Chemical Composition of Humic Substances Extracted From Salt Affected Egyptian Soils

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Abstract: Humic substances composed of humic acid (HA), fulvic acid (FA) and humin (HM) represent the most microbially recalcitrant and stable reservoir of organic carbon in soil. In order to identify the chemical compositions, humic substances were extracted from normal, (non-saline), saline, alkaline and newly reclaimed salt affected soils collected at0-30 cm surface layer during the summer of 2010. Elemental analysis, solid-state carbon-13 nuclear magnetic resonance (^{13}C-NMR) acquired with cross-polarization magic-angle spinning (CPMAS) and infrared (IR) spectroscopy measurements were used to characterize the chemical composition in the humic substances. Variations in chemical, functional groups and spectroscopic measurements were observed among the extracted humic and fulvic acids. More humic substances were extracted from the normal soil than other soil types, with the majority being humic acid. Data from elemental analysis and ^{13}CNMR spectroscopy indicated that humic and fulvic acids extracted from the normal and saline were more aromatic than those of alkaline and newly reclaimed soils. Fulvic acid extracted from all soils contained mostly aliphatic, O-substituted alkyl, and carboxylic groups and small amounts of carbonyl groups. Based on the spectroscopic analysis of IR Spectroscopy, no significant differences were detected among different types of humic substances. It cleared that humic acids extracted from the newly reclaimed soil were less humified than those of the other soils. Therefore, it is important to look for the suitable management practices for each type of soils.

1. Introduction

Salt-affected soils present in all continents and under most climatic conditions. Their distribution, however, is relatively more extensive in the arid and semi-arid regions as compared with the rained regions. Taking into account the variation in their characteristics, each type of these soils require specific approaches for their reclamation and management to maintain their long term productivity (Abroleand Yadav, 1988). For any long-term management practice, it is necessary to understand the origin of salt-affected soils and their classification, keeping in view the physico-chemical characteristics, processes leading to their formation and the suitable approaches for their reclamation and management.

Salt affected soils contain large amounts soluble salts that adversely affect the growth of most crop plants. For purposes of definition, saline soils are those which have an electrical conductivity of the saturation soil extract of more than 4dSm^{-1} at 25°C

(Richards, 1962). The majority of salt-affected soils in Egypt are located in the Northern- Central part of the Nile Delta and on its Eastern and Western edges. Nine hundred thousand hectare suffers from salinization problems in cultivated irrigated areas; Sixty percent of the cultivated lands of Northern Delta region are salt- affected; twenty percent of the Southern Delta and Middle Egyptian region and twenty five percent of the Upper Egypt regions are salt- affected soils (CAMPAS, 1989).

It is well known that fertility of soil is also related to soil organic matter (SOM) content. Nevertheless, humic substances are the major component of soil organic matter. The humified SOM or humic substances (HS) composed of humic acid (HA), fulvic acid (FA) and humin (HM) represent the most microbially recalcitrant and stable reservoir of organic carbon in soil (Piccolo *et al.*, 1992). Researches on humic substances show that they have multiple effects in maintaining soil quality and enhancing plant growth and yield (Sangeetha *et*

al., 2006, Fiorentino *et al.,* 2006 and Gersende *et al.,* 2008). Humic substances pronounced positive effects on plant growth and nutrition (Chen *et al.,*2004 and Elena *et al.*, 2009), pointing out the positive effects on seed germination, seedling growth, root initiation, root growth, shoot development and the uptake of macro and microelements. Also humic substances are able to improve soil quality parameters(viz. aggregation, aeration, permeability, water holding capacity and micronutrient availability (Tan, 2003).Additionally, humic substances might show anti-stress effects under salinity stress conditions (Masciandaro *et al*., 2002 and Kulikova *et al*., 2005). The chemical composition, structures and conformation of humic substances may vary greatly, depending on its origin (Leinweber *et al.*, 1996, and Baigorri *et al.,* 2009). Moreover, chemical characteristics of humic substances are affected by agricultural practices (Ding *et al*., 2002). Thus, identification of the overall chemical structure of humic substances is important to understand and elucidate its interactions with organic or inorganic contaminants.

Solid-state NMR spectroscopy is a powerful tool to study the structure of SOM because it is nondestructive, it can detect insoluble organic matter, and it can provide comprehensive structural information (Preston, 1996). Nearly all of the many SOM studies involving[13]C solid state NMR used routine techniques of ^{13}C cross polarization/magic angle spinning (CP/MAS).

