

Interaction of Humic Substances and Aluminum Formation of Insoluble Associates

Mira Petrović and Marija Kaštelan-Macan

Faculty of Chemical Engineering and Technology, Laboratory of
Analytical Chemistry, Marulićev trg 19, 10000 Zagreb, Croatia

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Summary

The interaction of aluminum with soil humic (HA) and fulvic acids (FA) and formation of insoluble associates have been studied under laboratory conditions. The standard test procedure involved a series of experiments at one humic (and fulvic) concentration (50.0 mg/L and 68.5 mg/L, respectively) with varying concentrations of Al(III)-ions (0.5–5 mmol/L). The amounts of aluminum and humic substances precipitated were measured in the pH range from 2 to 10.

It was found that, at any pH and regardless of mass ratio Al/HA, more than 85% of HA precipitate with aluminum. The formation of insoluble Al-fulvate is a pH-dependent reaction with precipitation maximum between pH=4–6.

The principal mechanism in an acidic medium (pH<5) is complex formation through salicylate-type functional groups with binding capacity (at pH=4) 2 mmol Al/g HA and 3.8 mmol Al/g FA. At higher pH the reaction mechanism is primarily sorption of humic substances on »in situ« formed Al(OH)₃.

Keywords: humic substances, humic acid, fulvic acid, Al(III)-ion interaction

Introduction

Naturally occurring organic matter, and especially the most stable components humic and fulvic acids, play an important regulatory role in determining the speciality, toxicity and mobility of aluminum ions. During weathering the series of aluminum-hydroxides of variable charge and composition from Al(OH)²⁺ to Al(OH)₆³⁻ are formed. In acidic environments (soil and water) ionic aluminum has toxic effects on some aquatic and terrestrial organisms. While inorganic complexes are toxic, complexes of aluminum and naturally occurring organic substances (mainly humic substances) are apparently non-toxic (1,2). Studying the effects of organic acids on aluminum toxicity in subsoils, Hue *et al.* (3) found out that aluminum detoxifying capacity of carboxylic acids was positively correlated with the relative position of OH/COOH groups on their main C chain, positions that favored the formation of stable 5- or 6-bond ring structures with Al. Humic substances (HS) contain a large number of oxygen-bearing functional groups (carboxyl, hydroxyl, carbonyl, phenolic and methoxyl) having a great affinity to coordinate with Al-ions (4–6). One of the factors that influence aluminum mobility is solubility of aluminum-humic complexes. These complexes can be

either water-soluble or water-insoluble depending on environmental conditions (7). The formation of water-insoluble associates reduces aluminum mobility and its availability to plant roots.

The objectives of this investigation were (i) to examine the effect of solution parameters (pH, concentrations) on the interaction between Al-ions and soil humic substances and formation of water-insoluble associates and (ii) to determine the relative efficiency of dissolved humic acids and dissolved fulvic acids in associating with aluminum species.

Experimental

Materials

Humic (HA) and fulvic (FA) acids were isolated from the surface O_a horizon of a forest uncultivated soil by alkaline extraction. The complete procedure was described previously (8). Humic and fulvic acids were characterized in terms of elemental composition, content of acidic functional groups and absorbances in UV and

in visible range. The results are presented in Table 1. Elemental composition was determined using CHN-600, LECO analyzer. Total acidity and carboxyl functional group amount were determined by the method of Schnitzer and Gupta (9).

checked and readjusted when required. The precipitate formed was separated by filtration (filter paper-blue ribbon). The equilibrium concentrations of Al(III) and humic substances in the filtrate were determined by standard methods. Concentration of Al(III)-ions was determined

Table 1. Characteristics of humic and fulvic acids studied

Humic substances	Elemental composition		Acidic functional groups		Absorption coefficients	
	<i>w</i> /%		<i>n</i> /mmol <i>m</i> /g			
HA	C	55.95	Total acidity	7.0	$\epsilon'_{270}/g^{-1} L cm^{-1}$	23.50
	H	4.33				
	N	2.00	-COOH	4.6	A_2/A_3^{**}	3.09
	O*	37.70				
	ash	6.20	-OH (phenolic)	2.4	A_4/A_6^{***}	6.54
FA	C	49.11	Total acidity	9.8	$\epsilon'_{270}/g^{-1} L cm^{-1}$	21.63
	H	4.34				
	N	1.99	-COOH	6.0	A_2/A_3	3.25
	O*	45.56				
	ash	3.80	-OH phenolic	3.8	A_4/A_6	11.20

