

Study of Complexation Behavior 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 the nutrients and environmental pollutants. The complexes of humic acid with macro and micro nutrient metals serve as ecofriendly organo-mineral fertilizer. In this study, lignite extracted humic acid-metal (Fe, Mg, Zn) complexes were prepared and characterized. 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 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 bidentate manner predominantly with carboxylic acid moiety of humic acid. Thermal gravimetric analysis indicated the higher value of humic acid decomposition as compared to their metal complexes. The thermal stability observed order is HA- Zn > HA-Fe > HA- Mg. The X-ray diffraction pattern pointed toward the non-crystalline nature of humic acid and their respective complex's due to having few intense and some small diffuse peaks in the 2θ range from 0 to 80° . Hence the humic acid-metals complexes increase the soil humic content along the availability of essential nutrient that enhance the loam biotic action.

1. Introduction

Humic materials are the major significant fractions of the soil and they play a vital part in developing soil fertility [1]. Humic matter is an organic substance that is spread in sediments, terrestrial land, and natural water [2,3]. Lakes, bog, soil, oxidized bituminous coal, weathered coal, peat, lignite, and vegetation / wildlife remains are the sources of humic acid [4]. The 185.5 billion ton of coal assets over all of coal areas are expected in Pakistan's coal assets [5]. All categories of the coal have humic acid (HA) but the most potent and readily useable form of HA is present in lignite [6]. Lignite has pulled in impressive consideration as its saves account for about 45% of worldwide coal assets [7,8]. However, the straight and extensive use of lignite is critically controlled due to its rich oxygen functional assemblies, higher moisture content and slight calorific value [9, 10].

The higher yield of HA is obtained through hydrothermal method which is an effective approach [11]. Humic acids (HA) are the divisions of humic materials that are insoluble in acidic solution, incompletely soluble in water, and dissolvable in alkaline media. There several functional groups are present in HAs like carboxylic acid, phenolic, enolic, ether, and quinine [12]. Carboxylic and phenolic groups are most dominant in humic acid composition [12]. Fertilizer proficiency is enhanced by the use of liquid or dry humic substances to soil and also improved the take up of magnesium (Mg) and calcium (Ca) when plants are watered with fluid suspensions of humic acids [13]. Combining the humic materials like HA which are resulting from organic and mineral fertilizers unique compounds may developed which would be significantly beneficial for agriculture production [14].

Some of the chief frequently revealed features of humic materials in the nature having the abilities of forming complexation with different metals [15]. The formation of these complexes is all about due to the presence of building blocks in construction of humic substances like phenolic,

carboxylic and ketonic groups that are necessary for reacting with metals [14]. Therefore, a number of reports have been studied the organic complexes of humic substances containing metals may increase or decrease the amount of various minerals by plants grown in soil [16]. There are many useful applications of complexes which are formed by the binding of humic acids (HAs) with metal cations like the adsorption of toxic metals from soil and the accessibility of nutrients from soil to plants [12].

Humic acid and metal species interact electrostatically as the cationic species are transferred to their thermodynamically favored sites within the structure [17]. It is commonly acknowledged that cations are of different nature due to various electronic configuration of metals by which they are formed [18]. Humic substances fraction binding with metals, on the other hand, provide information about humic substances structure and their fraction differences. The stability of metal humic complex is affected by type of metal ion, concentration of solution and molecular size of humic substances components [19].

Humic acids show an imperative part in the behavior and providence of metal ion species in natural environment. They can influence the movement of metals through ground water and soil [15, 20]. Heavy metal pollutants movement and bioavailability is influenced by the complexing reactions of humic acid with heavy metals [21]. 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 they have many functions in higher plants [22]. Organo-mineral fertilization is the combination of organic matter (HA) and mineral matter having more advantages in order to availability of macro (Mg), and micro (Zn) nutrients [23].

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 appropriate shortage of elements in soil [24]. In plants magnesium (Mg) is needed for the working of ATP in living cells and also for chlorophyll synthesis [25]. The presence of zinc (Zn), a micronutrient in soil is essential for the growth of plants. The slow and steady release of zinc for plant utilization is enabled by soluble forms of Zn-HA complexes [26]. Complexing ability of HA with iron (Fe) is very significant for phosphorus nutrition to plants [27].

The compact contact of humic materials with metals concludes in the arrangement of a complex HSs-nutrients, in this way employing the accessibility and their transportation for the plants, which gives humic substances more attraction for agriculture fields [14]. The present research work was aimed to extract humic acid from lignite and formulation of metal complexes with zinc, magnesium and iron metals. These metal complexes were characterized by FTIR, TGA, XRD and elemental analysis.

2. Materials And Methods

All experiments were conducted in 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. The extraction of humic substances is carried out according to the method of the International Humic Substances Society (IHSS).

2.1 Synthesis of metal complexes

The complexes of metals (Zn, Fe and Mg) with the humic acid were synthesized. For that purpose, put 0.1 gram of humic acid was into 84 mL of distilled water. For the dissolution efficiency of the humic acid into the water added 0.1 the pullet of potassium hydroxide KOH was dropped in the beaker to make the humic acid soluble in the distilled water. After the mixing of potassium hydroxide, the humic acid dissolved in the distilled water and then the pH of the solution was adjusted to 10.5. Then prepared 0.2M standard solution of zinc, iron and magnesium by using the different salts such as, zinc sulphate (ZnSO_4), Ferrous ammonium sulfate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$] and magnesium sulphate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) respectively. After that 10 mL solutions for complexes were prepared by adding 0.56g zinc sulphate, 0.63 g of iron sulphate and 0.45g of magnesium sulphate. The former solution was heated by using the hot plate at 30° to 40° for 30 minutes. After heating the first solution for 30 minutes the solution of zinc, iron and magnesium was mixed with the first solution and then shacked well by using magnetic stirrer for 30 minutes. After that the solution was remained at rest for 24 hours. Precipitates were observed after 24 hours. The precipitates, were separated from the solution mixture via filtering the technique using filter paper. Finally, the precipitates were washed through distilled water, and put into petri dish and were dried. After drying the precipitates that were metal complexes were used for further analysis.

2.2 Analytical Characterization

Ultraviolet-visible spectroscopy

Ultraviolet and visible spectroscopic measurements of HA was made between 200 to 800 nm by using Birchrom Libra 522 spectrophotometer using quartz cell (1cm x 1cm) at 20 °C.

Elemental Analysis

Elemental analysis is often used to find 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 sample by using Elemental Analyzer model EVR (Euro-EA Elemental Analyzer) in oxygen environment (15ml) at purging rate (80ml/min) and temperature is 100 °C.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of coal extracted humic aid and its metal complexes were recorded on a Happ-Genzel FTIR spectroscopic instrument according to method of using Potassium bromide pellets and sodium hydroxide.

Thermogravemetric analysis

Thermogravimetric analysis (TGA) of humic and its complexes was performed for determining the combustion capacity from ambient to high temperature (600-950 °C) by furnace (ADD).

X-ray diffraction (XRD)

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 Å). Interplanar distance (d) was calculated using the Bragg’s equation

$\lambda = 2d\sin\theta$

3. Results And Discussion

3.1 UV-Vis analysis of the extracted humic acids

Ultraviolet and visible spectroscopic measurements of the humic acids were made among 200 to 800 nm. E₄/E₆ value is the ratio of optical densities at specific wavelength of 450 and 650 nm used to conclude the degree of aromatization with normal Mw, size along with the O₂ contents in HS [28]. The E₄/E₆ ratio has inverse relation with the degree of condensation, aromaticity, and degree of humification of humic substances [29].