In recent years we have developed, adapted, and applied many new advanced solid-state NMR techniques for characterizing complex organic matter in plants, soils, water, and sediments (Mao and Schmidt-Rohr, 2005; Schmidt-Rohr and Mao et al., 2002; Levin et al., 2007; Mao et al., 2007;Mao et al., 20087). Nuclear magnetic resonance (NMR) techniques have been increasingly used in soil science, geochemistry and environmental science (Xu and Chen, 2006; Xu *et al.,* 2009). In particular,^{13}C NMR has been widely used to improve the understanding of SOM quality and composition in relation to terrestrial C and N cycling processes. These studies indicate that ^{13}C NMR spectra of humic acids extracted from soils belonging to various soil orders are different. Further, NMR studies by Saiz-Jimenez *et al.,* (1986) showed wide differences in the aromatic character of humic acids extracted from Inceptisols and Mollisols of Australia and Spain, respectively. Lobartini and Tan (1988) provided ^{13}CNMR spectra of humic acids extracted from Entisols, Inceptisols, Mollisols, Spodosols and Ultisols of Indonesia, the USA and Argentina and concluded that a distinctive spectrum was produced

from each humic acid studied. On the other hand, we found that the literature shows lack of nuclear magnetic resonance studies for salted affected soils.

Another nondestructive technique, infrared spectroscopy, usually in the form of FT-IR spectroscopy, is a relatively important yet simple tool for the characterization of organic matter (Giusquiani *et al.,* 1998; Fan *et al.,* 2000; Olk *et al.,* 2000; Tan, 2003; He *et al*., 2006). This technique provides detailed information about the oxygen-containing groups present in the complex molecules, since polar groups usually show very intense infrared signals (Francioso *et al.,* 1996).

Therefore, the main goal of this study is to clarify the changes of structural characteristics of humic substances (viz., humic and fulvic acids) by infrared (IR) and ^{13}C NMR (^{13}C CPMAS NMR) techniques and compare humic and fulvic acids extracted from the surface layer at 0-30cm of four different soils which were different degree of salinity/sodityin Egypt with the purpose to provide new information for improving soil fertility by organic matter addition.

2. Materials and Methods.
2.1. *Soil samples.*

Four surface soil samples at 0-30 cm were collected from one spot for each soil types by soil auger during summer of 2010seasonto represent normal soil located at Mansoura City, 31° 3′ N, 31° 23′ E, saline, alkaline and newly reclaimed salt affected soils located at the near of Manzala Lake, 31° 16′ N, 32° 12′ E, in Northeastern Egypt of the Nile Delta (Figure 1).

The soil samples were dried at 40°C for 24 hours and gently crushed to pass through a <2 mm sieve. The soil properties of the selected soils are shown in Table 1.

