



Gibberellic acid surface complexation on ferrihydrite at different pH values: Outer-sphere complexes versus inner-sphere complexes

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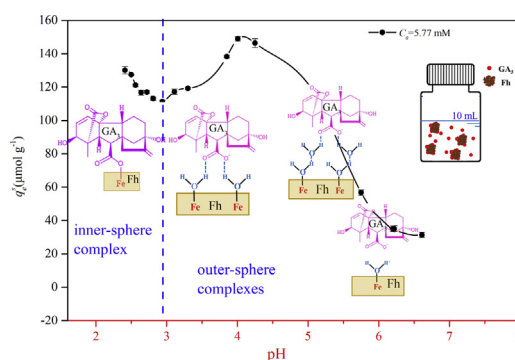
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HIGHLIGHTS

- The Fh-GA₃ surface complexation and retention on Fh depended strongly on pH.
- For pH > 2.9 two outer-sphere complexes stabilized by hydrogen bonds predominated.
- For pH ≤ 2.9, the monodentate complex was predominant and more irreversible.
- ~69–80% GA₃ could be replaced by nitrate at typical soil and groundwater pH values.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 June 2018

Received in revised form 18 August 2018

Accepted 2 September 2018

Available online 05 September 2018

Editor: P Holden

Keywords:

Gibberellic acid

Ferrihydrite

Surface complexation

Retention after desorption

pH

ABSTRACT

Gibberellic acid (GA₃) is a widely used plant growth regulator and environmental toxin especially in China, but no study has focused on the mechanism of the interactions between GA₃ and minerals/soils. In this study, the GA₃ surface complexation mechanism on ferrihydrite (Fh) was investigated by combining sorption–desorption batch experiments with Fourier transform infrared (FTIR) spectroscopy and moving-window two-dimensional (MW2D) correlation spectroscopy. The results showed that the Fh-GA₃ surface complexes and retention after desorption depended strongly on the pH. For pH > 2.9, electrostatic interactions played an important role in GA₃ sorption on Fh in two ways. One was directly forming an outer-sphere complex by electrostatic attraction to a minor extent. The other was acting as a driving force to facilitate the formations of surface hydration-shared ion pair (mainly formed at pH < 5.7) and solvent-surface hydration-separated ion pair (mainly formed at pH > 5.7). Those three outer-sphere complexes were partially reversible according to the high total desorption percentage of GA₃ (69–80%). For pH ≤ 2.9, the generated monodentate complex was observed and increased with decreasing pH, which showed more retention on Fh after desorption than the outer-sphere complexes according to the lower total desorption percentage of GA₃ (37%). At the typical soil and groundwater pH values (4.5–9), the outer-sphere complexes predominate, where GA₃ could be out-competed by nitrate and other anions and then easily desorbed from Fh. This increases the risk of groundwater contamination.

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1. Introduction

Gibberellic acid (GA₃), as a plant growth regulator, is widely applied in agriculture worldwide (Hafez et al., 2010; Chen et al., 2013; Shani et al., 2013). Since the end of the 20th century, China has become one of the largest GA₃ consumers, and its annual production is over 4000 tons in recent years (Mander, 1991; Lu et al., 2012), which leads to its high residues in agricultural products and natural environments. Shi (2011) reported that GA₃ residues were detected in soybean sprouts and early-maturing grapes at concentrations of 3.17 and 2.3 mg kg⁻¹, respectively, which were far beyond the standards issued by China (0.15 mg kg⁻¹) and Japan (0.2 mg kg⁻¹) (Shi, 2011; Shi, 2012). GA₃ is commonly associated with oxidative stress, a teratogenic effect and a carcinogenic effect in some animals (Celik et al., 2007; Troudi et al., 2010; Troudi et al., 2011). High GA₃ levels adversely affect the human endocrine system, because its molecular structure is similar to human steroids (Mander, 1992; Zhan et al., 2005). Therefore, it is important to study the transportation and fate of GA₃ in the environment.

The interaction of GA₃ with minerals/soils is important for understanding its migration and transformation in the soil/groundwater zone (Hu et al., 2001; Li et al., 2011; Qin et al., 2014). Hafez et al. (2010) reported that GA₃ could be sorbed on a Mg-Al layered double-hydroxide material (LDH) via anion-exchange with interlayer nitrate, and the formation of GA₃-LDH would inhibit the biodegradation of GA₃ as well as control its desorption quantity. Unlike man-made LDH, two-line ferrihydrite (Fh), the precursor of many crystalline forms of iron oxides and hydroxides (Cornell and Schwertmann, 2003), is ubiquitous in many near-surface environments (Schwertmann, 1987; Rancourt et al., 2001). Due to its extremely high surface area and reactivity, Fh always plays a substantial role in the sorption and desorption of pesticides on soils/sediments (Clausen and Fabricius, 2001; Kahle and Stamm, 2007; Sannino et al., 2009; Werner et al., 2013).