Table 3.1: Effect of co-solvent on yield of humic acids and their spectroscopic properties

Coal sample	Solvent	E ₄ /E ₆	Δlog K
LS-93	KOH	2.35	0.601

3.2 Elemental analysis

Rendering to the foundation of organic material and place of development, the elemental configuration of humic constituents, in addition to their assets may fluctuate. The elemental investigation is significant meanwhile it delivers knowledge around the overall conformation of the particle, even though defining the humic acid molecular formula epitomizes a task. 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 lower content of aliphatic means that there is a large content of aromatic groups which indicated the larger phenolic and carboxylic groups. These phenolic and carboxylic groups are the cause of formation of complexes. If the aromatic rings and humification is reduced, then the concentration of metal complexed is improved for alpha and gamma compositions at both pH in comparison beta places complex formation rises by the improved portions of carboxylic assemblies. It was shown that with the decrease of humification in humic acids, then the solidity of complexes at alpha and beta places reduces [26].

Table 3.2: 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		

Table 3.3: Physical state, color and melting points of humic metal complexes

HA complexes	Physical state	Color	Melting point
HA-Zn	Crystalline solid	Black	181°C
HA-Fe	Crystalline solid	Black	184°C
HA-Mg	Crystalline solid	Black	173°C

3.3 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, as well as offering limitations concerning the organizational description and it is also effective for identifying the functional groups presence.

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

Complexes with main vibrational assignments

Owing to the fact that 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 [30]. Carboxyl, hydroxyl groups, aromatic, and alcoholic, hydroxyls have been considered to be the main functional groups observed in HA (the main portion of humic substances) for metal complexation [31, 32]. We also will concentrate on its most interesting FTIR bands of such major groups that could play a key role in binding ions.

The FTIR of the HA-Zn complexes prepared using the ion-exchange method is shown in Figure 2. Around 1583 cm^{-1} and 1384 cm^{-1} , the two intensive bands can be identified. Symmetric (COO^-) and antisymmetric (COO^-) stretching vibrations, respectively [33] Carboxylate groups, can be attributed to these absorptions, suggesting that the HA-Zn complex of humic substances is formed predominantly by metal-carboxylate bonds. It would be difficult to classify the involvement of other functional groups (such as diketone groups and phenolic hydroxyls etc.) in metal complexing on the basis of FTIR analysis.

The approximate difference between the antisymmetric (COO^-) and symmetric (COO^-) carboxylate stretching frequencies of zinc (200 cm^{-1}) was proposed, suggesting that perhaps the metal-oxygen bonds throughout the zinc bonds are much more covalent. Figure 4.2 suggests 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 stated to be the existence of a peak approximately at 1700 cm^{-1} due to $\text{C}=\text{O}$ stretching [34].

Furthermore, in order 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 the majority of 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) turn out to be ever more intense for HA-Zn complexes [33]. It was studied by the use of Fourier transform infrared spectroscopy that the humic acids which are highly mummified have a tendency of bidentate linking complexation. If the humic acids are less humified than in this situation zinc tended to cause bidentate linking chelation [26]. The recent work describes the formation and description of complexes between humic substances particularly humic acid and fulvic acid isolated from wastes of hens and the zinc, copper, and iron ions [14]. The soil solution was appraised and is affected by deliver of such metals in a buffer solution. It was found that complex formation occurs due to the presence of carboxylic and phenolic groups [14].

The FTIR spectra of HA-Mg complex are shown in Figure 4.2. The peaks of the symmetric (COO^-) and antisymmetric (COO^-) stretching vibrations were identified after the analysis of HA. These groups of carboxylate groups, can be familiar to absorptions around 1566 cm^{-1} and 1381 cm^{-1} this suggesting that the HA-Mg complex of humic substances is formed mostly by metal-carboxylate bonds. Furthermore, in

order to the peaks of FTIR obtained 1566 cm^{-1} and 1381 cm^{-1} with disappearing of the absorption band at range of 1700 cm^{-1} - 1720 cm^{-1} of metal ion-complex, that was due to the interaction between both the metal cation (Mg^{2+}) and carboxylic groups. The absence of this group also means that the majority of 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 ion (Fe^{2+}) had a greater effect of the blocking sites. According to the pure HA there were intense peaks in the range of 3000 cm^{-1} to 2700 cm^{-1} . After the formation of the HA-Fe complex, these intense peaks were disappearing and obtained peaks in the region of 1566 cm^{-1} and 1381 cm^{-1} . Which indicate the deformation of H stretching Furthermore the below 1000 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 Figure 4. The peaks of the stretching of carboxylic groups were identified by the analysis of the FTIR. 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. The similar peaks values change for Fe-HA complexation were noted in already investigation [35].

Table 3.4: Comparative shifting of FTIR peaks of functional groups in HA and HA-Metal complexes

Functional groups	HA	HA-Zn	HA-Fe	HA-Mg
O-H 3540 – 3035	3390 cm^{-1}	3250 cm^{-1}	3270 cm^{-1}	3345 cm^{-1}
C-H 2950 – 2850	2919 cm^{-1}	Nil	2925 cm^{-1}	2921 cm^{-1}
COOH 1760-1500	1600 cm^{-1}	1574 cm^{-1}	1570 cm^{-1}	1566 cm^{-1}

3.4 Thermo gravimetric analysis

Metal-humic complexes increase the stability of metals which frequently permitting the metals to persist in solution to be with ease accessible without influencing the uptake of plants. Interaction between humic acid and metals like Na, K, Mg, and Zn is investigated with special emphasis. Humic acid enriched with these elements is useful in organomineral fertilization. Organomineral fertilization is the combination of organic matter (HA) and mineral matter having more advantages in order to availability of macro (Mg), and micro (Zn) nutrients that are needed at initial phases of plant development [23].

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

The mass loss at lower temperature was happened because metal ions interrupt the bond linkage between the humic substances and the individual components, due to which spread the individuals so it become reactive with heat and dissociate its structure. The decomposition carbohydrates present in the HA and the mass loss of the main functional groups as methyl, carboxylic, alcoholic groups and methylene was happened near about 300°C.

After the thermal analysis it is indicated that the HA has higher the value of the decomposition affinity with respect to the temperature as compared to the complexes as HA-Zn, HA-Fe and HA-Mg. However, the entropic contribution of the HA-Metal complexes smaller than according for 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 amount of the entropy in the process of degradation of humic acid, which combine with metal ions.

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

3.5 The X-ray Diffraction analysis

In particular, broad bands between 3.5 Å (assigned to the more compact carbon network, i.e. aromatic structure) as 04.31 Å are found throughout the diffraction spectra of HA (attributed to the structure of aliphatic carbons). In Figures 4.9 X-ray diffractograms of the HA are shown, and also their corresponding complexes. Many other fine and well-developed peaks typical of the crystalline structures are given by the diffractograms.