2.2. *Soil characterization*

Particle sizes distribution was determined using the pipette methods of Kilmer and Alexander (1949). According to the American Soil Taxonomy (USDA, 2010), these soils can be classified as, normal soil: *Typic Torrifluvents*; they are subject to flooding, but flooding is rare in some areas of the soils; saline soil; *Vertic Torrifluvents* having distinguished B horizon with wedge shaped structure, alkaline soil; *Typic Nartrargids* which saturated within 1 m of the soil surface for 1 month or more and newly reclaimed soil: *TypicTorrifluvents*. Normal soil was cultivated with wheat and corn crops for a long time, while the saline, alkaline and reclaimed soils were not cultivated and the newly reclaimed soil basically means improving their drainage conditions.
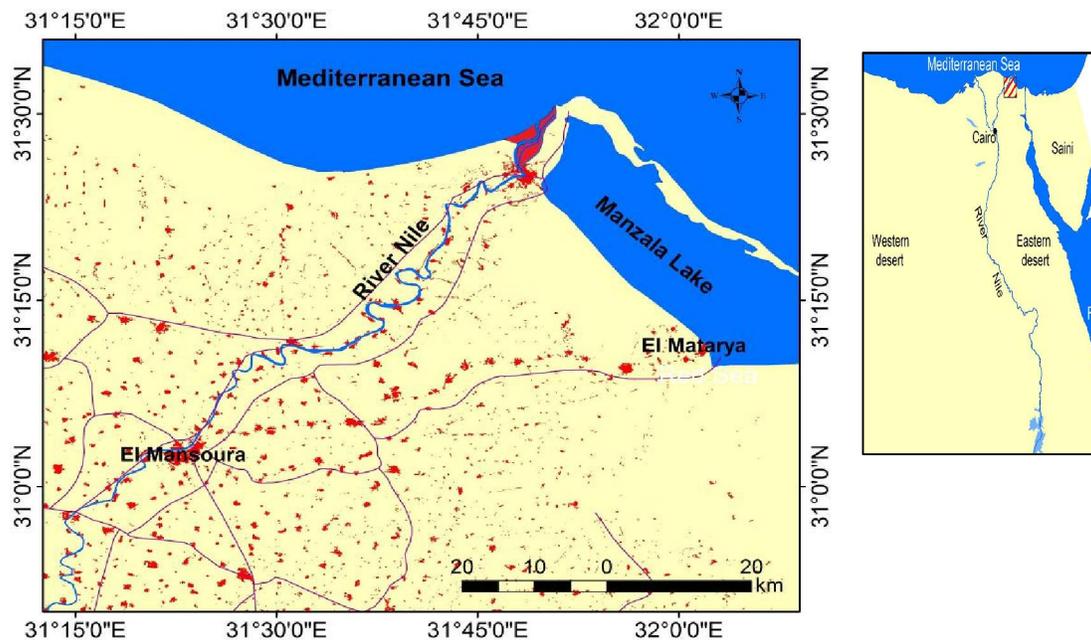
Figure 1. map of the experimental area and the location according to the GPS coordination.

Consequently, soil ripening will be started. Soil-ripening process includes all physical, chemical, and biological processes by whicha freshly-deposited mud is transformed into a dryland soil (Smits et al. 1962).

Soil pH and ECe were measured in soil paste and soil paste extract, respectively according to Jackson (1967). Sodium adsorption ratio was calculated using the following equation.

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{+2} + Mg^{+2}}{2}}}$$

Where, Na^+, Ca^{+2} and Mg^{+2} were $meqL^{-1}$ in soil paste extract. Exchangeable sodium percentage (ESP) was calculated according to Richards (1962), where.

$$ESP = 100 \frac{-0.0126 + 0.01475\ SAR}{1 + (-0.0126 + 0.01475\ SAR)}$$

Soil organic carbon (SOC) was determined by dry combustion (950°C) according to the methods of Nelson and Sommers (1982). Calcium carbonate ($CaCO_3$) was estimated using Collin, scalcimeter (Wright, 1939).

2.3. Extraction of humic and fulvic acids

Humic substances were extracted and purified using procedures outlined and distributed by International Humic Substances Society (Aiken, 1985). Briefly, 1000 g of 2-mm air dried soil was stirring in 0.1M NaOH (soil/solution ratio of 1:10) under an N_2 atmosphere for 24 h at room temperature. The extract was acidified with 6M HCl to a pH of ~1. Humic and fulvic acids were then separated by centrifugation at 10000 rpm for 15 min. The humic acid fraction was purified with 0.1 MHCl -0.3 M HF mixture, and then dialyzed in deionized water. Fulvic acids were purified with repeated passages through Amberlite XAD-8 no.A-6525, 1-0.5 mm resin (Sigma Chemical Co, St. Louis, MO), followed by washings with 0.3 M HF and dialyzed in the same way as humic acids. To ensure removal of salts, the fulvic acids were then passed four times in succession through Bio-Rad Ag MP-50, .05- to 0.2- mm resin (Bio-Rad Laboratories, Richmond, CA) in the H form. Both fractions (humic and fulvic acids) were then freeze-dried and stored.

2.4. Characterization of humic and fulvic acids

Carbon, hydrogen and nitrogen contents (oven-dry basis) were determined for humic and fulvic acid by dry combustion method as described by Mann and Saunder (1960). Oxygen was calculated by subtracting C% + H% + N% from 100.

Total acidity, carboxyl groups, and phenolic-OH groups were measured on all humic acids samples using the method described by Schnitzer (1982). Sufficient quantities of fulvic acids were not available for these measurements.

The IR spectra were obtained from discs containing about 1 mg sample and 200 mg KBr using the KBr pellet technique. The spectra were recorded in 200-4000 cm^{-1} range on a Beckman model IR spectrophotometer. Each sample was scanned 1 time with a resolution of 2 cm^{-1}.

