



CHARACTERIZATIONS OF SOME ORGANIC MATERIALS SOURCES AND ANALYSIS OF THE HUMIC ACIDS EXTRACTED FROM THEM

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ABSTRACT: Different organic materials such as town refuse, compost, sewage sludge and biogas have been used as sources of humic acids (HA). However, a systematic characterization of these organic materials and their comparison of humic acids which extracted from them have not been reported. This is essential to decide the relative merits and demerits of these substances as sources of humic acids. The objective of this work was to extract and characterize the chemical compositions of the different four organic materials and humic acids which extracted from them. Results showed that the four organic materials which used in this study were, generally, different in all studied properties. Sewage sludge sample recorded high values of moisture content, saturation percent, cation exchange capacity, organic carbon and organic matter content and lower values in each of bulk density, pH and EC as compared to other organic samples. Also, the highest value for each of total and available nitrogen (NH_4^+ and NO_3^-) was shown with sewage sludge and town refuse, respectively, while total and available phosphorus and potassium along with C/N ratio were recorded with compost sample. Furthermore, the four organic materials were different in total micronutrients and heavy metals. The highest value for each of Fe, Co and Ni was recorded with compost sample as well as similar results of Pb, Zn and Cu were observed with sewage sludge sample. Moreover, elementary composition of humic acids extracted from different samples was rich in carbon, nitrogen and oxygen and poor in sulfur except for sewage sludge sample. The C/N ratio was relatively high in HA extracted from biogas as well as HA from compost was superior in C/H, O/H, N+O/C and E4/E6 values. The lowest value of N/H was observed in HA extracted from biogas. On the other hand, obtained results reported that HA percentage was relatively high in biogas sample and the four organic materials can be arranged as following biogas > town refuse > compost > sewage sludge. Also, total acidity of humic acid samples reveals that, HA of sewage sludge was superior as compared to the other organic materials. The highest value for each of total carboxyl groups and carboxyl/phenol ratio was found with HA extracted from town refuse sample, whereas the greatest value of total phenolic groups was recorded with HA derived from sewage sludge. Furthermore, Infrared spectral (IR) analysis provides further useful information concerning the molecular structures and characteristic bonds and scanning electron microscopy (SEM) showed some crystal forms found in all HA samples. These results elucidated that the chemical composition and the molecular structure of HA samples varies as per the origin and environment where decomposition has occurred. Present study also documented that the spectroscopic and imaging techniques can be successfully used to bring out the finer differences among HA extracted from different organic sources.

Key words: Organic materials, town refuse, compost, sewage sludge and biogas, humic acids, infrared spectrophotometer IR, scanning electron microscopy SEM.

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INTRODUCTION

Organic materials must be characterized in order to predict and understand its behavior and chemistry. Numerous studies have been attempted to make out its structure and chemical composition; however, due to heterogeneity of samples, there is no definitive structure for organic matter although many structural models have been proposed (Meinelt *et al.*, 2004). Organic materials *i.e.*, town refuse, compost, sewage sludge and biogas have been used as sources of humic acids (HA). It is obligatory to know the chemical composition of each for further use as sources of humic acids. A humic substance is an end product of degraded materials that consists of transformed degradable compounds and dead microorganism tissues (Davies and Ghabbour, 1999). Recently, the extensions of sustainable agriculture and established organic farm have led to increasing applications of humic acids as source of organic fertilizer. Increase in the organic content of soils improves aeration, soil structure, increase the water holding capacity of the soil (Mangricha *et al.*, 2000).

Also, various studies about the characterization of HA extracted from different organic materials (town refuse, compost, sewage sludge and biogas) have been carried out. Most of the work reported is about the content of organic elements (C, O, N, H) and E4/E6 (degree of aromaticity) of HA from particular source. Few of them have also reported some inorganic elements such as S and P present in HA (Baddi *et al.*, 2003). On this background, an objective study was planned to characterize humic acids from various sources using chemical analysis. This included automatic analyzer, Fourier transforms infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

MATERIALS AND METHODS

The purpose of the present work was to evaluate some chemical properties of different organic materials along with extraction of humic acids from different sources. Chemical analyses of various humic acids sources were taken in consideration.

