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C Venkata Madhuri
PG Student, Department of Soil Science and Agricultural Chemistry, SV Agricultural College, Tirupati, Andhra Pradesh, India

V Munaswamy
Professor (RETD.), Department Soil Science and Agricultural Chemistry, SV Agricultural College, Tirupati, Andhra Pradesh, India

KV Naga Madhuri
Principal Scientist, Dept. Soil Science and Agricultural Chemistry, Regional Agricultural Research Station, Tirupati, Andhra Pradesh, India

Y Reddi Ramu
Associate Professor, Department Agronomy, SV Agricultural College, Tirupati, Andhra Pradesh, India

Corresponding Author:
C Venkata Madhuri
PG Student, Department of Soil Science and Agricultural Chemistry, SV Agricultural College, Tirupati, Andhra Pradesh, India

Effect of organic manures on soil organic matter quality in groundnut growing soils

C Venkata Madhuri, V Munaswamy, KV Naga Madhuri and Y Reddi Ramu

Abstract
A study on changes in organic matter quality as influenced by continuous application of organic manures was carried out during *Kharif*, 2016 in an ongoing long-term (9-years old) experiment at RARS, Tirupati. It is essential to know about the organic manure quality and transformation of soil OM which inturn influenced by the humic fraction. The continuous application of organic manures significantly increased humic acid fraction and oxygen containing functional groups of humic acid but decreased optical density (E_4/E_6 ratio) over control and RDF (Recommended dose of fertilizer i.e.20:40:50 N, P_2O_5, K_2O kg ha^{-1} for groundnut crop in *kharif* season). This indicated more aromatic character of humic acid. Different treatments recorded the following ranges of humic acid content from 0.23 to 1.26 g kg^1,total acidity (3.4 to 10.1 me g^{-1}), carboxyl groups (1.8 to 3.7 me g^{-1}), phenolic-OH groups (1.6 to 6.5 me g^{-1}) and E_4/E_6 ratio with narrow range (3.45 to 5.63) at harvest of crop. Potentiometric titrations curves of humic acid obtained from different organic manure treatments were sigmoid in nature, indicating their weak acidic nature. The conductometric titration curves showed slow conductance and the UV spectra were feature less i.e. similar in nature inspite of differences in composition and showed decreased optical density with increased wavelength.

Keywords: Humic substances, humic acid, organic manures, functional groups

Introduction
Groundnut (*Arachis hypogaea* L.) is an oilseed and protein rich crop which removes large quantities of nutrients (i.e.,160-180 kg of N, 20-25 kg P, 80-100 kg of K, 60-80 kg of Ca, 15-20 kg S to produce 2.0 to 2.5 t ha^{-1} of economic yield in groundnut. NRCG, 1994) [16] from the soil which cannot be met by single nutrient source. This crop is mostly grown under energy starved conditions of low soil fertility and rainfed situations. Use of organic manures may prove a viable option for sustaining the productivity. Soil organic matter (SOM) and various physical properties have been proposed as indicators of soil quality (Doran and Parkin, 1994) [4].

Soil organic matter is the single property which influences soil fertility, soil formation, soil biology, physical and chemical properties of soil (Malewar *et al.*, 1998 and Katyal, 2000)[13]. Humified organic matter which is transformed into humus will have a strong impact on soil fertility (Janzen, 1987) [9].

A better understanding of characteristics of humic substances is necessary to comprehenced the transformation of these fractions will undergo at different soil environment and different time interval. A very little information is available on the effect of organic manures on SOM fractions and its characteristics in groundnut crop. Hence the present investigation was proposed with main objective of effect of continuous application of various organic manures on changes in SOM and its quality.

Materials and Methods
A long-term experiment was initiated in the year 2007 at Regional Agricultural Research Station, Tirupati and the same experiment was selected for the present study with prime objective to assess the changes in organic matter fractions as influenced by continuous application of organic manures. The experimental site lies at a 13.5° N latitude and 79.5° E longitude with a total rainfall of 455.6 mm during the crop growing period of 2016. The experiment was laid out in a randomized block design, replicated four times with six treatments. The treatments include T_1: Control (no manure and fertilizers), T_2: RDF

(recommended dose of fertilizer i.e., 20 kg of N ha^{-1}, 40 kg of P_2O_5 ha^{-1}, 50 K_2O kg ha^{-1}), T_3 : Vermicompost at 2.5 Mg ha^{-1}, T_4 : Poultry manure at 4 Mg ha^{-1}, T_5: Farm yard manure at 10 Mg ha^{-1}, T_6 : Pressmud cake at 10 Mg ha^{-1}.Over a period of 9 years the above organic manures applied at the rate of 390 kgs of vermicompost, 624 kgs of poultry manure,1560 kgs of Farm Yard Manure and 1560 kgs of press mud cake to plot size of 173 m^2.

