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Extraction and Characterization of Humin from two Jordanian Soil

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ABSTRACT

The aim of this study was to separate and characterize humin from two locations in Jordan: Azraq Oasis (Inceptisols) and Ajloun forest (Vertisols) soils for the first time due to their richness in organic matter. Humin from those soils has been extracted and purified. They were characterized by FTIR, elemental analysis, TGA, SEM, XRD, solid and solution ^{13}C NMR. Also surface area, porosity and cation exchange capacity were determined. The Azraq humin has higher carbon percent that indicated high condensation than Ajloun humin. Also Azraq humin has higher ash percent due to presence of Kaolinite and Bentonite. The O/C ratio of Ajloun humin is higher than that for Azraq indicating it is richer in polar groups, and may reflect larger amount of carboxylic acid, phenolic and O-alkyl groups. The C/N ratio of Ajloun humin is lower than for Azraq which indicates that Azraq humin is in more advanced stage of humification. ^{13}C NMR measurements revealed that the aliphatic and aromatic percentages were higher in Ajloun humin, whereas the carboxylic acids and carbonyls were lower than those in Azraq humin. The SEM micrograph shows the layer structure (sheet) present; with high porosity. The cation exchange capacity values were 145.40 cmol/kg and 56.65 cmol/kg, for Azraq and Ajloun humin, respectively. Most pores radii are in the range of micropores and some of these in range of mesopores and macropores in the two humin.

Keywords: Inceptisols; Vertisols; humin; extraction; characterization.

INTRODUCTION

Humic substances (HS) are ubiquitous in the environment, occurring in all soils, waters, and sediments. In soils, they comprise up to 80% of soil organic matter (Hayes, 1998). They are the amorphous, highly transformed, darkly colored component of the organic matter, which consist of a wide range of functional groups (Stevenson, 1994; Hayes, 1998). They are the most important source of organic carbon in both terrestrial and aquatic environments (Stevenson, 1994), and play a major role in nature. They contribute to the growth of plants, which are responsible for the structure and physical–chemical properties of soil, and its majority of surface phenomena that occur in soil (Stevenson, 1994; Alvarez-Puebla et al., 2005).

Humic substances form an important pool of carbon(C) in the global carbon budget (Stevenson, 1994). The total mass of organic carbon stored in soils ranges from 1.100×10^{18} to 3.000×10^{18}g C, which are greater than atmospheric and living biomass C combined (Schlesinger, 1997). Additionally, humic substances influence soil fertility, soil development, and various soil chemical properties, including: cation exchange capacity (CEC), buffer capacity, pH, acid–base chemistry, and metal transport (Petersen, 1981; Buol et al.,1997), as well as serving as a source of energy for soil macro- and microorganisms (Paul and Clark, 1987).

Humin is the fraction of humic substances that is

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not extracted by traditional alkaline solution and insoluble at any pH, and has the highest molecular weight and the highest carbon content of the three humic fractions (Rice and MacCarthy, 1990). The postulated relationships are depicted by Stevenson (1994). Humin is very resistant to decomposition and to microbial degradation and is considered the ultimate product of the humification process.

Transport of the contaminants due to ground- and fresh-water dynamics is directly associated with both organic and inorganic soil components (Koopal et al., 2001). HS contain heteroatoms, mainly oxygen bound in carboxylic and hydroxyl groups. The complex nature of interaction between HS and metal cations is given by their heterogeneous, polyelectrolyte and polydispersive character given by the variety of functional groups located in various chemical environments of the three-dimensional structure of HS (Čežíková et al., 2001; Klučáková and Omelka, 2004; Martyniuk and Wieckowska, 2003).

The nature of binding ranges from purely electrostatic, non-specific interaction of metal cation with net negative charge on the surface of a humic macromolecule to specific interactions with the functional groups in the formation of complexes and chelates. Several interaction models have been proposed, in which the chemical heterogeneity of HS binding sites is usually reflected (Baker and Khalili, 2004). Numerous studies have demonstrated significant capacity of humic acids for binding metallic cations (Čežíková et al., 2001; Klučáková and Omelka, 2004;; Martyniuk and Wieckowska, 2003). Humin show high potential for metal ion sorption (De La Rosa et al., 2003 ***a, b;*** Alvarez-Puebla et al., 2004; Alvarez-Puebla et al., 2006) due to the presence of potential binding sites for metal ions.