Organic Material Samples Collection

Four organic material samples were chosen for this work. Town refuses was collected from Al-Ghar station for assembling urban wastes,

Zagazig city and removes of any metals or harmful substances then cut and encircled to become compost. Compost was obtained from Al-Arabia factory for organic compost, El-Khattara, Sharkia Governorate, Egypt. Rice straw and animal residues were mixed and subject to suitable heat and moisture to complete the decomposition processes and to obtain mature compost with good qualities. Sewage sludge was collected from station of sewage effluents remediation, Zagazig City. Biogas manure was taken from Recycling of Agric. Residues Training Center Moshtohor, Qalyubia Governorate, Egypt. Biogas manure was manufactured by drying the anaerobic cow dung effluent. Fresh cow dung was fermented in a biogas digester at retention time of 45-50 days.

Organic Material Analyses

Four studied samples were analyzed for physical and chemical characteristics. The physical analyses included moisture content as described by (Page *et al.* 1982) and bulk density according to (Vomocil, 1965). Chemical analyses included pH and Electrical conductivity (EC) (Richards, 1954), cation exchange capacity (CEC) (Page *et al.*, 1982). Organic carbon (OC) and organic matter (OM) (Jackson, 1973). Total macronutrients (N, P and K), micronutrients (Fe, Mn, Zn and Cu) and heavy metals (Pb, Cd, Co and Ni) were digested and measured as described by (Page *et al.*, 1982). Available macronutrients (NH₄ and NO₃), P and K were measured according to (Cottenie *et al.*, 1982).

Extraction and Purification of Humic Acids

Humic substances from different organic materials were extracted by using 0.5N NaOH as described by (Schnitzer and Skinner, 1968). Dry organic materials (50g) and 500 ml of NaOH solution was shaken 120 rpm under N₂ gas atmosphere in sealed bottles for 24 hours, then centrifuged for 15 minutes at 6000 rpm and the supernatant was removed then pH was adjusted to 2.0 by addition of 2N HCL and left overnight. The resulting brown precipitate was separated from the liquid phase by centrifugation (1500 g, 30 min.), the precipitate was freeze-dried for storage (unpurified humic acids). To purified dry humic acids, (2g) was treated with 100 ml from 0.5% HCl-HF solution (5 ml HCl and 5 ml HF L⁻¹), three times at room temperature according to (Schnitzer and Khan, 1972 and 1978).

Characteristics of Extracted Humic Acids

Elemental analyses for carbon, hydrogen, nitrogen and sulfur contents of the purified humic acids were performed by Antomatic analyzer CHNS (Vario el 111 elementer). Oxygen was calculated by subtracting total amount of carbon (%), hydrogen (%), nitrogen (%) and sulfur (%) from 100 (Schnitzer, 1975). Total acidity of humic acids was determined according to method described by (Wright and Schnitzer, 1959). Carboxyl groups of humic acids were, also, determined by calcium acetate $\text{Ca}(\text{OAc})_2$ method according to Wright and Schnitzer (1959). Phenolic OH groups were determined in humic acids samples by subtracting COOH group's content from total acidity according to Kononova (1966). E_4/E_6 ratio in humic acid samples was measured by absorption at 465 and 665 nm according to Schnitzer and Khan (1978).

Infrared Spectrophotometer

An infrared spectrum (IR) of humic acids was performed with Beckman-IR 250 double beam grating spectrophotometer. Scanning was done from 500 to 4000 cm^{-1} . The dried sample was prepared for infrared spectra using KBr pellets technique as described by Schnitzer (1977).

Scanning Electron Microscopy (SEM)

The surface morphology of the powdered humic acid samples was observed using scanning electron microscopy (SEM) technique.

RESULTS AND DISCUSSION

Organic materials pass too many stages through decomposition bio-oxidative process involved the mineralization and partial humification which leading to an establishment of a final product with certain humic properties (Zucconi and De Bertoldi, 1987).

Characteristics of Organic Materials Samples

Results presented in Table 1 show the physical and chemical properties of the organic material samples under study. The highest values for each of moisture (48.1%) and saturation percent SP (180) was observed with

sewage sludge samples, while the lowest one for each of moisture (9.17%) and SP (93%) was recorded with biogas manure and compost, respectively. The bulk density for all organic material sources were ranged between 0.42 and 0.87 Mg m^{-3} . These results are in agreement with those obtained by Huerta-Pujol *et al.* (2010)

With respect to chemical properties (pH, EC, CEC, OC% and OM%) of studied organic materials, results in Table 1 show that the lowest value for each of pH and EC was recorded with sewage sludge sample, while the highest one were observed with compost sample. The optimum EC value was mentioned by Sefidkar *et al.* (2013). Also, results of cation exchange capacity (CEC) revealed that the greatest value (63.2 cmolc Kg^{-1}) was observed with sewage sludge sample, while the least one (35.2 cmolc Kg^{-1}) was found with town refuse. The highest value for each of organic carbon (265 g Kg^{-1}) and organic matter (457 g Kg^{-1}) was recorded with sewage sludge sample as compared to other samples. From the above mentioned results, it may be worth to mention that values of both compost and biogas manure were very close. Also, the organic matter in most of the organic materials under study exceeded 200 g Kg^{-1} as a minimum limit stated by Ge *et al.* (2006). These results are in agreement with those obtained by Sadeghi *et al.* (2015) for mature compost.

