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Organo-metallic complex and its implications

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Abstract

Complex formation is the reaction of a metal ion and ligands through electron pair sharing and the resulting product is called the metal coordination compound. The metal ion is the electron-pair acceptor, and the ligand is the electron-pair donor. The metal ion serves as the central ion, and the organic ions are coordinated around it in a first coordination sphere.

Covelo *et al.*, 2008 studied the heavy metal sorption and desorption behavior of a Fibric Histosol with that of its organo mineral fraction (OMF) and reported that greatest sorption capacity was for lead and copper. Urrutia *et al.*, 2013 studied the physico-chemical characteristics of diverse types of humic-metal-phosphate acid complexes and reported that molecular size distribution of humic-metal-phosphate as a function of pH is similar to that of potassium or sodium humates and metal-humate complexes.

Eshwar *et al.*, 2017 studied the stability constant of Fe(II), Cu(II), Mn(II) and Zn(II) metal ion complexes with HA/FA at pH 7 and at 30 °C and reported that for humic acid the log k values was highest for Cu (II) and in case of fulvic acid the log k values was highest for Mn (II). Mukhopadhyay and Sanyal, 2004 studied the release potential of arsenic (As) from arsenic-humic/fulvic complexes by soluble phosphate nitrate salt and examined it in terms of the appropriate exchange isotherms and reported that phosphate had a greater degree of exchangeability with arsenic than did nitrate, at both the lower and higher concentrations and also reported that stability constant of synthetic HA/FA were greater than that of natural HA/FA.

Sinha and Bhattacharyya, 2011 studied the release isotherm of As from the HA/FA complexes extracted from vermicompost and FYM in presence of molybdate, nitrate, phosphate, sulfate and borate and reported that the greatest tendency to displace As from the complexes was shown by sulphate, molybdate, and nitrate. Datta *et al.*, 2001 studied the stability constant of complexes formed by the humic acid with Cd²⁺ ions in aqueous phase and reported that humic phenolic-OH group was involved in the formation of Cd²⁺-humic complex

Shahid *et al.*, 2012 studied the effects of different organic ligands like ethylene diamine tetra-acetic acid (EDTA), low molecular weight organic acids, humic substances on lead speciation and reported that EDTA forms soluble, stable, and phytoavailable Pb-chelates due to high binding lead affinity. He *et al.*, 2016 studied the binding behavior of Cu²⁺ to all ten HA fraction and reported that the FTIR and SEM-EDX image of HA fraction revealed that carboxyl and phenolic groups were responsible for the Cu²⁺ sorption on the ten sequentially extracted HA fractions process.

Higher molecular weight humic acids bind heavy metals more strongly than low molecular weight acids, and the study of soil organic fractions that can sorb heavy metals moderating its toxicity in the soil/crop system and preventing its entry in the food chain should be explored in future.

Keywords: Organo mineral fraction, stability constant, EDTA, FTIR, SEM-EDX

Introduction

Organo-metallic complexes are the chemical compounds containing at least one chemical bond between the carbon atom of organic molecules and a metal include alkaline, alkaline earth and transition metal. Complex formation is the reaction of a metal ion and ligands electron-pair sharing. The resulting product is called a metal coordination compound. The metal ion is the electron-pair acceptor, and the ligand is the electron-pair donor. The metal ion serves as the central ion, and the organic ions are coordinated around it in a first coordination sphere. The number of ligands bonded to the central atom in a definite geometry is called the coordination number. Some of the organic ligands can bind the metal ion with more than one donor functional group. This type of bonding forms a heterocyclic ring, called a chelate ring, the process of formation of chelate ring is called chelation. If one ligand molecule is involved in the formation is a monodentate chelate or complex, if two is involved in the formation then it is called bidentate and so on. The figure is of n-Butyllithium in which there are 4 lithium atom forming a tetrahedron, with 4 butyl groups attached to the faces. There are various linkage through which metal ion are liked with organic molecule. Monovalent cations (Na⁺, K⁺, etc) are held primarily by simple cation exchange through the formation of salts with COOH

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groups (RCOONa, RCOOK), multivalent cation (Cu^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , and others) have the potential for forming coordinate linkages with organic molecules. Soil organic matter consists of a mixture of plant and animal residues in various stages of decomposition, substances synthesized microbiologically, and or chemically, from the breakdown products and bodies of live and dead microorganisms and their decomposing remains. The higher plants release root exudates which combines with metal and form complexes. The binding of metal ions by humic colloids is a widely researched subject. Such metal-humic interactions would be expected to occur first at those sites which lead to the formation of coordinate to ring structure. Some investigations also emphasized the formation of chelate rings (Stevenson, 1994; McBride, 1994) [9, 5]. Micro-organism releases organic acid which combines with metal and form complex. Adsorption take place by clay insoluble precipitates and insoluble humus complexes and the fate of the reaction is leaching. The components of organo-metallic complexes are a) Ligand and b) Chelate.

a. Ligand: The compound which combines with metal ion is commonly referred to as the ligands. A covalent bond consists of a pair of electrons shared by two atoms, and occupying two orbitals, one of each atom. Essentially, a coordinate complex arises because the outer electron shell of the metal ion is not completely filled and can accept additional pair of electrons from atoms which have a pair of electron available for sharing. Examples of grouping contained in organic compounds which have unshared pairs of electron, and which can form coordinate linkages with ions, are shown in fig 1.

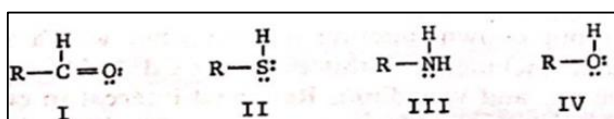


Fig 1: The structure of ligands

b. Chelate: is formed when two or more coordinate positions about the metal ion are occupied by donor groups of a single ligand to form an internal ring structure. Typical structures of chelate complexes with known biochemical compounds are shown in fig 2.

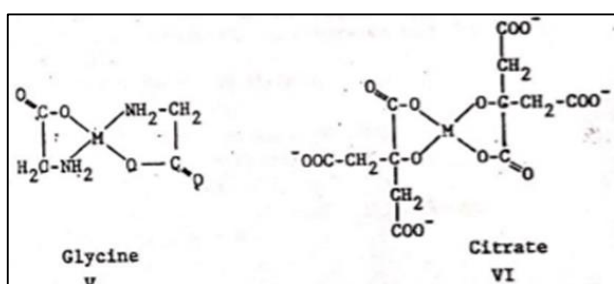


Fig 2: The structure of chelates

The significance of chelation reaction in soil is as follows:

a. Metal ion that would ordinarily convert to insoluble precipitates at the pH values found in productive agricultural soils would be maintained in solution. It is widely known that many biochemicals synthesised by micro-organisms, including amino acids and the simple aliphatic acids form soluble complexes with lead and other toxic heavy metals is of concern from the stand point of their transport to lakes and stream.