The form and structure of GA₃, as an organic acid with a carboxyl group, strongly influence its sorption mechanisms on iron oxides and hydroxides (Norén and Persson, 2007; Yeasmin et al., 2014). The sorption mechanisms of the carboxyl-containing organic acids on various mineral surfaces have primarily been studied by means of infrared spectroscopy, where the stretching vibrations of the carboxylate group have been used as the main diagnostic tool. On one hand, some researchers (Gu and Karthikeyan, 2005; Goyno et al., 2005; Greiner et al., 2014) interpreted frequency shifts of the carboxylate vibrations of organics sorbed on minerals in terms of some inner-sphere structures according to a set of empirical rules (shown in the Supplementary material (SM)). On the other hand, Norén and Persson (2007) reported that benzoate predominately formed some outer-sphere complexes, which were stabilized by hydrogen-bonding forces. In addition, the strong hydrogen-bonding interactions can have significant effects on the infrared spectra, and consequently, these complexes may be difficult to distinguish from inner-sphere complexes based on infrared spectroscopy alone (Majzlan and Myneni, 2005). Therefore, it is important to make that distinction by a combination of different analysis methods instead of only using the empirical rules.

In our previous study, batch experiments were conducted to investigate GA₃ sorption and desorption with different clay minerals (kaolinite and montmorillonite) as well as iron oxides and hydroxides (Fh, goethite and hematite) (Zhang et al., 2017). The results indicated that Fh had an important effect on the fate of GA₃ in the environment because GA₃ was only sorbed on Fh compared to the other four minerals. It was suggested that electrostatic sorption and surface complexation were possibly the main mechanisms. Unfortunately, the effects of different hydrogeochemical conditions (e.g., pH, GA₃ concentration and ionic strength) on the GA₃ sorption on Fh are still unknown. Especially, the pH would be an important factor influencing the sorption and desorption pattern because it determines the forms of GA₃ and the surface charge characteristics of Fh. Additionally, sufficient molecular evidences for different surface complexes (outer-sphere and/or inner-sphere complexes) at different pH values have not been reported.

Here, the GA₃ surface complexation mechanism on Fh was explored by the sorption-desorption batch experiments, Fourier transform infrared (FTIR) spectroscopy and moving-window two-dimensional (MW2D) correlation spectroscopy. The main objectives of this study were to: (1) evaluate the changes in the amounts of sorbed and desorbed GA₃ on Fh with various pH values under the given experimental conditions; (2) characterize Fh samples after sorption and desorption; (3) find sufficient molecular evidences for outer-sphere and/or inner-sphere complexes formed at different pH values; and (4) clarify the transportation and fate of GA₃ in the soil/groundwater zone.

2. Materials and methods

2.1. Materials

GA₃ (C₁₉H₂₂O₆; ~99% purity) stored at 4 °C was purchased from Acros Organics (Belgium, USA). GA₃ contains a carboxyl group in its molecular structure, and its acid dissociation constant (pKa) is 3.9. GA₃ was primarily in a protonated (neutral) form at pH < pKa (3.9) and in an anionic form at pH > pKa (Fig. S1). Fh was synthesized by the method reported by Schwertmann and Cornell (2000), and the detailed process is described in the SM. Its Brunauer-Emmett-Teller (BET) surface area and pH point of zero charge (pH_{PZC}) were determined by a Micromeritics ASAP 2046 (Norcross, Georgia, USA) and Zetasizer Nano Z (Malvern, United Kingdom), respectively. The BET surface area and pH_{PZC} of Fh were 244 m² g⁻¹ and 7.5, respectively, which were similar to the results reported in previous studies (Shimizu et al., 2013; Wang et al., 2013). Transmission electron microscope (TEM, Tecnai TF20, Eindhoven, Netherlands), X-ray diffraction (XRD, Rigaku D/max-rA, Japan) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi, United Kingdom) analyses were conducted to characterize the prepared Fh before and after the sorption of GA₃. The detailed results of XPS, TEM, and XRD are shown in the SM (Figs. S2–S5 and Table S1). The water used was purified by a Milli-Q (Millipore) ultra-pure water instrument (Merck Millipore, Darmstadt, Germany). Unless otherwise indicated, all other chemicals used were of analytical reagent grade or higher as received.

2.2. Sorption and desorption batch experiments

A series of batch experiments were conducted to investigate the sorption and desorption of GA₃ with Fh under different hydrochemical conditions in triplicate (Table 1). Fh (40 g L⁻¹) was pre-equilibrated overnight in a 0.01 mol L⁻¹ NaNO₃ solution prior to the sorption experiments. The suspension was continuously magnetically stirred at 700 rpm and adjusted to the desired pH by a NaOH or HNO₃ solution (1, 0.5 and 0.1 mol L⁻¹), and then, 5 mL aliquots of the homogeneous suspension were transferred to 20 mL amber glass vials with Teflon-lined screw caps. The total volume of aqueous phase in each of those vials was 10 mL, and the appropriate volumes of GA₃ solution and NaNO₃ solution were added to obtain the desired GA₃ concentration. All vials were shaken in a rotation shaker (QYC-2002C, Shanghai Fuma Test Equipment Co., Ltd., China) at 175 rpm and 25 °C for the 24 h equilibration time suggested by Zhang et al. (2017). Blank samples without GA₃ and control samples without Fh were evaluated to preclude the interference of Fh on GA₃ determination and the natural attenuation of GA₃, respectively.

After a predetermined equilibration time, all suspension samples were centrifuged at 4000 rpm for 30 min, and the final pH values were measured by a digital pH meter (Sartorius PB-10, Germany). Subsequently, the GA₃ concentration of the supernatant was analysed by high performance liquid chromatography (HPLC, LC-20AD, Shimadzu, Japan) with a determination method used in our previous study (Zhang et al., 2017). Finally, the GA₃ sorption quantity (q_e^s) was calculated by Eq. (1).

$$q_e^s = \frac{V(C_0 - C_e^s)}{M} \quad (1)$$

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