The soil samples were collected from each treatment at surface *viz.,* 0-15 cm before sowing and harvest of crop during *kharif*, 2016 which is used for isolation of humic substances and were extracted, purified and characterized using standard procedures (Kononova,1966) [11]. Humic acid and fulvic acids were separated after extraction with 0.5 N NaOH as humic fractions have differential solubility i.e. humic acid (alkali soluble), fulvic acid (acid soluble) was used as the criterian for separating them. But fulvic acid obtained after purification was present in very minute quantities and hence it was not characterized. Humic acid was characterized for functional groups like total acidity (Schintzer and Gupta, 1965) [18], carboxyl groups (Schintzer and Khan,1972) [19] and phenolic groups, spectral properties (E_4/E_6) ratio, UV spectra, potentiometric and conductometric titrations. Soil organic carbon was estimated by Walkley and Black wet oxidation method (1934) [26] as outlined by Jackson (1973) [8] and the same was expressed in g kg^{-1}.

Results and Discussion

Humic acid fractionation

Humic acid concentration of soil before sowing ranged from 0.25 g kg^{-1} to 0.92 g kg^{-1} with a mean of 0.59 g kg^{-1}.while at harvest it ranged from 0.23 g kg^{-1} to 1.26 g kg^{-1} with a mean of 0.75 g kg^{-1} (Table.1). Data showed that humic acid concentration increased from 21.3 to 40.6 per cent during sowing to harvest with application of different organic manures to groundnut crop. Significantly higher humic acid content was recorded in FYM applied treatment (T_5) compared to other organic manures. This could be due to improved microbial growth and a conductive environment for decomposition of organic matter, leading to the formation of more humic acids (Sharma and Gupta 1998) [20]. Gathala *et al.* (2007) [5] observed an increase in humic acid content (0.321%) with FYM application compared to control (0.239%) and RDF (0.269 %) in a long term experiment in a maize-wheat cropping system at Rajastan college of Agriculture farm, Udaipur. Humic acid production increased with decomposition in the present study. Singh and Amberger (1990) [21] also observed an increase in humic acid with time.

Table 1: Effect of long term application of organic manures on soil humic acid content (g kg^{-1}) and E_4/E_6 ratio before sowing and at harvest of groundnut crop.

Treatments	Humic acid (g kg^{-1})		%	E_4/E_6 ratio		Increase or decrease (%)
	Before sowing	Harvest	Increase or decrease	Before sowing	Harvest	
T_1: Control	0.25	0.23	-8.0	4.98	5.63	+13.1
T_2: RDF	0.32	0.45	+40.6	4.87	5.24	+7.6
T_3: Vermicompost 2.5 t ha^{-1}	0.47	0.57	+21.3	4.90	4.35	-11.2
T_4: Poultry manure 4 t ha^{-1}	0.69	0.87	+26.1	5.19	4.74	-8.7
T_5:Farm yard manure 10 t ha^{-1}	0.92	1.26	+37.0	4.50	3.45	-23.3
T_6:Press mud cake 10 t ha^{-1}	0.85	1.12	+31.8	4.51	3.57	-20.8
GM	0.59	0.75		4.83	4.50	
SE.m.±	0.03	0.04		0.80	0.43	
C.D (p = 0.05)	0.09	0.13		2.40	1.29	

Recommended dose of Fertilizer (RDF): 20:40:50 kg ha^{-1} N, P_2O_5, K_2O

The organic carbon content in all treatments significantly increased from 8 per cent to 50 per cent during sowing to harvest (Table.2). Among the organic manures highest organic carbon was recorded in FYM applied treatment (T_5). Increase in organic carbon content with application of organic manures were reported by Verma *et al.* (2005) [25] in long term fertilizer experiment in clay loam soils and by Gupta *et al.* (1988) [6] in coarse loamy soils of Hisar.

Characterization of humic fractions

The humic acid isolated and extracted from different treatments were analyzed for their functional groups. Humic acid was highly reactive natural polymer. Functional group analysis provided information on major oxygen containing functional groups of humic acid and are the index of their reactivity.