With respect to total macronutrients content in organic materials, results in Table 1 show that sewage sludge sample was superior in total nitrogen (32.2 g Kg^{-1}), while compost was superior in total P (6 g Kg^{-1}) and K (17.2 g Kg^{-1}). Such results are in agreement with those obtained by Zhang *et al.* (2009a).

Also, The C: N ratio for all organic material sources ranged between 8.22:1 and 18.7:1 resembling the optimum (less than 25: 1) for the mature compost as stated by Fathi *et al.* (2014). The highest C: N ratio was observed with compost sample, while the lowest one was found with sewage sludge.

Moreover, macronutrient availability reveal that both available ammonium and nitrate in town refuse sample were noted higher values (923 and 308 mg Kg^{-1} , respectively) as compared to other organic materials samples. This view point is in agreement with (Siuris, 2011). Biogas

Table 1. Physical and chemical analyses of investigated organic materials

Parameter	Organic source			
	Town refuse	Compost	Sewage sludge	Biogas manure
Moisture (%)	13.1	10.4	48.1	9.17
Saturation Percent (SP)	98.0	93.0	180	165
Bulk density (Mg m ⁻³)	0.87	0.80	0.42	0.62
pH (1:10)	6.77	7.61	6.36	7.59
EC (1:10)	5.54	6.20	4.00	4.01
CEC (cmole Kg ⁻¹)	35.2	50.5	63.2	52.8
OC, g Kg ⁻¹	164	205	265	218
OM, g Kg ⁻¹	282	353	457	375
Total macronutrients, g Kg⁻¹				
N	15.1	11.0	32.2	15.0
P	0.50	6.00	3.40	1.60
K	5.30	17.2	1.70	6.10
C/N ratio	10.9:1	18.7:1	8.22:1	14.5:1
Available macronutrients, mg kg⁻¹				
NH ₄ -N	923	301	648	283
NO ₃ -N	308	104	248	104
P	311	626	142	485
K	748	1365	109	763
Total micronutrients, mg kg⁻¹				
Fe	3043	3715	3138	3135
Mn	162	487	190	547
Zn	192	124	294	133
Cu	54.3	32.9	149	22.9
Total heavy metals, mg kg⁻¹				
Pb	13.7	16.5	29	0.0
Cd	11	8.5	9	2
Co	19	27	16.5	6
Ni	38	52	48	23

manure was recorded least values for ammonium and nitrates (283 and 104 mg Kg⁻¹, respectively) as well as compost sample was recorded similar value for nitrate. The highest value for each of phosphorus and potassium available was observed with compost sample, while the lowest one for each of both available P and K was obtained with sewage sludge sample.

It is worthy to notice that the total micronutrients (Fe, Mn, Zn and Cu) in organic material samples were different depending on the organic source. Total Fe ranged between 3043 and 3715 mg Kg⁻¹. The greatest value of total Fe was observed with compost sample, while the lowest one was obtained with town refuse. Total Mn ranged between 162 and 547 mg Kg⁻¹. The highest value of total Mn was recorded with biogas manure, while the lowest one was found with town refuse. Moreover, sewage sludge sample was recorded high level of both total Zn and Cu (294 and 149 mg Kg⁻¹, respectively), while the lowest value for each of total Zn and Cu was observed with compost and biogas samples, respectively. Similar results were observed by (Pawlowski *et al.*, 2013).

In addition, the levels of total heavy metals (Pb, Cd, Co and Ni) in Table 1 were varying according to the type of organic material. The total content of heavy metals ranges between (0 and 29 mg kg⁻¹) for Pb, (2 and 11 mg kg⁻¹) for Cd, (6 and 27 mg kg⁻¹) for Co and (23 and 52 mg kg⁻¹) for Ni. The lowest contents of heavy metals (Pb, Cd, Co and Ni) were found with the biogas sample, while the greatest ones of Pb and Cd were observed with sewage sludge and town refuse, respectively, whereas the greatest ones of Co and Ni were recorded with compost sample. These results were in harmony with those reported by Hernández *et al.* (2017).

