1998)^[50]. However, phenol is another functional group which donates the electron thus, the humic acid is electrically neutral besides it actively takes part in the redox potential (M. Schnitzer, 1977)^[48].

Table 5: NMR values of humic acids

Samples	Percentage of distributed carbon									
	0 - 90	110 - 160	160 - 190	(0 – 90 ppm)/(110 –						
	ppm	ppm	ppm	160 ppm)						
	Aliphatic C	Aromatic C	Carboxyl C	Caliphatic / Caromatic						
HA1	30.20 <u>+</u> 1.64	56.96 <u>+</u> 2.41	12.83 <u>+</u> 1.41	0.53						
HA2	36.64 <u>+</u> 1.82	46.86 <u>+</u> 2.12	16.68 <u>+</u> 1.21	0.78						

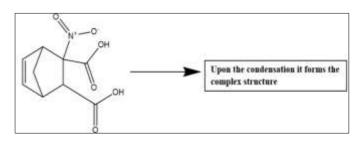
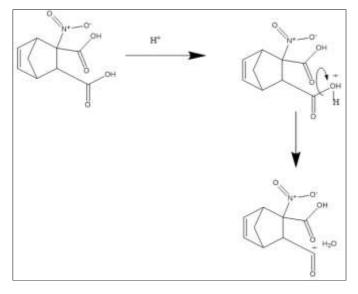


Fig 1: Basic Unit of humic acid (2-Nitrobicyclo [2.2.1] hept-5-ene-2, 3-dicarboxylic Acid) drawn in chemdraw software

pH and Humic acids

Since, humic acid contains high concentration of the hydroxyl group hence it is soluble more in neutral to alkaline condition (F. J. Stevenson, 1994)^[55]. However, the acidity humic acid varies with the chemical composition of the substrate (Thorn et al., 1989) ^[57]. The presence of excess lone pair electrons negative substance makes the compound in stretched due to stearic hindrance and thus are more prone to protonation which causes uncoiling (DeCocq & Bhattacharyya, 2019)^[18]. Therefore, humic acid under acidic condition becomes uncoiled and produces yellow color (light) while under alkaline condition coiled to produce the brown to black (dark) color. Hydroxyl group when protonated liberates water molecule hence the outer surface is hydrophobic while inner is hydrophilic (Mechanism 1). This water molecule is a becomes the store house of dissolved nutrient which are approaching for the adsorption. More the hydroxyl group, more would be the site of negative vicinity more would be the approach for the nutrient to be sorbed and thus, high exchange Capacity.

Under acidic condition



Mechanism 1: Expected behaviour of humic acid under acidic condition which is drawn in chemdraw software.

Under alkaline condition

The stereochemistry of the humic acid signifies that OH^- group attached with the compound lies in XY plain hence, the excessive hindrance for the OH^- ions at higher concentration takes place.

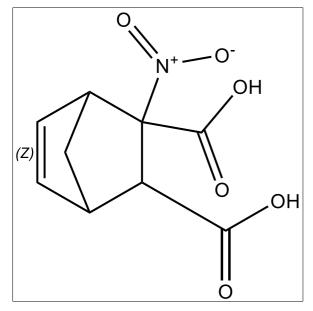
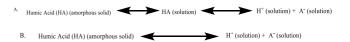


Fig 2: Stereochemistry of humic acid drawn with the help of chemdraw software (Z) is the z-axis component of the humic acid

As humic acid is an organic colloid whose negative charge density is inclined at XY plain (as per sterio diagram from chemdraw software). When any cation is swarming in an aqous medium, a potential is developed (called Zeta Potential) results the formation of electric double layer. The bukey of humic acid, cation and soil water tries to remain uncharged. Moreover, ions surrounding the particle prosecutes the charge protection i.e., at higher protection at lower strength and lower protection at higher strength.

At lower pH, the solubilization of humic acid is partial. Although, it is found to be dissolved in nature. The dissolution mechanism of the humic acid with water were presented by Kluc'áková & Pekar' in 1992, they stated that humic acid is semi solid (super cooled liquid) who produces soluble and insoluble fractions because of presence of electrolyte. This creates the difference in the extraction process which is discussed in the section extraction of humic acid. From the given below equations it is depicted that dissolution of humic acid in water are more complex than springle soluble in water, only some are water soluble. Thus, pH plays an important role in stabilization and solubilization of the cations.