Solid-State ^{13}C CPMAS NMR spectra for all humic acids were obtained on a Bruker CXP-100 spectrometer operating at 22.6 MHz. Samples were spun at the magic angle (54.7^o) at approximately 3 to3.5 kHz. Spectra based on 1200 scans were obtained using a contact time of 1 ms and a recycle time of 1s. Solid-state ^{13}C CPMAS NMR spectra for all fulvic acids were obtained on a Nicolet NT-150 spectrometer operating at 15MHz. Samples were spun at the magic angle at 3.8 kHz. Spectra based on 9000 scans were obtained using a contact of 1 ms and a recycle time of 1 s. Chemical shifts in the humic and fulvic acids were reported downfield from tetra methyl saline. The spectra were evaluated in a manner similar to that of Hatcher et al (1983).

3. Results and Discussion.

The organic carbon of the soil samples selected for this study range from 0.51% to 1.35% (Table 1). The normal soil (non saline) has OC content that are 2.5 times greater than that in the newly reclaimed salt affected soil. The pH values of all the studied soils are alkaline; the alkali soil has the highest pH value as a result of the high ESP value (18.07%). The saline soil has the highest EC(28.69 dSm^{-1}) whereas the newly reclaimed salt affected soil has the lowest EC (2.17 dSm^{-1}). The saline soil possesses the lowest CaCO$_3$ (1.62%) because the salts increase the solubility of calcium carbonate (Abrole and Yadav, 1988). The mineral fractions of the studied soils are dominated by clay (Table 1).

Table 1. Physical and Chemical properties for the investigated soils.

Soil properties	Alkaline	Normal	Newly reclaimed	Saline
Soil physical properties				
Particle size distributions (%)				
Sand	18.62	21.42	23.09	16.24
Silt	27.76	22.84	25.83	25.98
Clay	49.11	49.96	47.94	54.40
Soil texture	Clay	Clay	Clay	Clay
Soil chemical properties				
Organic carbon %	0.94	1.35	0.51	1.02
pH (1:2.5)*	8.70	7.92	8.12	8.02
ECedS m^{-1}*	3.83	1.14	2.17	28.69
SAR	15.88	4.98	11.51	11.75
ESP %	18.07	5.72	13.18	13.41
CaCO$_3$%	2.89	3.45	2.26	1.62

● Soil paste (1 soil:2.5 water).

3.1. Chemical analyses of humic substances

Yields of humic substances extracted from all four soils are expressed as a percentage of total organic carbon (TOC) content (Table 2). Thirty-nine to 52% of the TOC content of the soils was extracted. These values are similar to those reported by Lowe (1969).

Table 2. Yield of humic and fulvic acids expressed as a percentage of the total organic carbon

Soil Samples	Total Organic C (TOC %)	Yield of humic substances (%)		
		Humic acids	Fulvic acids	Total
Alkaline	0.94	28.59	16.62	45.21
Normal	1.35	38.04	14.13	52.17
Newly reclaimed	0.51	18.48	20.61	39.09
Saline	1.02	34.65	15.08	49.73

The normal and the saline soils yielded approximately 2 times more humic acids than the newly reclaimed soil. In contrast, the yields of fulvic acids were much lower than those of humic acids in all soils. Approximately, fulvic acids were similar among the normal, saline and alkaline soils, but higher in the newly reclaimed salt affected soil. This may be attributed to the high rate of decomposition of organic matter in this soil as a result of optimum soil conditions vz good drainage conditions which increase the activity of soil microorganisms. So, fulvic acids were more readily mineralized by the microorganisms in soil than humic acids (Ruchko, 1984) and Sonbol and El-Arquan (1978) pointed out that fulvic acids are the first stage of the formation of humic acids, therefore the significant higher fulvic acids and the lower humic acids in the newly reclaimed salt affected soil represent the initial stage

of formation for humic substances. According to the results presented in Table 3, the elemental composition of the humic acids extracted in this study range from 51.14 to 55.37% C, 3.75 to 4.68% H, 3.69 to 4.16% N and 36.81 to 40.02% O of oven dried humic acid.

Table 3. Elemental composition and ratios of humic and fulvic acids.

