Influence of catechin on precipitation of aluminum hydroxide

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ARTICLE INFO

Article history:

Received 17 March 2008

Received in revised form 11 June 2009

Accepted 22 June 2009

Available online 28 July 2009

Keywords:

Aluminum hydroxide

(+)-Catechin

Al hydrolysis

Complexing and hampering

ABSTRACT

Polyphenols (catechins) are vital biomolecules in tea plants, *Camellia sinensis*, which are well adapted to acid soils with high availability of phytotoxic Al species. Since the mechanism of Al resistance in tea plants by catechin remains obscure, this study investigates the influence of catechin on aluminum transformation. It is found that the pH of the suspensions decreased with aging. The hydrolytic precipitates of Al were subjected to surface area, X-ray diffraction (XRD), Fourier-transform infrared absorption spectroscopy (FT-IR), transmission electron microscopy (TEM), thermal, and chemical analyses. At the initial Al concentration of 2×10^{-2} M sample, in the absence of catechin for 180-d aging, only 59.7% of the Al is remained in the filtrate, including readily, moderately extractable and nonextractable fractions. However, in the presence of catechin, above 70.5% of the Al is present in the filtrate. The readily, moderately extractable and nonextractable Al fractions with 8-quinolinolate method are decreased with increasing concentrations of catechin after 180-d aging. Specific surface area of the Al precipitates increases with increasing concentrations of catechin. In the absence of catechin, the Al precipitates with prolonged aging are mostly crystalline gibbsite. X-ray diffraction analysis and TEM observations also show the structural distortion within the hydrolytic precipitates of Al in the presence of catechin. FT-IR spectra show that catechin substantially inhibits the formation of crystalline aluminum hydroxides. X-ray noncrystalline to poor-ordered hydrolytic reaction products of Al are formed in the presence of catechin. TEM images also show that the Al precipitates form under the perturbation of catechin are fine, shapeless and hollow colloids that are deformed and aggregated. Thermal analysis shows that the hydrolytic reaction products of Al lost their structural water gradually when catechin concentration is raised from 0 M (control) to 4.0×10^{-3} M, indicating that greater structural disorder occurs with increasing catechin concentration in the Al systems.

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1. Introduction

Aluminum can be released from aluminosilicate minerals into soil solution due to the acidity generated by natural and anthropogenic processes. High reactivity of Al leads to hydrolytic reactions and to strong complexation with naturally occurring organic acids commonly present in soils (Huang, 1988; Vance et al., 1996; Sanabria et al., 2008). The relative distribution of the hydrolyzed and complexed Al species is determining factor for Al mobility in soil solution and toxicity to natural ecosystems (Bertsch and Parker, 1996). Aluminum can be polymerized into various polynuclear species. Aluminum salt solutions are neutralized with a base, the hydrolysis of Al results in the initial formation of amorphous and poorly crystalline Al hydroxide, which will subsequently transform into crystallized Al hydroxides upon aging. There are three polymorphs of Al hydroxides, by gibbsite, bayerite and nondstrandite (Wang et al., 2003). Their crystal structures vary only in the arrangements of the stacking sequences of $\text{Al}(\text{OH})_3$ layers. However, the formation of crystalline or noncrystal-

line Al hydroxides is influenced by the ionic environment in the systems. For instance, chloride (Turner and Ross, 1970) and sulfate (Hsu, 1973) at high concentrations, silicic acid (Luciuk and Huang, 1974) and tannic acid (Colombo et al., 2004; Yu et al., 2006, 2007), inhibit the formation of crystalline Al hydroxides.

The chemistry of Al transformation as influenced by organic acids common in soils and sediments has been well documented (Kwong and Huang, 1977; Kodama and Schnitzer, 1980; Kwong and Huang, 1981; Huang et al., 2002; Colombo et al., 2004; Yu et al., 2006, 2007; Hu et al., 2008). Catechin is a vital biomolecule in tea plants which are well adapted to acid soils with high availability of phytotoxic Al species. However, the influence of catechin on the transformation of Al remains to be uncovered.