* from the difference

** A_2/A_3 is ratio of absorbance at $\lambda=250$ and $\lambda=365$ nm

*** A_4/A_6 is ratio of absorbance at $\lambda=465$ and $\lambda=665$ nm

The stock solutions of humic and fulvic acids of approximately 100 mg/L, each were prepared by dissolving powdered samples in redistilled water and by adding dropwise a solution of 0.1 mol/L NaOH until clear solutions were obtained. The solutions were then filtered by 0.45 μm »Millipore« membrane filter. The exact concentrations of humic and fulvic acids were determined by measuring TOC (total organic carbon) using an IONICS Carbon Analyzer model 1555. The mass concentrations of humic and fulvic acids were calculated on the basis of elemental analysis data. The concentrations of stock solutions were as follows: humic acids 100.1 mg/L, fulvic acids 137.0 mg/L.

A 10^{-1} mol/L standard stock solution of Al(III) was prepared from analytical reagent grade $Al(NO_3)_3 \cdot 9H_2O$. For the preparation of more dilute solutions the stock solution was diluted with redistilled water.

Procedure

The standard test procedure involved a series of beakers at one humic (or fulvic) concentration with varying concentrations of Al(III)-ions. The humic substances-Al(III) binding experiments were done at room temperature (22 ± 1 °C) by adding aliquots of Al(III) stock solution to 50 mL of humic acids and fulvic acids solution, respectively. The pH of solutions of humic and fulvic acids was preadjusted to an acidic level (pH \approx 4) with dilute HCl. After the addition of Al(III) pH was adjusted with dilute HCl or NaOH to the desired value (2-10). Buffers were not used to avoid possible competition. Total volume of mixtures was adjusted to 100 mL with redistilled water. The overall concentration of humic acids was 50.0 mg/L, fulvic acids 68.5 mg/L, while the concentration of aluminum(III) in final volume ranged from 13.3 mg/L ($5 \cdot 10^{-4}$ mol/L) to 133.0 mg/L ($5 \cdot 10^{-3}$ mol/L).

Each system was allowed to stand with intermittent shaking at room temperature for 24 hours. The pH was

by complexometric titration (10), while the concentration of humic substances was determined spectrophotometrically ($\lambda=370$ nm) using a Specol 210 spectrophotometer (Zeiss-Iskra MA 9325). The amounts of humic substances and aluminum precipitated were calculated by mass balance. The fractions of aluminum and humic substances in solid phase were calculated as a difference between their initial concentrations and equilibrium concentrations in the aqueous phase. Solid phase (humic substances-Al associate) was dried at 50 °C and stored over silica gel for several days to remove water. Afterwards, Fourier transformed infra red spectrum was taken on KBr pellets using a Fourier transform IR spectrometer Perkin-Elmer 2000 (Perkin-Elmer).

Results and Discussion

The formation of insoluble Al-humic complexes (associates) was studied under laboratory conditions by direct interaction of Al-ions and dissolved humic and fulvic acids. The experiments were performed without background electrolyte. Fractions of aluminum and humic substances in solid phase were measured as a function of pH at constant mass ratio of aluminum and humic substances in the mixture.

Fig. 1 illustrates the effects of pH on the precipitation of fulvic acids and aluminum from the mixture containing 68.5 mg of fulvic acids/L and 20.55 mg of Al/L (mass ratio (Al/FA)=0.30). The results show that insoluble reaction product is formed when FA interact with aluminum. The interaction between aluminum and fulvic acids and formation of insoluble products are pH dependent reactions. With the rise of pH from 2 to 4 the amount of fulvic acids in the solid phase rapidly increases. The precipitation maximum of the FA occurs at pH-values between 4 and 6, afterwards the fraction of fulvic acids in solid phase reduces.

