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A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects

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ABSTRACT

Analytical isotherm equations such as Langmuir and Freundlich isotherms are widely used for modeling adsorption data. However, these isotherms are primarily useful for simulating data collected at a fixed pH value and cannot be easily adapted to simulate pH-dependent adsorption effects. Therefore, most adsorption studies currently use numerical surface-complexation models (SCMs), which are more complex and time consuming than traditional analytical isotherm models. In this work, we propose a new analytical isotherm model, identified as the modified Langmuir-Freundlich (MLF) isotherm, which can be used to simulate pH-dependent adsorption. The MLF isotherm uses a linear correlation between pH and affinity coefficient values. We validated the proposed MLF isotherm by predicting arsenic adsorption onto two different types of sorbents: pure goethite and goethite-coated sand. The MLF model gave good predictions for both experimental and surface complexation-model predicted datasets for these two sorbents. The proposed analytical isotherm framework can help reduce modeling complexity, model development time, and computational efforts. One of the limitations of the proposed method is that it is currently valid only for single-component systems. Furthermore, the model requires a system-specific pH. vs. affinity coefficient relation. Despite these limitations, the approach provides a promising analytical framework for simulating pH-dependent adsorption effects.

1. Introduction

The effects of pH variation on adsorption of inorganic contaminants (e.g., arsenic, lead) on metal oxide surfaces (e.g., HFO, goethite) are primarily simulated using surface complexation models (SCMs) (Davis and Kent, 1990; Dzombak and Morel, 1990; Westall and Hohl, 1980). This numerical approach is intricate and computationally intensive when compared to simpler analytical models such as Langmuir and Freundlich isotherms. Unfortunately, none of the currently available analytical isotherm models are capable of predicting pH-dependent adsorption effects in a consistent manner. Hence, there is a need to develop adsorption isotherms that can describe pH-dependent adsorption effects. If developed, such pH-dependent isotherm models can potentially be integrated into large-scale contaminant transport codes such as MT3DMS (Zheng and Wang, 1999) and RT3D (Clement et al., 1998) to simulate pH dependent transport scenarios. Presently, these transport codes are integrated with computationally intensive, complex geochemical packages such as MICROQL, MINTEQ or PHREEQC (Clarlton and Parkhurst, 2002) to simulate scenarios involving pH-dependent transport [e.g., (Brown et al., 2000; Cederberg et al., 1985; Filius et al., 1999; Parkhurst et al., 2004; Prommer et al., 2003)]. Coupling of surface complexation models to transport codes is complex task that requires considerable code-development efforts. Hence several researchers have used simpler isotherm models to model transport involving adsorption reactions (Di Natale et al., 2008; Genc and Ulupinar, 2010; Khan et al., 2009; Palmer and Wittbrodt, 1991; Radu et al., 2008). Also, when transport codes are coupled to geochemical models the resulting tool would require considerable computer time to complete realistic field

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simulations. On the other hand, it is much easier to couple isotherm models to transport codes to develop computationally-efficient simulation tools.

Distribution coefficient (K_d) based models were commonly used for contaminant transport modeling. However, constant K_d models fail to capture pH-dependent adsorption behavior (Bethke and Brady, 2000). Several researchers have suggested intermediate models which can link K_d with soil properties such as pH and ionic strength. Anderson and Christensen (1988) showed that K_d varied linearly with pH for Cd, Co, Ni and Zn adsorption. Sakata (1987) showed that K_d for arsenic(III) adsorption varied linearly with iron content. Samper et al. (2010) observed that K_d for adsorption of Cs^+ ions varied with ionic strength in nuclear repositories. However, many of these studies were field studies and none of them provide an alternative analytical framework for modeling pH dependent reactive transport processes.