Properties of Humic Acids Extracted from Different Organic Materials

The elemental composition of humic acids extracted depended upon the type of the organic material. Carbon is the major element in organic structures; it is metabolized initially in the form of carbon dioxide and converted to organic carbon mainly through the photosynthetic activities of higher plants and to a lesser extent by microorganisms. About 90% of the dry matter of plants is composed of carbonyl levels

of varying complexities. Total carbon content of humic acids in Table 2 ranged between 497 and 541g Kg⁻¹. The highest content was found with sewage sludge sample and the lowest one was observed with compost sample. These results are in agreement with those obtained by Allam (2005). Also, total nitrogen content in humic acids varies according to the kind of organic material. Sewage sludge was superior for total nitrogen content (68.1g Kg⁻¹) followed by total N content (67.5 g Kg⁻¹) in town refuse sample, while the biogas sample was contained the lowest one (38 g Kg⁻¹). These results are in agreement with those obtained by El-Ghozli (1998). Results in Table 2 show that the highest C/N ratio (14.1) of humic acid was observed with biogas sample, while the lowest one (7.87) was recorded with town refuse. These results are in agreement with that obtained by El-Ghozli (1994) who found that C/N ratio of the studied humic acids differed according to the nature of organic residues.

Hydrogen Content and C/H Ratio

Results in Table 2 show that hydrogen contents ranged between 50.3 and 66 g Kg⁻¹ in the humic acid which extracted from different organic materials. The highest content of hydrogen (H) in humic acid was 66 g Kg⁻¹ in town refuse sample followed by 63.3 g Kg⁻¹ in sewage sludge sample as compared to the other organic samples. The variations among the C/H ratios of humic acids extracted from the different organic sources are relatively small, ranging between 8.05 and 9.88. However, El-Ghozli (1998) found that the contents of hydrogen in isolated HA from different organic residues were relatively smaller. The obtained results are in accordance with those obtained by Allam (2005). Last studies noticed that the hydrogen content of some humic acids extracted from different organic materials varied between 27.8 and 67.1 g Kg⁻¹.

Oxygen content, C/O and O/ H ratios

Oxygen (O) content ranged between 320 and 400 g Kg⁻¹ in the extracted humic acids (HA) samples. The highest content found in extracted HA from compost sample. Such results indicated that humic acid originated from the compost sample and obtained more oxidized function groups as compared with those originated from the other different humic acids

Table 2. Elementary composition of humic acid extracted from different samples

Sample	C g Kg ⁻¹	N g Kg ⁻¹	H g Kg ⁻¹	O g Kg ⁻¹	S g Kg ⁻¹	C/N ratio	C/H ratio	C/O ratio	O/H ratio	N/H ratio	(N+O)/C	E ₄ /E ₆
Town refuse	531	67.5	66.0	335	-	7.87	8.05	1.58	5.08	1.02	0.76	5.01
Compost	497	52.6	50.3	400	-	9.44	9.88	1.24	7.96	1.05	0.91	6.73
Sewage sludge	541	68.1	63.3	320	7.60	7.94	8.54	1.69	5.06	1.08	0.72	4.81
Biogas manure	536	38.0	59.7	366	-	14.1	8.98	1.47	6.13	0.64	0.75	4.68

C/H: Atomic ratio of carbon to hydrogen

C/O: Atomic ratio of carbon to oxygen

C/N: Atomic ratio of carbon to nitrogen

(N+O)/C: Atomic ratio of sum of nitrogen and oxygen to carbon

E₄/E₆ of humic acids is the ratio of the absorbance at 465 nm to that at 665 nm.

residual. This is could be attributed to the increase with time in the oxygenated functional groups (COOH, phenolic OH, alcoholic OH and methoxyl groups). The lowest content of oxygen (O) was found in HA extracted from sewage sludge and town refuse. Similar result was obtained by **El-Ghozli (1998)** who found that the total oxygen content of humic acids extracted from organic residues, generally fluctuated between 320 and 335.

The lowest C/O ratio was found in humic acid originated from compost and biogas manure. Such trend could be attributed to the relatively lower carbon content simultaneously with higher oxygen content of humic acids derived from compost and biogas manure. Also, the variations through the O/H ratio of humic acids derived from different treatments are relatively small and ranged between 5.06 and 7.96.