Total acidity of humic acid in soil before sowing varied from 4.2 me g^{-1} to 8.9 me g^{-1} with a mean of 6.6 me g^{-1} (Table.3) while at crop harvest it ranged from 3.4 me g^{-1} to 10.1 me g^{-1} with a mean of 7.67 me g^{-1}. Data showed that total acidity of humic acid content increased from sowing to harvest with application of different organic manures to the groundnut crop.

Table 2: Effect of long term application of organic manures on organic carbon (g kg^{-1}) content before sowing and at harvest of groundnut crop

Treatments	OC (g kg^{-1})		(Organic carbon) Increase or decrease (%)
	Before sowing	Harvest	
T_1: Control	2.20	1.60	-27.3
T_2: RDF	2.80	3.70	+32.1
T_3: Vermicompost @ 2.5 t ha^{-1}	2.50	3.60	+44.0
T_4:Poultry manure @ 4 t ha^{-1}	2.80	4.20	+50.0
T_5:Farm yard manure @ 10 t ha^{-1}	5.00	5.90	+8.00
T_6:Press mud cake @ 10 t ha^{-1}	4.60	5.80	+26.1
GM	3.34	4.18	
SE.m.±	0.25	0.52	
C.D (p = 0.05)	0.75	1.56	

Recommended dose of Fertilizer (RDF): 20:40:50 kg ha^{-1} N, P_2O_5, K_2O

Carboxyl groups of humic acid in soil before sowing (2016) varied from 2.2 me g^{-1} to 3.4 me g^{-1} with a mean of 2.78 me g^{-1}, while at crop harvest (2016) ranged from 1.8 me g^{-1} to 3.7 me g^{-1} with a mean of 3.02 me g^{-1}(Table.3).This carboxyl groups of humic acid increased from sowing to harvest of groundnut crop with the application of organic manures. The results were in conformity with findings of Inbar *et al.* (1990) [7] who extracted humic substances from cattle manure compost at different stages of decomposition and Srilatha *et al*. (2013) [22] who observed increased total acidity and carboxyl groups with FYM application compared to RDF by long-term application of fertilizers and manures in the farm of RARS, Polasa in rice-rice cropping sequence in an Inceptisol.

Phenolic groups of humic acid in soil increased with application of different organic manures from sowing to harvest. The results of Yadhav and Jha (1988) [27] indicated that phenolic group composition increased by application of organic manures. Close observation of data revealed that the functional groups viz., total acidity, carboxyl groups and phenolic-OH groups were higher in organic manure treatments compared to control and RDF (Table.3). Higher content of total acidity and phenolic groups in surface layers indicates that they had less potential for interaction with metal and clays. The easier movement and decomposition of COOH groups of aliphatic compounds compared to aromatic compounds tends to increase the relative proportion of phenoloic–OH groups in surface layers. More phenolic groups in soil indicate the organic matter in that particular soil was in more humified state (Lavti and Paliwal, 1981) [12]. At harvest of crop humic acid content was positively and significantly correlated with total acidity (0.945**) and phenolic groups (0.938**). Total acidity was also positively and significantly correlate with carboxyl groups (0.832*) and phenolic groups (0.983**) (Table.4).

Table 3: Effect of long term application of organic manures on functional groups of humic acid in soil before sowing and at harvest of groundnut crop.

TREATMENTS	Content (me g^{-1})					
	Total acidity		Carboxyl group (-COOH)		Phenolic group (-OH)	
	Before sowing	Harvest	Before sowing	Harvest	Before sowing	Harvest
T_1: Control	4.2	3.4	2.2	1.8	2.0	1.6
T_2: RDF	4.8	7.0	2.3	3.0	2.5	4.0
T_3:Vermicompost 2.5 t ha^{-1}	5.4	6.7	3.1	3.4	2.3	3.3
T_4:Poultry manure 4 t ha^{-1}	7.7	9.0	2.8	2.9	4.9	6.1
T_5:Farm yard manure 10 t ha^{-1}	8.9	10.1	3.4	3.7	5.5	6.4
T_6:Press mud cake 10 t ha^{-1}	8.6	9.8	2.9	3.3	5.7	6.5
GM	6.60	7.67	2.78	3.02	3.82	4.65
SE.m.±	0.22	0.31	0.06	0.07	0.19	0.25
C.D (P = 0.05)	0.67	0.94	0.17	0.22	0.57	0.75

