Study of Complexation Behaviour of Lignite Extracted Humic Acid with Some Divalent Cations

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***Abstract*— In biogeochemical cycles, humic substances are natural electron shuttles in transforming nutrients and environmental pollutants. Humic acid complexes with macro and micronutrient metals are eco-friendly organo-mineral fertilisers. This study prepared and characterised lignite-extracted humic acid-metal (Fe, Mg, Zn) complexes. The proximate analysis exhibited the moisture, volatile matter, ash and fixed carbon contents of extracted humic acid of 02.61%, 17.31%, 57.18% and 22.90%, respectively. The percentage of metal ions in humic acid complexes ranges from 3.5-7.25%. The FTIR analysis of coal-extracted humic acids-metal complexes showed Zn, Mg and Fe ions complexed in a bidentate manner predominantly with the carboxylic acid moiety of humic acid. Thermal gravimetric analysis indicated a higher value of humic acid decomposition than their metal complexes. The thermal stability observed order is HA- Zn >HA-Fe>HA- Mg. The X-ray diffraction pattern pointed toward the noncrystalline nature of humic acid and their respective complexes due to having few intense and small diffuse peaks in the 2θ range from 0 to 80°. Hence, the humic acid-metals complexes increase the soil humic content and the availability of essential nutrients that enhance the loam's biotic action.**

Keywords*— *Characterisation, Humic Acid–Metal Complex, Synthesis, TGA, XRD Analysis

I. Introduction

Humic materials are the major significant fractions of the soil and are vital in developing soil fertility [1]. Humic matter is an organic substance spread in sediments, terrestrial land, and natural water [2]. Lakes, bog, soil, oxidised bituminous coal, weathered coal, peat, lignite, and vegetation/wildlife remains are the sources of humic acid [3]. In Pakistan's coal assets, 185.5 billion tons of coal assets are expected [4]. All categories of coal have humic acid (HA), but the most potent and readily useable form of HA is present in lignite [5]. Lignite has pulled in impressive consideration as its savings account for about 45% of worldwide coal assets [6],[7]. However, lignite's straight and extensive use is critically controlled due to its rich oxygen functional assemblies, higher moisture content and slight calorific value [8],[9].

The higher yield of HA is obtained through the hydrothermal method, a practical approach [10]. Humic acids (HA) are the divisions of humic materials that are insoluble in acidic solution, incompletely soluble in water, and dissolvable in alkaline media. Several functional groups are present in HAs, like carboxylic acid, phenolic, enolic, ether, and quinine [11]. Carboxylic and phenolic groups are most dominant in humic acid composition. Fertiliser proficiency is enhanced by using liquid or dry humic substances in soil. Also, it improves the take up of magnesium (Mg) and calcium (Ca) when plants are watered with fluid suspensions of humic acids [12]. Combining humic materials like HA from organic and mineral fertilisers, unique compounds may develop, significantly benefiting agriculture production [13].

Some of the chiefs frequently revealed features of humic materials in nature having the ability to form complexation with different metals. The formation of these complexes is all due to the presence of building blocks in the construction of humic substances like phenolic, carboxylic and ketonic groups that are necessary for reacting with metals [13]. Therefore, several reports have shown that organic complexes of humic substances containing metals may increase or decrease the amount of various minerals in plants grown in soil [14]. There are many valuable applications of complexes formed by binding humic acids (HAs) with metal cations, like the adsorption of toxic metals from soil and the accessibility of nutrients from soil to plants [11].

Humic acid and metal species interact electrostatically as the cationic species are transferred to their thermodynamically favoured sites within the structure [15]. It is commonly acknowledged that cations are different due to the various electronic configurations of metals by which they are formed [16]. Humic substance's fraction binding with metals, on the other hand, provides information about humic substances' structure and their fraction differences. The stability of the metal humic complex is affected by the type of metal ion, the concentration of solution and the molecular size of humic substance components [17].

Humic acids are imperative in the behaviour and providence of metal ion species in the natural environment. They can influence the movement of metals through groundwater and soil. Heavy metal pollutants' activity and bioavailability are influenced by the complex reactions of humic acid with heavy metals. The binding potential of humic acids with metals to form complexes makes them beneficial in numerous functions. Zn, Fe, Cu and Mn are all micronutrients and have many functions in higher plants. Organomineral fertilisation is the combination of organic matter (HA) and mineral matter, having more advantages to the availability of macro (Mg) and micro (Zn) nutrients [18].