Sulfur Content and N/H Ratio

Results presented in Tables 2 clear that sulfur content in humic acid ranged between 0 and 7.6 g Kg⁻¹. Results revealed that the N/H ratio of humic acids ranged between 0.64 and 1.08. The highest N/H ratio was observed with humic acids derived from sewage sludge followed by that derived from compost. The lowest one was observed with humic acid derived from biogas manure. Such results could be due to relatively higher in nitrogen content combined with lower H content of humic acids derived from town refuse, compost and sewage sludge.

Results in Table 2 show that the polarity index (N+O)/C of humic acids was ranged between 0.72 and 0.91. The highest polarity index (N+O)/C was recorded with HA derived from compost, while the lowest one was observed with HA derived from sewage sludge. Similar results were obtained with (**Chen *et al.*, 2015**). Also, polarity index decreased with increasing sorption. **Wang *et al.* (1997)** explained that sorption increases with increasing number of carboxyl groups per molecule and acidity of carboxyl groups. Furthermore, the binding of carboxyl groups in organic matter to clay mineral surfaces is generally strong due to complexation with surface metals (**Kubicki *et al.*, 1999**), thus the sorption is barely reversible (**Avena and Koopal, 1998**). In this study, the HA fraction rich in carboxylic functionality may bind to clay surface through ligand exchange with the surface hydroxyl groups or through carboxylate bridging with Al ions present on the edge surfaces by electron donor-acceptor mechanism. **Weber *et al.* (1992)** suggested that N value can be taken as an index of site energy distribution, *i.e.* the smaller the N, the more heterogeneous the sorption sites. Therefore, the early extracted HA fractions with small N values may have a more heterogeneous structure or composition than the later ones with high N values. As a chemical mixture can be separated into each individual component or be purified to a relatively homogeneous mixture by solvent extraction, HA after several times of extraction may have a more homogeneous chemical composition.

In addition, the ratio of E4/E6 of HA is the ratio of the absorption at 465 nm to that at 665 nm has been used for the characterization of humic compounds derived from different organic materials. It is indicative of the degree of condensation of the aromatic nucleus in humic acid (Riffaldi *et al.*, 1983). Added that E4/E6 data provided further evidence of the heterogeneity of HA progressively extracted from the organic materials, consistent with the elemental composition. Generally, E4/E6 ratio is highly related to the humification degree (decomposition of organic matter) and molecular weight of OM. Results in Table 2 show that E4/E6 ratios was relative high in HA derived in compost (6.73) followed by HA from town refuse (5.01) and sewage sludge (4.81); the lowest ratio was found in biogas (4.68). This results are in agreement with those obtained by Kononova (1966) who reported that E4/E6 ratios ranging between 3.0 and 7.0 for humic acids.

Total Acidity and Acidic Groups of Humic Acids

The sum of the dissociable hydrogen of COOH and phenolic-OH groups in humic acids samples of both aromatic and aliphatic origins was defined by Schnitzer and Gupta (1965) as total acidity.

Humic acids percentage

Results in Table 3 report that the percentage of humic acids in different types of organic materials varied from 7.20 to 20.8, depending on the type of four organic materials used. The results of HA percent in both biogas and town refuse are converging which recorded 20.8 and 20.0, respectively. The inferior of humic acids percentage (7.20%) was recorded in HA from sewage sludge sample.

Total acidity of humic acids

Results in Tables 3 represent the amount of total acidity of humic acids of the four tested organic materials. The total acidity of the extracted humic acids from the organic materials ranged between 733 and 1233 me g⁻¹ humic acids.

Results found that the highest value of total acidity (1233 me g⁻¹) was found with humic acid extracted from sewage sludge, while the lowest

one (733 me g⁻¹) was observed with HA extracted from biogas. Such results are in agreement with those obtained by El-Ghozli (1998).

Carboxyl (COOH), Phenolic-OH Groups and Their Ratio in Humic Acids

Humic acids contain a variety of reactive functional groups such as carboxylic, phenolic, amine and thio groups that can react with the complex of metals. The values of COOH and phenolic-OH groups of humic acids extracted from the four organic materials were presented in Table 3. The values of carboxylic groups of humic acids extracted from the tested organic materials were higher than the values of phenolic-OH groups. Regarding values of carboxyl groups, results in Table 3 show that the highest value (860 me g⁻¹ HA) was observed with humic acid derived from town refuse, while the lowest value (560 me g⁻¹ HA) was recorded with humic acid extracted from biogas. The corresponding values of phenolic-OH groups were 433 and 106 me g⁻¹ HA for humic acid extracted from sewage sludge and town refuse, respectively.