- Organic complexing agents may influence the availability of trace elements to higher plants, as well as to soil micro- and macro-faunal organisms.
- Under certain circumstances the concentration of a metal ion may be reduced to a nontoxic level through complexation.
- The interaction of Al^{+3} with organic matter may be considerable importance in controlling soil solution levels of Al^{+3} in acid soils.

There are various studies which are related with the complex formation of organic matter with micronutrient and the heavy metals.

Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by Fibric Histosol and its organo-mineral fraction: Covelo *et al.*, (2008) [11] studied the heavy metal sorption and desorption behaviour of fibric histosol with that of organo-mineral fraction.

In this case study a organo-mineral fraction was separated out by a wet-sieving procedure where 50g sample were suspended in 100 mL of water by shaking for 2h in the presence of glass beads and the fraction passing a 0.1 mm sieve. A sorption solution was prepared equal mass concentrations (between 5 and 400 mg L^{-1}) of Cd^{+2} , Cr^{+3} , Cu^{+2} , Ni^{+2} , Pb^{+2} , and Zn^{+2} as their nitrates in acetate buffer of pH 4.5.

This study shows the graph which is plotted showing the amount of each metal sorbed by the H horizon and its organo-mineral fraction (OMF) and the other graph showing the amounts retained at the end of the desorption stage of the experiments—[Fig3, Fig4]

In OMF the sorption and retention of copper and lead increases almost linearly with the initial concentration of sorption solution, specially above 100-200ppm. There are abundant lead and copper that are unoccupied even at highest sorption solution, while the sorption of other metal showed saturation. In whole soil Pb sorption increases linearly, while the curve of Cu and Cr show fluctuation as in whole soil this pair of metal has specific binding site and they compete for this metal. These metal autocatalyze their own sorption and inhibit the other metal.

The best fitting of sorption and desorption isotherm can be visualized from Table 1. The model of all metal have a good fit of Langmuir with the exception of copper as Cu competes with other metal for more sorption. But in Langmuir model there is a exception that there is no interaction among sorbate molecules that each binding site can bind one sorbate molecule called monolayer sorption, therefore Cu has poor fit of Langmuir.

From Figure 5 the Correlation between observed maximum sorption and the Langmuir equation parameter β for the whole H horizon and its OMF can be observed. In this β reflect the number of binding sites, and the maximum amount of sorbate that can be sorbed. For OMF there is excellent co-relation between the sorption capacity β and the experimental maxima in comparison to the whole soil.

Physico-chemical characterization of humic-metal-phosphate complexes and their potential application to the manufacture of new types of phosphate-based fertilizers are studied below. Urrutia *et al.*, (2013) [10] studied the physico chemical characteristics of diverse type of humic metal phosphate complexes. In this case study, material like five polyether-sulfone membranes (Millipore) of 0.22 μm , 100, 50, 10, and 5kDa molecular weights cutoffs (MWCO) were taken.

The graph plotted in this study shows the size distribution at different pH for humic acid (HA), iron-humic acid complex (FeHA), and phosphor-iron-humic acid complex (PFeHA). From the graph at pH 4, 80% of total C was concentrated to 0.22µm to 100 kDa fraction (Figure 1), at pH 6, 60% was found concentrated in 100-500 kDa fraction (Fig 6), and pH 8 humic acid fraction corresponds to 10-5kDa size (Fig 7). In fig 8 When the pH increases there is deprotonation of functional group and the negative charge which develops in the chain repel each other causing stretching of molecules and as the pH increases the molecule get stretched and breaks down leading to smaller molecule fraction. But in case of FeHA complex or phospho-iron-humic complex, although the pH is increasing but there is presence of Fe and PFe complex to prevent the stretching of molecules.

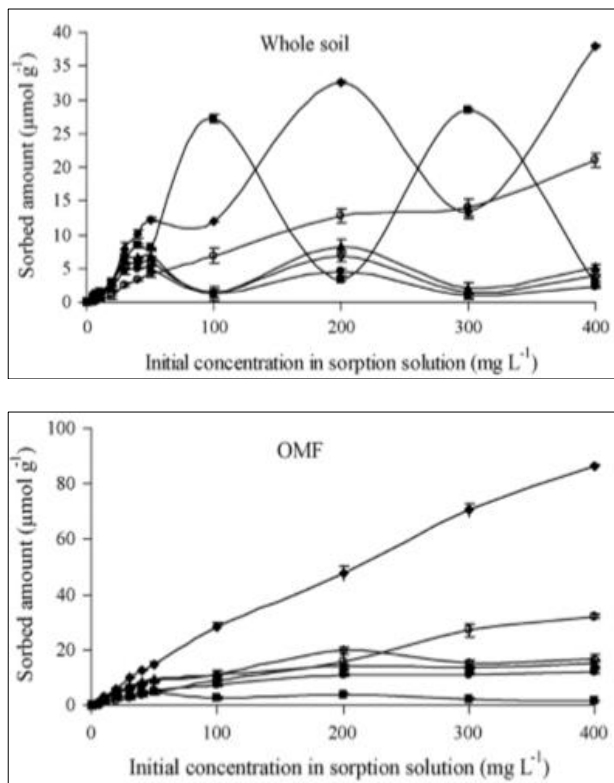


Fig 3: Simultaneous sorption of six heavy metals by a Fibric Histosol (whole soil) and its organo-mineral fraction