Copper (Cu), iron (Fe), calcium (Ca), zinc (Zn), magnesium (Mg), potassium (K), sodium (Na), and several other elements are complexed with humic acids to reduce the appropriate shortage of elements in soil [19]. Magnesium (Mg) is needed in plants to work ATP in living cells and for chlorophyll synthesis [15]. The presence of zinc (Zn), a micronutrient in soil, is essential for the growth of plants. Soluble forms of Zn-HA complexes enable zinc's slow and

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steady release for plant utilisation [20]. The complexing ability of HA with iron (Fe) is very significant for phosphorus nutrition in plants [21].

The humic acid was extracted from lignite to synthesise zinc, magnesium and iron metals. FTIR, TGA, XRD and elemental analysis characterised these metal complexes.

II. Materials and Methods

All experiments were conducted in the chemistry laboratory, department of Chemistry, Government College University Faisalabad, Pakistan. The coal sample was collected from the Industrial Biotechnology Division, National Institute for Biotechnology & Genetic Engineering (NIBGE), Jhang Road, Faisalabad. Humic substances are extracted using the International Humic Substances Society (IHSS) method.

A. Synthesis of metal complexes

The complexes of metals (Zn, Fe and Mg) with the humic acid were synthesised. Put 0.1 gram of humic acid into 84 mL of distilled water. For the dissolution efficiency of the humic acid in the water added, 0.1 pullet of potassium hydroxide KOH was dropped in the beaker to make the humic acid soluble in the distilled water. After mixing potassium hydroxide, the humic acid dissolved in the distilled water, and then the pH of the solution was adjusted to 10.5. Then, a 0.2M standard solution of zinc, iron and magnesium was by using different salts such as zinc sulphate (ZnSO4), Ferrous ammonium sulfate [Fe(NH4)2(SO4)2] and magnesium sulphate (MgSO4.6H2O) respectively. After that, 10 mL solutions for complexes were prepared by adding 0.56g of zinc sulphate, 0.63 g of iron sulphate and 0.45g of magnesium sulphate. The former solution was heated using the hot plate at 30̊ to 40˚ for 30 minutes. After heating the first solution for 30 minutes, the zinc, iron and magnesium solution was mixed with the first solution and then shaken well using a magnetic stirrer for 30 minutes. After that, the answer has remained at rest for 24 hours. Precipitates were observed after 24 hours. The precipitates were separated from the solution mixture by filtering the filter paper technique. Finally, the precipitates were washed through distilled water, put into a petri dish and dried. After drying, the metal complex depositions were used for further analysis.

B. Analytical Characterization

Ultraviolet and visible spectroscopic measurements of HA were made between 200 to 800 nm using a Birchrom Libra 522 spectrophotometer using a quartz cell (1cm x 1cm) at 20 OC. Elemental analysis is often used to find the nature and origin of humic substances. Elemental analysis was carried out to find the percentage of carbon, hydrogen, oxygen and sulphur content of the different coal samples by using Elemental Analyzer model EVR (Euro-EA Elemental Analyzer) in an oxygen environment (15ml) at purging rate (80ml/min) and temperature is 100 0C. The Fourier Transform Infrared (FTIR) Spectroscopy of coal-extracted humic aid and its metal complexes were recorded on a Happ-Genzel FTIR spectroscopic instrument according to the method using Potassium bromide pellets and sodium hydroxide. Thermogravimetric analysis (TGA) of humic and its complexes was performed to determine the combustion capacity from ambient to high temperature (600-950 °C) by furnace (ADD). X-ray diffractometry measurements of humic acid and its complexes raised bog were performed with the powder diffraction technique using nickel-filtered copper radiation CuKα (λ = 1.5017 À). Interplanar distance (d) was calculated using the Bragg's equation: $\lambda = 2d\sin\theta$

III. Results and Discussion

A. UV-Vis analysis of the extracted humic acids

Ultraviolet and visible spectroscopic measurements of the humic acids were made between 200 to 800 nm. E4/E6 value is the ratio of optical densities at specific wavelengths of 450 and 650 nm used to conclude the degree of aromatisation with normal Mw, size, and the O2 contents in HS [22]. The E4/E6 ratio is inverse to the degree of condensation, aromaticity, and humification of humic substances [23]. See Table I.

TABLE I. Effect of co-solvent on yield of humic acids and their spectroscopic properties

Coal sample	Solvent	E_4/E_6	**Δ**log K
LS-93	KOH	2.35	0.601

B. Elemental analysis

Rendering to the foundation of organic material and place of development, the elemental configuration of humic constituents and their assets may fluctuate. The primary investigation is significant; meanwhile, it delivers knowledge about the overall conformation of the particle, even though defining the humic acid molecular formula epitomises a task. Table II shows the elemental composition and atomic ratios of humic acid isolated from the sample. The presence of carbon content is lower as compared to the oxygen content. It is observed that the higher proportions of H/C and O/C and lower ratio N/C. The composition of humic acid having a lower content of aliphatic means that there is a significant content of aromatic groups, which indicates the larger phenolic and carboxylic groups. These phenolic and carboxylic groups are the cause of the formation of complexes.

