Experimental and modeling studies of sorption of tetracycline onto iron oxides-coated quartz

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ABSTRACT

The interaction of tetracycline (TET) with pure quartz (Q) and two iron oxides-coated quartz including quartz/ferrihydrite (Q_1) and quartz/goethite (Q_2) was investigated. The iron oxides-coated quartz were synthesized by precipitation suspension method and characterized by XRD, Fourier transform infrared spectroscopy (FTIR), surface area measurements and chemical analyses. Sorption of TET onto mixed oxides was studied under a wide range of conditions (time, sorbate concentration, pH, ionic strength, foreign divalent cations (Ca^{2+}, Pb^{2+}) and temperature). Kinetic data were treated using the pseudo-second-order model. The sorption isotherm of TET was fitted using a Langmuir model for both solids. The presence of complexing cation divalents decreased the sorption of TET to solid surface, but the variation of ionic strength (NaCl addition) was of less importance. The adsorption of TET was strongly affected by the pH at three temperatures with maximum adsorption close to the pK_a values. The adsorption increased with temperature increasing at low pH values, while at high pH values, it decreased with temperature increasing. Thermodynamic parameters (ΔG°, ΔH° and ΔS°) calculated from the temperature-dependent sorption data showed that the sorption reactions are endothermic and spontaneous for both mineral oxides. The experimental data of TET sorption can be described by surface complexation model assuming one type of site and binuclear surface complexes. The results of this study suggest that pH, temperature, surface charge of solids and presence of complexing divalent cations should be considered when predicting sorption of TET onto mineral oxides and its fate in soil and environment.

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1. Introduction

Tetracyclines (TET) are a class of antibiotics used in human medicine and widely used in veterinary medicine for treatment and prevention of infectious diseases [1]. TET constitutes one of the most important antibiotics families ranking second in production and usage worldwide [2]. It has been suggested that 90% of administered dose of antibiotics may be excreted through urine and faeces [3]. Thus, tetracyclines and pharmaceuticals antibiotics have been detected in surface water and in groundwater [4–6]. For this reason the fate and behavior of antibiotics in the environment are becoming a growing concern in most recent research. Sorption to solid surface is a major process affecting the transport and fate of antibiotics in the environment [7,8]. The sorption phenomenon is strongly influenced by solution chemistry and also by solid surface properties. Sorption of TET on whole soils, clays, pure oxides,

humic acids has been previously studied [9–11]. In this study, the sorption of TET to naturally occurring iron bearing minerals such as iron oxides-coated quartz has been investigated. Iron oxides-coated materials are one of the most abundant reactive surfaces typically present in near-surface and groundwater [12]. Therefore, it is important to evaluate their sorption capacity towards TET and their effect on the mobility of TET in soils. In addition, the complexation of TET with iron mineral surface where the chemical environment of iron is modified by mixing with silica quartz merits to be investigated. For this purpose, two mixed oxides including quartz/ferrihydrite and quartz/Goethite were prepared and characterized. In addition to their widespread abundance in soils and sediments, these iron phases were chosen because of their different crystallinity and surface area, which could affect the properties of iron-coated materials.

In this present work, series of batch experiments are conducted to characterize the sorption of TET onto iron oxides-coated quartz. First, sorption kinetic and sorption isotherm of TET were investigated and the data were fitted using the common models. Secondly, the effect of several physicochemical parameters (pH,

Table 1
Physical and chemical characteristics of TET

Chemical structure	
Molecular weight (g/mol)	480.90
Water solubility (mmol/L)	0.52–117
Log K_{ow}	−1.19
pK_1	3.3
pK_2	7.7
pK_3	9.7

Data extracted from Ref. [10].

ionic strength, foreign divalents cations (Ca^{2+}, Pb^{2+}) and temperature) was studied. Thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH), and standard entropy (ΔS°) were also evaluated by applying the Van't Hoff equation.

The most widespread model for reactions between oxyhydroxides and ligands is the surface complexation model, which is often used to fit experimental curves describing the variation of the amount of sorbed species as a function of the pH value [13]. In this work, the ability of a diffuse-layer model (DLM) assuming one type of site and one surface complexation reaction to describe the sorption of TET with iron oxides-coated quartz was examined.