The chemical and physical properties of humin are only partially understood. Some of the main functions of humins within the soil are to improve the soil's water holding capacity, soil structure, soil stability, and to function as a cation exchange system (Pettit, 2007). Thermochemolysis techniques revealed the presence of a number of components in humin fragments including a series of fatty acid methyl esters, methoxy alkanes, and aromatic and polar groups (Grasset and Amblès, 1998). Humin complexes are considered as macro organic substances because their molecular weight (MW) ranges from about 100,000 to 10,000,000 Dalton. It is extremely porous and the surface area is very large (Almendros and Sanz, 1991). The availability of pores and internal surface are useful in the adsorption process (De La Rosa et al., 2003 ***a, b***). The porosity of humin was determined using gas adsorption method and found the surface area per gram from different soils from 43.1 m^2 to 57.3 m^2 (Alvarez-Puebla et al., 2005). Their colloidal character and high surface functionality make humin excellent adsorbents with a superior capacity for the retention of ionic and molecular pollutants that will facilitate the processes of mobilization/immobilization of these in the environment (Alvarez-Puebla et al., 2004). Humin show high potential for metal ion sorption (De La Rosa et al., 2003 ***a, b;*** Alvarez-Puebla et al., 2004; Alvarez-Puebla et al., 2006) due to the various potential binding sites for heavy metal ions. So, humin can efficiently adsorb different heavy metal ions from aqueous solutions and it strongly affects the sorption behavior and fate of contaminants in soil and sediments (Wang and Xing, 2005; Pan et al., 2006). Lichtfouse (1999) proposed the following model of humin, which explains the stabilization of soil organic matter by encapsulation of small polar molecules (physical sequestration), binding of functional biomarkers (chemical sequestration) and selective aliphatic biopolymers (Figure 1).

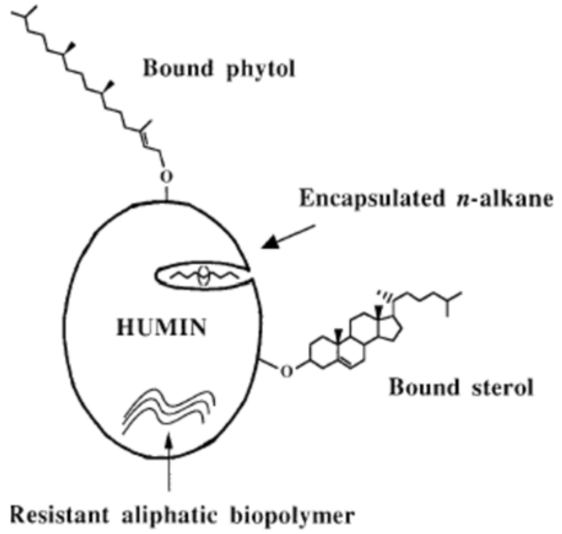


Figure 1: Model of humin (Lichtfouse, 1999).

For the first time humin from two soils in Jordan: Azraq Oasis east of Jordan (Inceptisols) and Ajloun forest north west of Jordan (Vertisols) have been separated and characterized inorder to understand the nature of organic matter in these soils. The first site is an oasis in the desert and the second is a semi arid forest. The humin fraction isolated was purified and then characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and (solid and solution)^{13}C nuclear magnetic resonance (^{13}C NMR). Also the surface area, porosity and cation exchange capacity (CEC) were determined in order to understand the humin nature, structure and properties.

2. Experimental

2.1. Materials

All chemicals were obtained from commercial sources as either analytical reagent grade or chemically pure grade and were used as received. The chemicals were purchased from the corresponding companies: H_2SO_4 98% (Gainland Company), $NaClO_4$ (Acros), HF (BDH), NaOH (LOBA), HNO_3 68-70 % (Tedia) and dimethyl sulfoxide (DMSO) (Carlo Erba Reactifs)

2.2. Extraction of humin

Soil samples used were from Azraq Oasis (East of Amman – Jordan) and Ajloun forest (North of Amman – Jordan). Three soil samples were air dried, then sieved to remove any sand or stone or tree leaves, then crushed and homogenized prior to extraction in an atmosphere of N_2 gas. The soil was repeatedly extracted according to Song et al. (2008) and Simpson et al. (2007) with 0.10 M NaOH in (1:10) ratio and shaken for 24 h. Exhaustive extraction was then carried out in the same way using 0.10 and 1.00 M NaOH with 6.00M urea (1 /1) ratio. Then further extraction carried out in the same way using DMSO and 6% H_2SO_4 in (94:6) ratio followed by separation using separatory funnel. Further purification to remove any ash was done using concentrated HF and finally the product was dried at 70 °C for 24 h. The yield from Ajloun was 2.9% while from Azraq was 1.1%.

2.3. Instrumentation

FT-IR spectra of extracted humin were recorded using Thermo Nicolet NEXUS 670 FT-IR Spectrophotometer. KBr powder was dried at 200 °C for 24 h, and then was homogenized with humin (1:100) in ball grinder. The tablets (diameter 1 cm, thickness 0.1 cm) were prepared using hydraulic press. The sample was mounted in the FT-IR sample holder. The infrared spectrum was recorded in the wave number range 400 - 4000 cm^{-1}. Elemental analyses of the two humin samples were done by using Euro Vector 3000 Elemental Analyzer. The ash test content was determined by ignition at 800 °C for 3 h and repeated until a fixed weight was obtained. The thermal gravimetric analysis (TGA) of the humin samples were studied using NETZCH STA 409 PG/PC Thermal Analyzer in the temperature range (0-1000) °C at a heating rate of 20 °C/min. XRD of humin samples were recorded using Philips X pert pro, operated at 30 KV and 30 mA, scatter slit: 1 deg, receiving slit: 0.3 mm, drive axis: 2 theta, scan speed: 2 deg/min and sampling pitch: 0.02 deg. X-rays are generated by impinging copper metal target with high-energy electrons in a vacuum. Samples (2.0-6.0) mg, were dissolved in 0.6 ml DMSO then two drops of 4% D_2SO_4 were added to the sample to ensure complete dissolution and then transferred to a 5 mm NMR tube for solution ^{13}C NMR analysis by Bruker DRX-300 spectrometer (Simpson et al., 2007). Solid ^{13}C NMR for humin samples were done by Bruker ^{13}C CPMAS (150 MHz). The FEI inspect f50 scanning electron microscope was used to record micrographs of the particles after coating with platinum then the energy dispersion spectrum (EDS) was used to determine the elements present. Nitrogen adsorption and desorption isotherms of humin were measured using QuantaChrom® NovaWin2 instrument to calculate the surface area and pore size according to Brunauer–Emmett–Teller (BET) method.