Binding of cationic metals with humic acid

The ability of Humic acids to chelate and complexates with the cationic metal and makes available for the plants at specific pH as well as remediate heavy metal contamination via adsorption (Chen & Stevenson, 1986)^[15]. The mechanism of interaction of metal with humic acid follows the similar trend as H⁺ (Von Wandruszka, 2000)^[63]. Higher the charge, molecular weight and concentration of metal, higher would be the capacity results the formation of pseudo-micelles domains and cause detergent effect. ¹³C-NMR spectroscopy results that lower molecular weight of humic acid contains high amount of phenolic and carboxylic group and therefore, these fractions can bind the metal efficiently.

Extraction of humic acid

Humic acids in the soils are found the combination of inorganic mineral constituents. To extract there is need to break the bond between them (A. M. Posner, 1966)^[45]. The common method adopted for the extraction is valid for almost all the sources of humic acid is under follows (Fig - 3) however, the concentration of the extractant varies with the change in the sources and bond strength between them.

Lignite coal were firstly refluxed with methanol / acetyl bromide + benzene to remove soluble non-humic substance and insoluble humic substance were extracted with dilute NaOH/Na₂CO₃. It produces insoluble humin substance and soluble organic fraction on centrifugation consists of fulvic and humic acids. This soluble organic fraction when treated with acid (pH-2-3) it results insoluble humic acid and soluble fulvic acids when centrifuged. The obtained humic acid is dialyzed and freezed to get crude humic acid and finally pure humic acid. Again, treatment of Ba-salt on soluble fulvic acid it results (Ba-fulvate) as precipitate which can be separated from the rest of humic substance (F. J. Stevenson, 1994, Yuan et al., 2015)^[55, 68].

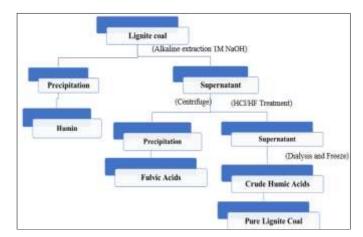


Fig 3: Extraction of pure lignite humic acid from lignite coal

Types and chemicial composition of lignite coal derrived humic acids

The humic acid when extracted from the different sources of lignite mines results in three different colored namely yellow, brown and black humic acid (Dubey and Raha, 2020) ^[24]. Yellow colored humic acid is deficient in nitrogen and sulphur content but an approaching constrainent among the chemical composition in these had been reported (Youngs and Frost, 1963) ^[67]. Therefore, the characterestic ratios H:C, O:C,

C:N, E4:E6 etc is used to differentiate between them (Table – 6). The lower availibility of sulphur tends lower E3:E5 ratio (aromaticity with sulpur) in yellow compared to rest (being black as highest). C:H ratio of yellow humic acid is lower however it is high in O:C ratio being black and brown as intermediate and high respectively shows yellow colored humic acid among them is more alaphatic (Youngs and Frost, 1963)^[67]. The above facts protends E4:E6 ratio, total acidity, carboxylic group and phenolic group (Table – 6).

Table 6: Chemical co	nposition of the various kind of lignide coal derrived	humic acids

HAs	С	Н	0	S	Ν	H/C	O/C	C/N	E ₃ /E ₅	E4/E6	Α	Car	Р
Y	58.123	4.013	22.020	-	-	1.01	0.342	-	2.78	1.92	523	315	208
Br	58.983	4.571	17.712	2.089	0.740	1.12	0.271	78.480	4.40	3.42	618	379	239
Bl	59.240	4.616	18.583	2.072	0.906	1.12	0.282	64.109	4.67	3.91	678	408	270

 $\begin{array}{l} HAs - Humic \ acids, \ Y - Yellow \ humic \ acid, \ Br - Brown \ humic \ acid, \ Bl - Black \ humic \ acid, \ C - total \ carbon, \ H - total \ hydrogen, \ O - oxygen, \ S - sulphur, \ N - nitrogen, \ A - Total \ acidity \ (C \ mol \ kg^{-1}), \ Car - Carboxyl \ group \ (C \ mol \ kg^{-1}), \ P - Phenolic \ groups \ (C \ mol \ kg^{-1}) \end{array}$

