



Sorption of tylosin on clay minerals



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HIGHLIGHTS

- Sorption of tylosin on montmorillonite was much higher than that on kaolinite.
- Sorption of tylosin decreased as pH increased.
- Intercalation happened on montmorillonite.
- The sorption of tylosin on montmorillonite is a monolayer sorption.

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ABSTRACT

The equilibrium sorption of tylosin (TYL) on kaolinite and montmorillonite was measured at different solution pH using batch reactor systems. The results showed that all the sorption isotherms were nonlinear and that the nonlinearity decreased as the solution pH increased for a given clay. At a specific aqueous concentration, the single-point sorption distribution coefficient (K_D) of TYL decreased rapidly as the solution pH increased. A speciation-dependent sorption model that accounted for the contributions of the cationic and neutral forms of TYL fit the data well, suggesting that the sorption may be dominated by both ion exchange and hydrophobic interactions. The isotherm data also fit well to a dual mode model that quantifies the contributions of a site-limiting Langmuir component (ion exchange) and a non-specific linear partitioning component (hydrophobic interactions). X-ray diffraction analyses revealed that the interlayers of montmorillonite were expanded due to the uptake of TYL. TYL molecules likely form a monolayer surface coverage.

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1. Introduction

As a main manufacturer and consumer of antibiotic chemicals in the world, China produced about 210,000 tons of antibiotic chemicals annually, of which 85% was utilized in animal agriculture and medicine, particularly as growth promoters in livestock (Sarmah et al., 2006; Luo et al., 2011). These antibiotics can only be absorbed partially in the digestive tract, and 50–80% of them are excreted as unmetabolized compounds (Gavalchin and Katz, 1994; Vaclavik et al., 2004), becoming associated with manure and wastewater. When manure is applied in agricultural lands, these chemicals can enter aquatic environments, possessing serious threat to both surface and groundwater quality and living organisms (Hamscher et al., 2002; Kolpin et al., 2002; Hamscher et al., 2005; Zuccato et al., 2005; Davis et al., 2006; Stooß et al., 2007; Xu et al., 2007; Peng et al., 2008; Hoese et al., 2009; Li

et al., 2011; Luo et al., 2011). Their presence in aquatic systems may also increase resistance of bacteria to antibiotic functions of these chemicals, raising great concern about their transport, fate, ecological effects and risk in the environment (Halling-Sørensen et al., 1998; Kümmerer, 2001; Aubry-Damon et al., 2004; Allaire et al., 2006; Khachatryan et al., 2006; Sarmah et al., 2006). Unlike nonpolar toxic organic pollutants, these bioactive agents often contain polar or ionic functional groups, which could lead to complicated interaction mechanisms with environmental solids (Gu et al., 2007; Wang et al., 2009).

Tylosin (TYL), a macrolide antibiotic produced by *Streptomyces fradiae*, is active against most gram-positive bacteria, mycoplasma and certain gram-negative bacteria. It is one of the most widely used additives in livestock feed and veterinary medicine in China. TYL is a weakly alkaline molecule with a pK_b value of 7.1 (Wollenberger et al., 2000; Babic et al., 2007), and has an ionizable dimethylamine group. The chemical exists predominantly as a cationic species in neutral to acidic pH ranges typical of the natural environment. The TYL molecule could be bonded on negatively charged sites of soils and is largely retained in soils and sediments

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as reported by Kim and Carlson (2007). Furthermore, TYL could be released to the aqueous phase due to increased soil pH resulting from fertilization (Blackwell et al., 2009). However, the assessment models developed based on hydrophobic organic compounds were insufficient to describe the behavior of veterinary pharmaceuticals including TYL in soils and sediments (Tolls, 2001; Franco and Trapp, 2008; Franco et al., 2009). In order to modify the models, it is necessary to understand the interactions between antibiotics and soils/sediments as well as clays as important component.

Prior studies of TYL sorption have focused primarily on manure and soils (Rabølle and Spliid, 2000; Loke et al., 2002; Clay et al., 2005; Allaire et al., 2006; ter Laak et al., 2006a, 2006b; Blackwell et al., 2007). Bewick (1979) had reported that distribution coefficients (K_D) values of TYL on sandy loams to clay soils were about 8–128 L kg⁻¹ and correlated positively with the contents of clay. The positively charged TYL can interact with negatively charged surfaces and functionalities in manure and soils such as minerals. Clays are common minerals in soils and sediments. They can play an important role on the transport of TYL in the environment. Prior studies revealed that cation exchange could be primarily responsible for the sorption of TYL on clays especially under acidic conditions (ter Laak et al., 2006a; Essington et al., 2010). Moreover, van der Waals forces also could play an important role on the distribution of TYL between soil and water. Sassman et al. (2007) reported that TYL sorption in soils were positively correlated to the specific surface area, clay content and cation exchange capacity (CEC) of the soils whereas the hydrophobic interactions may contribute partially to the overall sorption. Loke et al. (2002) reported that the distribution of TYL in manure was predominately related to hydrophobic bindings to organic matter instead of ionic bindings even though TYL has an aliphatic amine group on the molecule. Nevertheless, multiple mechanisms are expected for the uptake of TYL on soils.