2.4. Cation exchange capacity experiments

Cation exchange capacity (CEC) was determined using adsorption of copper ions by humin (Haenam and Dongil, 2001). The CEC of the samples were obtained by the difference in Cu(II) content in the initial and final solution as determined by atomic absorption spectrometry and the CEC was calculated from the quantity of Cu(II) adsorbed.

The humin cation exchange capacity (meq /100g or cmol/kg) was calculated using the following equation:

$$\text{CEC} = \frac{(C_i - C_e)V}{m} \times \frac{100}{1000}$$

Where:

C_i: Initial copper ion concentration (meq/L).

C_e: Final copper ion concentration (meq/L).

V: volume of copper ion solution added (mL).

m: mass of humin (g).

3. Results and discussion

3.1. FT-IR

The FT-IR spectrum of the humin exhibits characteristic absorption bands for the major bonds involved in the humin. The results of the FT-IR (Table 1) analysis showed absorption bands in the regions: 3400-3300 cm^{-1} for the stretching of H-bonded (OH-group) (3348 cm^{-1} in Azraq humin and 3338 cm^{-1} in Ajloun humin), 2950-2800 cm^{-1} for aliphatic CH stretching, (symmetric stretching nearly at 2850 cm^{-1} in Azraq and Ajloun humin, asymmetric stretching nearly at 2920 cm^{-1} for both), 1750-1720 cm^{-1} for C=O stretching, 1650-1600 cm^{-1} for aromatic C=C stretching, 1300-1000 cm^{-1} for CO stretching and the peak at 1043 cm^{-1} in Azraq humin and 1057 cm^{-1} in Ajloun humin for CO stretching of polysaccharide or Si-O tension due to presence of quartz or/and clay minerals and the band at 798 cm^{-1} is due to quartz. The same peak appear in the FTIR analysis of humin from Fluka Company (Alvarez-Puebla et al., 2004) and for bentonite from Azraq (Al-Jarriri and Khalili, 2010). This is similar to what has been found for humin from Fluka Company (Alvarez-Puebla et al., 2004). The IR spectrum also showed other peaks in Azraq humin at 3697 cm^{-1} and 3617 cm^{-1} and a small weak band at 697 cm^{-1} indicating the presence of kaolinite, the same peaks appeared in Fluka humin (Alvarez-Puebla et al., 2004).

Table 1: FT-IR for Azraq and Ajloun humin.

Azraq humin	Ajloun humin	Assignment
3348 cm^{-1}	3338 cm^{-1}	the stretching of H-bonded OH-group
2850 cm^{-1}	2850 cm^{-1}	aliphatic CH symmetric stretching
2920 cm^{-1}	2920 cm^{-1}	aliphatic CH asymmetric stretching
1714 cm^{-1}	1716 cm^{-1}	C=O stretching
1613 cm^{-1}	1642 cm^{-1}	aromatic C=C stretching
1043 cm^{-1}	1057 cm^{-1}	CO stretching of polysaccharide, or Si-O tension due to quartz or/and clay
798 cm^{-1}	742 cm^{-1}	due to quartz
3697 cm^{-1}		indicating the presence of kaolinite
3617 cm^{-1}		
697 cm^{-1}		

3.2. Thermal properties

The thermal stability of the humin was investigated by thermogravimetric analysis (TGA) under dry nitrogen atmosphere. The TGA curve of the humin displayed almost one stage characteristics with a slow loss of mass due to dehydration starting from 60 °C to 140°C for Ajloun and to 160°C for Azraq. A relatively fast loss between 140°C to about 480 °C for Ajloun humin and 160°C to about 480 °C for Azraq humin. Flaig et al. (1975) mentioned that below 500 °C the superposition of thermal degradation of carbohydrates, dehydration of aliphatic structures and decarboxylation of carboxylic groups are considered to occur, while at higher temperature the breakdown of aromatic structures are involved. The ash percent is 20% and 4.5 % for Azraq and Ajloun humin respectively. These results are in agreement with that for Italian humic acid by Dell 'Abate et al. (2002).

3.3. Elemental Analysis

Elemental analysis was done to show the percentage of each element in the two humin (Table 2).

Table 2: Elemental analyses of the two humin (Azraq, Ajloun) and Fluka company humin.