TABLE II. Elemental composition and atomic ratios of humic acid isolated from sample

Elements (%)		**Atomic Ratio**	
C	40.50	H/C	1.65
H	5.25	N/C	0.13
N	7.23	O/C	0.81
O	45.35		

C. Vibrational assignments of FTIR

Fourier transform infrared spectroscopy (FTIR) is very applicable for studies of metals and humic acid interactions, reveals imperative features of divalent positive ions complexation, and offers limitations concerning the organisational description. It is also effective for identifying the functional group's presence. Complexes with primary vibrational assignments

Because humic substances establish numerous known binding sites such as amine (-NH), hydroxyl (-OH), carboxyl (-COOH), and metal ions of various metals (heavy metals) have revealed strong attractions [24]. Carboxyl, hydroxyl groups, aromatic, and alcoholic hydroxyl have been considered the main functional groups observed in HA (the central portion of humic substances) [25]. We also concentrated on the most interesting FTIR bands of such major groups that could play a key role in binding ions. Table III shows the vibration peaks of FTIR analysis of HA and HA-metal complexes.

TABLE III. VIBRATION PEAKS OF FTIR ANALYSIS OF HA AND HA-METAL COMPLEXES

Bond stretching	Wave number (cm^{-1})
C-H	2950 – 2850
O-H	3540 – 3035
C-O	1200 -1215
C=O	1650 – 1550
C=C	1678 – 1688
COOH	1760-1690
Zn	500
Fe	490
Mg	480

Fig. 1 shows the FTIR of the HA only. The FTIR of the HA-Zn complexes prepared using the ion-exchange method is shown in Fig. 2. Around 1583 cm-1 and 1384 cm-1, the two intensive bands can be identified. Symmetric (COO-) and antisymmetric (COO-) stretching vibrations, respectively. Carboxylate groups can be attributed to these absorptions, suggesting that the HA-Zn complex of humic substances is formed predominantly by metal-carboxylate bonds. Classifying the involvement of other functional groups (such as diketone groups and phenolic hydroxyls, etc.) in metal complexing based on FTIR analysis would be challenging.

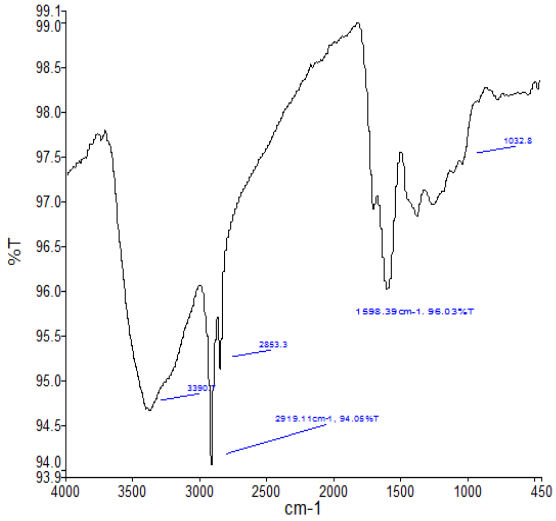

Fig. 1. FTIR spectra of HA

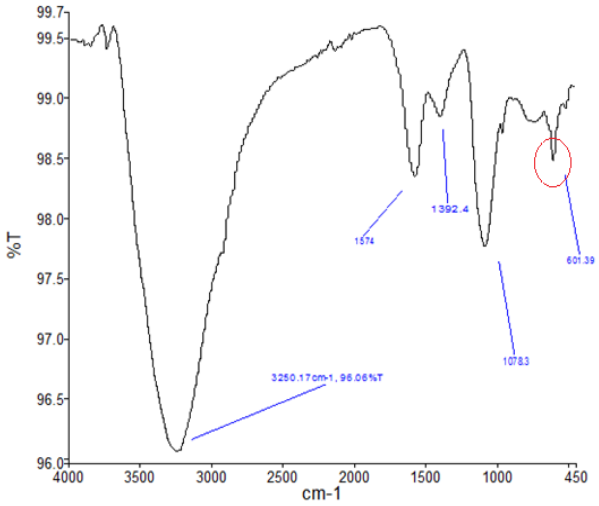

Fig. 2. FTIR spectra of HA-Zn

The approximate difference between the antisymmetric (COO-) and symmetric (COO-) carboxylate stretching frequencies of zinc (200 cm-1) was proposed, suggesting that the metal-oxygen bonds throughout the zinc bonds are much more covalent. Fig. 2 indicates that the value was (199 cm-1) between all these bands, thereby confirming the active formation of the HA-Zn complex. The most significant aspect of the FTIR spectrum of HA substances was a peak approximately at 1700 cm-1 due to C=O stretching [26].

