

Silicon Binding in Soil Humic Substances

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Research Article

Keywords: Humic acid, Silicon, binding, organo-mineral complex

Posted Date: December 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-905591/v2>

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Abstract

In the present study, an attempt has been made to probe the nature of silicon-humus bonding as it occurs in nature ('untreated') as compared to the samples wherefrom the metalloid ions have been removed ('treated'). Infrared (IR) spectroscopy revealed the role of carboxylic acid groups of Humic acid (HA) in metal complexation. Si-O absorption reduced considerably in treatment to remove metalloid ions, but it remained quite strong in the treated samples indicating a strong Si-O linkage with humus. In XRD analysis, treated samples showed stronger γ -bands. DTA analysis indicated structural strain on the humic molecule induced by complexation with metalloid ions. Treated HAs had higher acidity values compared to the untreated samples. Treatment for removal of metal ions caused an increase in cation exchange capacity while a reduction of E_4/E_6 ratio. Treated HAs also showed higher molecular weights (M_v) compared to the untreated samples. Removal of metals renders certain groups free which form intermolecular bonds. On the basis of analytical data, it was observed that there is still some silicon bonds within humic acid molecule, even after removal of silicon by forcing conditions. Association of silicon with humus in soils are quantitatively and qualitatively different from other metal ions and it is clear that humic acid molecule possess silicon-humus bond like pure organo-metallic compounds.

Introduction

Humic substances (HSs), which are ubiquitous in natural environments, are organic macromolecules primarily derived from the degradation of plant and microbial materials. The binding of metal ions to HSs is of great interest because of its importance in regulating metal speciation, toxicity, bioavailability and transport in the environment (Stevenson, 1994).

HS is the most widely encountered natural complexing ligands, which tends to chelate various metal ion present in the environment. In humic acid (HA) metal complexes, humic acid can change the properties of metal ions. Metal solubility can be increased when metals are complexed with free HA or decreased when metals are scavenged by humic films or mineral surfaces (Calac et al., 2009). As a result metal bioavailability and toxicity get affected (Monterio et al., 2013).

Humic substances in soils are naturally associated with metal ions (Stevenson, 1994; Ghosh and Schnitzer, 1981; Yan and Korshin, 2014; Zhou et al., 2015; Ding et al., 2019) and the phenomenon is more pronounced with tropical soils. However, most of the studies on humic substances have been made with samples of temperate origin although it was known that the characteristics of tropical samples are different (Griffith & Schnitzer, 1975). Tropical samples contain higher amount of ash. This ash mainly contains silicon, iron and aluminium. It is not just the amount of these metal ions in the tropical samples but its unusually strong bonding to the humic molecule (Griffith & Schnitzer 1975) which makes it so decisive in modifying the properties of humic substances. Humic substances- metal binding (Kerndroff and Schnitzer, 1980; Plaza et al., 2006; Zhaung et al., 2014; Zhou et al., 2015) can affect metal migration

and bio-availability. As a result, HS-metal interactions are of strong research interest and metal binding by HSs is being studied very thoroughly (Kinniburgh et al., 1996; Ghabbour et al., 2007; Fuentes et al., 2013; Liu et al., 2014; Orłowska et al., 2017).

The objective of this study was to explore the nature of new silicon humus bonding for understanding the soil organic matter functions and reactivity.

In this work, humic substances were treated with the usual methods of ash-removal to reduce, as much as possible, the aforesaid inorganic ions and then these treated samples were compared by various physicochemical means with the untreated ones.