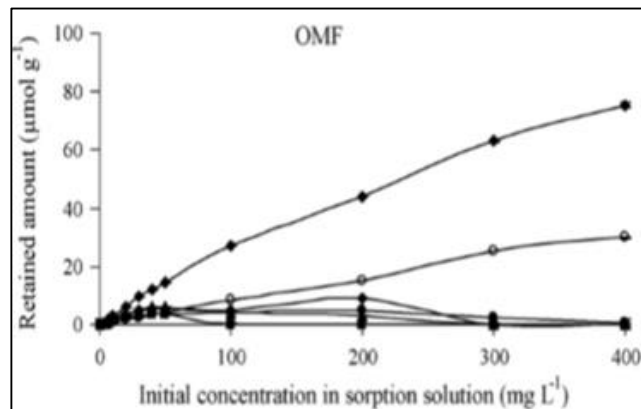
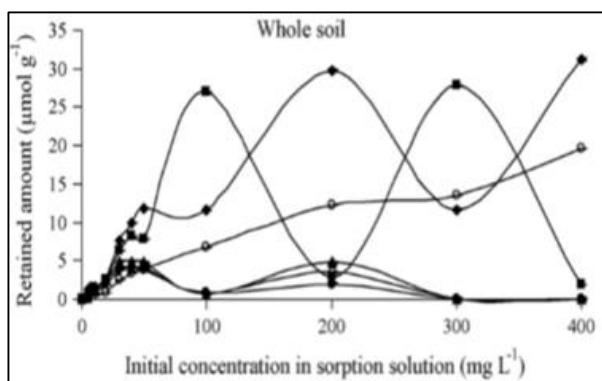


Fig 4: Retention of sorbed heavy metals after equilibrium with buffers by (whole soil) and organo-mineral fraction

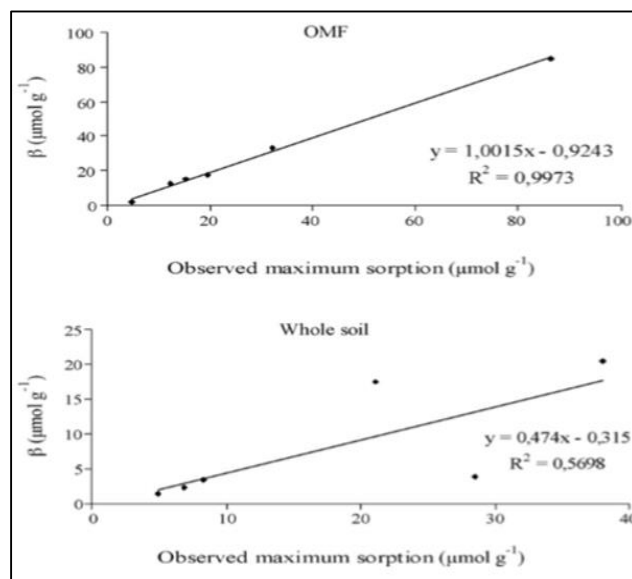
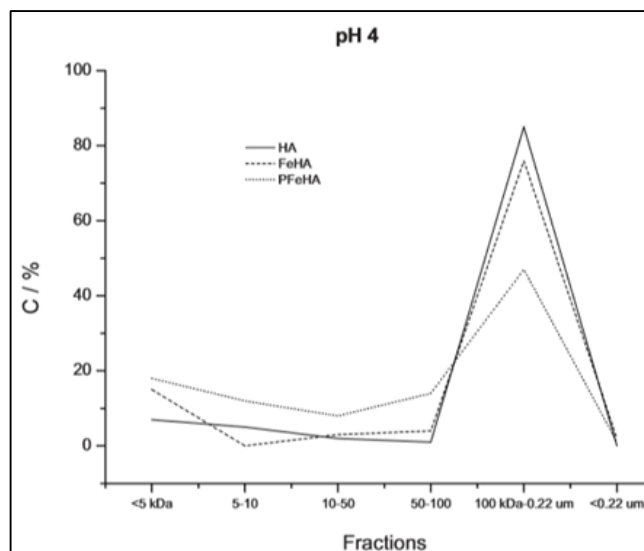


Fig 5: Correlation between observed maximum sorption and the Langmuir equation



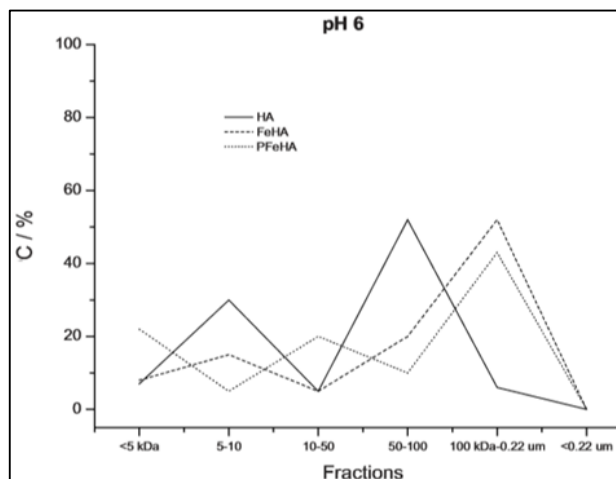


Fig 6 & 7: Size distribution at different pH for Humic acid (HA), iron-humic acid complex (PFeHA), and phospho-iron-humic acid complex (PFeHA)

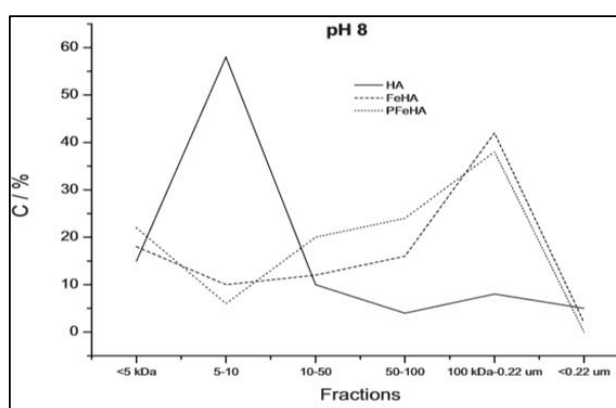


Fig 8: Size distribution at different pH for Humic acid (HA), iron-humic acid complex (PFeHA), and phospho-iron-humic acid complex (PFeHA)

Stability constant of complexes

This is one of the important parameter in determining the thermodynamic stability of metal complexes and their effectiveness in increasing or decreasing the availability of metal cation to plants. When the metal ion function as the central group which is usually the case with complex of small group series of type MA are formed.

Complexation Behaviour of Humic and Fulvic acid Acids with Metal Ion and their Assessment by Stability Constants where Eshwar *et al.*, 2017 [3] studied the stability of different micronutrient with the Humic acid fractions. In this study the X- value was determined, which refers to the numbers of mole to HA/FA that reacted with one mole of metal ion and $\Delta Gr^0 = -RT \ln K$.

As per the findings Moles of HA and FA reacted with one mole of metal ion [Fe (II), Cu (II), Mn (II), Zn (II) in the formation of complex (x values)] [Table 2]Copper is having the highest value of X, as the moles of HA/FA that will combine with Cu is more. Ability of metal ions [Fe (II), Cu (II), Mn (II) and Zn (II)] to form complexes with humic acids (1/x values) [Table 3]. The lower (1/x) value, the greater is the combining ability of these metal with HA/FA acid. The graph showing different stability constant of metal humic acid complex in fig 9, 10. The graph showing the stability constant of metal fulvic acid complex in fig 11, 12.