Furthermore, to form a metal ion complex, the interaction between both the metal cation and carboxylic groups results in the disappearing of absorption peaks at 1700 cm-1 - 1720 cm-1 and the emergence of new bands at around 1583 cm-1 and 1384 cm-1 allocated to COO- and its stretching respectively. The absence of this group also means that most COOH groups have been converted into the COO type. In contrast to the (COO-stretching), the band near about 1617 cm-1 of pure HA, along with the change to lower frequencies, which also confirms the formation of HA-Zn and the band at about 1583 cm-1 (COO-stretching) turns out to be ever more intense for HA-Zn complexes [27].

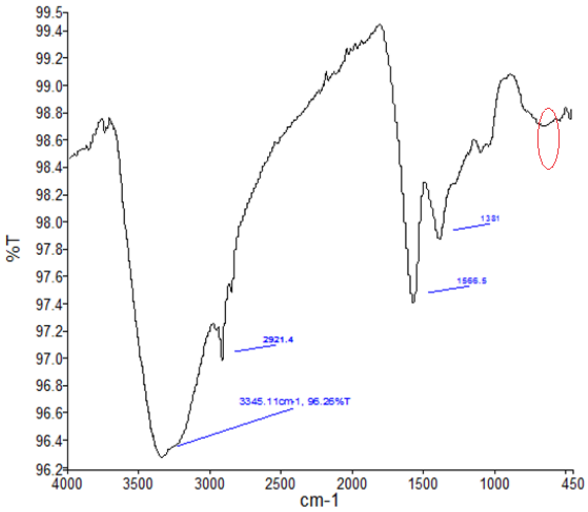

Fig. 3. FTIR spectra of HA-Mg

The FTIR spectra of the HA-Mg complex are shown in Fig. 3. The peaks of the symmetric (COO-) and antisymmetric (COO-) stretching vibrations were identified after the analysis of HA. These carboxylate groups can be familiar to absorptions around 1566 cm-1 and 1381 cm-1, suggesting that the HA-Mg complex of humic substances is formed mainly by metal-carboxylate bonds. Furthermore, the peaks of FTIR obtained 1566 cm-1 and 1381 cm-1 with the disappearance of the absorption band at the range of 1700 cm-1 - 1720 cm-1 of metal ion-complex, Which was due to the interaction between both the metal cation (Mg2+) and carboxylic groups. The absence of this group also means that most COOH groups have been transformed into the COO type. In comparison to the (COO-stretching) band near 1617 cm-1 of pure HA along with the change to lower frequencies, which also confirms the formation of HA-Mg, we obtained the band at 1566 cm-1 (COO-stretching) becomes ever more intense for the HA-Mg complexes.

Iron ions (Fe2+) had a more significant effect on the blocking sites. According to the pure HA, there were intense peaks in the 3000 cm-1 to 2700 cm-1 range. After forming the HA-Fe complex, these extreme peaks disappeared and obtained peaks in 1566 cm-1 and 1381 cm-1, which indicates the deformation of H stretching. Furthermore, the below 1000

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cm-1 band indicates the presence of nitrogenous ring structures in the complex due to the pyrimidine and purine of HA. It also provided a binding site for the metal ion with HA. The FTIR spectra of the HA-Fe complexes are shown in Fig. 4. The analysis of the FTIR identified the peaks of the stretching of carboxylic groups. Absorptions of about 1566 cm-1 and 1381 cm-1 can be standard in these classes of carboxylate groups, representing that the HA-Fe complex of humic substances is formed primarily by bonds of metal-carboxylate.

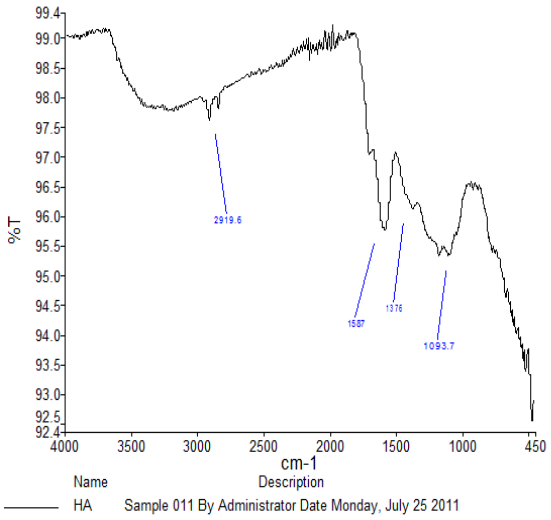

Fig. 4. FTIR spectra of HA-Fe

D. Thermo gravimetric analysis

Humic acid showed mass loss graphs as a function of the temperature at two significant peaks: the first at a lower temperature approximately 280 °C), as well as the second at a temperature above 400 °C. Eliminating water contents happened up to 200 °C accompanied by eliminating main functional groups present in the sample between 250 to 280 °C.