Humin source	% C	%O	% N	% H	Atomic H/C ratio	Atomic O/C ratio	Atomic C/N ratio	% Ash
Azraq	55.68	17.63	2.95	3.75	0.80	0.24	22.02	20.0
Ajloun	44.96	40.41	3.41	6.72	1.79	1.20	15.38	4.5
Fluka*	39.8	37.5	0.21	5.02	1.53	0.71	1.13	16.5

* Alvazera-puebla et al, 2005.

The elemental analysis of the two humin indicates that the ratios of C, O, H and N are different from one soil to another. These data shows that the %C in Ajloun humin is less than Azraq humin, but %O, %N and %H are higher in Ajloun humin. The two humin have higher %C than Fluka company humin reported by Alvarez-Puebla et al. (2005). This suggest that there is more humification (more condensation) process in Azraq humin than in Ajloun; because of the weather conditions (higher temperatures and humidity) in Azraq (Oasis) region compared with Ajloun (High mountains).

The H/C, O/C and C/N atomic ratios are calculated in (Table 2) as indicators of the saturation degree, polarity and stage of decomposition, respectively (Balcke et al., 2002; Ding et al., 2002). The H/C ratio of Ajloun humin is higher than that for Azraq, which indicates that Azraq humin is more condensed and less protonated than Ajloun. This suggests a well-developed carbon lattice and higher molecular weight of Azraq humin, and support the increase in aromaticity. The O/C ratio of Ajloun humin is higher than that of Azraq and Fluka's, this indicates that Ajloun humin is richer in polar groups, and may reflect larger amount of carboxylic acid, phenolic and O-alkyl groups (Balcke et al., 2002). The C/N ratio of Ajloun humin is lower than for Azraq and higher than Fluka. This indicates that Azraq humin is in a more advanced stage of decomposition than that of Ajloun, which is more than Fluka's (Ding et al., 2002). Also the ash percentage for Azraq humin is more than those of Ajloun and Fluka humin due to the presence of bentonite and kaolinite.

3.4. XRD Analysis

The XRD patterns for the two humin are presented in Figure (2) and Table 3. The band at 3.53 Å (G-band) is due to tightly condensed aromatic carbon in a similar way to graphite, and it indicates that aromatic carbons are more than aliphatic in Azraq humin (Schnitzer et al., 1990). A peak at 3.02 Å and 2.89 Å in Azraq humin and at 3.15 Å in Ajloun humin indicate graphite like structure, these peaks also appear in Azraq humic acid done by Khalili and Ajjouri (1987). A peak at 1.94 Å in

Ajloun humin and 2.04 Å and 1.93 Å in Azraq humin indicate the presence of aromatic structure (Khalili and Ajjouri, 1987). In the XRD data (Table 3) of Ajloun humin other peak appeared at 1.65 Å indicating the presence of alpha quartz (Alvarez-Puebla et al., 2004). In Azraq humin, there are other peaks indicating quartz at 1.77 Å and 3.31 Å (Alvarez-Puebla et al., 2004). All the previous peaks confirms with Fluka humin done by Alvarez-Puebla et al. (2005). Others peaks appear in Azraq humin indicating the presence of more minerals than in Ajloun humin.