Recommended dose of Fertilizer (RDF): 20:40:50 kg ha^{-1} N, P_2O_5, K_2O

The per cent contribution of carboxyl groups towards total acidity of humic acid in soils before sowing of crop ranged from 33.72 to 57.41 with a mean of 44.33 per cent, while at harvest ranged from 32.22 to 52.94 with a mean of 41.51 per cent. Contribution of phenolic groups – OH towards total acidity of humic acid in soils of before sowing of crop ranged from 42.59 to 66.28 with a mean of 55.66 per cent, while at harvest it ranged from 47.06 to 67.78 with a mean of 58.49 per cent. Similar observations was given by Lavti and Paliwal (1981) [12] who reported that presence of high levels of phenolic - OH groups in Pusa soils than other functional groups. Results of present experiment are in contrast to findings of Nagamadhuri (1996) [14], Srilatha *et al.* (2013) [22] who observed more of COOH groups contribution to total acidity than Phenolic-OH groups.

Table 4: Correlation between humic acid content and functional groups of humic acid content at harvest.

	Humic acid content	Total acidity	COOH groups	Phenolic -OH groups
Humic acid	1			
Total acidity	0.945**	1		
COOH groups	0.759	0.832*	1	
Phenolic-OH groups	0.938**	0.983**	0.716	1

* and ** indicate a significant difference at $P < 00.05$ and $P < 00.01$, respectively

Characterisation of humic fractions for spectral properties:

E_4/E_6 ratio:

Measurement of absorption in different regions of electromagnetic spectrum has been used for qualitative and quantitative investigation on humic acid (Stevenson, 1982) [23]. E_4/E_6 ratio of humic acid in soil before sowing ranged from 4.5 to 5.19 with a mean of 4.83 while at harvest it ranged from 3.45 to 5.63 with a mean of 4.50. E_4/E_6 ratio of humic acid in soils under various organic manures applied treatments was significantly varied. At harvest lower E_4/E_6 ratio was recorded in organic manure treatments compared to control and RDF before sowing of crop (Table.1). This indicated humic acid in soils at harvest had higher aromaticity and higher humification degree compared to soils of before sowing. Similar results of decrease in optical density with application of organic manures was reported by Szombathova et *al*. (2004) [24] and by Aranda *et al*. (2011) [2] in a study on influence of soil type and management on organic matter quality.

Potentiometric and conductometric titrations:

Potentiometric titration curves have been used to characterize the acidic functional groups in humic acid. The potentiometric titration curves of humic acid extracted from soils under different treatments before sowing and at harvest showed similar in nature with each other (Fig.1 and Fig. 2). In potentiometric titrations with standard 0.1 N NaOH, gradual rise in pH was recorded with the addition of base indicating a high buffering capacity of humic acids. Potentiometric titration curves were sigmoidal in nature indicating an appeerent monobasic character and had a single break indicating weak acid polyelectolytic character of humic acid. The findings of Nagamadhuri *et al.* (1998) [15], Reddy and Rao (2000) [17] also indicated weak acidic behavior of humic acid in different farming systems.

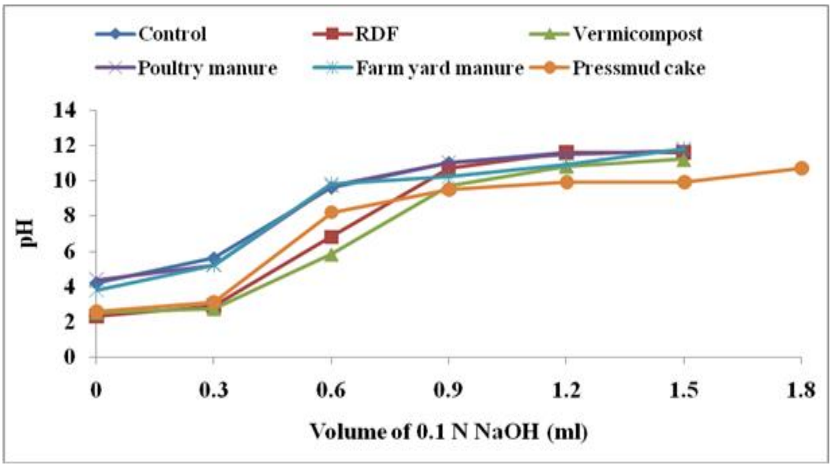

Fig 1: Potentiometric titration curves of humic acid in soil as influenced by long term application of organic manures before sowing of crop.

