



Modeling of Cd adsorption to goethite-bacteria composites

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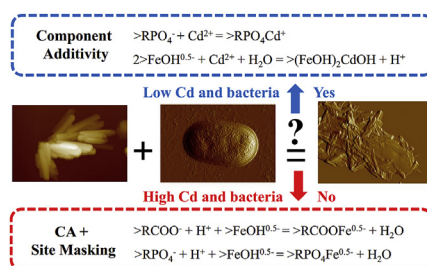
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HIGHLIGHTS

- Both CA and “CA-site masking” models were established for Cd adsorption on goethite-bacteria composites.
- Models are conditional on mineral/bacteria ratio and Cd concentration.
- Both models were precisely supported by thermodynamic reaction data.

GRAPHICAL ABSTRACT



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ABSTRACT

The accurate modeling of heavy metal adsorption in complex systems is fundamental for risk assessments in soils and associated environments. Bacteria-iron (hydr)oxide associations in soils and sediments play a critical role in heavy metal immobilization. The reduced adsorption of heavy metals on these composites have been widely reported using the component additivity (CA) method. However, there is a lack of a mechanism model to account for these deviations. In this study, we established models for Cd adsorption on goethite-*Pseudomonas putida* composites at 1:1 and 5:1 mass ratios. Cadmium adsorption on the 5:1 composite was consistent with the additivity method. However, the CA method over predicted Cd adsorption by approximately 8% on the 1:1 composite at high Cd concentration. The deviation was corrected by adding the site blockage reactions between *P. putida* and goethite. Both CA and “CA-site masking” models for Cd adsorption onto the composites were in line with the ITC data. These results indicate that CA method in simulating Cd adsorption on bacteria-iron oxides composites is limited to low bacterial and Cd concentrations. Therefore the interfacial complexation reactions that occur between iron (hydr)oxides and bacteria should be taken into account when high concentrations of bacteria and heavy metals are present.

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1. Introduction

The cycling of heavy metals in natural environments can be strongly affected by adsorption onto solid particle surfaces. Clay-sized minerals, bacteria and humic substances are among the most active adsorbents due to their large specific surface areas and

high affinity for heavy metals (Brown et al., 1999; Filgueiras et al., 2002; Plathe et al., 2013; Shi et al., 2013; Fisher-Power et al., 2016). They are often found to be spatially associated and to form tight composites with each other in soils and sediments (Fortin and Langley, 2005; Huang et al., 2005, 2015). To understand and evaluate the fate and risk of heavy metals in soil systems, it is therefore necessary to accurately simulate and predict heavy metal adsorption onto these complex systems.

Surface complexation models (SCM) are powerful tools for calculating ion adsorption processes. SCM has been widely used in describing heavy metal adsorption on different minerals and organic matters. For metal (hydr)oxides, the surface sites are derived from the crystallographic structure (Hiemstra et al., 1989), and the so-called charge distribution multi-site complexation (CD-MUSIC) model has been successfully applied in simulating the adsorption of Ca, Pb, Cd and Cu onto iron or aluminum (hydr)oxides (Randall et al., 1999; Weerasooriya et al., 2002; Boily et al., 2005; Weng et al., 2005, 2008; Xiong et al., 2015). Models have also been built for a range of toxic metals on phyllosilicates such as illite (Lackovic et al., 2003), montmorillonite (Stadler and Schindler, 1993; Gu et al., 2010; Wang et al., 2016a) and kaolinite (Gu and Evans, 2008). These models are able to distinguish between the bidentate non-specific adsorption on the basal surfaces and the monodentate inner-sphere complexes on edge sites. In contrast to minerals, the surface charges of bacteria result predominantly from organic functional groups. A number of SCMs have been previously employed to interpret the charge properties of bacteria. For example, the continuous pKa distribution approach coupled with the Donnan model was able to explain the proton reactions on *Rhodococcus erythropolis* (Plette et al., 1995), *Bacillus subtilis* and *Escherichia coli* (Martinez et al., 2002), as well as Cd adsorption onto *Rhodobacter sphaeroides*, *Alcaligenes eutrophus* (Seki et al., 1998) and bacterial exopolysaccharides (Lamelas et al., 2006). Besides, 3 or 4 discrete site nonelectrostatic models (NEM) have been used to describe adsorption in bacterial systems (Fein et al., 1997, 2005; Borrok and Fein, 2005; Fein, 2006; Yu et al., 2014), whilst spore surface of *B. subtilis* have been simulated by the 5-site NEM (Harrold and Gorman-Lewis, 2013). Several models such as diffuse layer model (DLM) (Borrok and Fein, 2005), constant capacitance model (CCM) (Ha et al., 2010; Wang et al., 2016a), and basic Stern model (BSM) (Moon and Peacock, 2011) have been adopted to account for the electric double-layer on heavy metals adsorption by bacteria.