Soil Samples	Ash%	C%	H%	N%	O%	Elemental ratios		
						H/C	O/C	N/C
Humic acids								
Alkaline	1.20	54.94	4.23	4.02	36.81	0.92	0.50	0.063
Normal	1.10	55.37	3.75	3.69	37.19	0.81	0.50	0.057
Newly reclaimed	1.01	51.14	4.68	4.16	40.02	1.10	0.58	0.069
Saline	0.95	54.32	3.92	3.81	37.95	0.87	0.52	0.060
Fulvic acids								
Alkaline		41.68	3.66	2.81	51.85	1.05	0.93	0.058
Normal		43.96	3.42	2.24	50.38	0.93	0.86	0.044
Newly reclaimed		40.57	3.81	2.94	52.68	1.13	0.97	0.062
Saline		42.45	3.54	2.69	51.32	1.00	0.91	0.054

The maximum value of C element was 55.37% occurred with the normal soil, meanwhile the minimum value of the same attribute was 51.14% found in the newly reclaimed soil. In the contrast, the maximum values of H, N and O% were 4.68, 4.16 and 40.02% occurred with the newly reclaimed soil. While, the minimum values of the current once were 3.75, 3.69 and 37.19% found in the normal soil, respectively. The composition is similar to that of an ideal soil humic acid reported by Schnitzer (1977) and humic acids extracted from a Gray Solonetz and a Brown Solod reported by Lowe (1969). Some trends, however, are apparent. The carbon content of the humic acid extracted from the newly reclaimed salt affected soil is lower and the oxygen content is higher than those of humic acids extracted from the other soils as illustrated by the differences in O/C ratios (Table 3). This suggests that humic acids of the newly reclaimed soil are less humified than humic acids of the other soils.

The differences in hummification may be indicative of how long these soils have been cultivated. Some other differences can also be noted between the extracted humic acids. The humic acid extracted from the alkaline and the newly reclaimed soils have wider H/C of 0.92 and 1.10, respectively, N/C ratios of 0.063 and 0.069 than the other two soils, respectively. Generally, H and N contents increased with decrease in organic carbon content of soil (Visser, 1983).Wider H/C ratios are indicative of humic substances with less condensed or more open aromatic type structures and a relatively high content of aliphatic components (Visser, 1983). The results indicate that the humic acids extracted from the alkaline and the newly reclaimed soils were not as structurally condensed as the humic acids extracted from the normal and the saline soils.

As shown in Table 3, elemental composition of the fulvic acids range from 40.57 to 43.96% C, 3.42 to 3.81% H, 2.24 to 2.94% N and 50.38 to 52.68% O of oven dried fulvic acids. The maximum value of C element was 43.96 % occurred with the normal soil, meanwhile the minimum value of the same attribute was 40.57% found in the newly reclaimed soil. On the other hand, the maximum values of H, N and O% elements were 3.66, 2.81 and 51.85% occurred with the newly reclaimed soil. While, the minimum values of the current once were 3.75, 3.69 and 37.19% found in the normal soil, respectively. Similarly, the fulvic acid extracted from the alkaline and the newly reclaimed soils have wider H/C of 1.05 and 1.13, respectively, N/C ratios of 0.93 and 0.97 than the other two soils, respectively. The composition is similar to that of an ideal fulvic acids reported by Schnitzer (1977) and Stevenson (1994). Steenlink (1985) reported that the H/C, O/C and N/C ratios for fulvic acids typically clustered around 0.01, 0.09 and 0.05, respectively. The data generated in this study suggest some slight compositional differences between the fulvic acids extracted from the different soils. Total acidity values of the humic acids range from 6.12 to 7.29, carboxylic groups from 4.49 to 5.30 and phenolic OH groups from1.61 to 1.99 meq g^{-1} HA (Table 4).

Functional groups analyses were not performed on fulvic acids because of insufficient sampler. Humic acid extracted from saline soil contains higher quantities of total acidity, carboxylic and phenoloic- OH groups than those extracted from the other soils. The high values for carboxylic groups indicate the inherent reactivity of the humic acids.

Table 4. Total acidity, carboxylic and phenolic OH groups of humic acids.

Soils	meq/g. HA		
	Total acidity	Carboxylic groups	Phenolic-OH*
Alkaline	7.08	5.21	1.87
Normal	6.78	5.17	1.61
Newly reclaimed	6.12	4.49	1.63
Saline	7.29	5.30	1.99

*Determined by difference between total acidity and carboxylic groups.