Moreover, results in Table 3 also show that COOH/phenolic-OH groups ratios ranged between 1.85 and 8.10 in humic acids extracted from organic materials. The different ratios of COOH/phenolic-OH were relatively big. This may be due to the low differences between the values of COOH group in organic materials of different origins. Generally, the differences in the content of total COOH groups and total phenolic-OH groups could be related to the chemical composition of organic residues as well as the effect of humification processes (Rivero *et al.*, 1998).

Infrared Spectra

Infrared spectral analysis provides further useful information concerning the molecular structures and characteristic bonds Sakellariadou (2006). Results in Fig. 1 and Table 4, were in agreement with the results of Madejová (2003) and Garcia-Gomez *et al.* (2005) which reported that the absorption bands could be interpreted as the following: (a) the 3400 cm⁻¹ band is the one where a strong absorption due to hydrogen bonding hydroxyl groups occurs (-OH stretch from-COOH and -OH) like that in Qin *et al.* (2015); (b) the 2920 and 2860 cm⁻¹ absorption bands are attributed to the asymmetric and

Table 4. The main bands present in infrared spectra of four different humic acid samples

Wave number (cm ⁻¹)	Functional groups
3300-3500	-OH stretch from -COOH and -COH
2800-3100	-CH stretch from -CH, -CH ₂ and -CH ₃ groups of aliphatic chains
1600-1650	aromatic -C=C vibration; -C=O stretch from H-bonded conjugated ketones; -COO- asymmetric stretch
1510-1550	aromatic -C=C stretch and/or N-H deformation and C=N stretch from secondary amides
1380-1400	-OH and -CO deformation from alcoholic and phenolic -OH; -COO- symmetric stretch
1200-1260	-CO stretch and -OH bending from -COOH
1020-1100	-CO stretch of polysaccharides; Si- Ostretch from silicate impurities

symmetric stretching vibrations, respectively, of aliphatic C-H bonds in methyl and/or methylene units; (c) the band at 1710 cm⁻¹, which in terrestrial humic acids appears as a deep shoulder, is assigned to C=O stretch of carboxyl and carbonyl groups; (d) the 1600-1650 cm⁻¹ band is assigned to aromatic C=C double bonds conjugated with C=O and/or COO-; (e) the absorption at 1540 cm⁻¹ is the amide band due to peptidic linkages; (f) the band at 1385 cm⁻¹ is assigned at O-H deformation and C-O- stretch of phenols, COO-group vibrations, C-H deformation of CH₃; (g) the absorption around 1220 cm⁻¹ is assigned to the C-O stretching vibration and OH bending deformations, due mainly to carboxyl groups; (h.) an intense band around 1035 cm⁻¹ is assigned to alcoholic and polysaccharide CO stretch and OH deformation and, eventually, Si-OH bend in silicate impurities. In the present study, the IR spectra show that significant bands occur. The IR absorption characteristics resemble each other significantly, while the relative intensities of specific bands vary. Thus, through a thorough study of the IR spectra, it appears that all samples showed characteristic peaks for the following: hydroxyl, methyl, methylene, aromatic bond, carbonyl, carboxyl, phenol, alcohol, polysaccharide and silicate impurities. While in this study it found that the sample sewage sludge is devoid of -OH and -CO deformation from alcoholic and phenolic -OH; -COO- symmetric stretch.

Scanning Electron Microscopy (SEM)

In general, all HA samples analyzed are rich in carbon and oxygen. SEM can be useful to bring out the fine differences among HA extracted from various sources. SEM photo (Fig. 2) show some crystal-like forms aggregate along with various shapes; these results elucidated that the molecular structure of HA samples varies as per the origin and environment where decomposition has occurred. Fig. 2 shows the granular structure of various HA that have been extracted from the four different organic sources. This characteristic promotes a high metal adsorption (Xu *et al.*, 2006). The metals in this fraction can form bridges with carboxyl groups, interact by chemisorption with oxidized C groups and form coordination compounds (Pandey *et al.*, 2000) with other functional groups of humic acids, such as hydroxyl, phenol, and methoxy functional groups. Compacted micro aggregates were found in the samples; however, the aggregate size of the biogas (Fig. 2) was greater than those of the other fractions. Changlung *et al.* (2007) reported that the aggregation phenomenon is important to the transport of metal ions in natural environments. Zhang *et al.* (2009b) reported that humic acids in dilute solutions form thin thread and net-like structures that grow into larger rings and sheets with increasing humic and cation concentrations.