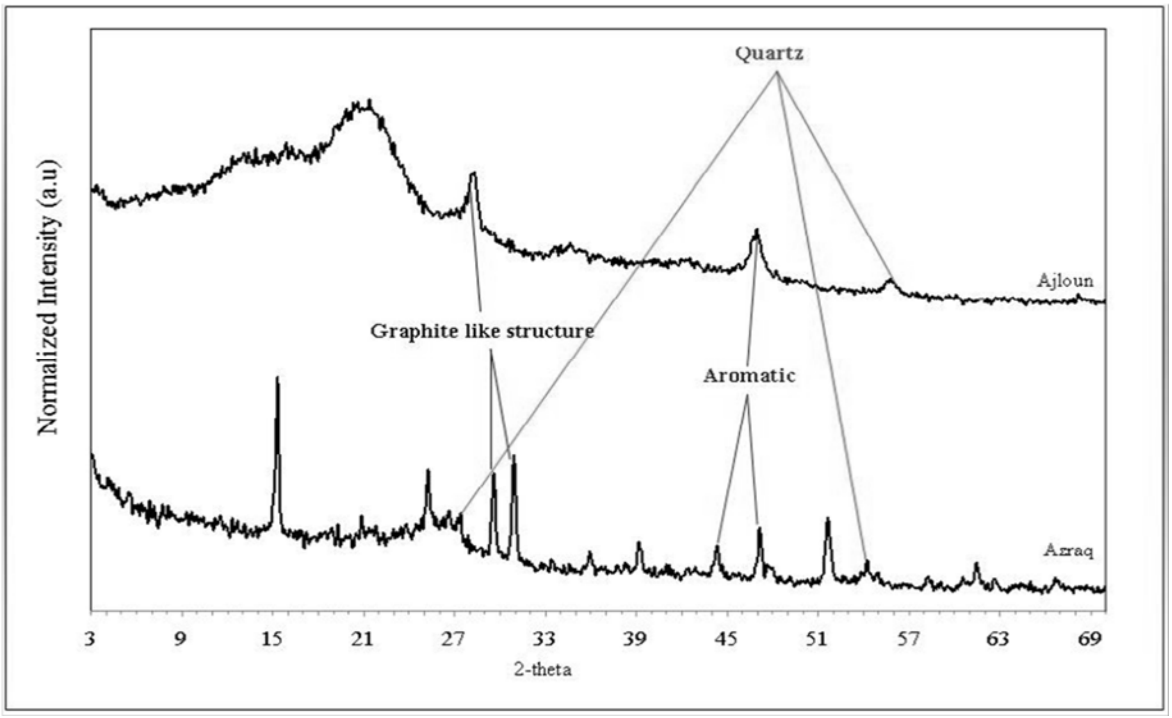


Figure 2: XRD pattern of Ajloun and Azraq humin.

These minerals mainly bentonite with peaks appear at 2.50, 1.51 and 1.40 Å, (Al-Jarriri and Khalili, 2010) and kaolinite at 2.30 Å (Alvarez-Puebla et al., 2004). These results agree with the percent of ash which is more in Azraq humin (20%) than in Ajloun humin (4.5%) and with the FTIR results.

3.5. Solution ^{13}C NMR

The results of solution ^{13}C NMR is shown in Figure 3. This Figure with integration values shows that there are three peaks in the aliphatic region; at 50-60 ppm region, 79-80 ppm region and 100-105 ppm region in the two humin samples with different integration values. In the aromatic region, there are two peaks at 110-120 ppm region and 145-155 ppm region. Another two peaks appear in the carbonyl region at 185-195 ppm and 205-215 ppm (Helal, et al., 2011). Also a peak in the carboxylic acid regions appears at 170-180 ppm region in the two humin. The integration of solution ^{13}C NMR shown in Table 4 shows the percentage of various carbon types in the two humin samples.

Table 3: XRD data.

Humin source	**Azraq**		**Ajloun**	
Mineral and structural feature	2Θ	d-spacing (Å)	2Θ	d-spacing (Å)
Kaolinite	39.19	2.30		
Bentonite	35.93	2.50		
	61.50	1.51		
	66.81	1.40		
Quartz	26.97	3.31		
	54.65	1.77	55.70	1.65
G band	25.25	3.53		
Graphite like structure	30.92	2.89	28.31	3.15
	29.60	3.02		
Aromatic	47.13	1.93	46.89	1.94
	44.34	2.04		

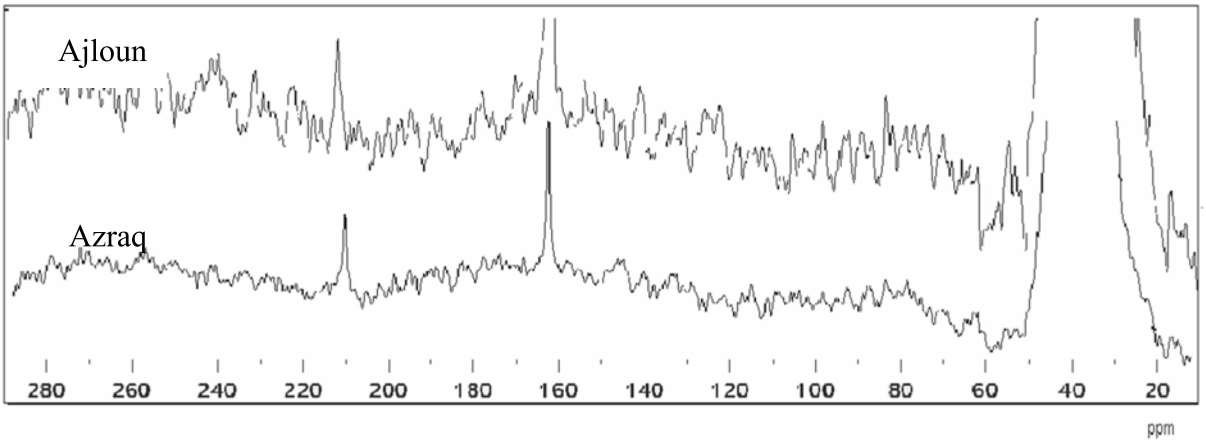


Figure 3: Solution ^{13}C NMR of Ajloun and Azraq humin.

From the values shown in Table (4) the aliphatic and aromatic percentages were higher in Ajloun humin, while the carboxylic and carbonyls were lower than those in Azraq humin. All aliphatic carbons were O-alkyl in the two humin, and the major part of the aromatic was phenolic. The phenolic integrations were 18.30 and 24.39 for Azraq and Ajloun humins, respectively. The phenolic part in Ajloun is more than that in Azraq. That is clearly confirmed with the %O from the elemental analysis. The results in Table (4) show that the Jordanian humin has lower aliphatic, nearly the same aromatic, higher carboxylic, aldehyde and ketone than humin extracted from Tennessee (USA) soil, but the two Jordanian humin have lower aliphatic and higher aromatic from that reported by Ussiri and Johnson (2003) for the soil from White Mountain region of New Hampshire in USA.