3.2.   Infrared Spectroscopy (IR)

Infrared spectra of both the humic and fulvic acids (Fig. 2 and 3) show a strong-OH absorption band at 3430 to 3250 cm^{-1} a C-H absorption band at 2960 to 2900 cm^{-1}, a C=O stretch of COOH absorption band at 1730 to 1710 cm^{-1}, and an aromatic C=C and an aromatic C-C absorption band at 1640 to 1610 cm^{-1}.
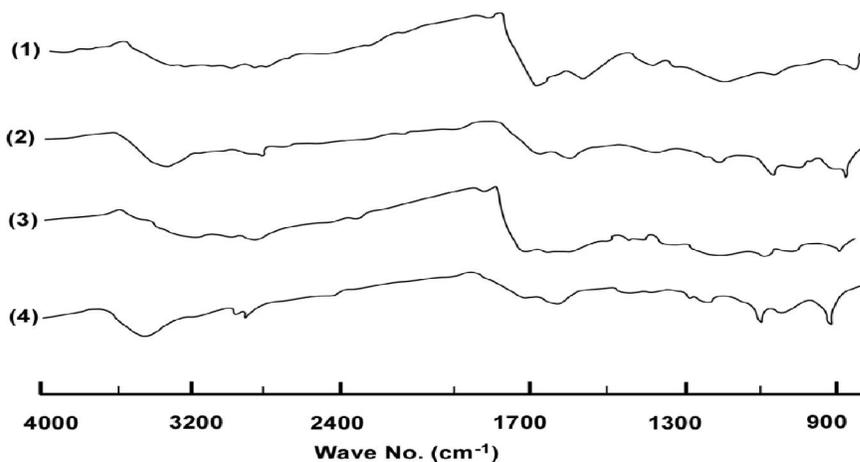
Fig.2. IR spectra for (1) Alkaline, (2) Normal, (3) Newly reclaimed and (4) Saline fulvic acids.
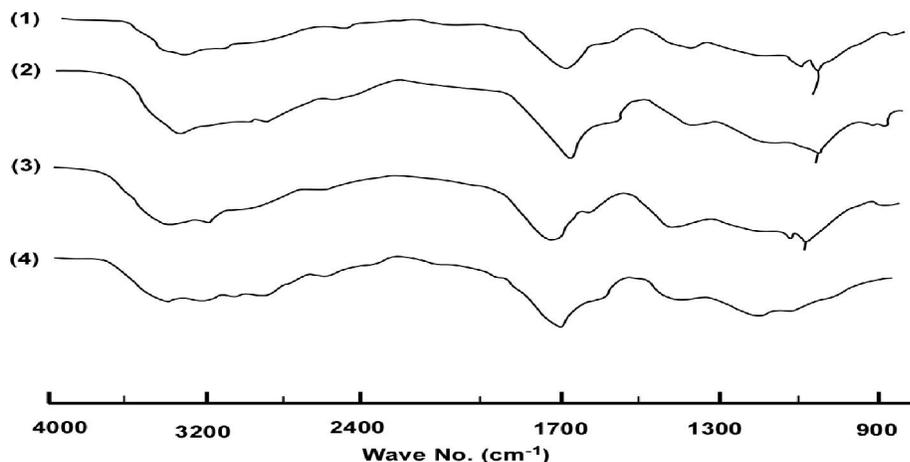
Fig.3. IR spectra for (1) Alkaline, (2) Normal, (3) Newly reclaimed and (4) Saline fulvic acids.

All humic acid spectra exhibit a weak band indicative of C=O stretching of amides and quinones at 1650 cm^{-1}. Other bands common to both the humic and fulvic acid spectra are attributable to weak -OH deformation and C-O stretching of phenolic-OH or COO-antisymmetric stretching at 1420 to 1390 cm^{-1} a C-O stretch and –OH deformation of COOH groups at 1230 to 1200 cm^{-1} and a C-O stretching of polysaccharide-like substances or Si-O of silicate impurities at 1110 to 1080 cm^{-1}. These findings are coincided with Olk et al., 2000 and Wang and Chang, 2001 and Tan, 2003, they reported that the IR spectra

showedthe peaks and/or bands at 1706–1719 cm^{-1} (carboxyl as wellas aldehydic and ketonic carbonyl), and at 1623–1664 cm^{-1}(C=C stretching vibrations in olefinic and aromatic compounds).The spectra also showed the peaks and/or bands at1365–1402 cm^{-1}(C–H deformation of CH2 and CH$_3$, saltsof carboxylic acid and/or aliphatic CH), 1229–1230 cm^{-1}(C–O stretching vibrations of esters, ethers, and phenols), and 1088–1095 cm^{-1} (C–O stretch). In addition, all humic acids exhibit a =C-H out- of- plane bending of aromatic and alkene structures at 900 cm^{-1} (Pavia *et al.,* 1979).