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 on the basis of the percentage used for understanding. The patterns are referred to the horizontal chains' aliphatic groups, whereas the other bands are attributed to the aromatic rings inside an

order close to that of the graphite plan (002). This research was effectively used by [14]. Researchers who reinforced the effects of this kind of technique, whereby BG= band G (correlates to the 2nd angle of 25.50 °, or 00.35 nm mostly in X-ray diffractogram); Bγ= band γ (correlates to either the 2nd angle of 20.50 °, either 00.43 nm mostly in X-ray diffractogram); 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 percent higher disparity. The substance of humification as well as aromaticity, furthermore, is not only relevant to something like the qualitative structure including its functional groups, as well as to the structural reorganisation of certain substances, such as the changes that arise because when humic fraction is metal-complex. We emphasise that the given peaks aren't all that extreme and for HA-Zn, HA-Fe and FA-Mg complexes, which would have hindered the measurement of the aromatic as well as aliphatic carbon.

4. Conclusion

The E_4/E_6 ratio has inverse relation with the degree of condensation, aromaticity, and degree of humification of humic substances. The higher proportions of H/C and O/C and lower ratio N/C showed that large aromatic character is present. The complexes of humic substances are formed predominantly by metal-carboxylate bonds. The thermo- gravimetric resistance showed by the HA as compared with the gravimetric analysis showed that there is continuously mass loss happened and show little resistance as compared to the analysis of FA. HA has higher the value of the decomposition affinity with respect to the temperature as compared to the complexes as HA-Zn, HA-Fe and HA-Mg. the complexes of HA achieved the larger percentages for the band G and higher resistance to thermal degradation. The humic metal complexes may also use as nutrients for plants.

Declarations

Data availability

All the tables and figures are presented in the manuscript on the basis of the results was described.

Conflict of interest

There is no conflict of interest among the authors for publication of present research work.