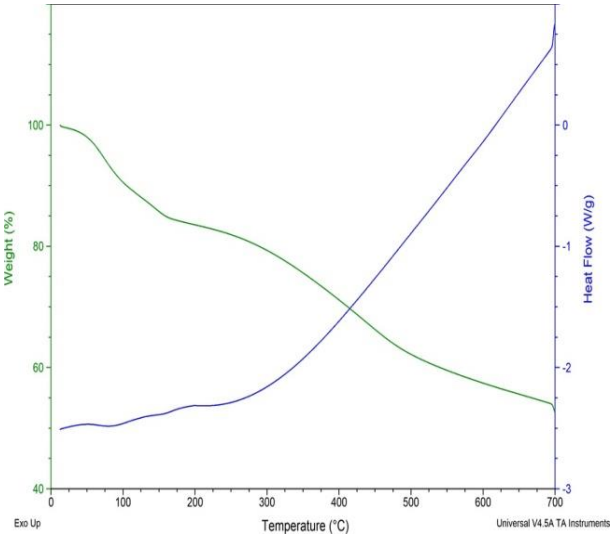

Fig. 5. Thermogravimetric curves of HA

The mass loss at lower temperatures happens because metal ions interrupt the bond linkage between the humic substances and the individual components, which spreads the individuals, so it becomes reactive with heat and dissociates its structure. The decomposition of carbohydrates in the HA and the mass loss of the main functional groups as methyl, carboxylic, alcoholic groups and methylene happened near about 300°C. See Fig. 5 for the thermogravimetric curves of HA.

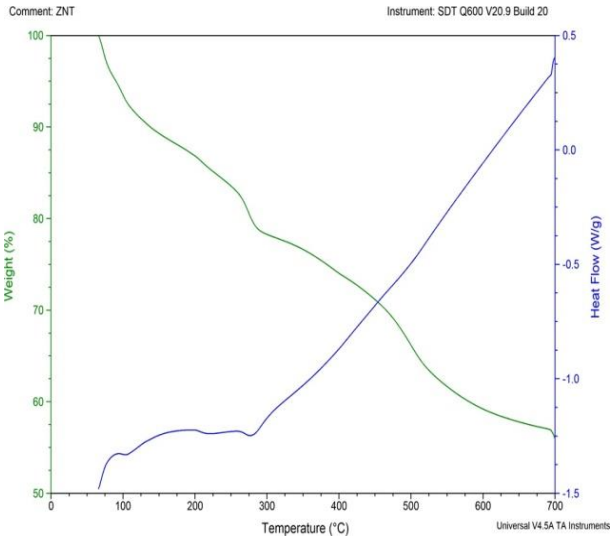

Fig. 6. Thermogravimetric curves of (HA-Zn)

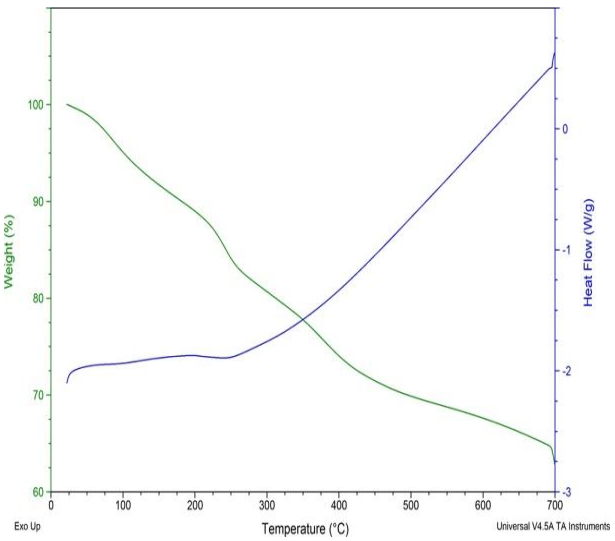

Fig. 7. Thermogravimetric curve of (HA-Fe)