It is interesting to note that the spectra of fulvic acids exhibit a weaker band at 1640 to 1610 cm^{-1} than those of the humic acids, which indicates that there was less aromatic character in the fulvic acids than the humic acids. The IR spectral patterns of humic acids and fulvic acids in this study are similar to those reported by Taha and Modihish (2003). No differences are evident by IR spectroscopy among the humic and fulvic acids extracted from the different four soils in this study. Infrared analyses did reveal that humic and fulvic acids were composed of aromatic, aliphatic, carbonyl (as carboxylic acids, ketones and phenolic-OH) groups and polysaccharide-like components and that the fulvic acids were not as aromatic as the humic acids.

^{13}C CPMAS NMR Spectra

The ^{13}CNMR spectra for the extracted humic and fulvic acids are presented in Figs. 4 and 5, respectively. Each spectrum was divided into four regions of resonance frequencies for major organic structures. The most significant peaks in each resonance frequency region were identified and the significance of each region discussed. In the aliphatic regions (0-50 ppm), spectra of humic acids from the alkaline and the newly reclaimed soils exhibit a broad peak (18-32 ppm), whereas those of the normal and the saline soils show a relatively well-defined peak at 32 to 34 ppm (Fig. 3). The result suggests that, although humic acids from all soils contained methyl-C in long chains and alkyl-C bonded to aromatic ring structures (Taha *et al.,* 2000), the humic acids extracted from the alkaline and the newly reclaimed soils may have contained a more heterogeneous mixture of aliphatic structures than the normal and the saline humic acids.
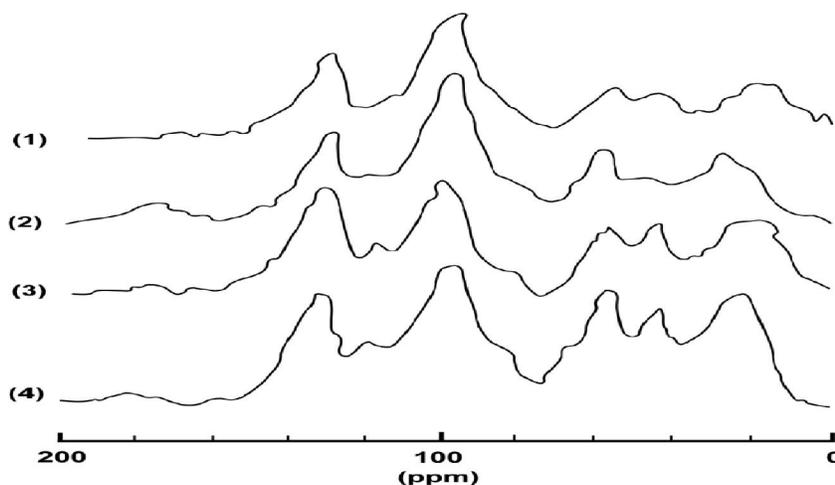
Fig. 4. Solid – state ^{13}C NMR of (1) Alkaline, (2) Normal, (3) Newly reclaimed and (4) Saline humic acids.

In the O-alkyl region (50-110 ppm), peaks are evident in the spectra of all humic acids at 57 to 58 and 73 to 74 ppm. The peak at 58 ppm has been attributed to methoxy associated with lignin and lignin-like products (Piotrowski *et al.,* 1984), whereas the 74 ppm peak has been attributed to carbohydrates (Preston *et al*., 1997). The most intense peak in the humic acids spectra of this study occurred at 129 to 134 ppm, which Schnitzer and Preston (1986) have attributed to aromatic structures substituted with alkyl groups. Minor peaks, indicative of phenolic-OH groups, also occurred at 153 to 154 ppm in all humic acids.