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Figures

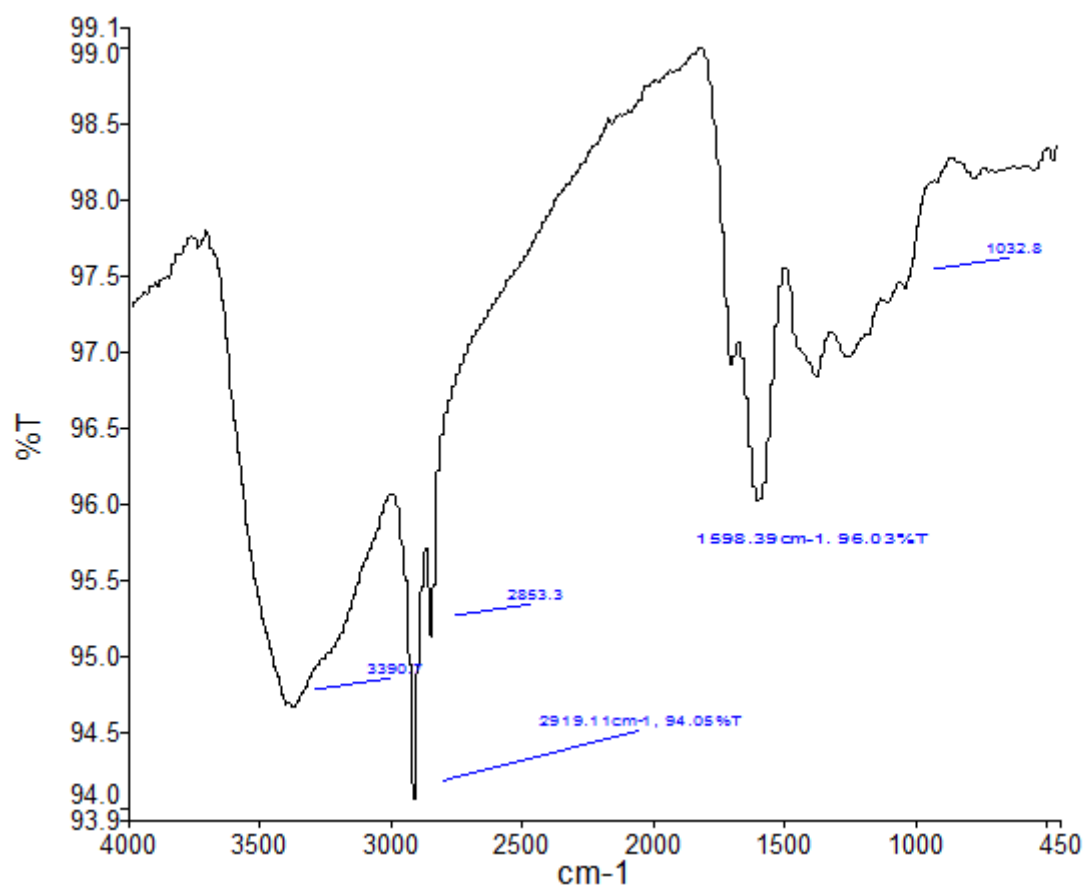


Figure 1

FTIR spectra of HA

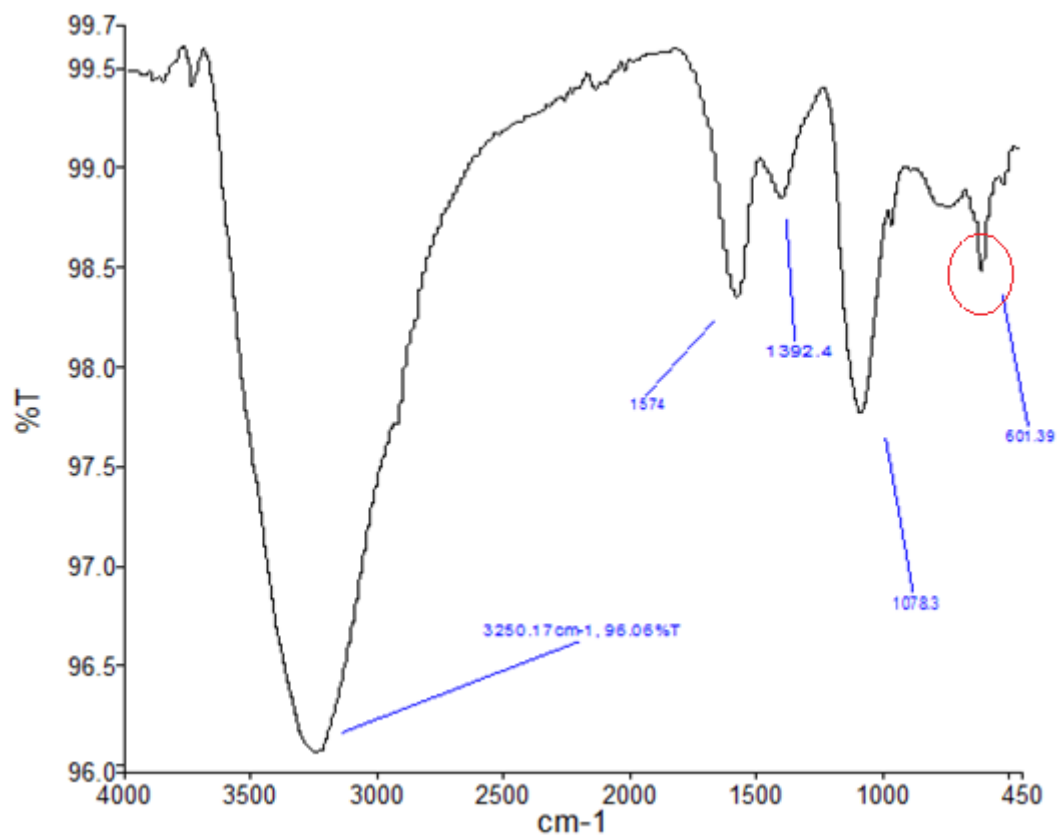


Figure 2

FTIR spectra of HA-Zn