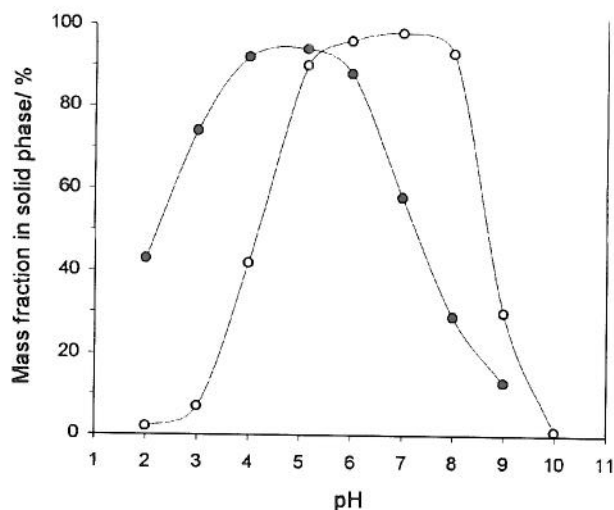


Fig. 1. Precipitation of fulvic acids and aluminum from the mixture as a function of pH, $\gamma(\text{Al})=20.55 \text{ mg/L}$, $\gamma(\text{FA})=68.5 \text{ mg/L}$, mass ratio (Al/FA)=0.30; fulvic acids (●), Al (○).

The precipitation of humic acids-aluminum associates is presented in Fig. 2. The results show that regardless of pH, more than 85% of humic acids precipitate from the solution containing 50.0 mg of humic acids/L, and 12.5 mg of Al/L (mass ratio (Al/HA)=0.25). The precipitation maximum is observed at pH=5-6 where 98% of humic acids appear in insoluble form. To discern the influence of aluminum complexation reaction from the reaction induced by variations of H^+ -concentration the precipitations of humic and fulvic acids were measured, as a function of pH, in solutions without aluminum. Free fulvic acids were found to be completely soluble in water over the pH range studied (2-10), while the solubility of humic acids decreased as the concentration of H^+ -ions increased (Fig. 3a). The higher solubility of fulvic acids is a result of the abundance of charged and highly polar groups in the structure. As it can be seen from the results presented in Table 1, fulvic acids

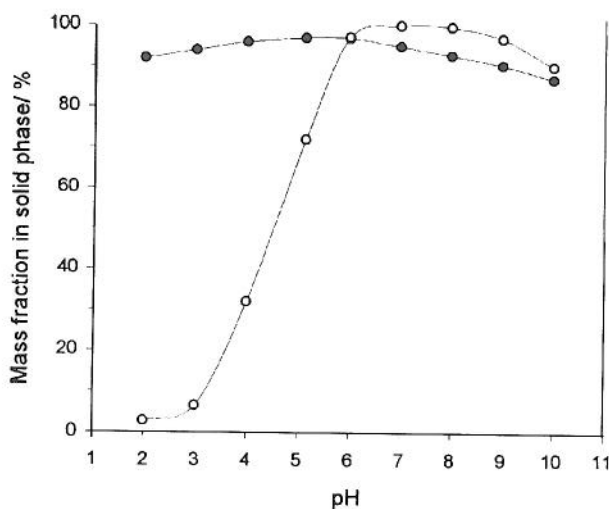


Fig. 2. Precipitation of humic acids and aluminum from the mixture as a function of pH, $\gamma(\text{Al})=12.5 \text{ mg/L}$, $\gamma(\text{HA})=50.0 \text{ mg/L}$, mass ratio (Al/HA)=0.25; humic acids (●), Al (○).

contain more oxygen but less carbon, and have a higher content of carboxylic and phenolic groups than humic acids. Fig. 3b shows the fractions of aluminum in solid phase in the pH range from 2 to 10. The precipitation curve of aluminum generally follows the pattern with three distinguished areas: in the first one at $\text{pH}<4$ dissolved species $[\text{Al}^{3+}$ and positively charged hydroxo complexes: $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$] are dominant. Most of the authors agree that hydrated ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and polynuclear species such as $\text{Al}_6(\text{OH})_{15}^{3+}$ predominate in the acid solution, while $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_3(\text{OH})_6^{3+}$ and mononuclear species are the main products of hydrolysis (II). At $\text{pH}>4$ the phase changes and precipitation of solid $\text{Al}(\text{OH})_3$ occurs, whereas at $\text{pH}>8$ dissolution and formation of dissolved negatively charged hydroxo complexes [from $\text{Al}(\text{OH})_4^-$ to $\text{Al}(\text{OH})_6^{3-}$] prevail.