Materials And Methods

Isolation of Humic Acid

Humus was isolated from Ap horizon (0-15 cm) of two soils, viz., Jalpaiguri and Baruipur, West Bengal, India, with three replications. Humic acid were isolated by conventional methods that is describe briefly below:

Soil carbonates were removed by mechanical stirring of the sample for 30min with 2M H_3PO_4 . The treatments were repeated three times. Soil sample were then washed with distilled water until the suspension reached a pH of 7. Free carbonate in soil sample were then extracted with 0.1M sodium pyrophosphate (pH 9.8) followed by 0.1M NaOH using a sample extractant ratio of 1:10. For each extraction step, the mixture was shaken mechanically for 3h, followed by centrifugation at 15,000g for 15 min and final filtration of the supernatant through a Whatman no.42 filterpaper. Each procedure was repeated three times. The combined alkaline extracts were then acidified with HCl to pH= 1, left standing for 24h in a refrigerator to allow the complete precipitation of HA, and then centrifuged at 30,000g. The HA precipitates were purified by dissolution in 0.1M NaOH. The suspension was centrifuged at 30,000g, the residue was discarded, and the alkaline supernatant was acidified with HCl to pH= 1. The suspension was left standing for 12h at room temperature (about 293K). This purification procedure was repeated three times. The precipitated HA were then recovered with distilled water, dialyzed until free of Cl^- ions, dried.

The 'HA' sample was treated with a large excess of 0.5% (v/v) HF-HCl mixture for 72 hours; the solution was removed by centrifugation and the process repeated thrice more. The solid sample was thereafter washed by centrifugation, dialyzed and vacuum dried, as before. This sample was designated as 'treated HA'.

Characterization of humic acid

Elemental analysis of humic acids was performed by complete oxidation through instantaneous combustion of small portion of the sample. The percentage of carbon, hydrogen, nitrogen and sulphur

was determined on ash free basis using LECO Model CHNS-932 Elemental Analyzer and oxygen by difference to 100: $0\% = 100 - (C + H + N + S) \%$. In order to determine the silicon, aluminum and iron contents, the samples were analyzed following the methods described by Sparks (1996). For the analysis of Al^{3+} and $Fe^{3+/2+}$, fusion of the sample was done with tri-acid mixture ($HNO_3 + H_2SO_4 + HClO_4$). While for Si^{4+} , it was fused with solid NaOH in a Ni-crucible. Silicon was determined as sulphomolybdate, aluminum as alizarin red-S and iron as o-phenanthroline complexes following spectrophotometric methods.

E_4/E_6 ratios were determined by dissolving 1 mg of HA in 5 ml of 0.05 M $NaHCO_3$ and measuring optical densities at 465 and 665 nm (Chen et al., 1977). Total acidity was determined conductometrically following Schnitzer and Gupta (1965).

The IR spectra were recorded on KBr pellets by mixing 1-2mg of sample was made into pressed discs with 200mg KBr. This was scanned over $4000-400cm^{-1}$ on a Perkin Elmer 577 double beam spectrometer.

The XRD patterns of the HA's both treated and untreated, were recorded on a Phillips PW 1140 diffractometer using Ni-filtered $CuK\alpha$ radiation. The samples were packed in a sample holder. Scanning angles ranging from 5 to $60^\circ (2\theta)$ were run at $2^\circ (2\theta)/min$.

Viscosity measurements were done with the help of a Ubbelohde viscometer at $30^\circ C \pm 0.1$. Solutions of HAs were prepared by dissolving the samples in 0.1 N NaCl where their macromolecular structures do not change with sample concentration (Ghosh & Schnitzer, 1980) and adjusting the pH strictly to 7.0, so that the pH-effect is uniform in all the solution.

Metalloid-ion interactions:

The metalloid ion adsorption methods are the same as recommended by Schnitzer and Hansen (1970).

To determine interaction of Si^{4+} with HA, 20 mg of the treated HA, was taken in a 150 ml conical flasks; 2,5,10,20,30,40 ppm standard aqueous metal solution was added to these sets along with 2.5 ml of 1(N) NaCl solution. There after pH was adjusted to 2.0 and volume made up to 25 ml the mixture was shaken for three hours and equilibrated by allowing the solution to stand for 24 hours at room temperature. After allowing time for solids to settle, a requisite amount of solution was pipette out. The amount of Si^{4+} in this solution was pipette out. The amount of Si^{4+} in this solutions were determined calorimetrically. Si^{4+} ions fail to respond any interaction under this experimental condition (Table -6).