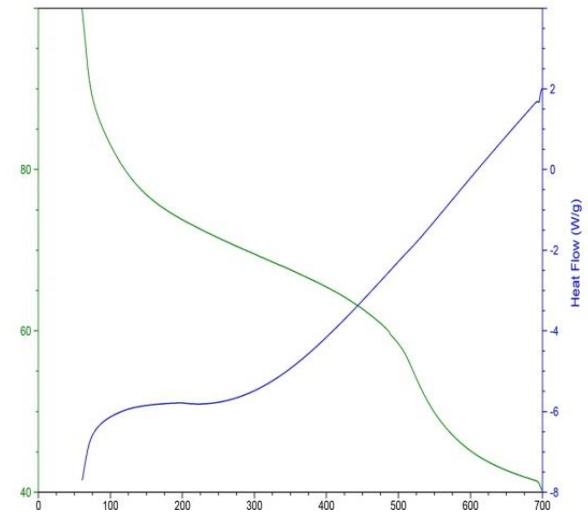

Fig. 8. Thermogravimetric curve of (HA-Mg)

The other results are shown in Fig. 6, Fig. 7 and Fig. 8 for further analysis. After the thermal analysis, it is indicated that the HA has a higher value of the decomposition affinity concerning the temperature compared to the complexes HA-Zn, HA-Fe and HA-Mg. However, the entropic contribution of the HA-Metal complexes is smaller than according to the HA; hence, the metal ions increase the thermal stability of the Humic products in the light of the above figures. It is also observed that decreases of large entropy in the process of degradation of humic acid, which combines with metal ions.

The maximum weight loss of the HA complex occurs in the 300–500 ºC range, indicating thermal degradation. Sharma & Dubey (2014) reported the thermal degradation of the complex in the air atmosphere; 2.50% weight lost at 105°C indicates the dehydration of the HA complex. The maximum weight loss of about 91.6 % between 330 ºC and 590 ºC means both homogeneous combustion of volatiles and heterogeneous combustion of fixed carbon. Compared N2 and Ar atmospheres with CO2 atmospheres could considerably promote the combustion reaction and burnout temperature (Guo-dong et al., 2016). Thermo gravimetric analysis of HA complex showed excellent weight loss in temperature ranges from 400°C to 700°C, and HA complex showed lower TG behaviour due to high content of inert materials such as ash and low volatile content. HA complex started losing moisture from 30–170°C (Dwivedi et al., 2019). Rathnam et al. measured the reactivity of the Australian HA complex under simulated air (O2/N2) and oxy-fuel (O2/CO2) atmospheres using a TGA under non-isothermal conditions up to 1473 K.

E. The X-ray Diffraction analysis

In particular, broad bands between 3.5 Å (assigned to the more compact carbon network, i.e. aromatic structure) and 04.31 Å are found throughout the diffraction spectra of HA (attributed to the structure of aliphatic carbons). In Fig. 9, X-ray diffractograms of the HA and their corresponding complexes. The diffractograms give many other nuanced and well-developed peaks typical of crystalline structures.