In both systems examined: humic acids-Al and fulvic acids-Al, the precipitation curves of aluminum (Figs. 1 and 2) show some differences and retirement compared with the precipitation curve obtained in the solution containing no humic substances. In an acidic medium, especially at $\text{pH}<5$, a considerable amount of ionic aluminum is fixed in solid associate with humic substances. At $\text{pH}=4.0$, in conditions of full saturation, one gram of HA binds 2 mmol of Al in an insoluble associate, while FA binds 3.8 mmol of Al/g. Humic and

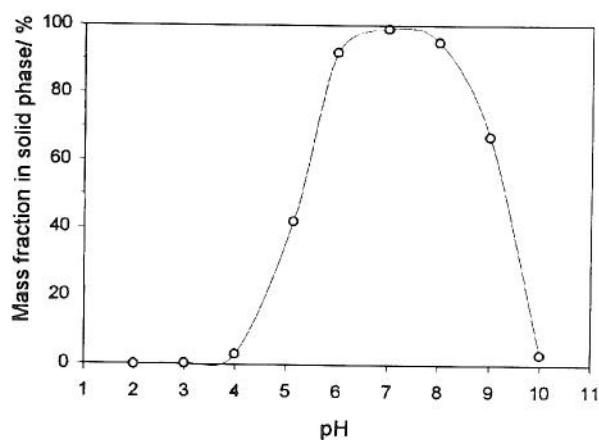
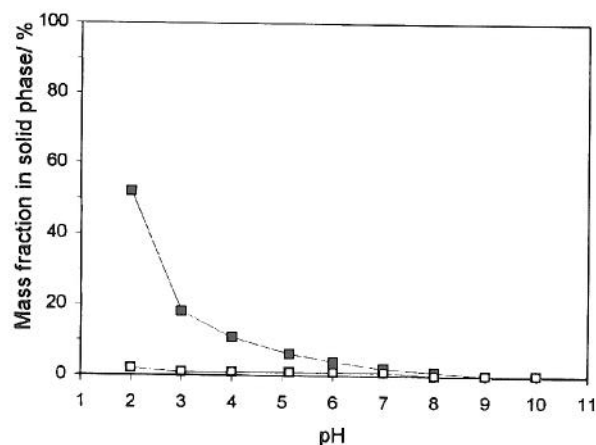


Fig. 3. Precipitation of humic substances (A) and aluminum (B) as a function of pH, $\gamma(\text{HA})=50.0 \text{ mg/L}$, $\gamma(\text{FA})=68.5 \text{ mg/L}$, $\gamma(\text{Al})=65.45 \text{ mg/L}$; humic acids (■), fulvic acids (□), Al (○).

fulvic acids apparently bind aluminum through salicylate-type functional groups having a relatively large conditional stability constant (12). Other possible binding sites in humic molecules are phthalic or aliphatic carboxyl groups, with a variety of molecular arrangements. FTIR-spectra of humic acids and humic-Al solid associate formed at pH=4.0 (mass ratio (Al/HA)=0.25), same as spectra of fulvic acids and fulvic-Al solid associate (formed at pH=4.0 in the solution with mass ratio (Al/FA)=0.30) are given in Figs. 4 and 5. The main difference between the spectrum of humic acids in H⁺-form and that of aluminum-humate is the disappearance of the bands centered at 1720 cm⁻¹ and 1220 cm⁻¹ and the appearance of new bands in the 1400-1450 cm⁻¹ region. The absorption band at 1720 cm⁻¹, due to the carbonyl of the unionized carboxyl group (13), disappears upon the reaction with aluminum, providing direct evidence for the participation of carboxyl groups in the complexation. The absorption band at 1220 cm⁻¹ assigned to the C-O stretching vibrations and OH bending deformations, due mainly to carboxyl groups, also disappears on producing the aluminum-humate. Similar changes are observed on infrared spectra of fulvic acids and aluminum-fulvate.