Natural organic matter (NOM) has a profound effect on the availability of nutrients for plant growth. Organic matter can be mineralized by soil microorganisms to release N, P and S. Organic matter also influences the supply of nutrients from other sources. Furthermore, organic substances in soil can exert physiological effects on plant growth. Many studies have also shown that some compounds such as polyphenols are present in crop residues and soils (Whitehead, 1964; Wang et al., 1971; Vrsalovic et al., 2005).

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Catechins have been considered to have significant beneficial effects on human health. Catechins such as (+)-catechin (C), (–)-epicatechin (EC), (–)-epigallocatechin (EGC), (–)-epicatechin gallate (ECG) and (–)-epigallocatechin gallate (EGCG), have recently received much attention as protective agents against cardiovascular disease and cancer (Dubey et al., 2002; Kim et al., 2003). It is generally believed that catechins, the principal bioactive compounds in tea, are responsible for the claimed therapeutic activities of tea. Polyphenols have high reactivity toward other phenolic or metal compounds, giving rise to compounds with complicated structures (Chen et al., 2006). These transformations affect sensory properties such as color and taste (Cheynier et al., 1988).

The high Al affinity of complexed phenolics has been recognized by analytical chemists (Roser et al., 2005). However, in natural systems, catechins are part of the environmental chemicals and their influence on the hydrolytic reaction of Al is not well understood. This study investigates the influence of catechin on aluminum transformation.

2. Materials and methods

2.1. Materials

(+)-Catechin was obtained from the Sigma Chemical Co (St. Louis, MO) and used without further purification. Aluminum chloride was supplied from Merck (DAC, USP). Double deionized water (DDW) was purified with a Milli-Q water system (Millipore, Bedford, MA) prior to use.

2.2. Methods

Solutions containing 100 mL of 0.1 M AlCl_3 were titrated to OH/Al molar ratio of 2.5 with 0.1 M NaOH in the absence and in the presence of catechin. In suspensions, Al concentrations at final volume were 2×10^{-2} M. The concentrations of catechin in the suspensions were 0, 1.0×10^{-4} and 4.0×10^{-3} M, respectively. All solutions were then aged at 25 °C for 0, 1, 7, 30, and 180-d. After each aging period, the pH of each suspension was measured. At the end of 180-d aging, each suspension was separated into its filtrate and precipitate phases by ultrafiltration through a 0.025 μm Millipore filter.

2.3. Examination of the filtrates

At the end of the selected aging periods, concentrations of the readily extractable, moderately extractable, and nonextractable Al were determined by the 8-quionlinolate method in the filtrate (i.e., <0.025 μm Millipore filter) (Turner, 1969). The terms “readily extractable” and “moderately extractable” Al as used here refer to Al extractable by 8-quionlinolate chemicals within shaking periods of 10 s and 30 min, respectively. The Al which cannot be extracted by 8-quionlinolate within 30 min is referred to as nonextractable Al fractions. The total Al in the filtrate was determined after digestion with a mixture of HNO_3 and HCl solution (Lim and Jackson, 1982). Amount of Al in the precipitate phase (>0.025 μm) was calculated by the difference between the initial Al concentration (i.e., 2×10^{-2} M) and the concentration of Al in the filtrate at the end of each aging period. The pH levels of the suspensions at the end of each aging period were measured using a Radiometer pH M83 pH meter.

2.4. Examination of hydrolytic products of aluminum

Samples of the precipitate phase were characterized by specific surface area, X-ray diffraction analysis (XRD), Fourier-transform infrared absorption spectrometry (FT-IR), transmission electron microscopy (TEM), and thermogravimetrics (TGA).

Specific surface area: Specific surface area was performed on 100 mg of precipitates using the Teller (BET) equation with a Nova 2000 analyzer (Quanta Chrome).

X-ray diffraction (XRD) analysis: The precipitates were examined by XRD using $\text{CuK}\alpha$ radiation on a Rigaku Geigerflex X-ray diffractometer equipped with graphite monochromator, operating at 35 kV and 15 mA at a step-scan of $0.02^\circ 2\theta/\text{s}$. The X-ray patterns were recorded in the range of $3\text{--}50^\circ 2\theta$.