A distinct peak appears in the 160 to 190 ppm range in all the studied humic acids, which is commonly assigned as carboxylic carbons including free carboxylic acids and esters with possible contributions from peptides and quinones (Amalfitano *et al.,* 1995). Minor peaks in the carbonyl region (190-240 ppm) of the spectra were evident for all four humic acids (Fig. 4).

The ^{13}C NMR spectra of the extracted fulvic acids are shown in Fig. 4. In the aliphatic region, spectra for all fulvic acids showed a broad, noisy peak between 30 and 41ppm.
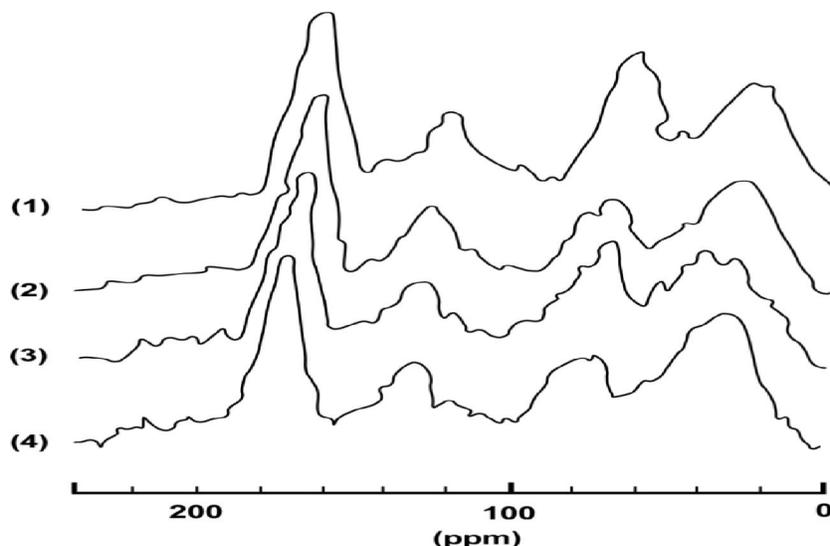
Fig.5. Solid – state ^{13}C NMR of (1) Alkaline, (2) Normal, (3) Newly reclaimed and (4) Saline fulvic acids.

The fulvic acids extracted from the alkaline and the newly reclaimed soils exhibited a shoulder peak at 17 to 18 ppm which indicated an aliphatic-side- chain C and C from terminal methyl groups (Li *et al.,* 2003), this suggests that there are some differences between the fulvic acids extracted from the normal, the saline and the alkaline and the newly reclaimed soils. All fulvic acids spectra exhibited a weak signal at 56 ppm that provided little evidence for lignin and lignin-like products.

Strong absorptions peaks at 70 to 72 ppm suggested that carbohydrate and carbohydrate- like components are major constituents. Hatcher *et al.,* (1983) have reported that soil fulvic acids are dominated by carbohydrate and carbohydrate-like components. Unlike the humic acids, the peaks indicative of aromaticity occurring between 130 and 137 ppm were not the most intense signals in the fulvic acids spectra, which indicates that although fulvic acids have some aromatic character, they are mainly alkyl substituted (Saleh*et al*, 1983). The most prominent peak in the fulvic acid spectra occurs between 172 and 174 ppm that is attributed to carboxylic acids, amides, and esters. A dominance of carboxylic acid adsorption peaks has been noted previously by Saiz-Jimenez *et al*., (1986) in spectra of soil fulvic acids. All fulvic acids spectra exhibited some minor peaks in the carbonyl region, but the signals are weak.

4.   Conclusion

Humic substances (HS) extracted from the different soil types of the normal, saline, alkaline and newly reclaimed soils in Egypt were studied using elemental analyses, infrared (IR), and CP/MAS^{13}C

nuclear magnetic resonance (NMR) spectroscopy. Data from elemental analysis and ^{13}C NMR spectroscopy indicated that humic and fulvic acids of the normal and the saline soils were more aromatic than those of the alkaline and the newly reclaimed soils. In addition, the data of the functional groups analysis and ^{13}C NMR spectroscopy revealed that humic acids extracted from the saline soil contained more carboxylic groups than those of the other soils. The spectroscopic properties for IRof the humic substances did not vary significantly with the different soil types. The humic acid extracted from the newly reclaimed soil was less humified than those of other soils.

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