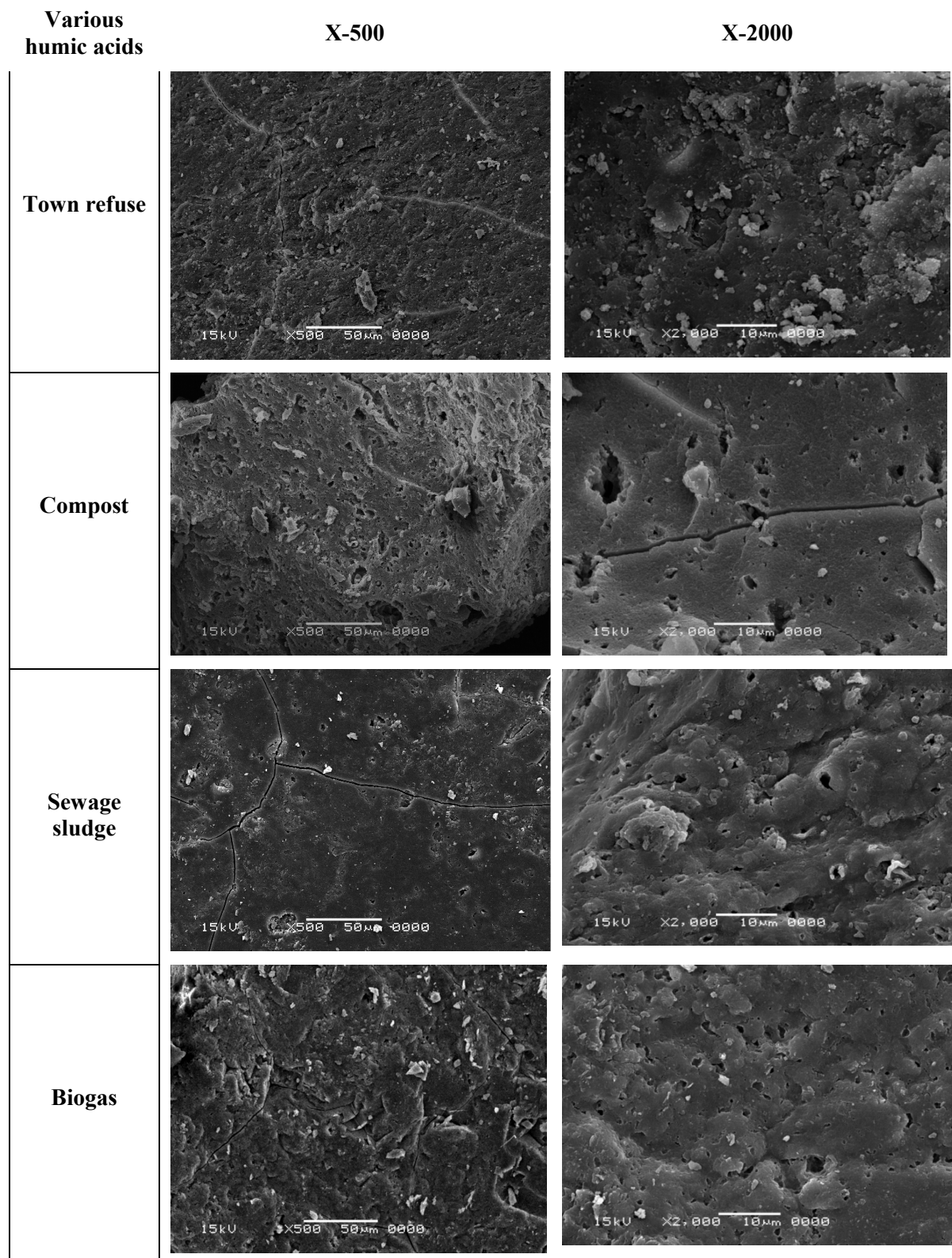


Fig. 2. The granular structure of HA samples from SEM at X- 500 and X-2000

Conclusion

Humic acids extracted from different organic materials usually used for many purposes. Hence, analyses of these materials by various techniques should be done. In this study results showed that HA exhibit different elemental compositions and spectroscopic characteristics. In general, all HA samples analyses were rich in carbon and oxygen and poor in nitrogen except sewage sludge. This study showed that the chemical composition and active groups of humic acids vary according to the sources which extracted from them, so different techniques must be used to determine their properties.