Fourier-transform infrared absorption spectrometry (FT-IR) analysis: 1 mg of the precipitates dried in a vacuum desiccator was ground and mixed thoroughly with 200 mg of oven-dried KBr powder of analytical reagent (Merck, DAC, USP). The powder was placed in a die and compressed into a transparent disk. The infrared spectra were recorded by using a Perkin-Elmer System 2000 double beam infrared spectrophotometer. The spectral resolution was 4 cm^{-1} .

Transmission electron microscopy (TEM) analysis: One drop of suspension was dried on a carbon-coated film on copper grids (3.05 mm in diameter), and then examined under a JEOL TEM (JEM 100 CXII) operated at 100 kV for selected area electron diffraction (SAED).

Thermogravimetric analysis (TGA): About 12 mg of air-dried samples were heated in a Fisher 260 furnace which was programmed to raise the temperature from 25 to 1000 °C at a rate of 10° min^{-1} . The weight loss during heating was recorded by a Cahn RG automatic electrobalance. The DTG patterns were obtained from the TGA analysis.

2.5. Statistical analyses

Statistical data were analyzed using analysis of variance (ANOVA). Duncan's Multiple Range Test was used in all experiments to test the differences amongst the means at $p < 0.05$.

3. Results

3.1. pH of suspensions

The suspension pH decreased with increasing aging days (Table 1). However, in the presence of catechin, pH levels are slightly decreased with prolonged aging. This is attributed to not only Al complexing with catechin but Al also performs to the development of the proton acceptors in the Al precipitates.

3.2. Percentage distribution of Al that is readily, moderately extractable and nonextractable fractions (<0.025 μm)

After 180-d aging in the absence of catechin, about 59.7% ($22.1 + 30.5 + 7.1\%$) to the initial Al concentration is present in the filtrate, which is included readily, moderately extractable and nonextractable Al fractions (Table 2). However, in the presence of catechin, above 70.5% ($20.3 + 42.2 + 8.0\%$) to the initial Al concentration is present in the filtrate. This is ascribed to the complexation of hydroxyl-Al by catechin perturbing the Al precipitation reaction. The fractions of moderately extractable and nonextractable Al are higher in the presence of catechin.

Table 1

The suspensions pH at initial Al concentration of 2.0×10^{-2} M as functions at different aging days, in the absence and presence of catechin (OH/Al molar ratio = 2.5).

Aging day	Initial catechin concentration (M)		
	0	1.0×10^{-4}	4.0×10^{-3}
0	5.50 ± 0.05	5.50 ± 0.04	5.50 ± 0.04
1	5.48 ± 0.04	5.47 ± 0.05	5.40 ± 0.05
7	5.15 ± 0.05	5.41 ± 0.03	5.34 ± 0.06
30	4.62 ± 0.03	5.23 ± 0.05	5.24 ± 0.04
180	4.08 ± 0.04	5.13 ± 0.06	5.12 ± 0.05

Table 2

Percentage of the precipitated Al and the readily, moderately extractable and nonextractable Al fractions (%), at initial Al concentrations of 2.0×10^{-2} M as influenced by catechin concentrations after 180-d aging (OH/Al molar ratio = 2.5).

Forms of Al ⁺	0	1.0×10^{-4} M	4.0×10^{-3} M
*Readily extractable Al [‡]	22.1 ± 0.8	20.3 ± 1.1	29.2 ± 1.5
Moderately extractable Al [‡]	30.5 ± 1.3	42.2 ± 0.9	33.4 ± 1.0
Nonextractable Al [‡]	7.1 ± 0.7	8.0 ± 0.8	14.1 ± 1.2
Precipitated Al [*]	40.3 ± 1.4	29.5 ± 0.5	23.3 ± 1.6

⁺ The suspensions was filtered through Millipore membrane with the pore size of 0.025 μm.

[‡] Fractionation of solution Al speciation, i.e., readily extractable, moderately extractable and nonextractable Al was based on Turner (1969).

* Least significant difference (LSD, $p \leq 0.05$) of Al precipitated (%) is 2.0.