The interaction of humic substances and aluminum at pH>5.5 is primarily a surface complexation and sorption on *in situ* formed Al(OH)₃ flocs. The interaction is based on a charge neutralization-precipitation mechanism where specific chemical interaction between posi-

tively charged hydrolyzed aluminum species and ionized carboxyl groups on the humic macromolecules occurs. Humic substances bear a net negative charge and the first step, caused by electrostatic effects, involve the rapid neutralization of the positive charge of Al(OH)₃ flocs. This neutralization is followed by the formation of aggregates of hydrophilic colloids consisting of negatively charged humic substance spanned by a bridge of positively charged aluminum species. As a consequence of chain structure growth the larger aggregates are formed. The extent of precipitation of insoluble Al-fulvate associate is dependent on Al/FA mass ratio. The results presented in Fig. 6. show that in neutral and basic solutions the fraction of fulvic acids bound in solid phase is small at low Al/FA mass ratio. As the amount of aluminum added to the mixture increases, the percentage of fulvic acids bound into the solid associate significantly increases. On the other hand, the precipitation of humic acids is not influenced by the Al/HA mass ratio. These observations can be explained in terms of total acidity and content of carboxyl and phenolic functional groups in humic and fulvic acids. As it can be seen from the data given in Table 1, the content of acidic functional groups is higher in fulvic acids, which has resulted in a proportional demand of aluminum to saturate the binding sites on the fulvic macromolecules.

Due to the complexity of the system studied it is difficult to determine all the variables that may influence

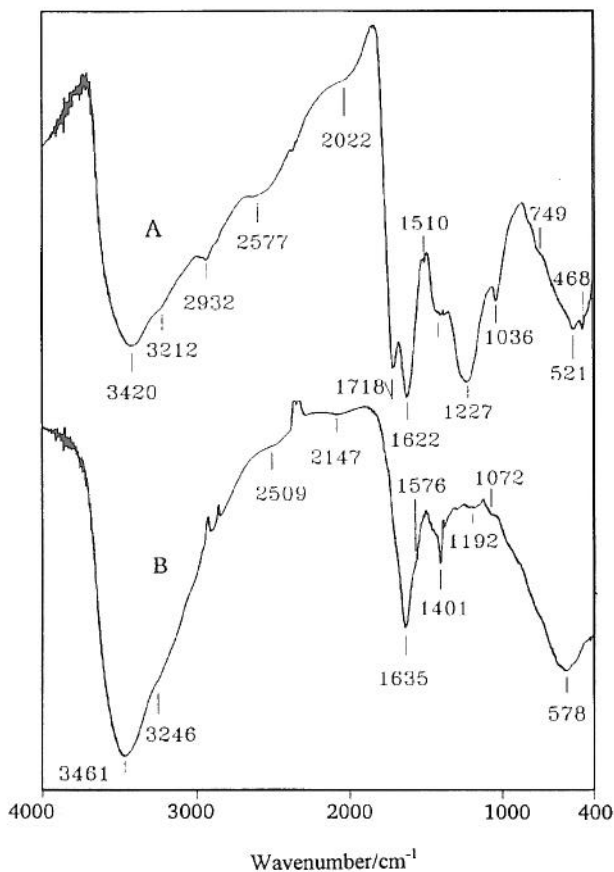


Fig. 4. FTIR-spectra of humic acids (A) and of solid associate Al-humate (B) formed at pH=4.0 in the solution with mass ratio (Al/HA)=0.25