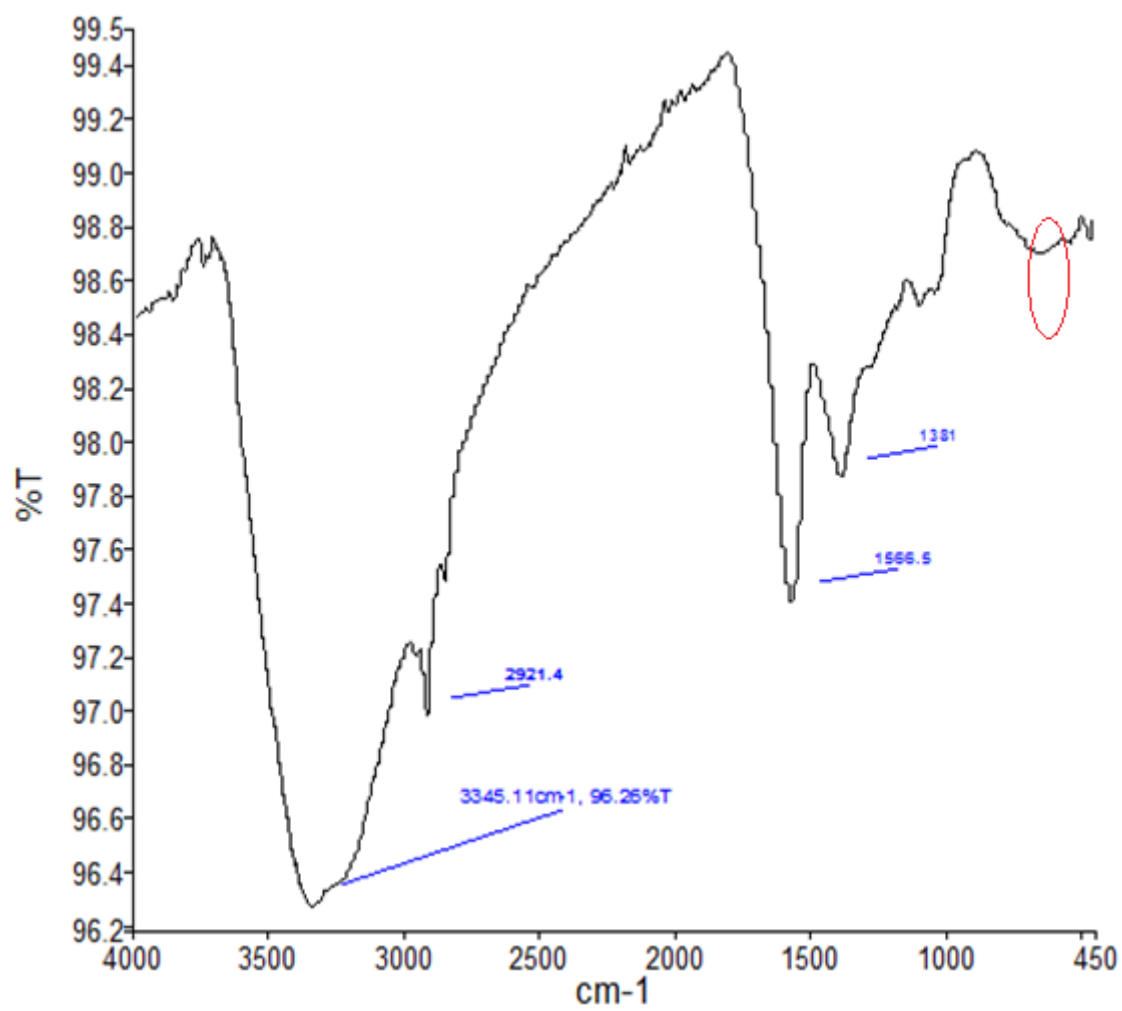


Figure 3

FTIR spectra of HA-Mg

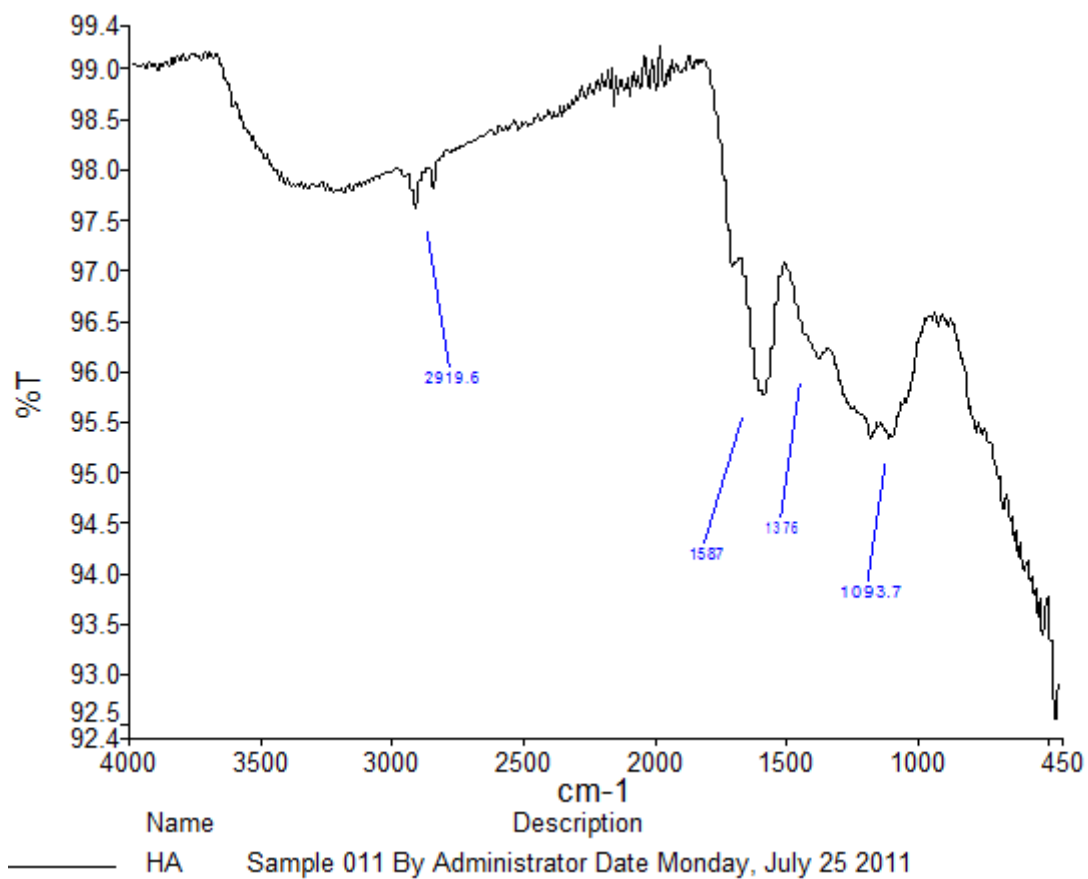


Figure 4

FTIR spectra of HA-Fe

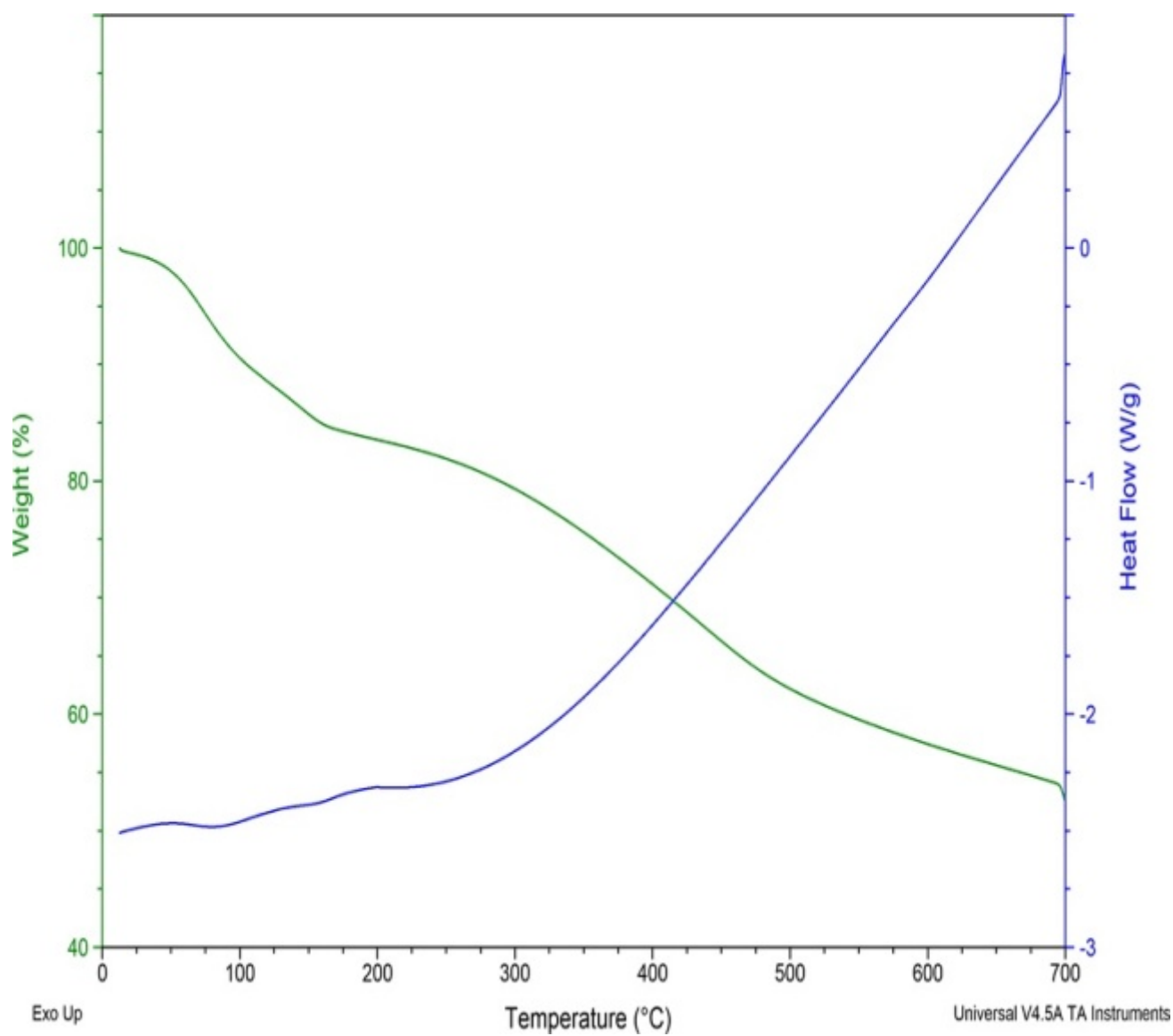
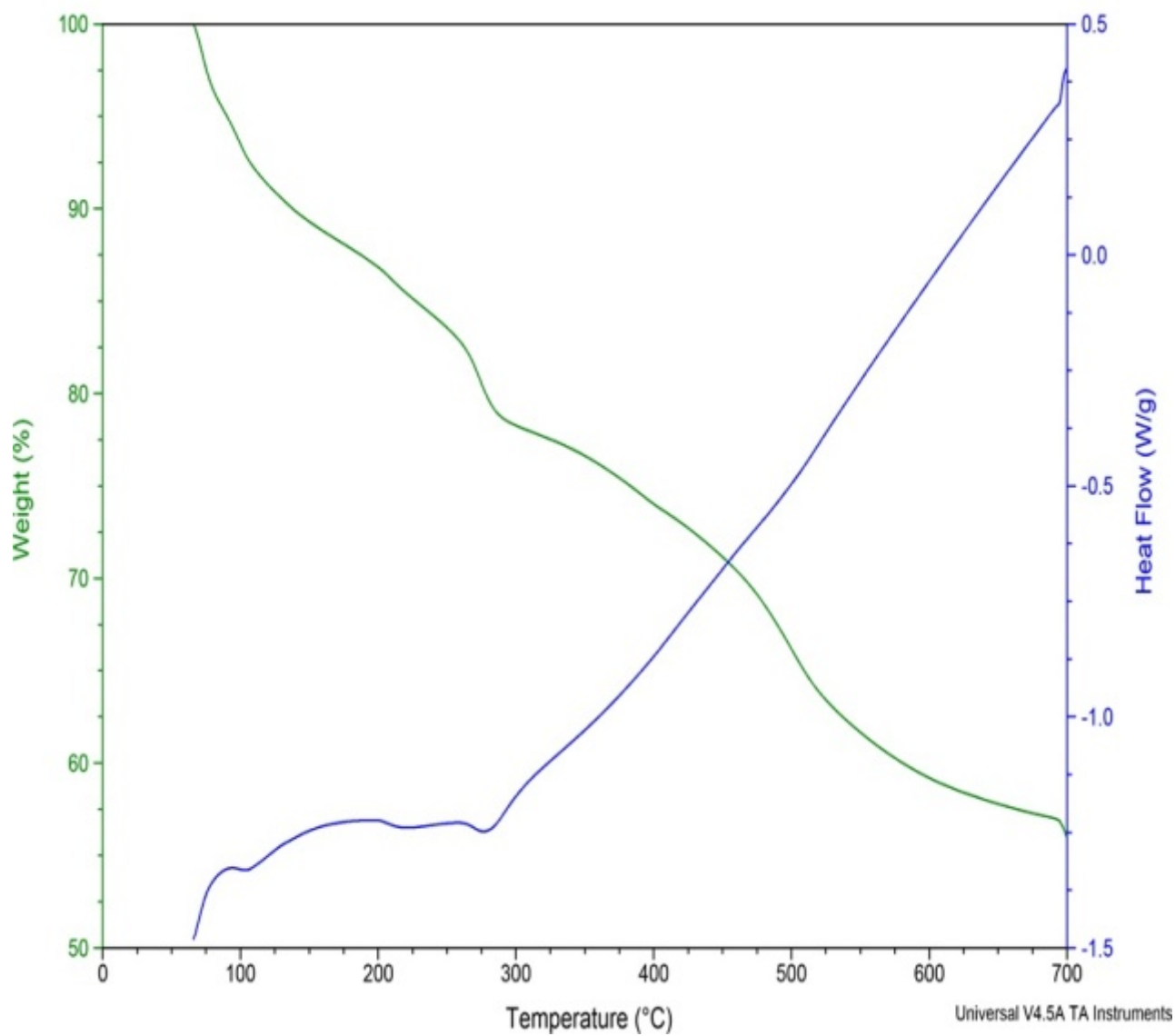