Standard free energy ($-\Delta Gr^0$) values for the complexation reactions of metal ion [Fe (II), Cu(II), Mn(II), Zn(II)] with humic acid fraction is shown in table 4. Standard free energy

ΔGr^0 value of copper is the highest because the electronic configuration of copper (29) is 3d10 4s1 having half filled s orbital which accept electron from the complexing agent and form the stable complex. Standard free energy ($-\Delta Gr^0$) values for the complexation reactions of metal ion [Fe (II), Cu(II), Mn(II), Zn(II)] with fulvic acid fraction is shown in table 5. In case of fulvic acid complex the coordinate bond formed between the complexing agent and the Mn (II) is most stable. Mukhopadhyay *et al.*, 2004 [6] studied the stability constant of complex formed by natural and synthetic HA/FA with heavy metal arsenic, as well as the release potential of arsenic from humic/fulvic complex by soluble phosphate and nitrate salt. In this case study humic acid from different source were extracted like.

Humic acid - HA₁: extracted from Ghentugachhi soil; HA₂: extracted from Gayeshpur soil; HA₃: synthesised from hydroquinone+cysteine.

Fulvic acid - FA₁: extracted from

Ghentugachhi soil; FA₂: extracted from Gayesphur soil
The stability constant of organo-arsenic complex can be determined by following equations:-

$$\log[(\lambda_0/\lambda) - 1] = \log K + x \log [HA]$$

The logarithm of stability constant of the arsenate/humate or fulvate complex (log k) was determined by:-

Where,

λ_0 is distribution constant in absence of HA/FA

λ is distribution constant in presence of HA/FA

Log k is stability constant of arsenic/HA or FA complex

x is the number of mol HA/FA that combine with one mol arsenic

[HA] is the concentration of HA/ FA in mol per L

$$\lambda_0 = \frac{\alpha_0 V}{(100 - \alpha_0)g}$$

λ_0 was determined from following equation :-

Where, α_0 is percent of total metal bound to exchange resin (100- α_0) is percent of total metal remaining in solution.

In table 6 amount of fresh alkali and the period of time required to attain a stable higher pH (10.8) of Humic/Fulvic acid. The naturally occurring humic sample HA₁ and HA₂ require longer time to attain the stable pH than HA₃ but require less amount of alkali. This is due to highly coiled, polycondensed structure of the natural HA and high molecular weight. Such coiled structure does not require participation of carboxylic and phenolic group in intramolecular hydrogen bond formation and not much acidity is locked up inside the coil. This is similar in case with FA₁ and FA₂.

Stability constant (log k) and mole ratio (x) of HA/FA Arsenic complexes at pH 5 is shown in table 7. For synthetic humic acid log k value is more which means that more acidic group are involved in it as well as having low molecular weight. The log k value is having positive relation with total acidity as well as negative relation with molecular weight.

Release of arsenic from HA₁-As and HA₂-As complex by aqueous phosphate and nitrate anions can be visualized in the

fig 13, 14. The release isotherm of phosphate and nitrate ion support the exchange process. At the initial stage, the extent of exchange was high for both nitrate and phosphate, but again for nitrate the extent of exchange was in equilibrium. Nitrate had a lesser tendency to displace arsenic than phosphate for both low and high concentration because of its high electronegativity, smaller size and coordination of nitrate ion.

Release of arsenic from FA₁-As and FA₂-As complex by aqueous phosphate nitrate [fig 15, fig 16]. The reason for release of arsenic from fulvic acid is same as that of humic acid. Retention and release of arsenic in arsenic-humic/fulvic equilibrium study was predicted by Sinha *et al.*, in 2011^[8] with the release isotherm of arsenic from HA/FA extracted from vermicompost/FYM, as well as the tendency of different oxyanions to displace arsenic from the complexes. In this case study humic acid and fulvic acid were extracted from different source like:-

- Humic acid/Fulvic acid extracted from vermicompost
- Humic acid/Fulvic acid extracted from FYM
- Humic acid/Fulvic acid extracted from municipal sludge
- Humic acid/Fulvic acid extracted from mustard cake
- Humic acid/Fulvic acid extracted from Ghentugachhi soil

Stability constant and mole ratio of As-HA/FA complexes at pH 5.0. The mole ratio of vermicompost FA is more than FYM, which indicate that more amount of HA/FA combine with one mole of metal ion. And this indicate that arsenic will be more tightly bounded to vermicompost and there retention release will be less as shown in fig 17.

The bar graph shown in fig 18 shows the efficiency of Organo-arsenic on retention release of Arsenic supports the fact that release of arsenic from the vermicompost complex is less. Release of As from organo-As complex in presence of different oxy anions can be seen in fig 18, molybdate ion has higher tendency to displace arsenic from organo-arsenic complex because molybdate ion has higher affinity for electron pair of electron of COOH group present in organic fractions. Datta *et al.*, 2001^[2] studied the stability constant and X value of cadmium-humic acid complex. In this case study humic acid used were extracted from different source

- HA₁: natural humic acid extracted from Mohitnagar soil
- HA₂: glycine and hydroquinone as starting materials
- HA₃: α -alanine and hydroquinone as starting material
- HA₄: cystine and hydroquinone as starting material
- HA₅: glycine and catechol as starting material

The structure of the synthetic material used in the synthesis of the humic acid is shown in fig 19. Stability constant and 'x' value of Cd²⁺ humic complexes at pH value 5 from metal HA complexation study are shown in table 8. HA₃ which was extracted from hydroquinone and α -alanine was having the higher X value and stability constant because of the phenolic acidity and since log k value is having positive relation with total acidity.