For this reason interaction of Si^{4+} with treated HA was also done at a pH of 6.0 and 8.5. For experiments at pH 8.5, 0.1 (N) NaOH was used to raise the pH. Since humic acids solublised at this pH, the interaction was done in the solution stage after adding the requisite amount of Si^{4+} solution. At the end of this interaction period, the pH of the solution was adjusted at 2.0; the HA precipitated from this solution was centrifuged off. The Si^{4+} in this solution was recorded. At pH 6.0 and 8.5 instead of adsorption, desorption of Si^{4+} takes place.

At the same time how much Si^{4+} can be dissolved out from the treated HA was determined in another experiment by treating HA with 0.2, 0.02, 0.002, and 0.0002(N) NaOH solutions. (Table 7)

As Si^{4+} dissolve from all the above experiments, extraction of silica was done in light of the procedure recommended by Hashimoto and Jackson (1960). Briefly, 200 mg of the treated HA sample was taken in a plastic beaker. Then 100 ml of 0.5 (N) NaOH was added to it and the solution boiled for exactly 2.5 min. It was then brought to room temperature, and the HA precipitated by adjusting the pH at 2 with HCl solution.

The precipitated was separated by centrifugation and repeatedly washed with 0.1 (N) HCl solution followed by water and then dried. Then amount of Si^{4+} of this treated samples are estimated and at the same time adsorption of Si^{4+} with that treated HA was done in the usual way as mention above.

Results And Discussion

Humus was extracted from highly weathered soils differed in mineralogical composition according to the parent material type (Table 1). The soils are Aeric Epiaqupts and Typic Haplusteps have developed on residuum derived from Deltaic Alluvium and Alluvium/ Colluvium. The some physical and chemical properties of these soils are listed in Table 2.

Elemental analysis and metal contents of humic acids is listed in table 3. All the treated samples contain certain amount of Si^{4+} , Al^{3+} and $\text{Fe}^{3+/2+}$ even after treatments to reduce metal ions. In the 'treated' HA the contents of all the ions were reduced by reduction in Si^{4+} level was less than Al^{3+} or $\text{Fe}^{3+/2+}$. All treated samples had comparable levels of metal ions.

The elemental analysis of treated HAs was unnecessary because on dry, ash-free basis, it will be the same with the untreated ones (Table 3). On treatment to reduce the metal ions, (i) Si^{4+} content reduces by about 80% in case of Jalpaiguri HA while for Baruipur HA, such reduction is around 92% (ii) Al^{3+} content reduces by about 97% for both Jalpaiguri and Baruipur HA samples, and (iii) $\text{Fe}^{3+/2+}$ content is lowered by 97% and 84% for Jalpaiguri and Baruipur HA sample, respectively (Table 3).

IR spectra (Figure 1) showed the following changes on reducing metal ions: (i) In the treated HAs the absorption of the 1630 cm^{-1} decreases whereas that of the 1720 cm^{-1} increases compared to the untreated HAs. (ii) Simultaneously, the $1400\text{-}1390\text{ cm}^{-1}$ band diminishes in intensity in the treated HAs, compared to that in the untreated HAs.

(iii) Similarly, the 1050 cm^{-1} is more prominent in the untreated samples whereas it is much less intense in the treated samples. All these indicate that as more polyvalent, metal ions are removed as in treated samples, more carboxylic groups are rendered free. Carboxylic groups react with metal ions to form metal carboxylate bonds. At the same time, hydrogen bonding of C=O of carboxyl or quinines are destroyed. Positions of carboxyl C=O and OH vibrations are, therefore, deformed from their normal positions.

(iv) The sharp decrease in the 1040 cm^{-1} in the treated samples compared to untreated ones is probably due to reduction in the level of Si-O bonded to HA following treatment to reduce metal ions. This infers that a strong Si-O linkage existed in the HA which can only be partially removed by chemical treatment.