Table 4: Integration results of solution ^{13}C NMR showing the percentage of various carbon types in humin samples.

Humin source	Aliphatic	Aromatic	Carboxylic	Aldehyde and Ketone
Azraq	34.53	29.48	20.55	15.44
Ajloun	39.82	32.42	12.90	15.31

3.6. Solid ^{13}C NMR

The results of solid Cross polarization magic-angle spinning ^{13}C NMR (CPMAS ^{13}C NMR) is shown in Figure 4. This Figure shows that there are many types of carbon, such as: Aliphatic carbon (alkyl 0-50 ppm and O-alkyl 50-110 ppm), aromatic 110-140 ppm (phenolic 140-160 ppm appears only in Ajloun humin) and carboxylic carbon 160-200 ppm, with different intensity in the two humin. These results agree with Amherst peat soil humin and Florida peat soil humin with a different intensity (Wang and Xing, 2005). Ajloun humin has higher intensities for all types of carbon; these results agree with solution ^{13}C NMR results. The main features occur between 20-30 ppm aliphatic C (especially those in the long CH_2 –chains), 49 ppm aliphatic C (for CH_4), 65 ppm for O-alkyl, 95 ppm for di –O-alkyl C, 130-140 ppm for aromatic, 140-149 ppm phenolic for Ajloun humin only and 160-180 ppm for carboxyl C. These results agree with solution ^{13}C NMR except the features in alkyl region disappear in solution ^{13}C NMR because the solvent appear in this region, while the features in the carbonyl region appear in solution ^{13}C NMR and disappear in CPMAS ^{13}C NMR.

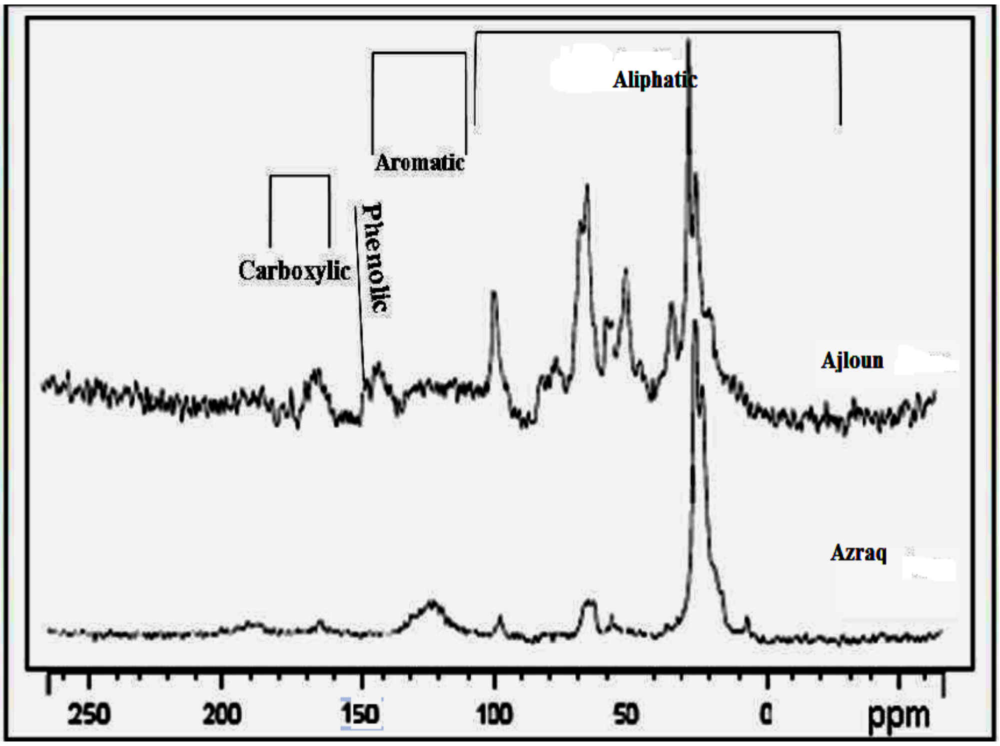
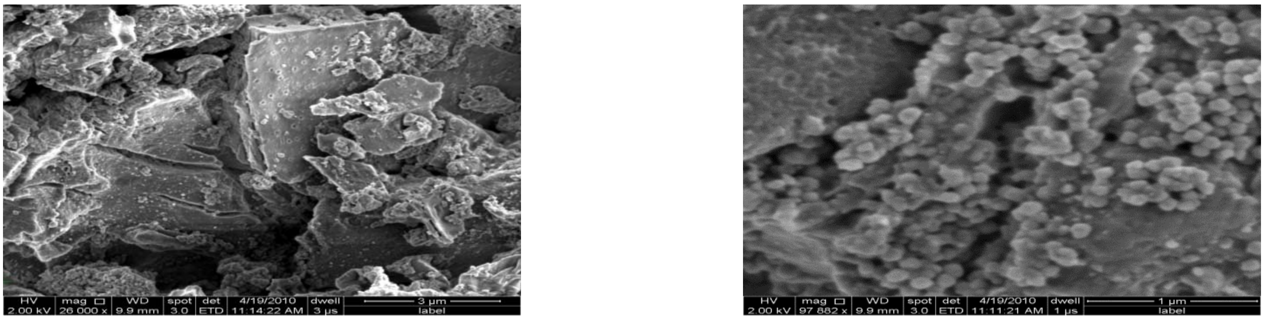


Figure 4: Solid ^{13}C NMR for Ajloun and Azraq humin.