Shahid *et al.*, 2012^[7] studied the efficiency of EDTA, low molecular weight organic acids (LMWOA_s) and humic substances (HS). Binding constant of different organic ligands for Pb EDTA, low molecular weight organic acid and humic substances were taken and found that stability value of EDTA is more in comparison to other which can be seen in table 8. Efficiency of EDTA, citric acid (CA) and FA to bind Pb in nutrient at pH 7. Small concentration of EDTA can combine with Optimum amount of lead. EDTA forms soluble, stable and phyto-Available Pb chelates due to high binding affinity

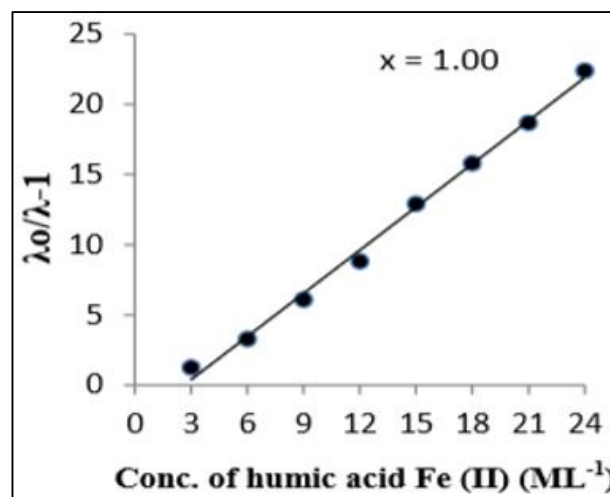
as shown in table 8. Binding characteristics of Cu²⁺ to natural humic acid fractions sequentially extracted from the lake sediment was studied by He *et al* in 2016^[4], they studied the binding behaviour of Cu(II) to all ten fraction HA fraction. In this case study different fractions of humic substances were taken:-

- Former fractions (F1, F2)
- Medium fraction (F3, F4, F5, F6, F7)
- Latter fraction (F8, F9, F10)

Elemental composition and functional groups of extracted HA_s can be seen from fig 20. The concentration of H and N increases on going from former, medium to latter fractions. As the H/C ratio increases it confirms the aliphatic character, O/C and (O+N)/C usually ranges from 0.66 to 0.53 and 0.72 to 0.61 respectively, which indicate fractions were having more oxygen containing functional group and high polarity.

F₉ and F₁₀ fraction have higher value which indicate complex structure of HA. Small size fraction was more aromatic and polar in nature where as large size fraction were more aliphatic in nature. The phenolic and carboxylic content decreases therefore total acidity decreases. UV-visible analysis for the ratios of absorbance for humic acids at 250 and 365 nm (E2/E3 ratios) and at 465 and 665 nm (E4/E6 ratios). U.V visible spectroscopy gives a better understanding of HA by (E2/E3) and (E4/E6) ratio. E4/E6 ratio related with aromaticity which decreases on going from former to latter fraction, while E2/E3 is related with aliphatic character which increases and polarity decreases as shown in fig 21.

Scanning electron microscope (SEM) images of A, B, C were former (F2), medium (F5), latter (F9) fractions and a, b, c were corresponding HA-Cu, respectively. SEM was widely used to characterise the shape, size and structure of humic substances, which is shown in fig 22 they provide information about the physico-chemical reaction. HA forms thin sheet, thread and structure in the figure A, B, C which shows that HA fraction has heterogenous surface and it is ambiguous. The figure shows that former fractions adsorb more copper. The adsorption capacity of copper on HA increases with increased concentration which can be seen from fig 23. At low concentration, the adsorption capacity increases till 50mg/L and then it flat down with high concentration. The adsorption capacity of former fraction were higher than the latter ones, due to more acidity. High carboxyl, phenolic and aromatic character in earlier fraction adsorb copper more.