(v) On the other hand, in the treated HA samples, the 3400 cm^{-1} absorption decreases. Assuming that some OH groups are involved in the metal-humic bonds in the untreated HA samples, the removal of metal ions should cause an increase in OH absorption. The contrary behavior suggests that during the removal of metal ions from HA by the methods employed, M-OH bonds (M=metal) are also abstracted. These probably contributed to a significant extent in the 3400 cm^{-1} absorption and may be the reason for the decrease in intensity of the 3400 cm^{-1} band in the treated samples. At this stage, it may be conjectured that during the process of humus formation, $\text{Fe}^{3+/2+}$, Al^{3+} , Si^{4+} etc. ions do not incorporate into the humic substances in purely ionic forms, rather, they may react as some partially hydroxylated forms like $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Si}(\text{OH})_3^+$, $\text{Si}(\text{OH})_2^{2+}$, $\text{Si}(\text{OH})^{3+}$, etc. This explains why untreated HA contains some M-OH bonds together with M-HA bonds, (vi) There is also a sharpening of phenoxy C-O (1250 cm^{-1}) in the treated samples. This may be caused by the release of some phenoxy C-O groups, from bonding with metals, (vii) The 1200 cm^{-1} is absent in the untreated samples whereas the treated samples show this band due to opening of some oxygen containing functional groups.

Although Si-O absorption around 1000 cm^{-1} reduces considerably on treatment, this was still quite strong in the treated samples indicating a strong Si-O linkage with humus. A reduction in the absorption around 3400 cm^{-1} was also noted on treatment, which suggest the contribution of metal-OH absorptions in the untreated samples.

The X-ray diffractograms are shown in figs. 1 and the data derived therefrom are presented in Table 5. The noteworthy information in this context are as follows: (i) A strong reflection at 9.60 \AA (at 9.82 \AA with Jalpaiguri HA only) is observed with all the samples. This is due to a silicate as humic molecules produce only weak reflections, even a very small quantity of silicate present can yield relatively stronger diffraction bands. (ii) The band around 7.5 \AA may also be due to silicate organic band is extremely strong and this indirectly suggests that the tropical humic substances will be richer in metal ions than the temperate ones. (iii) All the samples show the well-known γ -band, between 4.03 and 4.12 \AA . (iv) The other reflections shown by the samples are of not much significance.

On treatment to reduce metal ions, the significant changes in XRD (Figure -1) is that the γ -band (4.03 to 4.12 \AA) becomes more prominent and reflections due to silicate ($9.60 - 9.82\text{ \AA}$) weaken. The bands like one at 7.5 \AA assigned to silicate phase and the well known 002 band, due to ordering of condensed aromatic layers normal to their planes (Kodama & Schnitzer, 1967), are exhibited by both 'treated' and 'untreated' samples.

Treated HAs show exotherms at much higher temperatures (Table 4), viz. with Jalpaiguri HA at 605°C instead of 540°C and with Baruipur HA at 600°C instead of 440°C . Ghosh and Schnitzer (1982) observed

that the thermal stability of humic substances is decreased as they are complexed with metals. They inferred that complexing by metals exert strains in the humic structure thereby lowering its resistance to thermal stabilities. On treatment, an additional endotherm at 435°C for Jalpaiguri HA and 480°C for Baruipur HA are observed. Strain got free by removal of metals is likely to be responsible for this.

There is substantial increase in total acidity values on treatment to reduce metal ions. With Jalpaiguri HA, such increase is from 475 to 860 cmol (+) kg⁻¹ (about 80%) while for Baruipur HA, the change is from 660 to 860 cmol (+) kg⁻¹ (about 30%). One can conclude that the groups which are responsible for total acidity is humic molecules; which includes weakly acidic functional groups apart from carboxyl and phenolic hydroxyl, are rendered free on removal of metal ions.