3.3. Percentage distribution of Al in the phase of precipitates (>0.025 μm)

The amount of Al in the phase of precipitates (>0.025 μm) after 180-d aging decreases with increasing catechin concentrations (Table 2). Catechin hinder the hydrolytic reaction of Al. In the absence of catechin, 40.3% of the initial Al was precipitated. The addition of 1.0×10^{-4} M catechin to the same system reduced the Al precipitated to 29.5% at the end of the 180-d aging. The precipitation of Al fraction was further decreased to 23.3% when the initial concentration of catechin was raised to 4×10^{-3} M.

3.4. Specific surface area of Al precipitates

Specific surface area of Al precipitates increase with increasing the initial catechin concentration after 180-d aging (Table 3). The data clearly show that increasing the catechin concentration caused greater structural distortions within the Al precipitates, thus increasing the specific surface area.

3.5. X-ray diffractograms (XRD) of the precipitate phase

In the absence of catechin, the reaction products after 180-d aging are mostly crystalline gibbsite (Fig. 1a). However, in the presence of catechin (i.e., 1×10^{-4} and 4×10^{-3} M) at the same initial OH/Al molar ratio and Al concentration, the hydrolytic reaction products are XRD noncrystalline materials (Fig. 1b and c).

3.6. FT-IR spectra of Al precipitates

The wavenumber of FT-IR spectra in the absence of catechin at 3620, 3521 and 3469 are assigned to gibbsite (Table 4). The IR absorption bands at 3472, 1639, 1072 and 570 cm^{-1} are assigned to stretching vibration of the OH bond, bending modes of the H_2O , Al–O bond and Al–O stretch (AlO_6) (Meher et al., 2005). On the other hand, the IR absorption bands at 3620, 3527, 3488, 1023 and 561 cm^{-1} are absent in the presence of catechin. This indicates that Al complexes with catechin, cause the loss of some function groups in the IR spectra of the precipitates.

Table 3

Influence of catechin on the specific surface area of Al precipitates after 180-d aging.

Catechin concentration (M)	Specific surface area (m^2/g)
0	13 ± 1.1
1.0×10^{-4} M	25 ± 1.5
4.0×10^{-3} M	47 ± 1.3
*LSD ($p \leq 0.05$)	1.7

*LSD: least significant difference.

Fig. 1. X-ray diffractograms of Al precipitates at initial Al concentration of 2.0×10^{-2} M and OH/Al molar ratio of 2.5: (a) in the absence of catechin, (b) in the presence of 1.0×10^{-4} M catechin, and (c) in the presence of 4.0×10^{-3} M catechin after 180-d aging.

3.7. Surface morphology of Al precipitates

In the absence of catechin, the Al precipitates are gibbsite (hexagonal plates) (Fig. 2a and b). This is supported by the XRD (Fig. 1a) and selected area electron diffraction pattern (SAED) (data not shown). In contrast, in the presence of 4.0×10^{-3} M catechin, the Al precipitates are noncrystalline to XRD (Fig. 1b and c) and SAED. They are fine, shapeless and hollow colloids that are deformed and aggregated. The sizes of the aggregate materials range from 0.5 μm to 2 μm (Fig. 2c and d).

3.8. Thermal analysis

The hydrolytic precipitation products of Al form in the absence of catechin lost the structural water at the critical temperature (80°–110 °C) as indicated by the intense peak (Fig. 3a). The loss of the structural water of the Al precipitates form at the initial catechin concentration of 1.0×10^{-4} M is much lower (Fig. 3b) compared to the Al precipitates form in the absence of catechin (Fig. 3a). By contrast, the former lost much more adsorbed water than the latter. As the initial catechin concentration is increased to 4.0×10^{-3} M, the loss of

Table 4

Assignment of FT-IR spectra at OH/Al molar ratio = 2.5 after 180-d aging.