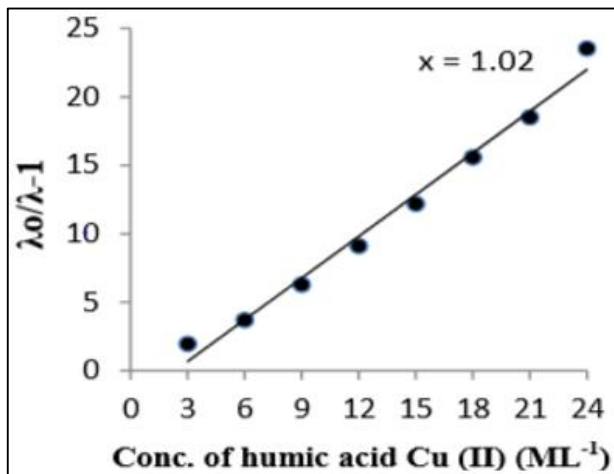


Fig 9: Stability constants of metal – humic acid complexes

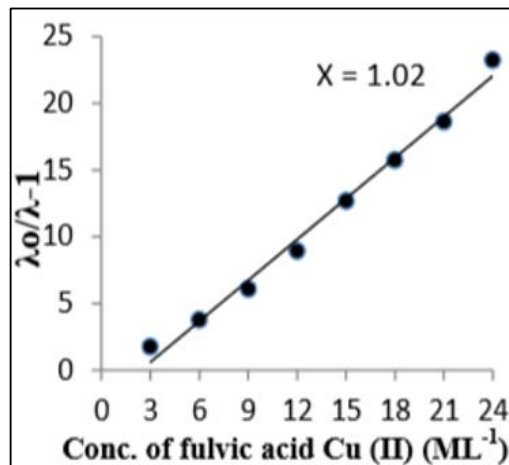


Fig 11: Stability of metal – fulvic acid complexes

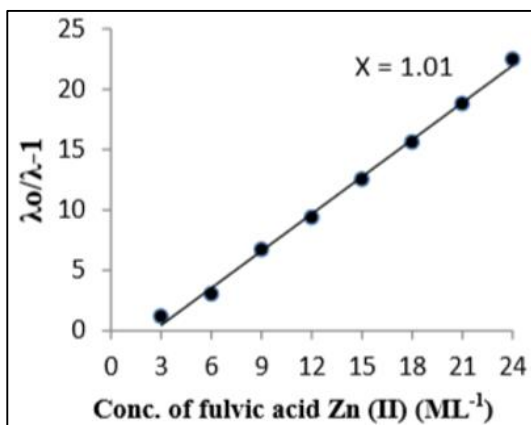
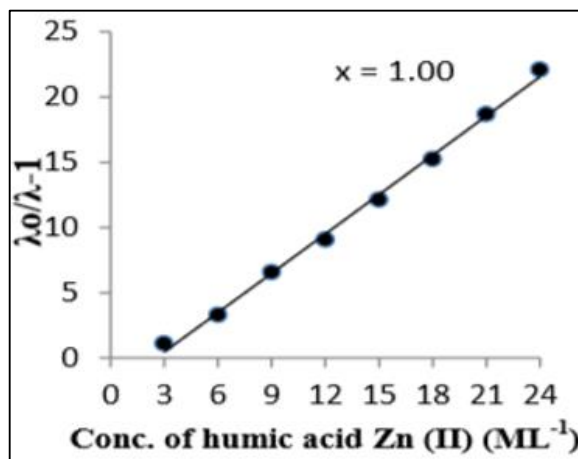
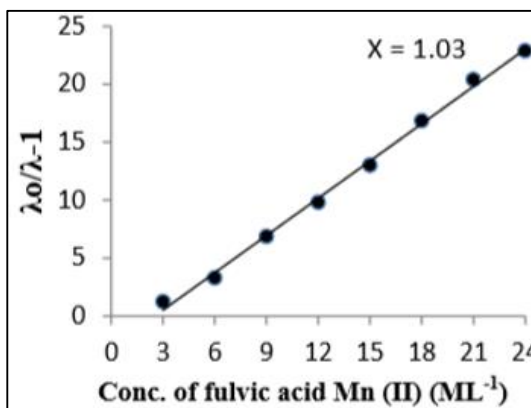
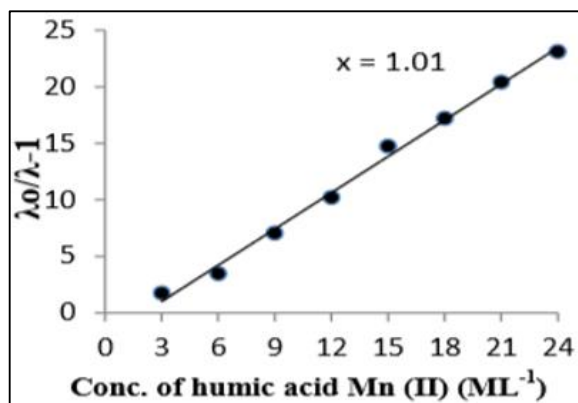
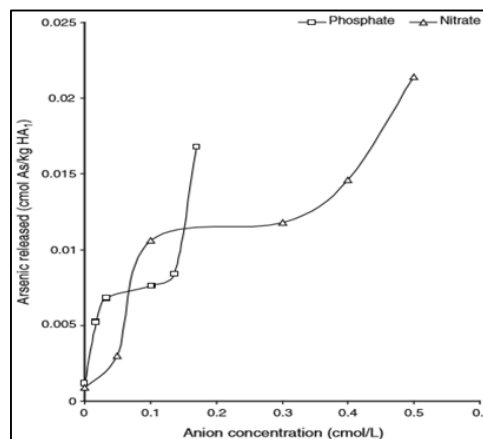
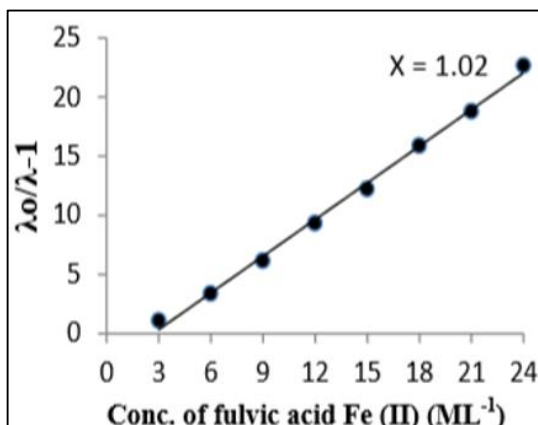


Fig 10: Stability constant of metal – humic acid complexes

Fig 12: Stability of metal – fulvic acid complexes



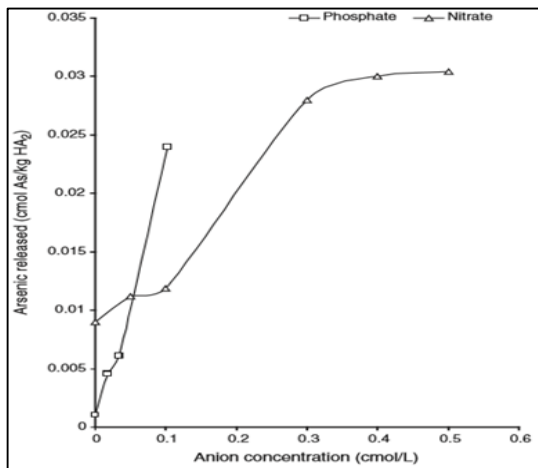


Fig 13 & 14: Release of arsenic from HA₁-As and HA₂-As complex by aqueous

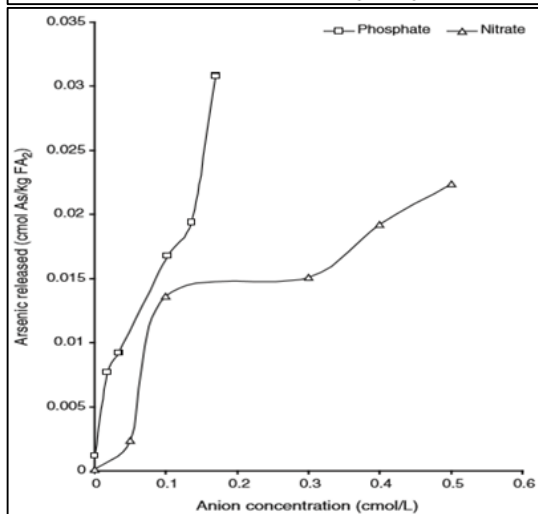
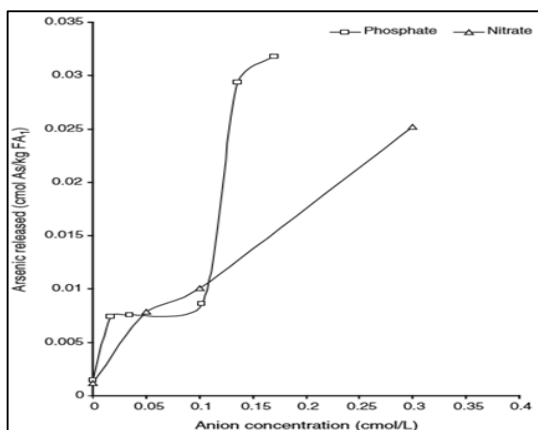


Fig 15 & 16: Release of arsenic from FA₁-As and FA₂-As complex by

HA or FA samples	Mole ratio (x)	Stability constant (logK)
HA/MS	0.41±0.09	3.54±0.19
HA/ FYM	0.55±0.07	4.12±0.22
HA/ MC	0.35±0.07	2.04±0.20
HA /VC	0.53±0.10	4.86±0.21
HA/S	0.39±0.03	2.64±0.25
FA/ MS	0.74±0.03	6.03±0.18
FA / FYM	1.07±0.11	8.65±0.18
FA/ MC	0.62±0.45	5.37±0.20
FA / VC	1.15±0.07	10.27±0.19
FA/S	0.66±0.07	4.55±0.20