3.7. Scanning Electron Microscope (SEM)

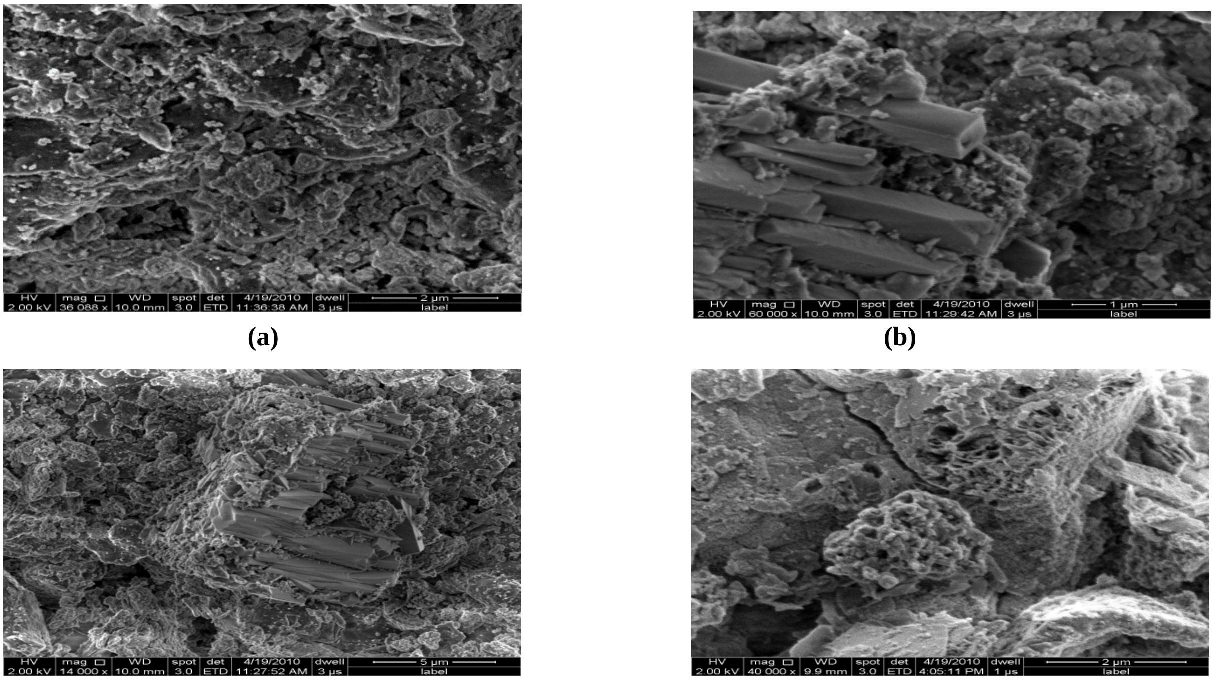
The SEM micrograph of Azraq humin Figure (5a) shows layer like structure (flats) which agrees with XRD 3.53 Å (G-band) indicating the presence of graphite like structure, gaps and holes are also exist and there are crystals. At high magnification Figure (5b), clearly shows the aggregated nano grains of the humin. Those are randomly distributed within the range of 50-120 nm.



(a) **(b)**

Figure 5: SEM micrographs for Azraq humin at magnifications (a) 26000x. (b) 97882x.

The SEM micrograph of Ajloun humin (Figures 6a and 6c) showed the layer structure (sheet) that agrees with the XRD graphite layer structure results, the aggregation and the high porosity of the humin with low presence of crystals. Figure (6b) shows the sheet structure and the presence of crystals with rode shape due to the presence of quartz crystals. Figure (6d) shows a lot of holes and gapes with different size and high porosity.



(a) **(b)**

(c) **(d)**

Figure 6: SEM micrographs for Ajloun humin at different magnifications (a)36088x (b)60000x (c)14000x (d)40000x.

3.8. Cation Exchange Capacity (CEC) of Azraq and Ajloun humin

The cation exchange capacity values depend on pH and temperature (Brady et al., 2008). The highest values were 145.40 cmol/kg and 56.65 cmol/kg, at pH 6.00 and 45°C and at pH 5.00 and 45°C for Azraq and Ajloun humin, respectively. These values showed that the CEC for Azraq is higher than that of Ajloun humin. The Azraq humin values are within the range (100-300) cmol/kg of CEC reported by Petti (2007). This can be explained by the higher percentage of carboxylic content in Azraq than Ajloun humin (Table 4).

3.9. Surface area and porosity of Azraq and Ajloun humin.

Nitrogen adsorption/desorption isotherms of the two humin were done according to IUPAC classification, the humin samples showed N_2 adsorption/desorption isotherm type III hysteresis, meaning there is a wide range of pore sizes in humin. The shape of the adsorption isotherm curve itself represents a continuous progression with increasing loading from monolayer to multilayer adsorption and then to capillary condensation, indicating relatively weak attractive interactions between the adsorbent and the adsorbate (Lowell et al., 2004).