Effect of humic acid on the physical properties of the soil

Most of the physical properties of the soil are static in nature due to non-variability of the texture with time however, a small significant change might occur under long term experimentation. Aggregate stability is one of the physical characterestics of the soil which indicates the degree to which soil can resist against dispersion. It gives the signature of soil organic matter content, porosity, drainage, water availibility for plants, compaction and to some extent biological properties. Of the physical prtoperties of soil aggregate stability depends upon the soil structure (More % of clay content more would be the force required to break due to binding action (cementing action). Roseta *et al.*, (2006) in Nigeria studied the effect of humic acid on the physical properties of the soil and reported that

- 1. Higher the concentration of the humic acid higher the stability of the aggregate.
- 2. More the ageing time more is the stability (i.e., lower concentration of humic acid also pretunds more stable structure compared to higher concentration provided lower concentrated is being aged for longer time period)

Effect of humic acid in the nutrient dynamics in soil Nitrogen

Changes in the ammonium and nitrate concentration after the application of urea with and without humic acid was under long term experiment in soil microcosoms revealed that the urease activity initially clouts similarly and hasten in first three days in both the microcosoms. It resembles peak at 5th days for urea treated microsoms only and lowered fastly as compared to humic acid microsoms which were found stable. Additionally, a strong correlation between ammonia dissappearence and nitrate accumulation had been reported. Biologically, arobic bacteria with increase in porosity too had been observed which might be due to the fact that humic acid alters the rate of release of ammonia by imparing urease activity. High arobic bacteria indicates that there is continuous supply of ammonium which is crucial for nitrifiers (Dong *et al.*, 2008) ^[22].

Phosphorous

The impact of lignite coal derrived humic acid shows that high phosphorous reserves was allocated in calcarious compared to non-calcarious soil and on application of humic acid the ligand adsorption competation for phosphorous increases in calcarious soil compared to non-calcarious soil but the dynamics remains non-significant. The high reduction in phosphorous concentration after application of humic acid is mainly due to efficiency of chelation and complexation which inverts from treatement level, growing media and its origin (Vaughan and Linehan, 2004)^[61].

Potassium

Humic acid stimulates the retension and release of potassium in soil either by dissolving potassium bearing minerals or unblocking interlayer to release potassium and then absorbing. The rate and fate of the potassium dynamics have proportional similar resemblence as with the other organic matter (Andrews, 2021)^[4].

Secondary and micronutrients

AB-DTPA extractable cationic micronutrient as well as secondary nutrient increases due to chelation and complexation produced by weak acid base pair exceept copper whose concentration decreases with unknown reason.

Effect of humic acid on the biological properties of the soil

Biologically, humic acid conceives a significant changes for the microbeal diversity and enzymes produced by microbes which actually takes part in the metabolism of soil-humic acid-organic matter consortium, soil - humic acid - plant consortium. The results of long term experiment for several crop revealed that soil urease, phosphates, sucrase significantly increases after the application of humic acid. It is due to the fact that humic acid rich in organic matter which improves physico-chemical as well as biological properties thereby increase enzymetic activity too (Li et al., 2019)^[35]. However, many studies revealed the decrease in urease activity due to formation of complex with humic acid. Changes in the aerobic population size compared to total bacterial population size showed that the numbers were higher in Urea treatment than in Urea + HA (slow release of ammonia). It is because of the sudden increase in NH₄⁺ and quick accumulation of nitrates could enhance nitrifiers and other active group growth, which might change the total community (Li et al., 2019 and Dong et al., 2009)^[35, 23].

Microbeal community has also been found to increase. More precisely, the number and type of the bacterial colony decreases while fungui colony increases in the continuous cropping system because humic acids are organically rich materials which makes the acidic pH of soil. Lowered pH favours the growth of fungui (Li *et al.*, 2019)^[35].

Conclusion

Humic acids acts as an boon in organic coridor which surplus the fertility status at the cost of environmental pollution. The following are the bullets conclusion which are drawn from the above manuscript why the humic acid shouldn't be used:-

- Lignite coal derived Humic acid contains high percentage of hydrocarbons (esp. aromatic) which chelate and complexates with the rarest heavy metals.
- Application of HA at low rate improved the stability of micro aggregates and at high rate improved macro aggregates.
- Addition of lignite HA buffered the change in microbial community composition, numbers, AOB population size and potential nitrification.
- Formation of metal bridges by HA between mineral surfaces & P decreased P sorption in non-calcareous soils.
- Humates enhance crop productivity by improving physical, chemical and biological properties of soil. Apart from these it too acts as growth stumulents.
- Effectiveness of humates is more under stress than normal soil.

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