2. Materials and methods

2.1. Chemicals

Tetracycline hydrochloride was obtained from Sigma–Aldrich and was used without any purification. TET has three pK_a values causing it to exist as cationic, zwitterionic and anionic forms (Table 1). Speciation diagram of TET as a function of pH has been reported in literature [10]. Calcium chloride $CaCl_2$ was obtained from Prolabo, Lead chloride ($PbCl_2$) from Fisher scientific S.A. hydrochloride acid and sodium hydroxyde from Prolabo were used.

2.2. Analytical methods

Because the maximum absorption peak of TET varies with pH, calibration curves were obtained by using the standard TET solutions with known concentrations at various pH (3–10). TET was quantified by UV/Vis spectroscopy (CARY 1, Varian. Inc.) at maximum wavelength of 358 nm over the range of pH tested. Before analysis, the suspensions were filtered through 0.22 μm polyvinylidene fluoride (PVDF) syringe filters (Millipore) that were shown not to sorb TET. Blank samples were prepared and monitored for each batch experiment. The blank samples did not indicate any significant compound degradation or sorptive losses on the glassware or desorption of "organics" from the tube walls during the course

of the experiment. The detection limit of UV–visible spectroscopy is about 0.1 μmol/L of organic compound. Aqueous concentrations of Pb, Ca and Fe were determined by Inductive Coupled Plasma spectroscopy (ICP-AES). The quantification limit of Fe by ICP-AES is about 10^{-2} μmol/L.

2.3. Preparation of the iron oxides-coated quartz

Quartz (CHEMPUR, 99%) called Q, with a grain size range of 0.3–10 μm was used. The mineralogy of the sand was characterized by X-ray diffraction and was found to be exclusively quartz.

The solid Q_1 was prepared by precipitation homogeneous suspension procedure. Iron oxide was precipitated in quartz suspension heated to 60 °C by drop-wise addition of $FeCl_3$ and NaOH solutions as explained in Refs. [14–16]. The simultaneous drop-wise addition of NaOH and $FeCl_3$ was continued to reach a pH 7 and the temperature was kept at 60 °C for 1 h. After pH adjustment, the suspension was stirred for 2 h at ambient temperature. The precipitates were filtered and were washed with distilled water till free of chloride anions. The product thus obtained was dried in an oven at 70 °C for 24 h.

The solid Q_2 was prepared by oxidation/precipitation from homogeneous solution. Goethite was synthesized by combining the two methods of Clarke and Hall [17] and Engel and Hilsenbek [18]. 33 g of $FeCl_2\cdot 4H_2O$ was dissolved in 200 mL of water flushed with N_2 to remove dissolved oxygen and then mixed with 10 g of quartz in glass reaction vessel. 3.1 g of $NaClO_3$ were added to oxidize the $FeCl_2$. Then, 500 mL of 0.52 mol/L of $NaHCO_3$ were added to the mixture to reach a pH value of 7. The suspension was stirred for 5 days at ambient temperature. The solid thus obtained was washed several times and then dried.

The two synthesized iron oxide-coated quartz were stored at ambient temperature until further use.

2.4. Sample characterization

In order to verify the crystal structure of minerals, samples of solids were analyzed by X-ray diffraction using an automated powder diffractometer with Mo Kα radiation (λ = 0.71069 Å). The bulk Fe over the sand was obtained by acid dissolution followed by quantification of Fe by ICP-AES. The specific surface area of the iron oxides was determined by multipoint N_2-BET analysis using a Coulter (SA 3100) surface area analyzer. The particle size distribution was measured by a dynamic light-scattering method using Laser scattering particle size (HARIBA, LA 200). The site density or the concentration of the replaceable surface groups of oxide was determined by measurement of the amount of fluoride adsorption on the surface [19]. Potentiometric titrations of the iron oxide-coated quartz were conducted in thermostated double walled pyrex cell at 293 K in 0.001, 0.01 and 0.1 M NaCl solutions according to the method of Parks and de Bruyn [20]. The N_2 gas was constantly passed through the suspensions to bubble out the CO_2. The pH value of the suspension was adjusted with titrant solutions (HCl or NaOH) and recorded with the Orion pH meter model 710A having combination glass electrode. The blank titrations were also performed with similar solutions in the absence

Table 2
Some properties of synthesized iron oxides-coated quartz

Mineral	Fe content (wt%)	wt% of iron oxide	Mean particle diameter (μm)	SSA (m²/g)	Site density (μmol/m²)	PZC
Q quartz	0	0	2	5.6	–	3
Q_1 quartz/ferric hydroxide	37.1	59.6	10.3	121	3.8	6.8
Q_2 quartz/goethite	33.4	53.0	2.8	148	3.3	6.7