Fig 17: Stability constant and mole ratio of As–HA/FA complexes at pH 5.0

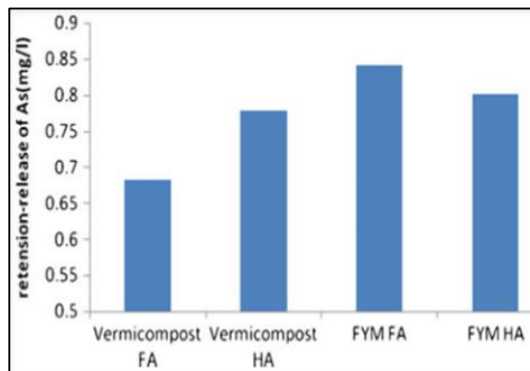


Fig 17: Efficiency of organo-As on retention – release of as

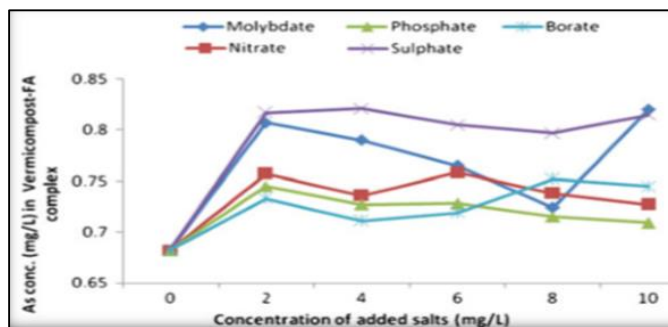


Fig 18: Release of as from organo-As complex in presence of different

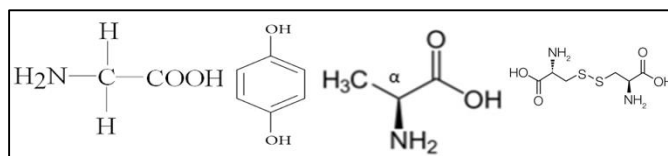


Fig 19: The structure of synthetic material used in synthesis of humic acid

Fractions	C (%)	H (%)	N (%)	O (%)	H/C	O/C	C/N	(O+N)/C	Total acidic group (mmol/g)	Carboxyl group (mmol/g)	Phenolic group (mmol/g)
F1	48.92	4.45	3.80	42.83	1.09	0.66	15.02	0.72	6.06	1.60	4.46
F2	49.03	4.21	4.03	42.73	1.03	0.65	14.20	0.72	5.98	1.50	4.48
F3	51.80	4.48	4.51	39.22	1.04	0.57	13.41	0.64	6.02	1.86	4.16
F4	49.09	5.20	4.98	40.73	1.27	0.62	11.50	0.71	5.56	1.42	4.14
F5	51.87	5.44	5.30	37.39	1.26	0.54	11.42	0.63	4.88	1.08	3.82
F6	49.83	5.49	5.45	39.22	1.32	0.59	10.66	0.68	5.02	0.80	4.24
F7	52.48	5.65	5.39	36.49	1.29	0.52	11.37	0.61	4.18	0.40	3.78
F8	52.41	5.35	5.02	37.21	1.23	0.53	12.17	0.61	3.24	0.28	2.98
F9	48.34	5.53	6.08	40.04	1.37	0.62	9.28	0.73	3.86	0.64	3.22
F10	48.60	5.59	5.88	39.93	1.38	0.62	9.64	0.72	3.18	0.58	2.60

Fig 20: Elemental composition and functional groups of extracted HAs

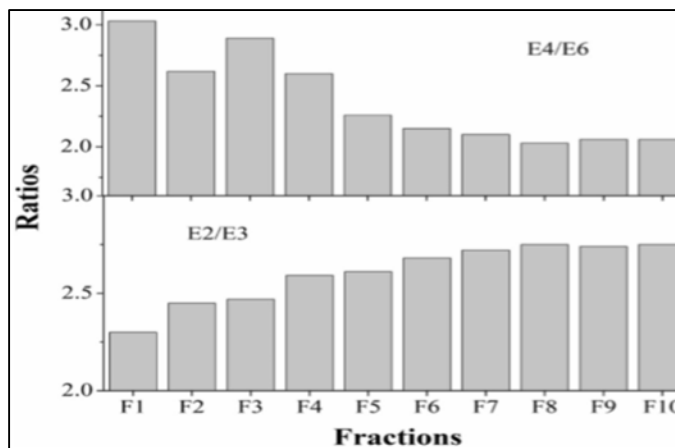


Fig 21: UV-visible analysis for the ratios of absorbance for humic acids at 250 and 365

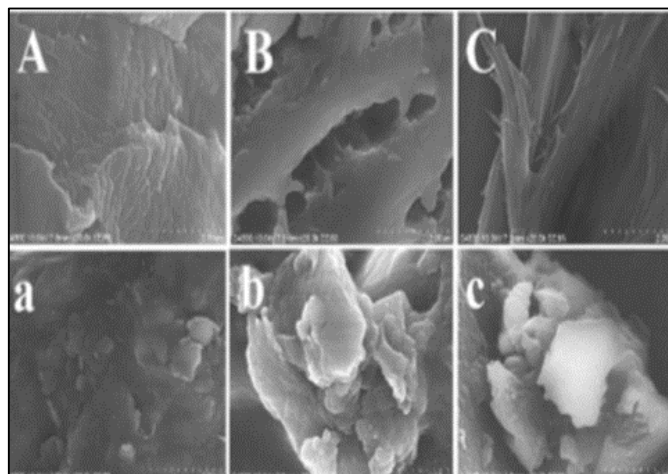


Fig 22: SEM images of A, B, C were former (F2), medium (F5), latter (F9) fractions an a, b, c were corresponding HA-Cu, respectively