Modeling of heavy metal adsorption on binary complexes has received increasing attention over the recent years. The composites exhibit contrasting sorption behaviors when compared to their end members by the component additivity (CA) approach. For example, the Langmuir equation underestimated Cu adsorption by about 6% on montmorillonite-*Pseudomonas putida* (Fang et al., 2010b) and smectite-*P. putida* composites (Chen et al., 2009). On the contrary, simple additivity models predicted 17%–193% higher adsorption of Sr, Cd, Pb and Cu on bacteria-iron (hydr)oxides composites (Martinez et al., 2004; Kulczycki et al., 2005; Langley et al., 2009; Fang et al., 2010a). Similarly, a 10% over prediction was reported for Cd adsorption to the composites of ferrihydrite (HFO) and *Comamonas* spp. when a 4-site NEM for bacteria and DLM for HFO were combined (Song et al., 2009). These overestimations may be due to the masking of iron oxide >FeOH sites by phosphate (Omoike et al., 2004; Omoike and Chorover, 2006; Fang et al., 2012) and carboxyl groups (Parikh and Chorover, 2006; Ojeda et al., 2008; Gao et al., 2009) present on the bacterial surface. In comparison, Cd adsorption onto the composites of bacteria with kaolinite, montmorillonite or HFO at various mass ratios were proven to be additive (Alessi and Fein, 2010; Du et al., 2016; Wang et al., 2016a). The additivity was also observed by BSM for Cu adsorption onto

HFO-*B. subtilis* composite at about 5:1 and 2:1 mass ratios (Moon and Peacock, 2013). These modeling results were supported by the long-period x-ray standing wave analysis, confirming that the reactive sites on metal oxides are not passivated by the biofilms (Templeton et al., 2001, 2003; Wang et al., 2016b).

To date, studies regarding heavy metal adsorption by binary composites have mainly focused on applying the additivity method. There is a need for a model that can simultaneously incorporate the site masking and heavy metal adsorption on iron (hydr)oxides-bacteria composites. Thus, in this study, we first investigated the functional groups of goethite-*P. putida* composites using potentiometric titration and isothermal titration calorimetry (ITC). Then, the adsorption capacity and heat for Cd were measured by batch experiment and ITC technique, respectively. Finally, we develop a surface complexation model to describe the ligand exchange reactions between *P. putida* and goethite and the model parameters were further used to adjust the deviations in CA method and to calculate the distribution of Cd on goethite-*P. putida* composites.

2. Materials and methods

2.1. Preparation of bacteria, montmorillonite and their mixtures

The strain of *Pseudomonas putida* X4 was cultivated to reach mid-exponential phase in Luria broth medium as described by Wu et al. (2014). Goethite was synthesized according to the method of Atkinson et al. (1967). The goethite-bacteria composites were prepared by mixing the mineral and bacterial suspension at 1:1 and 5:1 ratios (dry-weight basis), respectively, and incubated at pH 6.5 for 12 h to achieve equilibrium. The mixtures were then used for subsequent experiments. The detailed procedures for sample preparation are shown in the [Supporting Information](#).

2.2. FTIR and AFM measurement

The infrared spectra of *P. putida* and the composites were characterized by in situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Vertex 70 spectrometer, Bruker Optik GmbH). The horizontal 45° ZnSe ATR crystal stage was coated with a goethite film and the bacterial adsorption was conducted by allowing the bacterial suspension flow at a speed of 1 mL/min for 100 min. Morphology measurements were performed using a Multimode 8 atomic force microscope (Bruker). The mineral-bacteria aggregate was immobilized by drying on a mica surface. An area of 3 μm \times 1.7 μm with 300 scan lines were performed to catch single bacteria. The specific procedures for sample preparation and data analysis are shown in the [Supporting Information](#).

2.3. Potentiometric titrations

The reaction for proton on goethite, bacteria and composite systems was performed in triplicate using a Metrohm automatic potentiometric titrator, Switzerland. The suspensions (10 g L⁻¹, 40 mL) in 0.01 M NaNO₃ were placed in a sealed titration vessel maintained under a positive pressure of N₂. An aliquot of 0.1 M HNO₃ was added at the beginning of the experiment to lower the pH to approximately 3. The cell suspension was equilibrated for 30 min and titrated to pH 10.5 with 0.1 M NaOH. A stability of 0.004 pH/min was attained for each titration. The suspension was titrated back to pH 3 by adding a 0.1 M HNO₃ solution. No significant hysteresis was observed between the base and acid legs. The base legs were used to determine the acid–base parameters. The AFM detection shows that the *P. putida* cells maintained integrity for 3 h at both pH 10.5 and 2.5, but the strong acid and base conditions resulted in increased cell surface roughness, and the

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