Figure 5

Thermogravimetric curves of HA

**Figure 6**

Thermogravimetric curves of (HA-Zn)

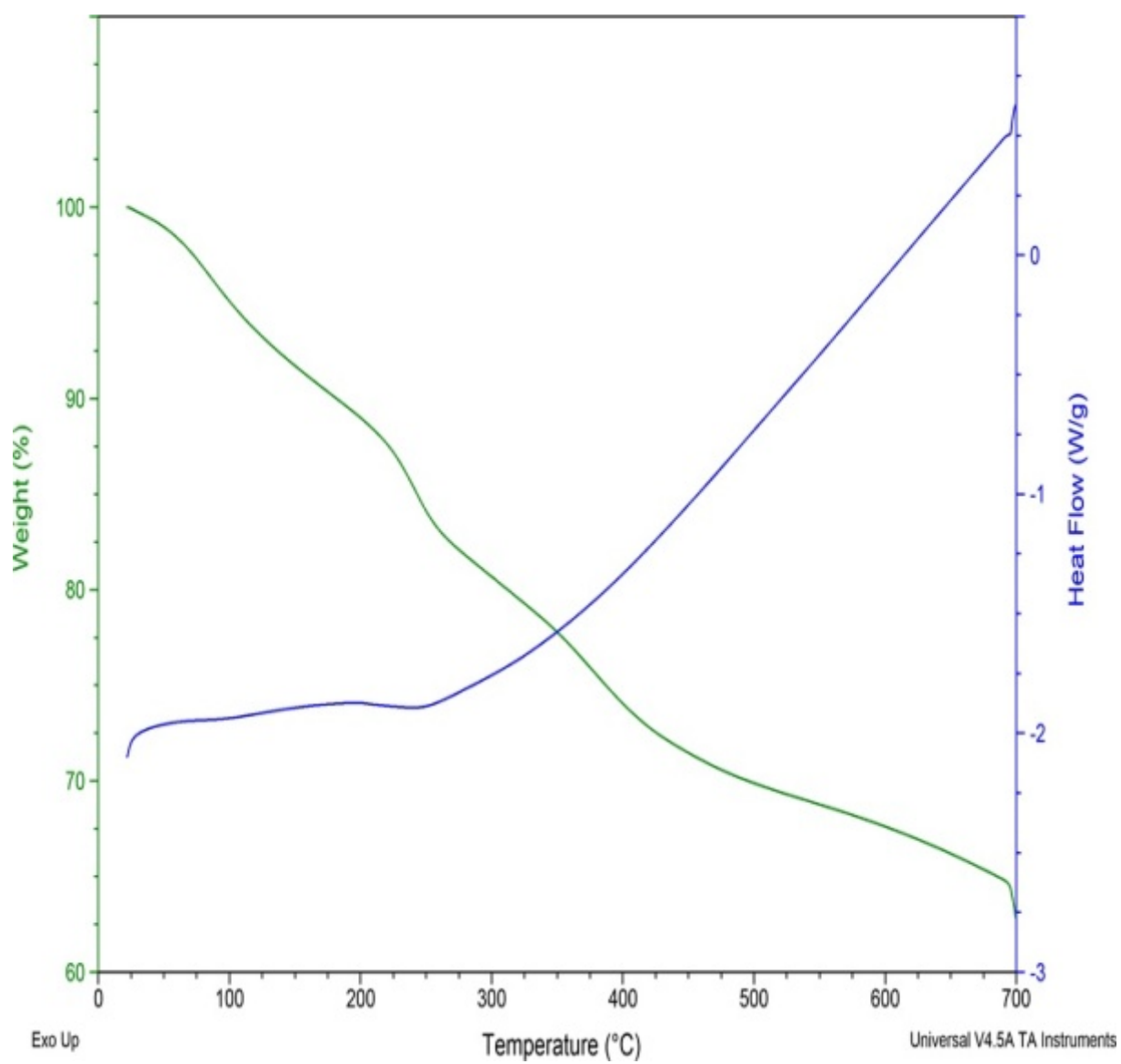


Figure 7

Thermogravimetric curve of (HA-Fe)