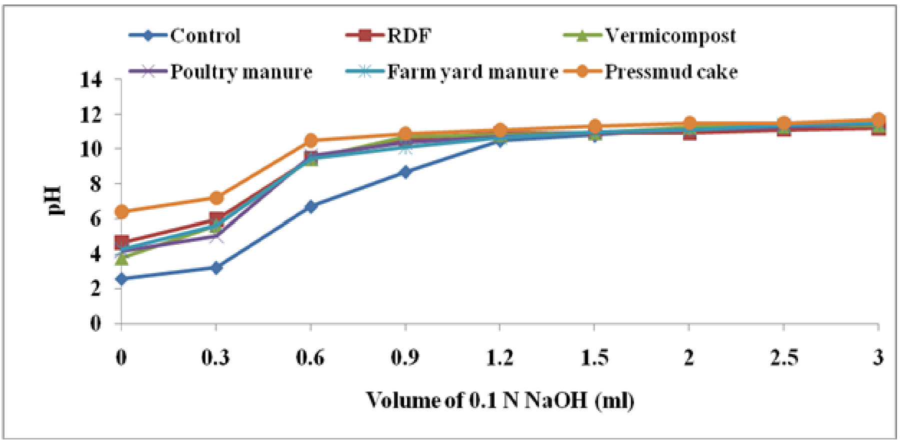

Fig 2: Potentiometric titration curves of humic acid as influenced by long term application of organic manures at harvest of crop.

Humic acid extracted from soils of different treatments were conductmetrically titrated against 0.1 N NaOH. Conductometric titration curves of humic acid extracted from different treatments before sowing and at harvest showed similar in nature (Fig.3 and Fig. 4). From the curves, it was clear that the conductance increased slowly in the beginning to neutralize its acidity followed by a sharp rise in curve with addition of NaOH. Low conductance of HA was due to purification, because while purification HA dialysed almost free of ions (Adhikari *et al*., 1972) [1]. The results of the present investigation were similar to findings of Srilatha *et al*. (2013) [22] in the experiment conducted for physico-chemical characterization of humic substances under long-term application of fertilizers and manures in an Inceptisol.

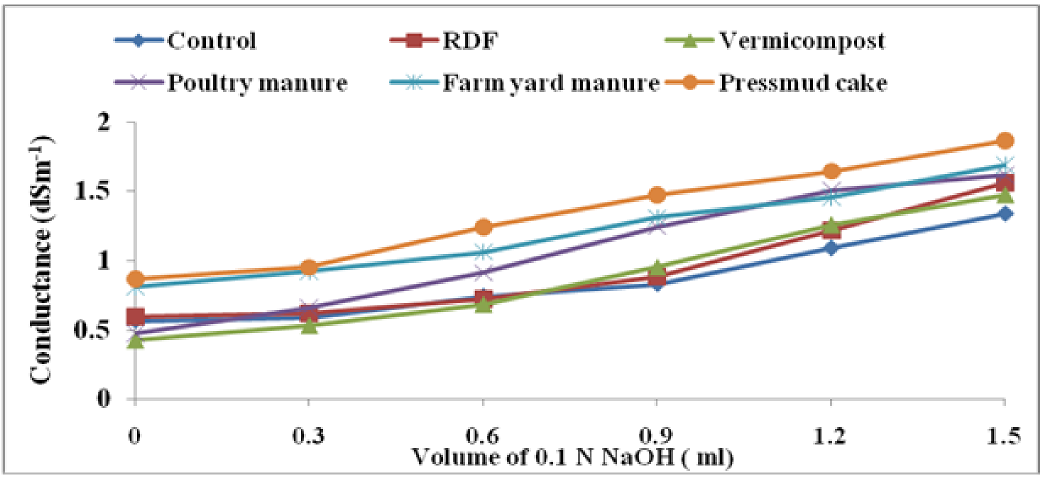

Fig 3: Conductometric titration curves of humic acid in soil before sowing of crop as influenced by long term application of organic manures.