Catechin concentration	Wavenumber of IR spectra	Wavenumber of IR spectra (Meher et al., 2005)	Assignment
0	3620	3620	Gibbsite
	3527	3521	Gibbsite
	3488	3469	Gibbsite
	3470	3472	Stretching vibration of OH Bond
	1645	1639	Bending moments of H_2O
1.0×10^{-4} M	1023	1072	Al–O bond
	561	570	Al–O stretch (AlO_6)
	3465	3472	Stretching vibration of OH Bond
	1637	1639	Bond bending moments of H_2O
4.0×10^{-3} M	3471	3472	Stretching vibration of OH Bond
	1645	1639	Bond bending moments of H_2O

Fig. 2. Transmission electron micrographs (TEM) of Al hydroxides after 180-d aging: (a) and (b) of gibbsite particles in the absence of catechin; (c) and (d) of X-ray noncrystalline Al precipitates, in the presence of 4.0×10^{-3} M catechin.

the structural water is not evidenced (Fig. 3c) anymore, but the loss of the adsorbed water is greatly increased.

4. Discussion

The influence of catechin on the specific surface area of Al precipitates is ascribed to the complexation of Al by catechin and indicated by the stability constant of Al-catechin complexes (Kwong and Huang, 1981). Organic compounds with a molecular weight less

than 150 are not significantly adsorbed by physical forces on the surfaces of clay minerals (Greenland, 1965). In the present study, the catechin's molecular weight is 290.3, which is related to the physical or chemical adsorption onto Al precipitates, in addition to the complexation reactions of Al with catechin in the structural network of the precipitates (Table 2). Table 2 demonstrates that nonextractable and precipitated Al fractions decrease with increasing catechin concentrations, however, the readily and moderately extractable Al fractions show the reversed trend.

The hydrolytic reaction products of Al in the absence of interfering ligands have been thoroughly documented in the literature (Hsu and Bates, 1964; Luciuk and Huang, 1974; Kwong and Huang, 1977; Wang et al., 2003; Yu et al., 2007). The X-ray diffractograms show the structural distortion within the hydrolytic reaction products of Al when catechin is present in the system. This is because catechin can occupy with the coordination sites of Al. This hampers the development of hydroxyl bridging mechanism and also distorts the arrangement of hexagonal units that are present in crystalline aluminum hydroxides.

In the absence of catechin, the polymeric Al possessed positively charged edges capable of undergoing hydrolysis which leads ultimately to the development of the precipitated crystalline aluminum hydroxides (Kwong and Huang, 1977). Catechin apparently blocks the coordination sites of the terminal-Al through complexation, and thus, hampers the hydroxyl-bridging mechanism in the hydrolysis and polymerization of Al, which is fundamental to the formation of crystalline Al hydroxide precipitates. Therefore, the FT-IR data are in agreement with the XRD data, showing that catechin can inhibit the formation of crystalline aluminum hydroxides.

The degree of the structural distortion of the Al precipitates increase with increasing initial catechin concentration. The findings from the thermal analysis (Fig. 3) are in agreement with the XRD (Fig. 1), FT-IR (Table 4), TEM (Fig. 2), and SAED data. These findings support the reasoning that catechin hampers the hydroxyl bridging mechanism in the hydrolytic reaction of Al, which is fundamental to the crystallization of Al hydroxides.

Fig. 3. DTG patterns of Al hydrolytic reaction products: (a) in the absence of catechin, in the presence of (b) 1.0×10^{-4} M catechin and (c) 4.0×10^{-3} M catechin after 180-d aging.

5. Conclusions

X-ray, FT-IR and thermal analyses, and TEM image reveal the fact that structural perturbation of Al precipitation, through complexation and coprecipitation of catechin with Al results in the formation of short-range ordered Al precipitates. These Al precipitates have highly specific surface area, fine, shapeless and hollow colloids which are aggregated. The size of aggregated materials ranges from 0.5 to 2 μm . The findings obtained in the present study are of fundamental significance in advancing the frontiers of knowledge on low temperature geochemistry and biogeochemistry of Al and the impact on the environment and ecosystem.

Acknowledgments

We thank the National Science Council, Taiwan, The Republic of China, for financial support by NSC grants 88-2313-B002-279, 89-2313-B002-279, 90-2213-B002-279 and 92-262-B-002-018.

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