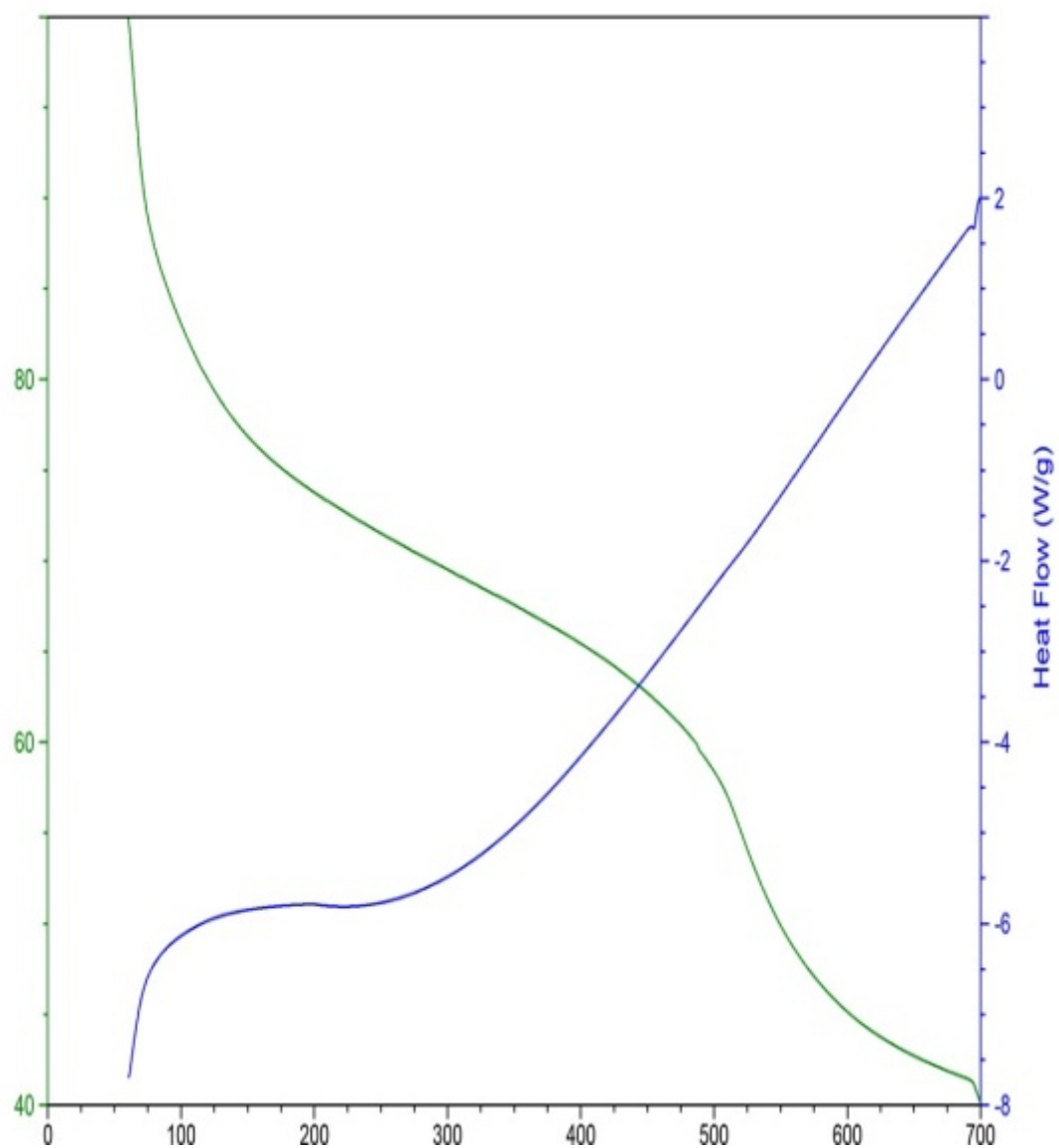


Figure 8

Thermogravimetric curve of (HA-Mg)