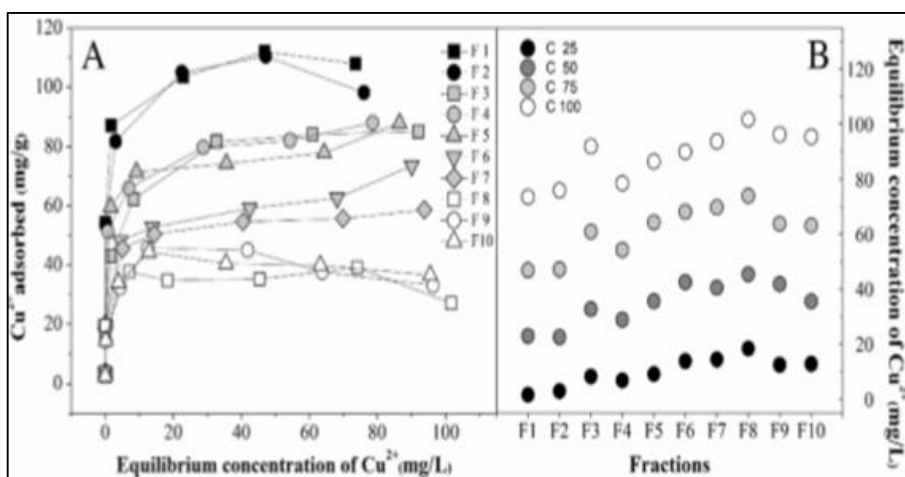


Fig 22: Adsorption isotherm of Cu²⁺ on HA fractions

Table 1: Best fitting sorption and desorption isotherms

Sorbent	Metal	Best fitting model	R ²	Equation
Sorption isotherms				
Whole H horizon	Cd	langmuir	0.73	Y=0.68x-43.76
	Cr	langmuir	0.57	Y=0.25x+88.69
	Ni	freundlich	0.77	Y=0.37x+0.16
	Pb	langmuir	0.65	Y=0.29x-50.91
	Zn	langmuir	0.92	Y=0.06x+2.21
OMF	Cd	langmuir	0.65	Y=0.44x-10.72
	Cr	langmuir	0.99	Y=0.08x+13.92
	Cu	langmuir	0.89	Y=0.51x-63.62
	Ni	langmuir	0.96	Y=0.07x+16.92
	Pb	langmuir	0.99	Y=0.03x+1.85
Zn	langmuir	0.95	Y=0.06x+17.7	
Desorption isotherms				
Whole H horizon	Cd	Neither model fitted		
	Cr	Neither model fitted		
	Ni	freundlich	0.91	Y=0.54x+0.30
	Pb	Neither model fitted		
	Zn	langmuir	0.96	Y=0.04x+0.62
OMF	Cd	Neither model fitted		
	Cr	langmuir	0.67	Y=1.04x-54.99
	Cu	Neither model fitted		
	Ni	langmuir	0.97	Y=0.01x+1.19
	Pb	Neither model fitted		
Zn	Neither model fitted			

Table 2: Moles of HA and FA reacted with one mole of metal ion [Fe (II), Cu (II), Mn (II), Zn (II) in the formation of complex (x values)]

Source	Metal ions			
	Fe (II)	Cu (II)	Mn (II)	Zn (II)
Fulvic acid	9.65	9.68	9.72	9.61

Table 3: Ability of metal ions [Fe (II), Cu (II), Mn (II) and Zn (II)] to form complexes with humic acids (1/x values)

Source	Metal ions			
	Fe (II)	Cu (II)	Mn (II)	Zn (II)
Humic acid	1.00	0.98	0.99	1.00
Fulvic acid	0.98	0.98	0.97	0.99

Table 4: Standard free energy ($-\Delta G^0$) values for the complexation reactions of metal ion [Fe (II), Cu(II), Mn(II), Zn(II)] with humic acid fraction

Source	Metal ions			
	Fe (II)	Cu (II)	Mn (II)	Zn (II)
Humic acid	9.56	9.68	9.66	9.56

Table 5: Standard free energy ($-\Delta G^0$) values for the complexation reactions of metal ion [Fe (II), Cu(II), Mn(II), Zn(II)] with fulvic acid fraction

Source	Metal ions			
	Fe (II)	Cu (II)	Mn (II)	Zn (II)
Fulvic acid	9.65	9.68	9.72	9.61

Table 6: Amount of fresh alkali and the period of time required to attain a stable higher pH (10.8) of Humic/Fulvic acid

HA/FA sample	Amount of fresh alkali required (mol/kg)	Time required (h)
HA ₁	0.600	6.82
HA ₂	0.730	10.3
HA ₃	10.1	2.67
FA ₁	14.6	16.2
FA ₂	6.96	11.6

Table 10: Efficiency of EDTA, citric acid (CA) and FA to bind Pb in nutrient at pH 7

EDTA (μM)	Pb ²⁺ (%)	Pb-EDTA (%)
0	69	0
1	57	18
5	10	86
10	1	99
CA (mM)	Pb ²⁺ (%)	Pb-CA (%)
0.1	66	5
1	41	41
5	7	90
10	1	98
FA (mg l ⁻¹)	Pb ²⁺ (%)	Pb-FA (%)
1	65	14
5	33	56
10	15	80
40	1	99

Conclusion

Higher molecular weight humic acids bind heavy metals more strongly than do the lower molecular weight acids and among humic acid and fulvic acid log k values were higher with metal-FA than metal-HA. Humic fractions has better ability to form complex with copper where Synthetic humic acids is having higher log k values than natural humic acid.

Future aspect

The soil organic fractions can sorb heavy metals, moderating its toxicity in the soil/crop system and preventing its entry in the food chain. The Pesticide residues can form stable complexes with soil organic compound and thus can help in combating the harmful effects.

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Table 7: Stability constant (log k) and mole ratio (x) of HA/FA Arsenic complexes at pH 5

HA/FA Samples	x	Log x
HA ₁	0.505	2.63
HA ₂	1.530	7.91
HA ₃	1.530	8.32
FA ₁	1.830	8.35
FA ₂	0.802	4.31

Table 8: Stability constant and 'x' value of Cd²⁺ humic complexes at pH value 5 from metal HA complexation study

HA samples	x	Log k
HA ₁	2.59 ± 0.08	12.4 ± 0.07
HA ₂	1.99 ± 0.02	12.6 ± 0.10
HA ₃	2.69 ± 0.06	13.3 ± 0.03
HA ₄	1.58 ± 0.02	7.85 ± 0.07
HA ₅	1.51 ± 0.06	9.10 ± 0.07

Table 9: Binding constant of different organic ligands for Pb

Complex	Pk
Pb-citrate ⁻	5.7
Pb-(citrate) ₂ ⁻⁴	6.6
Pb-EDTA ⁻²	197
Pb-HEDTA ⁻	22.5
Pb-HA (pk ₁)	4.1
Pb-HA (pk ₂)	8.8
Pb-FA (pk ₁)	3.2
Pb-FA (pk ₂)	9.4

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