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خصائص بعض مصادر المواد العضوية وتحليل حامض الهيوميك المستخلص منها

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أجريت الدراسة الحالية باستخدام أربعة أنواع من المواد العضوية (قمامة المدن - سماد الكمبوست - الحمأة - مخلفات إنتاج الغاز الحيوي) كمصادر مختلفة لحامض الهيوميك (HA)، هذه المواد لم تأخذ القدر الكافي من الدراسة وتوصيفها ومقارنة خصائص الأحماض الدبالية المستخلصة منها، وترجع أهمية هذه الدراسة إلى ضرورة تحديد مزايا وعيوب استخدام هذه المواد كمصادر لحامض الهيوميك، حيث تم توصيف التركيب الكيميائي للمواد العضوية الأربعة وكذلك أحماض الهيوميك المستخلصة منها، وقد أظهرت النتائج أن المواد العضوية المستخدمة في هذه الدراسة (قمامة المدن - سماد الكمبوست - الحمأة - مخلفات إنتاج الغاز الحيوي) كانت وبشكل عام مختلفة في جميع خصائصها المدروسة، حيث سجلت الحمأة أعلى القيم فيما يتعلق بالمحتوى الرطوبي، نسبة التشبع، السعة التبادلية الكاتيونية، ومحتوى الكربون والمادة العضوية وعلى النقيض، فقد سجلت أقل القيم فيما يخص الكثافة الظاهرية ودرجة الحموضة وقيم التوصيل الكهربى وذلك بالمقارنة مع المواد العضوية الأخرى المستخدمة، كما أوضحت النتائج أن أعلى محتوى للنيتروجين الكلي والميسر بصورتيه الامونيومية والنتراتية ($\text{NO}_3^- - \text{NH}_4^+$) كان في الحمأة وقمامة المدن على التوالي، في حين سجل سماد الكمبوست أعلى محتوى للفوسفور والبوتاسيوم الكلي والميسر بالإضافة إلى نسبة C/N، بينما اختلف محتوى المواد العضوية الأربعة من المغذيات الدقيقة والمعادن الثقيلة، حيث تم تسجيل أعلى قيم لعناصر Fe و Co و Ni في سماد الكمبوست بينما أعلى قيم لعناصر Pb و Zn و Cu كانت في الحمأة، وقد أظهر التركيب الكيميائي لأحماض الهيوميك المستخلصة أنها كانت غنية بالكربون والنيتروجين والأكسجين وفقيرة في محتواها من الكبريت ويستثنى من ذلك حمض الهيوميك المستخلص من الحمأة، بينما كانت نسبة C/N مرتفعة نسبياً في حامض الهيوميك المستخلص من مخلفات إنتاج الغاز الحيوي. كما أظهر حامض الهيوميك المستخلص من سماد الكمبوست أعلى القيم فيما يخص نسب C/H و O/H و N+O/C و E4/E6، وقد لوحظ أن أقل قيمة لنسبة N/H كانت في حمض الهيوميك المستخلص من مخلفات إنتاج الغاز الحيوي، من ناحية أخرى، أوضحت النتائج أن نسبة حامض الهيوميك في مخلفات إنتاج الغاز الحيوي كانت الأعلى مقارنة بباقي المواد العضوية المستخدمة يليها قمامة المدن، سماد الكمبوست ثم الحمأة، على الترتيب، كما دلت النتائج أن الحموضة الكلية لحامض الهيوميك المستخلص من الحمأة كانت الأعلى مقارنة بأحماض الهيوميك المستخلصة من المواد العضوية الأخرى، وأن حامض الهيوميك المستخرج من قمامة المدن اختلف على أعلى محتوى من مجاميع الكربوكسيل ونسبة الكربوكسيل/الفينول، بينما اختلف محتوى حمض الهيوميك المستخلص من الحمأة على أعلى محتوى من مجموعات الفيينول الكلية، أظهر التحليل الطيفي بالأشعة تحت الحمراء (IR) معلومات إضافية فيما يتعلق بالتركيب الجزيئي والروابط في الأحماض المستخلصة، كما أظهر المسح بالمجهر الإلكتروني (SEM) الأشكال البلورية لهذه الأحماض والتي أكدت اختلاف التركيب الكيميائي والجزيئي للأحماض تبعا للمادة المستخلصة منها والبيئة التي تحللت فيها هذه المواد، وقد أثبتت الدراسة الحالية أن التقنيات الطيفية والتصويرية يمكن استخدامها بنجاح لإظهار الاختلافات بين أحماض الهيوميك المستخلصة من مصادر عضوية مختلفة.

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