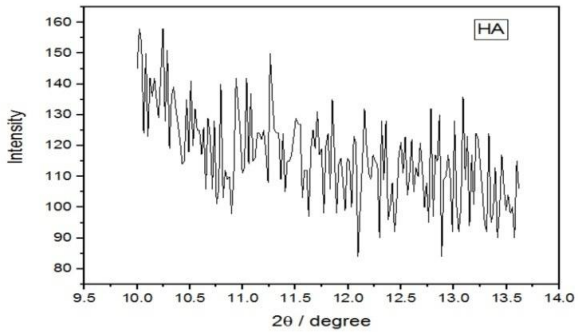

Fig. 9. XRD spectra of HA

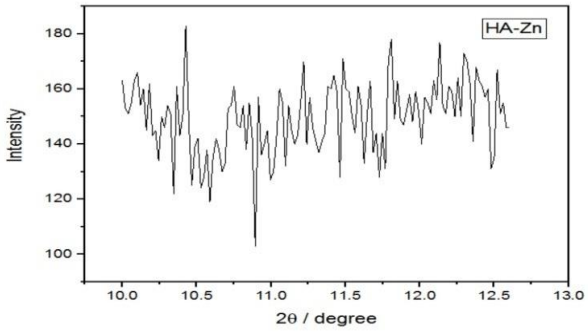

Fig. 10. XRD spectra of HA-Zn

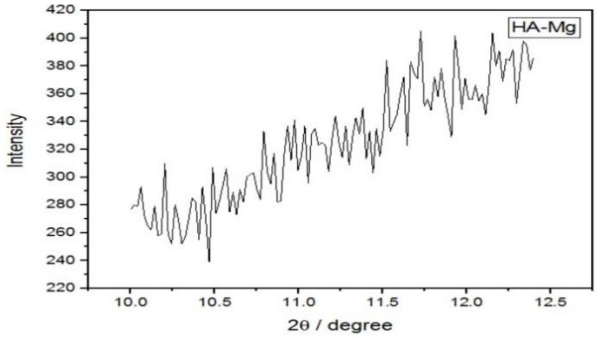

Fig. 11. XRD spectra of HA-Mg

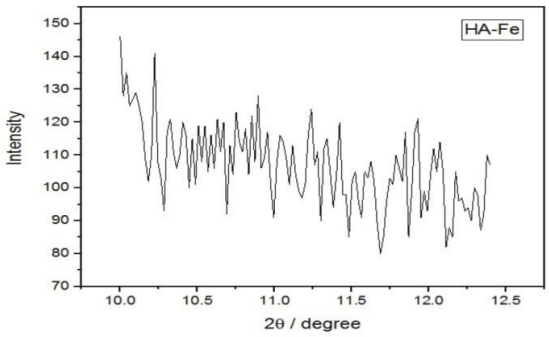

Fig. 12. XRD spectra of HA-Fe

Furthermore, because it is a macromolecule which may differ in composition and does not yet have a fully defined crystal lattice, experiments concerning the aromatic rings are recorded throughout the literature based on the percentage used for understanding. The patterns are referred to as the horizontal chains' aliphatic groups. In contrast, the other bands are attributed to the aromatic rings inside an order close to the graphite plan (002). This research was effectively used by [13]. Researchers who reinforced the effects of this kind of technique, whereby BG= band G (correlates to the second angle of 25.50 °, or 00.35 nm mostly in X-ray diffractograms); Bγ= band γ (correlates to either the second angle of 20.50 °, either 00.43 nm mostly in X-ray diffractograms); BG= peak area= high-level area of band G; Bγ= peak area = peak area of band γ. HA had identical aromatic carbon contents ratios, with HA having a 05.25 per cent higher disparity. Humification and aromaticity are relevant to the qualitative structure, including its functional groups and the structural reorganisation of certain substances, such as the changes that arise when the humic fraction is metal-complex. We emphasise that the peaks are not extreme for HA-Zn, HA-Fe and FA-Mg complexes (see Fig. 10, Fig. 11, and Fig. 12), which would have hindered the aromatic and aliphatic carbon measurement.

IV. Conclusion

The E4/E6 ratio is inverse to the degree of condensation, aromaticity, and humification of humic substances. The higher proportions of H/C and O/C and a lower ratio of N/C showed that a sizeable aromatic character is present. The complexes of humic substances are formed predominantly by metal-carboxylate bonds. The thermo-gravimetric resistance demonstrated by the HA compared with the gravimetric analysis showed continuous mass loss and little resistance compared to the study of FA. HA has a higher value of the decomposition affinity concerning the temperature compared to the complexes HA-Zn, HA-Fe and HA-Mg. The complexes of HA achieved more significant percentages for the band G and higher resistance to thermal degradation. The humic metal complexes may also used as nutrients for plants.

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REFERENCES

[1] Eshwar, M., Srilatha, M., Rekha, K. B. & Sharma, S. H. K. (2017). Characterisation of metal complexes with humic fractions by potentiometric titrations. International Journal of Communication Systems, 5(5): 1463-1466.

[2] Ghabbour, E. A., Shaker, M., El-Toukhy, A., Abid, I. M. & Davies, G. (2006). Thermodynamics of metal cation binding by a solid soil-derived humic acid: Binding of Fe (III), Pb (II), and Cu (II). Chemosphere, 63(3): 477-483.

[3] Manzak, A., Kurşun, C. & Yıldız, Y. (2017). Characterisation of humic acid extracted from aqueous solutions with polymer inclusion membranes. Journal of the Taiwan Institute of Chemical Engineers, 81: 14-20.

[4] Zara, M., Ahmad, Z., Akhtar, J., Shahzad, K., Sheikh, N. & Munir, S. (2017). Extraction and characterisation of humic acid from Pakistani lignite coals. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39(11): 1159-1166.

[5] Pehlivan, E. & Arslan, G. (2006). Uptake of metal ions on humic acids. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 28(12): 1099-1112.

[6] Zhang, Y. Y., Zong, Z. M., Sun, Y. B., Liu, F. J., Li, W. T., Wang, Y. N. & Wei, X. Y. (2018). Investigation on the structural feature of Shengli lignite. International Journal of Mining Science and Technology, 28(2): 335-342.