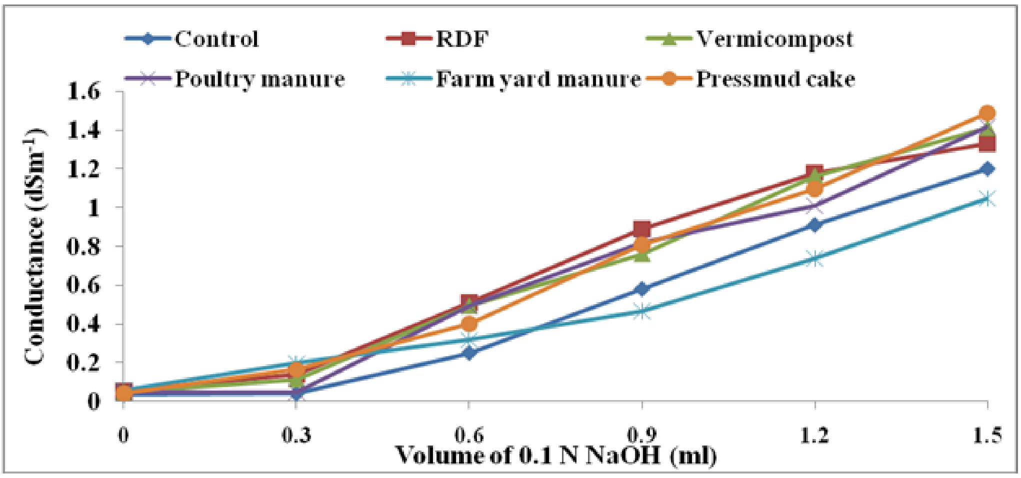

Fig 4: Conductometric titration curves of humic acid in soil as influenced by long term application of organic manures at harvest of crop.

UV spectra of humic acid

Ultraviolet spectra of humic acid extracted from soils of various organic manures treatments before sowing and at harvest are showed in Fig.5 indicating that these were featureless with a decreasing optical density with increasing wavelength. UV spectra of humic acid emanated from different organic manure treatments were steeper in nature which indicates more aromatic character of humic acid (Dkhar *et al*. 1986) [3].

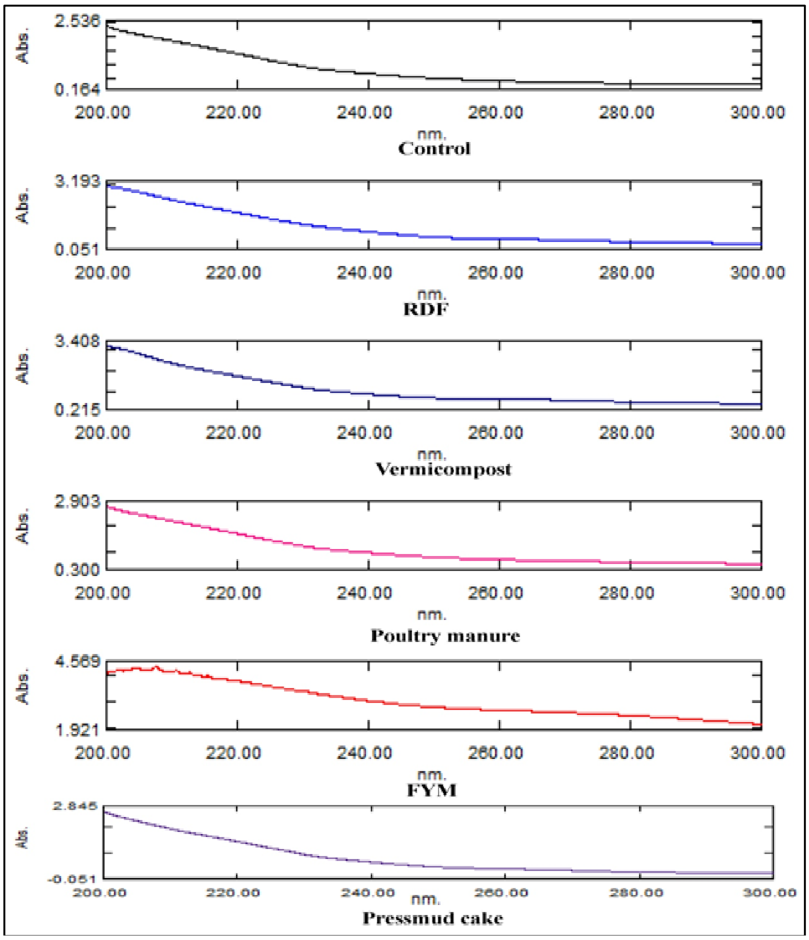

Fig 5: UV Spectrum of humic acid as influenced by long term application of organic manures in different treatments.

Conclusion

Humic acid extracted from different organic manures and oxygen containing functional groups viz., total acidity, carboxyl groups and phenolic groups of humic acid are significantly increased by the pressmud cake and FYM treatments. E_4/E_6 ratio is in narrow range. Potentiometric, conductrometric cuves indicates weak acid character of humic acid and UV spectra featureless indicates similar nature of humic substances inspite of different treatmental composition. Long term application of organic manures increased the soil organic matter quality apart from the supply of essential nutrients for sustainable crop growth.

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