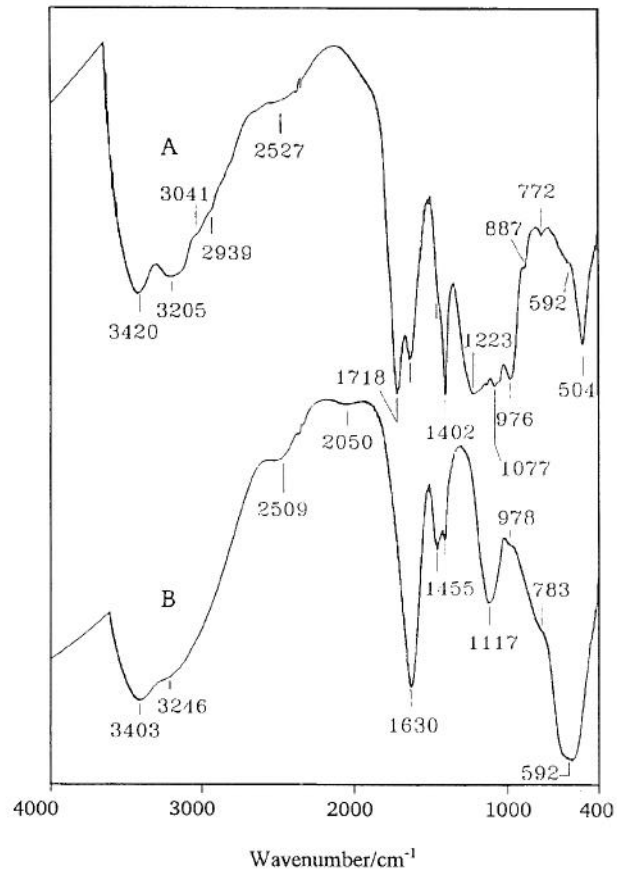


Fig. 5. FTIR-spectra of fulvic acids (A) and of solid associate Al-fulvate (B) formed at pH=4.0 in the solution with mass ratio (Al/FA)=0.30

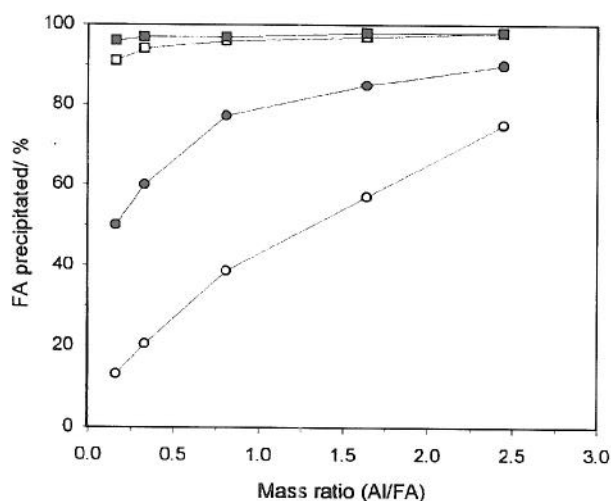


Fig. 6. The precipitation of fulvic acids as a function of Al/FA mass ratio; pH=4 (□), pH=5 (■), pH=7 (●), pH=9 (○).

the formation of insoluble associate formed by the reaction of aluminum and natural humic substances. However, it is possible that several reactions take place simultaneously, especially at pH>5.5 (chelation, sorption and coprecipitation). The type of predominant interaction will depend on the specific condition (pH, aluminum concentration, concentration of humic substances and their characteristics).

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Međudjelovanje humusnih tvari i aluminijske Nastanak netopljivih asocijata

Sažetak

Ispitivano je međudjelovanje aluminijske i humusnih (HA) i fulvinskih kiselina (FA) te nastanak u vodi netopljivih asocijata. Mjereno je taloženje aluminijske i humusnih tvari pri pH=2–10 iz otopina koje sadržavaju 50,0 mg HA/L, odnosno 68,5 mg FA/L te aluminijske čija je koncentracija bila 0,5–5 mmol/L.

Nađeno je da se u cijelom ispitivanom području pH-vrijednosti i pri svim ispitivanim masenim omjerima Al/HA taloži više od 85% humusnih kiselina. Taložnje čvrstog Al-fulvata ovisi o pH-vrijednosti sustava i najveće je pri pH=4–6.

Osnovni mehanizam interakcije u kiselj otopini (pH<5) jest kompleksiranje aluminijske na aktivna mjesta (salicilatne funkcionalne skupine) u humusnim makromolekulama, pri čemu kapacitet vezanja (pri pH=4) iznosi 2 mmol Al/g HA, odnosno 3,8 mmol Al/g FA. Pri višim pH-vrijednostima do taloženja u prvom redu dolazi zbog sorpcije humusnih tvari na »in situ« nastali koloidni Al(OH)₃.