On the other hand, the pore size distribution graphs of humin samples showed that the most probable pores diameters of humin samples are almost at 18.00 Å and other probable maximums could be seen around 29.00 and 55.00 Å and 14.00 Å for Azraq humin, while for Ajloun humin they could be seen around 24.00, 39.00 and 55.00 Å. Therefore, most pores radii are in the range of micropores and some of these in the range of mesopores and macropores in the two humin. These results are in agreement with Fluka humin values reported by Alvarez-Puebla et al. (2005). The pore size and surface area data of humin samples were reported as the following: the average pore diameters were 17.64 and 13.33 Å, these values and multi point BET were 7.71 and 7.84 m^2/g for Azraq and Ajloun humin respectively. There is no value for surface area done by N_2 and BET for any humin, but Alvarez-Puebla et al. (2005) used CO_2 and DR method for the surface area for Fluka humin and got a value of 57.3 m^2/g. This difference is due to that N_2 cannot penetrate into the micropores in humin. This is in agreement with the results of a pervious study done to determine the surface area of humic acid for three samples from Amsterdam-Netherlands done by Jonge and Mittelmeijer-Hazeleger (1996). They found that there is a large difference between the BET –N_2 (at 77 K) surface area of 0.89-4.94 m^2/g and the CO_2 (at 273 K) surface area of 94-174 m^2/g. These results could be explained as follows: microspores less than 0.5 nm can be penetrated only by CO_2 and not N_2 due to activated diffusion and the capillary condensation of N_2 in pores of 0.2-0.5 nm (Jonge and Mittelmeijer-Hazeleger, 1996).

4. Conclusions

The two Jordanian humin are very stable, extremely porous with high surface area, high functionality of carboxylic acid, phenolic and O-alkyl groups, with layer structure and differ slightly than known humin from other region. The Azraq humin higher carbon percentage indicates higher condensation and less protonation than Ajloun Humin. Also Azraq humin has higher ash percentage due to the presence of kaolinite and bentonite. The Azraq humin is in more advanced stage of humification because the aromatic carbons are more than the aliphatic. They have graphite like layer structure (sheet); and high porosity. The cation exchange capacity values depend on the pH and temperature. The CEC for Azraq is higher than Ajloun humin. The most probable pore diameters are in the range of micropores and some in the range of mesopores and macropores in the two humin.

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فصل وتشخيص الهيومن من موقعين في الأردن

صفاء المومني[1] و فواز الخليلي[2]

ملخص

إن الهدف من هذه الدراسة هو فصل وتشخيص الهيومن من موقعين في الأردن: واحة الأزرق (انسيبتسيول) وغابات عجلون فيرتيسول) لأول مرة بسبب ثرائهما في المادة العضوية. تم استخلاص الهيومن من الموقعين وتنقيته. ومن ثم تم تشخيص الناتج بواسطة طيف الأشعة تحت الحمراء، تحليل العناصر، وكذلك التحليل الكمي الحراري، و المسح المجهري الإلكتروني، وحيود الأشعة السينية، والرنين المغناطيسي لنظير الكربون 13 للسائل و الصلب. كما تم دراسة مساحة السطح والمسامية وسعة التبادل الكاتيوني. تشير نسبة الكربون المرتفعة في هيومن الأزرق إلى تكثيف عالٍ بالمقارنة مع الهيومن من عجلون. كما يتميز هيومن الأزرق بارتفاع نسبة الرماد بسبب وجود الكاولينيت والبنتونيت. إن نسبة C /O في هيومن عجلون أعلى من تلك الموجودة في الأزرق مما يدل على أنها أكثر ثراء بالمجموعات القطبية ، وقد تعكس وجود كمية أكبر من مجموعات حمض الكربوكسيل ، الفينول و O –ألكيل. كما ان نسبة C/ N في هيومن عجلون هي أقل من النسبة في هيومن الأزرق والتي تشير إلى أن هيومن الأزرق هو في مرحلة متقدمة من التكوين. كشفت قياسات الرنين المغناطيسي النووي لنظير الكربون 13 أن النسب المئوية للمجموعات الأليفاتية والعطرية كانت أعلى في هيومن عجلون ، في حين أن أحماض الكربوكسيل والكربونات كانت أقل من تلك الموجودة في هيومن الأزرق. كما دلت صورة المسح المجهري الإلكتروني على وجود بنية طبقية (رقائق) مع مسامية عالية. بلغت قيم سعة التبادل الكاتيوني 145.40 سنتيمول / كيلوغرام و 56.65 سنتيمول / كغم ، بالنسبة لهيومن الأزرق وعجلون على التوالي. وأن معظم المسام نصف قطرها في نطاق ميكروبورز وبعضها في نطاق ميزوبورز و ماكروبورز في هيومن ألازرق وعجلون.

الكلمات الدالة: انسيبتسيول، فيرتيسول، هيومن، استخلاص، تشخيص.

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