



Insights into tetracycline adsorption onto goethite: Experiments and modeling



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HIGHLIGHTS

- pH greatly influences tetracycline adsorption on goethite, while ionic strength does not.
- The adsorption was successfully predicted by a basic Stern model with CD approach.
- The tricarbonylamide group and the phenolic group are involved in adsorption.
- Two inner-sphere surface complexes $\equiv\text{FeTCH}_2^{0.5+}$ and $\equiv\text{Fe}_2\text{TC}$ are proposed.

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ABSTRACT

The surface adsorption behavior of tetracycline (TC), a zwitterionic antibiotic, to goethite was investigated as a function of pH, ionic strength and TC concentration using batch adsorption experiments and structural information was derived from attenuated total reflectance Fourier transform infrared spectrum observations. The spectroscopic results suggested that the tricarbonylamide group and the phenolic diketone group of the TC molecule were involved in interacting with the goethite surface depending on the pH level. A charge distribution surface complexation model was developed to describe the macroscopic adsorption trends. Two inner-sphere surface complexation species could successfully describe observed adsorption trends: under acidic condition TC may interact with the surface of goethite, forming a monodentate complex through the tricarbonylamide group, while under alkaline condition forming a more stable bidentate complex via the tricarbonylamide and phenolic diketone groups. The model could well predict the adsorption behavior of TC under a relatively wide range of pH, ionic strength and surface coverage. However, since the model did not fully consider the molecular size of TC, the model might overestimate the adsorption when TC surface coverage is higher than $1.42 \mu\text{mol m}^{-2}$.

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1. Introduction

Tetracyclines (TCs), one of the most widely used antibiotic families in the world, are often used to treat and prevent diseases in animals and are incorporated into animal feeds to enhance growth and feed efficiency in healthy livestock (Hu et al., 2010; Luo et al., 2011; Sarmah et al., 2006). Most TCs administered to livestock are excreted unmetabolized (Ji et al., 2009; Pils and Laird, 2007). Considering the high excretion rates of bioactive compounds and the potential of promoting the evolution of microbial populations resistant to TCs, the fate and behavior of TCs in the environment have become a source of growing concern in recent years (Thiele-Bruhn and Beck, 2005). With the land-based application of livestock wastes to agricultural fields, sorption to soils is a

major process affecting the transport and degradation of TCs in the environment (Kulshrestha et al., 2004). Hence, the assessment of the sorption and mobility of TCs in soils is important regarding their risk to the environment and human health.

TC is an amphoteric molecule with multiple ionizable functional groups: a tricarbonylamide group, a phenolic diketone group and a dimethylamino group (Fig. S1a). It can undergo protonation–deprotonation reactions and present different species depending on the solution pH (Parolo et al., 2008). Dissolved TC species may have net charges that are positive (H_3TC^+ , $\text{pH} < 3.3$), neutral (H_2TC^0 , $3.3 < \text{pH} < 7.68$), one negative (HTC^- , $7.68 < \text{pH} < 9.68$) or two negative (TC^{2-} , $\text{pH} > 9.68$) (Fig. S1b). It has been reported that TC can be highly adsorbed on clay minerals (Figuera et al., 2004; Pils and Laird, 2007; Wang et al., 2008), oxide minerals (Chen and Huang, 2010; Figuera and Mackay, 2005), humic substances (Gu et al., 2007; MacKay and Canterbury, 2005), soils (Wan et al., 2010; Zhang et al., 2011) and sediments (Wang et al., 2010; Xu and Li, 2010). The mechanisms of TC adsorption to clay minerals

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normally involve cation exchange reactions for cationic species (H_3TC^+) and surface complexation for zwitterions (H_2TC^0) (Figueroa et al., 2004). Unlike the well-characterized interaction of TC with phyllosilicate clay minerals, its sorption on oxide surfaces has received less attention. The adsorption of oxytetracycline onto goethite and hematite was investigated at various pH values and an adsorption maximum at pH 8 was observed, and a surface complexation mechanism was proposed (Figueroa and Mackay, 2005). Similar adsorption behavior was also reported between TC and goethite or ferrihydrite-coated quartz (Tanis et al., 2008), and iron hydrous oxide (Gu and Karthikeyan, 2005). It was suggested that the strong sorption was dominated by inner-sphere surface complexation. Moreover, FTIR spectroscopic evidence showed that tricarbonylamide and carbonyl groups might be responsible for the adsorption (Gu and Karthikeyan, 2005). Recently, one of our studies showed that different background cations (Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) showed little effect on the TC adsorption under pH range 3–10, also indicating a surface complexation mechanism involved (Zhao et al., 2011). However, the surface complexation species and electrostatic effect of the interaction between TC molecular and goethite surface remain unclear.

Models of the solid–solution interface are applied to understand and predict the reactivity of the surface. Surface complexation models (SCMs), a thermodynamic approach to describe the formation of surface complexes between dissolved solutes and surface functional groups, have been widely used to describe surface adsorption behavior, particularly the adsorption of various heavy metals onto minerals (Gu and Evans, 2008; Lund et al., 2008; Marcussen et al., 2009; Wang et al., 2006). Over the past decade, SCMs have also been successfully applied to adsorption of ionic organics to oxide minerals. A two-layer model was used to predict the adsorption of a series of organic acids onto goethite (Evanko and Dzombak, 1999). In recent years, SCM was successfully developed to describe the adsorption of glyphosate onto goethite surface (Jonsson et al., 2008), L-aspartate to rutile (Jonsson et al., 2010) and ofloxacin onto nano-anatase titanium dioxide (Paul et al., 2012). However, to our knowledge, there are only two studies that reported the modeling of TC adsorption onto iron oxide minerals so far. Figueroa and Mackay (2005) modeled the adsorption of oxytetracycline on goethite and hematite with two surface species and Tanis et al. (2008) used one binuclear surface species to model the surface complexation of TC onto goethite-coated quartz. These two studies did not clearly define the oxide surface-site heterogeneity and surface acid–base reactions. Meanwhile, they considered the stoichiometry of surface reactions, but ignored the possible electrostatic effect of the surface interaction.