On treatments, the E₄/E₆ ratio (Table 4) of Jalpaiguri HA reduces from 4.95 to 2.46 while such lowering in the case of Baruipur HA, is from 6.11 to 2.74. As E₄/E₆ ratio is an index of molecular size and weight (Chen et al., 1977) this substantial change indicates that metal ions which were removed, do not act as a bonding between humic molecules. On the contrary, on removal of these metal ions, groups which can form linkages between humic molecules become free and make bonds as H-bonds or homolytic bonds through free radicals, which is quite likely at pH 8.3.

With Jalpaiguri HA, on treatment to reduce metal ions, the viscosity average molecular weight (M_v), is increased from 4,715 to 8,030 an increase of about 70% (Table 4). Such increase is around 20% with Baruipur HA where in the absolute increase in M_v values are from 14,830 to 17,705. This data provide more conclusive evidence of the observation that metal ions do not act as a bridge between humic molecules; only intermolecular bonds are formed. On removal of the metal ions, the acid groups become free and promote intermolecular bonding, thereby increasing the molecular weight. It may be noted that the increase in total acidity value, on treatment to reduce metal ions for Jalpaiguri HA is about 80% while it is 30% for Baruipur HA. This molecular weight increase can be explained by mechanism discussed above with CEC and E₄ / E₆ values.

Treated HAs, from which the metal ions had been reduced, were interacted with Si⁴⁺ ions and in order to observed the reverse behavior and to understand how these metal ions interacted with HA. With Si⁴⁺, usually, desorption occurred at pH 2.0, 6.0 and 8.5 (Table 7). In order to prove the binding of Si⁴⁺ to HA, both Jalpaiguri HA and Baruipur HA was extracted with NaOH at various strengths. At the highest concentration of NaOH only 36.5-38.5% of remaining Si⁴⁺ could be dissolved (Table 7). The HA was then subjected to Hashimoto and Jackson Method (1960) for the removal of Si⁴⁺. The sample was subsequently studied for Si⁴⁺ adsorption. Even with this sample, only a small adsorption occurred (Table-6). It was observed that even after treatment with HAs with strong alkali solution at boiling condition only 40.50- 42.5 % of remaining Si⁴⁺ could be dissolved under such forcing condition. Thus, it is seen that although humus in nature is strongly bound with fairly large amount of Si⁴⁺, after removal of this Si⁴⁺, it cannot be re-incorporated into the humus structure.

In humic molecule there is a strong silicon-humus bond like pure organo- metallic compounds . It appears from this studies that the association of metalloid ions, with humus in soils is quantatively and qualitatively different from that of other metal ions. The unique interaction of HA with Si^{4+} could throw new light on nature of humic substances in soils.

Declarations

ACKNOWLEDGEMENT

I am gratefully indebted to Prof. (Dr.) K. Ghosh and Dr. C.Varadachari for stimulating me to think through this problem, valuable discussion, suggestion and constant help throughout the analysis periods and for the data to illustrate feasible solutions. This work is funded by the University of Calcutta from their research fund.

Notes

The author declares no competing financial interest.

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Tables

Table 1

Topographical location, Vegetation type, soil classification, parent material and Genetic horizon of soils

Site location	Topographical location	Vegetation type	Soil classification	Parent material	Genetic horizon
Baruipur	Baruipur, West Bengal, India 22°35'N, 88°44'E	Rice-Rice-Rice	Fine-loamy, Aeric Epiaquepts	Deltaic Alluvium	Ap-Bw-Bc
Jalpaiguri	Jalpaiguri, West Bengal, India 26°44'N, 89°21'E	Himalayan Forest	Coarse-loamy Typic Haplustepts	Alluvium/Colluvium	A-Bw-C