In this study, we investigated the sorption of TYL by clay minerals under different solution pH conditions. X-ray diffraction (XRD) analysis was employed to provide the insights of interlayer of clay minerals during sorption. We hypothesized that (1) cation

exchange could dominate the sorption process; (2) differences in sorption between clay minerals could be related to the variations in both the solution pH and CEC of the clay minerals; and (3) the interlayer of expandable clays may be accessible to TYL even though it has a large molecular size. We also evaluated an empirical model for estimating sorption using a sorption coefficient fraction of the species present as a function of pH and assuming species-specific sorption to cation exchange sites. The purpose of current study was to understand mechanism of TYL sorption on clay minerals and to provide further insight to the role of clay in its transport in aquatic systems.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical-reagent grades or higher purity and solvents used were of HPLC grade. TYL tartrate (>95%) was purchased from Sigma–Aldrich (St. Louis, MO) and used as received. Other chemicals were purchased from Guangzhou Chemical Reagent Co. (Guangzhou, China). Acetonitrile and formic acid were purchased from Merck (Darmstadt, Germany). Water was purified using Milli-Q® (Millipore, Guangzhou, China).

A primary stock solution of TYL at 1 g L⁻¹ was prepared with Milli-Q® water and stored at 4 °C for a maximum of 1 month. The initial aqueous solutions were prepared by diluting desired volumes of stock solution using 0.01 M KNO₃ solution. Both KOH and HNO₃ were used for pH adjustment.

2.2. Sorbents

Na-Montmorillonite and kaolinite purchased from The Clay Minerals Society (Chantilly, VA) were employed as the sorbents. The specific surface areas (SSAs) were measured with the ethylene glycol mono-ethyl ether (EGME) method, and the results were similar to the report by Figueroa et al. (2004). The method presumably measured both external and interlayer surface areas of the clay

Table 1
The physicochemical properties and sorption parameters of sorbents.

Sorbent	Montmorillonite			Kaolinite		
<i>Physicochemical properties</i>						
Surface area (m ² g ⁻¹)	617			20.8		
CEC ^a (cmol(+) kg ⁻¹)	42.9			4.40		
pH	6.80			5.50		
Freundlich parameters ^b						
	pH = 4	pH = 7	pH = 9	pH = 4	pH = 7	pH = 9
log K _F (log[(μg g ⁻¹)/(μg L ⁻¹) ⁿ])	4.65	4.48	3.10	1.407	0.917	0.374
n (Unitless)	0.208	0.212	0.485	0.281	0.369	0.393
R ²	0.912	0.782	0.983	0.980	0.919	0.956
K _{D-SSA} ^c (L m ⁻²)						
C _e = 1000 μg L ⁻¹	3.15 × 10 ⁻¹	2.12 × 10 ⁻¹	5.80 × 10 ⁻²	8.55 × 10 ⁻³	5.08 × 10 ⁻³	1.72 × 10 ⁻³
C _e = 20,000 μg L ⁻¹	2.94 × 10 ⁻¹	2.00 × 10 ⁻¹	1.24 × 10 ⁻¹	9.92 × 10 ⁻⁴	7.67 × 10 ⁻⁴	2.79 × 10 ⁻⁴
K _{D-CEC} ^c (L cmol(+) ⁻¹)						
C _e = 1000 μg L ⁻¹	4.53 × 10 ³	3.04 × 10 ³	8.34 × 10 ²	40.42	24.02	8.12
C _e = 20,000 μg L ⁻¹	4.22 × 10 ²	2.87 × 10 ²	1.78 × 10 ²	4.69	3.63	1.32
Dual mode model parameters ^d						
	pH = 4	pH = 7	pH = 9	pH = 4	pH = 7	pH = 9
K _{DL} (L g ⁻¹)	10.78	2.27	0.973	8.02 × 10 ⁻³	2.11 × 10 ⁻³	3.63 × 10 ⁻³
Q (μg g ⁻¹)	1.94 × 10 ⁵	1.87 × 10 ⁵	1.63 × 10 ⁵	245.81	259	43.8
b (μg ⁻¹)	1.63 × 10 ⁻²	4.26 × 10 ⁻³	2.10 × 10 ⁻⁴	3.47 × 10 ⁻³	9.26 × 10 ⁻⁴	3.90 × 10 ⁻³
R ²	0.956	0.920	0.983	0.957	0.989	0.968
<i>Sorption coefficients of the different species</i>						
K _{D1} ^e (L m ⁻²)	0.424			0.004		
K _{D2} ^f (L m ⁻²)	0.054			0.001		

^a CEC, cation exchange capacity.

^b Freundlich parameters are defined by Eq. (1).

^c K_{D-SSA} and K_{D-CEC} are defined by Eq. (3).

^d Dual mode model parameters are defined by Eq. (5).

^e K_{D1}, the cation sorption coefficient, is defined by Eq. (4).

^f K_{D2}, the zwitterionic sorption coefficient, is defined by Eq. (4).

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