To describe the surface complexation behavior of an ionizable molecule, like TC, to a variable charged surface, like goethite, one of the most common and stable crystalline iron (hydr)oxides in natural environments, the surface electrostatic effect needs to be fully considered. Among the SCMs developed for ion binding to oxides, the CD-MUSIC (charge distribution multi site complexation) model (Hiemstra and VanRiemsdijk, 1996) has the advantage that it is based on the structure of the mineral surface, the structure of the adsorbed species and the structure of the electrostatic potential profile in the vicinity of the mineral–water interface (Weng et al., 2006). The CD-MUSIC model has been successfully applied in modeling boron (Goli et al., 2011), arsenate (Salazar-Camacho and Villalobos, 2010), MCPA (4-chloro-2-methylphenoxyacetic acid) (Iglesias et al., 2010a), paraquat (Iglesias et al., 2010b) and many other substances on goethite surfaces.

The aim of this work was to characterize the surface complexation behavior of TC to goethite surfaces and use the CD-MUSIC model to predict its adsorption over relatively wide pH, ionic strength and surface coverage conditions. Such a model could help to predict the distribution of TC in natural waters, and this contributes to a better understanding of its mobility and bioavailability in the environment.

2. Materials and methods

2.1. Materials and chemicals

Tetracycline (96% purity) was purchased from Sigma-Aldrich Co. (St. Louis, MO). Other chemicals, including NaNO_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, were of A.R. grade and were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water (resistivity = $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the study.

Goethite sample was synthesized according to the method described in our other study (Zhao et al., 2011). X-ray diffraction (XRD) was used to confirm the formation of goethite (D/MAX-RA, Rigaku, Japan). The specific surface area measured by N_2 -BET analysis was $63.53 \text{ m}^2 \text{ g}^{-1}$ (ASAP 2020, Micromeritics, USA), and the mean particle size was $3.04 \mu\text{m}$, as measured by a laser particle analyzer (Mastersizer 2000, Malvern Co., UK).

2.2. FTIR measurements

FTIR spectra were collected using a Vertex 70 V FTIR spectrometer (Bruker, Germany) equipped with a liquid-nitrogen-cooled MCT detector and a 022-2020 ZnSe crystal fitted in a horizontal attenuated total reflectance (ATR) cell (Pike Technologies). A total of 256 scans with a spectral resolution of 4 cm^{-1} were performed.

TC solutions (5 mM) within 2 g L^{-1} goethite suspension were prepared at different pH values (pH 3, 5, 7, 8, 10) adjusted with NaOH/HNO_3 . NaNO_3 solution (0.01 M) was used as background electrolyte. The samples were wrapped in aluminum foil to prevent exposure to light and shaken at 150 rpm at $25 \pm 0.5 \text{ }^\circ\text{C}$ for 24 h. After equilibrium, the tubes were centrifuged for 30 min at 2880 g , and the solid and supernatant were collected separately and immediately spread on the ZnSe crystal surface to obtain a thin layer; FTIR spectra were then measured. Spectra of goethite in 0.01 M NaNO_3 were also obtained at five different pHs in the absence of TC. Difference spectra attributable only to the TC–goethite surface complexes were obtained by subtracting the supernatant and goethite- NaNO_3 suspension signals from the corresponding spectra of the solid. For the spectra of aqueous TC at different pH values (pH 3, 5, 7, 8, 10), the spectral contributions from water were removed by subtraction of the spectrum of the background electrolyte solution (at the same pH) from the TC spectrum.

2.3. Batch adsorption experiments

The effects of pH and ionic strength on the adsorption were examined using batch experiments in 0.001 M , 0.01 M and 0.1 M NaNO_3 background electrolyte at pH 3–10. All of the adsorption experiments were conducted using 22 mL glass vials equipped with polytetrafluoroethylene-lined screw caps. The solid-to-water ratio was 2 g L^{-1} , the initial TC concentration was 0.1125 mM and the samples were mixed on a reciprocal shaker at 150 rpm at $25 \pm 0.5 \text{ }^\circ\text{C}$ for 24 h. The solutions were purged with N_2 to remove dissolved oxygen to prevent the possible oxygen-mediated degradation of TC (Ji et al., 2009). The final pH values were measured immediately following equilibration using an Orion 8272 PerpHect Ross Sure-Flow electrode. The suspensions were then centrifuged, and TC in the supernatant was analyzed using HPLC. For detailed measurement methods, readers can refer to Zhao et al. (2011) and Zhao et al. (2012). To take account for solute loss from processes other than adsorbent sorption, calibration curves were built separately at the same treatment and conditions (pH, temperature, equilibration time, etc.) as the adsorption samples without adsorbent. Before detected by HPLC, the pH values of both adsorption samples and calibration curve samples were adjusted to 2.5 using diluted HNO_3 solution. The method used to investigate the effect of surface coverage was similar to the method described previously, except with respect to the initial TC concentrations.

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