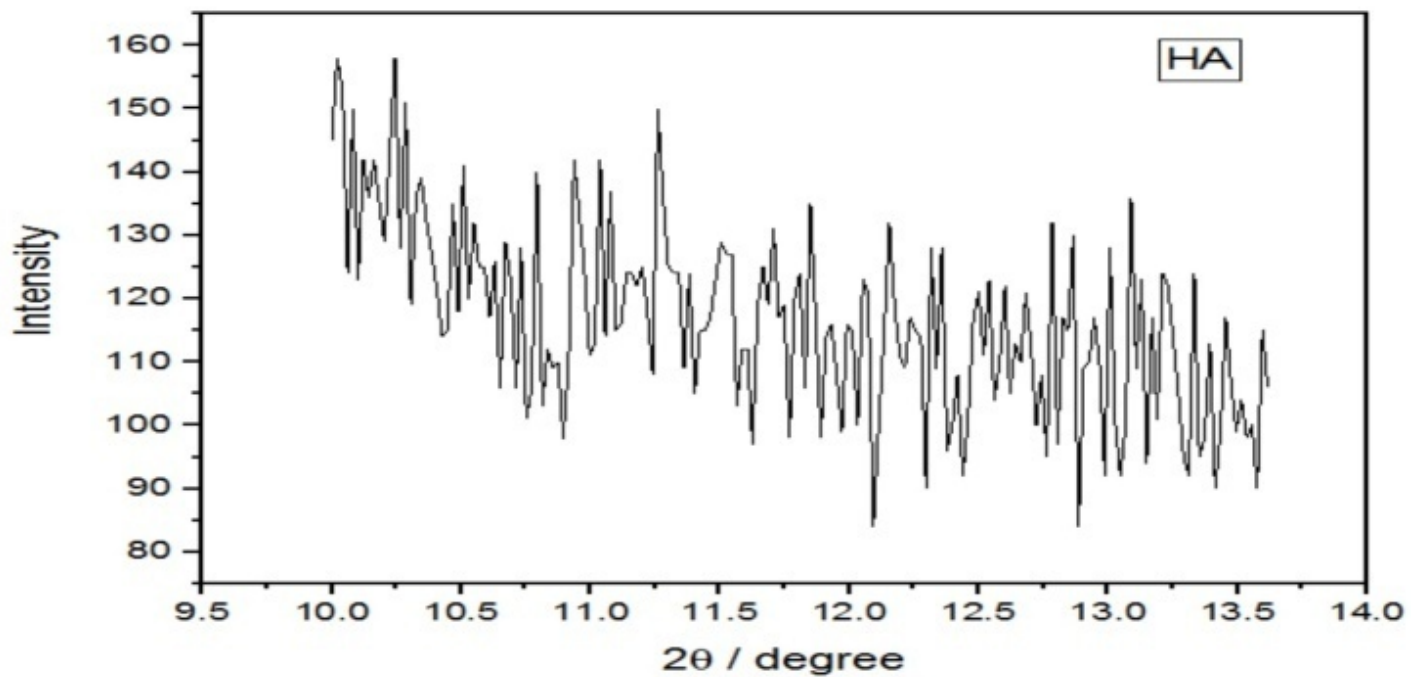


Figure 9

XRD spectra of HA

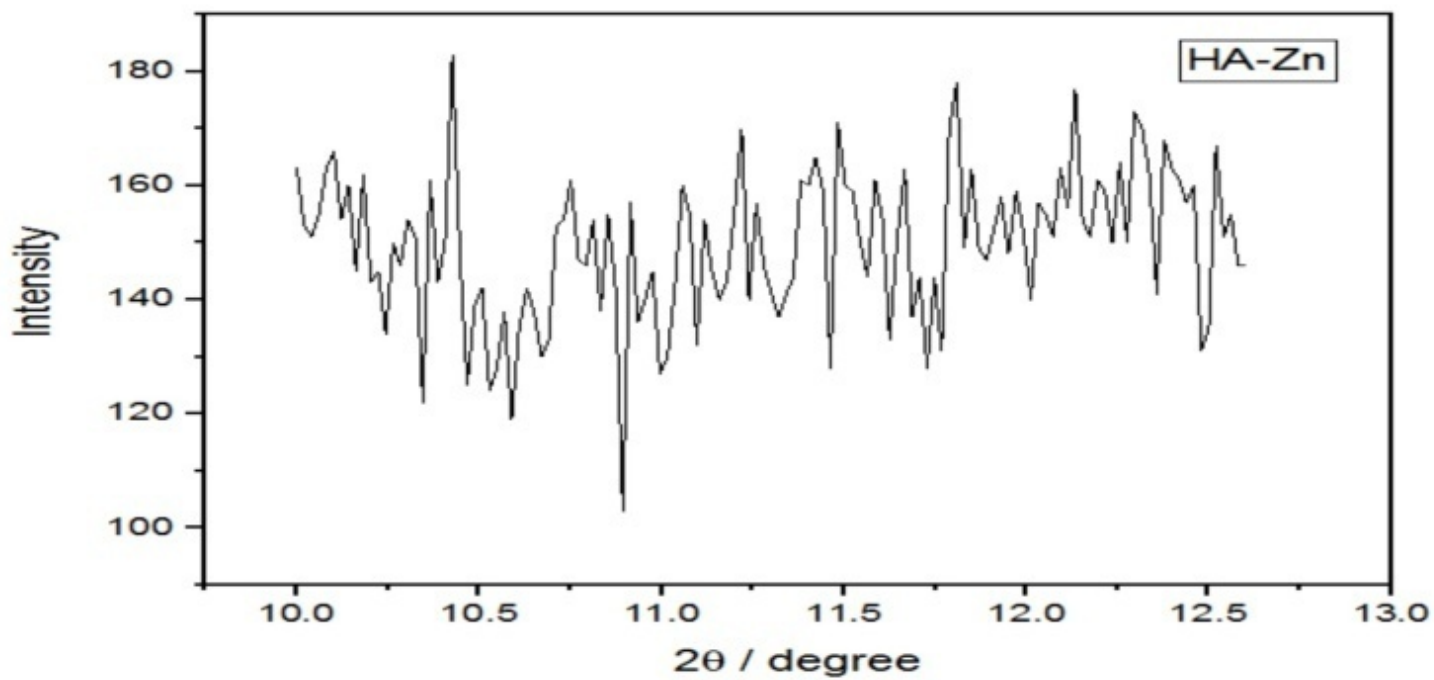


Figure 10

XRD spectra of HA-Zn

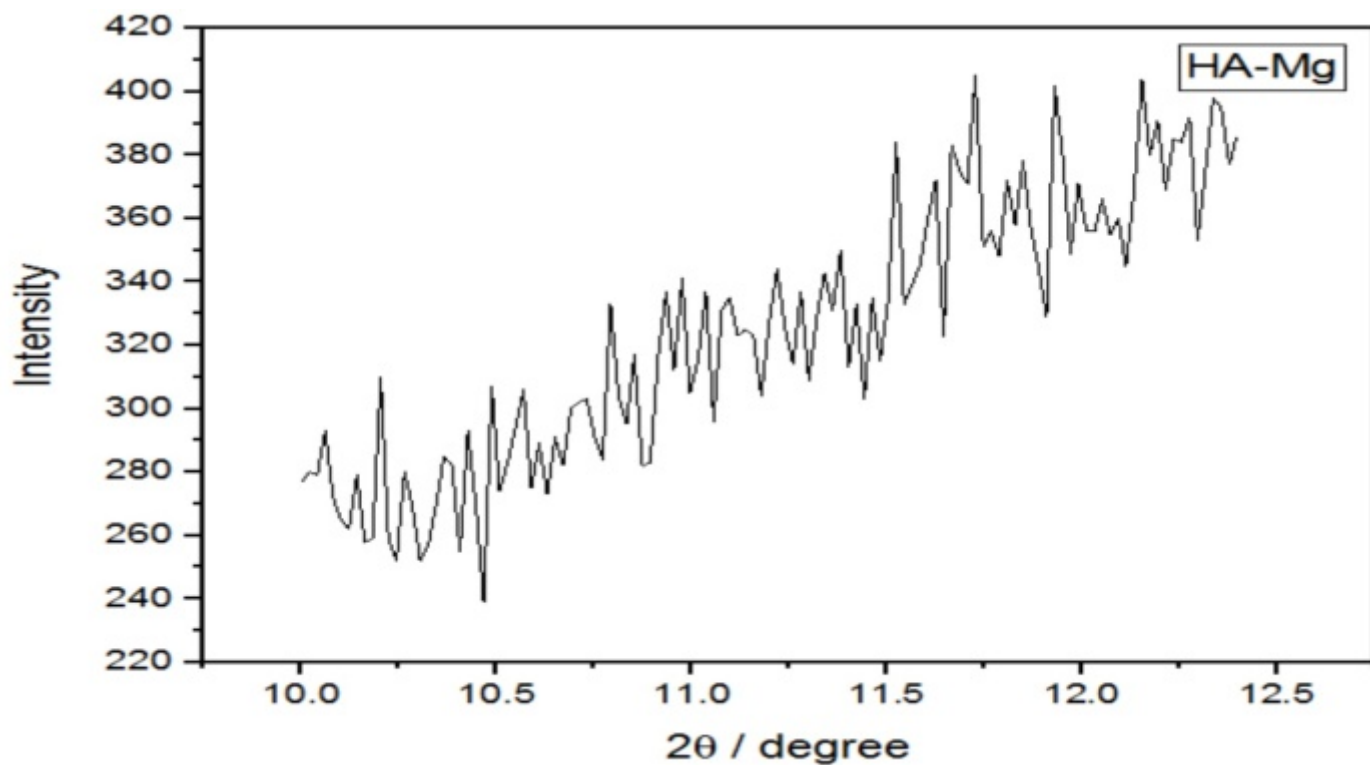


Figure 11

XRD spectra of HA-Mg

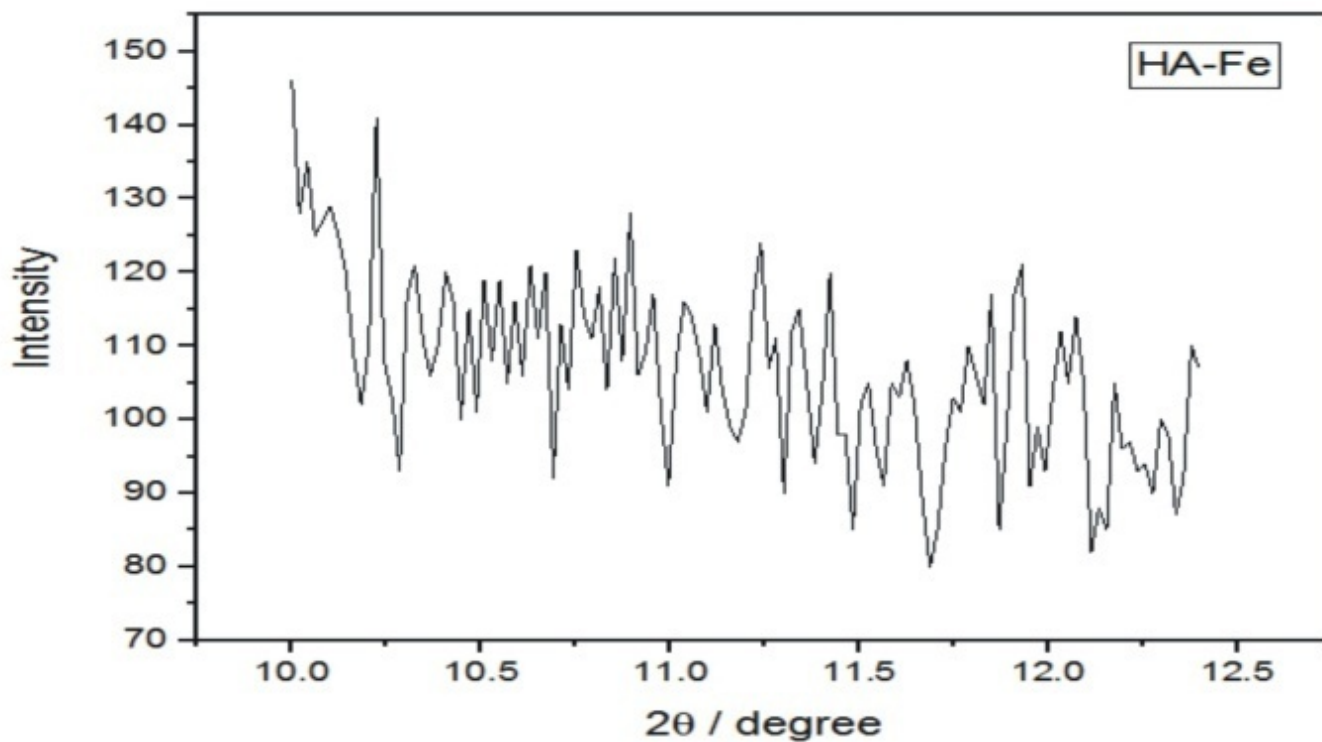


Figure 12

XRD spectra of HA-Fe