[7] Yuan, L., Zhang, N., Kan, J. G. & Wang, Y. (2018). The concept, model and reserve forecast of green coal resources in China. Journal of China University Mineral Technology, 47(1): 1-8.

[8] Wang, C., Xiao, Y., Li, Q., Deng, J. & Wang, K. (2018). Free radicals, apparent activation energy, and functional groups during low-temperature oxidation of Jurassic coal in Northern Shaanxi. International Journal of Mining Science and Technology, 28(3): 469-475.

[9] Xia, Y., Zhang, R., Xing, Y. & Gui, X. (2019). Improving the adsorption of the oily collector on the surface of low-rank coal during flotation using a cationic surfactant: An experimental and molecular dynamics simulation study. Fuel, 235: 687-695.

[10] Cheng, G., Niu, Z., Zhang, C., Zhang, X. & Li, X. (2019). Extraction of Humic Acid from Lignite by KOH-Hydrothermal Method. Applied Sciences, 9(7): 1356.

[11] de Melo, B. A. G., Motta, F. L. & Santana, M. H. A. (2016). Humic acids: Structural properties and multiple functionalities for novel technological developments. Materials Science and Engineering: C, 62: 967-974.

[12] Pettit, R. E. (2004). Organic matter, humus, humate, humic acid, fulvic acid and humin: their importance in soil fertility and plant health.Central Technological Institution Research, 43:1-17.

[13] Santos, A. M., Bertoli, A. C., Borges, A. C. C., Gomes, R. A., Garcia, J. S. & Trevisan, M. G. (2018). New organomineral complex from humic substances extracted from poultry wastes: synthesis, characterisation and controlled release study. Journal of the Brazilian Chemical Society, 29(1): 140-150.

[14] Garcia-Mina, J. M. (2006). Stability, solubility and maximum metal binding capacity in metal–humic complexes involving humic substances extracted from peat and organic compost. Organic Geochemistry, 37 (12): 1960-1972.

[15] Christl, I. & Kretzschmar, R. (2001). Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 1. Proton binding. Environmental Science & Technology, 35(12): 2505-2511.

[16] Baruah, M. K. & Upreti, M. C. (1994). Preferential uptake of Fe (III) by humic acid extracted from lignite. FuelChemistry, 73(2): 273-275.

[17] Ubner, M. (2004). Interaction of Humic Substances with metal cations, vol.4 ed. 2nd Tallinn University of Technology Press.

[18] Chassapis, K., Roulia, M., & Tsirigoti, D. (2009). Chemistry of metal–humic complexes contained in Megalopolis lignite and potential application in modern organomineral fertilisation. International Journal of Coal Geology, 78(4): 288-295.

[19] Nikbakht, A., Kafi, M., Babalar, M., Xia, Y. P., Luo, A. & Etemadi, N. A. (2008). Effect of humic acid on plant growth, nutrient uptake, and postharvest life of gerbera. Journal of Plant Nutrition, 31(12): 2155-2167.

[20] Boguta, P. & Sokołowska, Z. (2016). Interactions of Zn (II) ions with humic acids isolated from various types of soils. Effect of pH, Zn concentrations and humic acids chemical properties. Public Library of Science, 11(4): 123-155.

[21] Zanin, L., Tomasi, N., Cesco, S., Varanini, Z. & Pinton, R. (2019). Humic substances contribute to plant iron nutrition, acting as chelators and biostimulants. Frontiers in Plant Science, 10: 45-51.

[22] Huang, X., Wan, Y., Shi, B. & Shi, J. (2020). Effects of powdered activated carbon on the coagulation-flocculation process in humic acid and humic acid-kaolin water treatment. Chemosphere, 238: 124-637.

[23] Senesi, N., D'orazio, V. & Ricca, G. (2003). Humic acids in the first generation of euro soils. Geoderma, 116(3-4): 325-344.

[24] Yan, W. L. & Bai, R. (2005). Adsorption of lead and humic acid on chitosan hydrogel beads. Water Research, 39(4): 688-698.

[25] Hizal, J. & Apak, R. (2006). Modelling of copper (II) and lead (II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. Journal of Colloid and Interface Science, 295(1): 1-13.

[26] Zhu, H., Yin, J., Zhao, X., Wang, C. & Yang, X. (2015). Humic acid is a promising organic anode for lithium/sodium ion batteries. Chemical Communications, 51(79): 14708-14711.

[27] Dyab, A. K., Abdallah, E. M., Ahmed, S. A. & Rabee, M. M. (2016). Fabrication and characterisation of novel natural Lycopodium clavatum sporopollenin microcapsules loaded in situ with nano-magnetic humic acid-metal complexes. Journal of Encapsulation and Adsorption Sciences, 6(04): 109.