Table 2

Physiochemical analysis of the soils from which Humus were extracted

Location	pH (1:2)	EC (mSm ⁻¹)	O.C %	CEC CmolcKg ⁻¹	Sand, silt and clay (%)	Si gKg ⁻¹	SiO ₂ gKg ⁻¹	Total Fe	Fe ₂ O ₃	Total Al	Al ₂ O ₃
Baruipur	6.20	0.07	1.25	27.8	35,45,20	2.72	5.8	0.30	0.33	0.25	0.27
Jalpaiguri	5.2	0.05	1.2	27.2	52,31,17	21.1	45.4	0.23	0.27	0.09	0.12

Table 3

Elemental analysis and metal contents of HA samples

Sample		C	H	N	S	O	Si ⁴⁺	Al ³⁺	Fe ^{2+/3+}	Correlation value between treated and untreated sample		
		% (dry, ash free basis)					[(%) or mg Kg ⁻¹ x10 ⁴]			Si	Al	Fe
Jalpaiguri	untreated	55.6	4.5	4.0	Trace	35.9	1.98	4.32	7.38	-0.98198	-0.5	-0.75593
	treated						0.40	0.12	0.20	Correlation value between treated and untreated sample		
Baruipur	untreated	56.2	4.1	3.6	Trace	36.1	4.76	7.95	3.98	0.981981	-0.18898	0.720577
	treated						0.38	0.25	0.62			

Table 4
Thermal, Cation Exchange, E4/E6 and Viscosity parameters of HA samples

Sample		T(-) °C	T(+) °C	CEC cmol(+)/Kg ⁻¹	E4/E6	\overline{M}_v	Correlation value of CEC/ \overline{M}_v with thrice replication	Correlation value of CEC between untreated/treated sample with thrice replication	Correlation value of \overline{M}_v between untreated/treated sample with thrice replication
treated	100	435 605	860	2.46	8030	-0.99340			
Baruipur	untreated	110	440	660	6.11	14830	0.756636	-0.78571	0.866565
	treated	100	480 600	860	2.74	17705	-0.65465		

Table 5 X-ray diffraction patterns

Jalpaiguri HA Untreated		Jalpaiguri HA treated		Baruipur HA Untreated		Baruipur HA treated	
d in A ⁰	I*	d in A ⁰	I	d in A ⁰	I	d in A ⁰	I
9.82	100	9.60	47	9.60	46	9.60	43
7.37	37	5.98	6	7.76	7	4.11	100
4.12	29	4.03	100	5.90	7	3.40	11
2.47	17	3.18	22	4.07	100	3.20	11
1.70	12			3.20	26	2.60	7
				2.58	9		

I* : Relative Intensity

Table 6
Interaction of Si⁴⁺ with HA after treatments*

Sample	Concentration of Si ⁴⁺ solution added (in ppm)	Amount adsorbed (mg/100mg HA)
Jalpaiguri HA (Treated)	2	0
	5	0
	10	0.062
	20	0.042
	30	0.125
	40	0.083
Baruipur HA (Treated)	2	0
	5	0
	10	0.035
	20	0.046
	30	0.112
	40	0.125

Table 7**Amount of Si⁴⁺ dissolved from HA by varying strength of NaOH**

Sample	Strength of caustic soda (N)	pH	% of Si ⁴⁺ dissolved from 100mg HA
Jalpaiguri HA (Treated)	0.0002	10.3	7.25
	0.002	11.3	14.75
	0.02	12.3	18.50
	0.2	13.3	38.5
	0.5 *	13.34	42.50
Baruipur HA (Treated)	0.0002	10.3	6.12
	0.002	11.3	12.35
	0.02	12.3	17.85
	0.2	13.3	36.50
	0.5 *	13.34	40.50

*As per Hashimoto—Jackson method (1960).

Figures

Figure 1

On treatment to reduce metal ions, the significant changes in XRD (Figure -1) is that the γ -band (4.03 to 4.12Å) becomes more prominent and reflections due to silicate (9.60 - 9.82 Å) weaken. The bands like one at 7.5 Å assigned to silicate phase and the well known 002 band, due to ordering of condensed aromatic layers normal to their planes (Kodama & Schnitzer, 1967), are exhibited by both 'treated' and 'untreated' samples.