In the published literature, a few studies have attempted to fit standard adsorption isotherm equations to laboratory datasets collected at different pH values. Anderson et al. (1976) used the Langmuir isotherm to fit arsenate adsorption at different pH values. Hingston et al. (1971) used a modified Langmuir isotherm to model competitive adsorption of arsenate in presence of phosphate at different pH values. Ghosh and Yuan (1987) investigated adsorption of arsenic on activated alumina at different pH values using the Langmuir isotherm. Hsia et al. (1992) used a modified Langmuir isotherm to model arsenic adsorption on amorphous iron oxide. Yu and Kaewsarn (1999) used a modified Langmuir isotherm to describe pH dependent bio-sorption of heavy metals on marine algae. However, these studies have simply regressed various forms of Langmuir isotherm expressions by fitting the values of the affinity constant and adsorption capacity to pH-dependent sorption datasets. No attempts have been made to develop expressions for simulating the effects of pH variations on sorption using a framework that is consistent with SCM predictions. For example, SCM simulations show that adsorption of metal or metalloid species (such as arsenate) at different pH tends to increase with concentration of adsorbate and converges towards the maximum adsorption capacity value for the sorbent. Therefore, most SCMs advocate the use a single site density value which represents the maximum adsorption capacity of the system (Dzombak and Morel, 1990; Goldberg, 1986). However, attempt to arbitrarily force fit the Langmuir isotherm to various datasets (Anderson et al., 1976; Ghosh and Yuan, 1987; Wankasi and Tarawou, 2008) would yield different values of adsorption capacity at different pH values. Currently, there are no analytical adsorption modeling frameworks available in the literature that can be used as an analytical alternative to SCMs to simulate pH-dependent adsorption effects.

The objective of this paper is to develop an analytical framework for modeling pH-dependent adsorption effects. We have modified the Langmuir-Freundlich isotherm model to simulate pH-dependent adsorption effects and demonstrated its application using two different arsenic sorption datasets.

2. Modeling Methods: The Langmuir-Freundlich isotherm

In our earlier study (Jeppu et al., 2010), we presented several laboratory datasets for arsenic(V) adsorption on goethite-coated sands and pure goethite. We have also presented a scalable SCM formulation for modeling all these experimental datasets. In this effort we will utilize both the experimental data as well as the SCM parameters presented for arsenic adsorption in Jeppu et al. (2010) to test the proposed analytical modeling methods. Since Jeppu et al. (2010) work focused on arsenic sorption on goethite, we will use arsenic-goethite system as the test problem in this study.

The most widely used analytical isotherm for modeling adsorption of arsenic on iron-oxides are: Langmuir isotherm (Hingston, 1970; Kundu and Gupta, 2006; Raven et al., 1998; Thirunavukkarasu et al., 2001; Thirunavukkarasu et al., 2003) and Freundlich isotherm (Badruzzaman et al., 2004; Lin and Wu, 2001; Raven et al., 1998). The Langmuir-Freundlich isotherm, also known as Sip's equation, is a versatile isotherm expression that can simulate both Langmuir and Freundlich behaviors (Nahm et al., 1977; Sips, 1948; Sips, 1950). Rau et al. (2003) studied arsenate adsorption on metal-oxides using different types of adsorption isotherms and concluded that the Langmuir-Freundlich isotherm best described their data. In this study, we have used the Langmuir-Freundlich isotherm as the base model to describe all our arsenate adsorption data. The Langmuir-Freundlich isotherm can describe both the Langmuir-type and Freundlich-type adsorption behavior of arsenic and is suitable for modeling pH-dependent sorption effects. A general form of Langmuir-Freundlich isotherm equation for arsenic(V) adsorption can be written as (Turiel et al., 2003):

$$q = \frac{Q_m (K_a C_{eq})^n}{(K_a C_{eq})^n + 1} \tag{1}$$

Where,

q is the amount of As(V) adsorbed on the sand at equilibrium (mg As(V)/ g sand)

Q_m is the adsorption capacity of the system (mg of sorbate/ g sorbant), which can also be expressed as N_t , which is a measure of total number of binding sites available per gram of sorbent

C_{eq} is the aqueous phase concentration at equilibrium (mg/ L)

K_a is the affinity constant for adsorption (L/mg)

n is the index of heterogeneity

Fundamentally, both Langmuir and Freundlich isotherms can be mathematically viewed as the following weighted integral (Limousin et al., 2007):

$$q = \int_{-\infty}^{+\infty} g(K_a) \frac{K_a C_{eq}}{1 + K_a C_{eq}} dK_a \tag{2}$$

Where the statistical density function $g(K_a)$ represents the individual site density values of elementary isotherms with its own affinity constant K_a. The $g(K_a)$ distribution reduces to a Dirac's delta function for Langmuir isotherm, and it resembles a log-normal distribution for Freundlich isotherm (Limousin et al., 2007). The LF isotherm allows one to vary the density function for heterogeneous systems using a heterogeneity index n, which is allowed to vary from 0 and 1. The value of n for a homogeneous material is