



A simple model to predict chromate partitioning in selected soils from China



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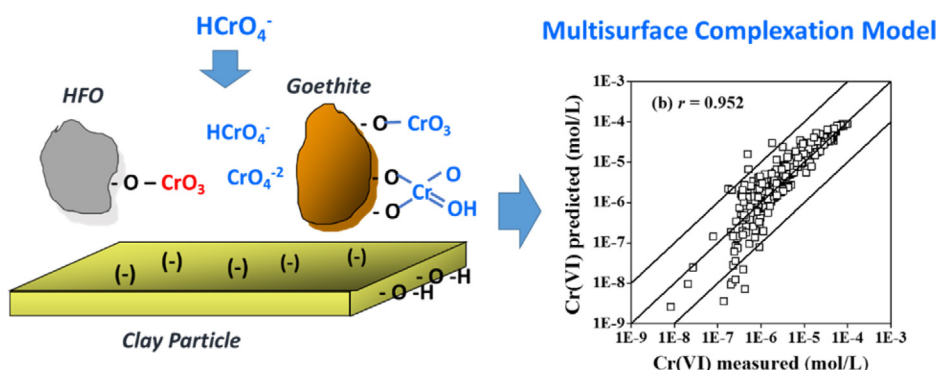
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HIGHLIGHTS

- Cr(VI) partition in soils is well-modeled by the CD-MUSIC model of Cr(VI) on goethite.
- Available phosphate should be considered in soils with a low Fe/P ratio (<1).
- The model is applicable in soils with wide-ranging properties and Cr(VI) levels.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 July 2016

Received in revised form 6 October 2016

Accepted 15 October 2016

Available online 17 October 2016

Keywords:

Chromate
Model
Soil
Goethite
Partition

ABSTRACT

Due to its mobility and toxicity, chromate [Cr(VI)] partitioning in soils, especially in the vadose zone, is an important environmental concern. The aim of this study was to develop a mechanism-based multi-surface complexation model using published parameters to predict the soil/water partitioning of Cr(VI) in 12 soils (previously depleted of organic matter) from China. The retention of Cr(VI) in soils was attributed to two reactive oxide surfaces: goethite and hydrous ferric oxide (HFO); however, modeling results showed that the best prediction was obtained with goethite alone, whereas the addition of HFO resulted in an overestimation of adsorption in some soils. Cr(VI) adsorption onto goethite could be described using our previously proposed CD-MUSIC model. In the absence of a specific value for the soil-reactive surface area of goethite, a general value of 45.8 m²/g was used. The available phosphate in soils was identified as a strong competitor for Cr(VI) adsorption; thus, for soils with a low Fe/P ratio (<1) the effect of phosphate on Cr(VI) retention should not be neglected. The simple method presented herein can be applied to soils with a wide range of properties, pH values, and Cr(VI) loading concentrations.

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1. Introduction

Cr(VI) is widely used in numerous industrial processes, such as electroplating, leather tanning, and wood preservation. However, it is also one of the most toxic chemicals known and has been linked to carcinoma, chromosomal mutations/aberrations, and DNA damage [1,2]. Because Cr(VI) mainly occurs as oxyanions with high solu-

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bility, it easily leaches into groundwater and thus poses a severe environmental threat. The maximum permissible Cr(VI) level in drinking water, as recommended by the World Health Organization (WHO), the USA's Environmental Protection Agency (EPA), and the EPA in China, is 0.05 mg L^{-1} (0.001 mmol/L). The leaching standard of Cr(VI) for hazardous waste, as recommended by the Chinese EPA, is 5 mg L^{-1} (0.096 mmol/L).

Because the solid-solution partitioning of metals is a key factor influencing their accumulation, mobility, and bio-availability in soils, it is essential to understand Cr(VI) partitioning in soils to predict the potential risk of its leaching into groundwater and its bioavailability to biomass. The fate of Cr(VI) in soil environments is strongly linked to its adsorption onto soil mineral surfaces. Among the many mineral groups, iron hydroxides are the most important reactive surfaces for Cr(VI) retention, given their surface charge properties, high adsorption capacities, and their abundance in soil environments. By contrast, the adsorption of Cr(VI) onto phyllosilicate clay minerals is negligible [3]. For example, at pH 4 the adsorption capacity of Cr(VI) onto goethite is 158 mmol/kg [4], but onto kaolinite it is only 8.6 mmol/kg [5]. Illite and montmorillonite retain even less Cr(VI) than kaolinite because of their higher negative surface charges [3,5]. Soil organic matter (SOM) provides important adsorption sites for most heavy-metal cations, but mainly serves as a reductant to reduce Cr(VI) to Cr(III), which is much less toxic and less soluble in soils [6,7].

Although the adsorption of Cr(VI) onto (hydroxyl)oxides has been extensively investigated and modeled, there have been few attempts to predict Cr(VI) retention in heterogeneous soils. Jardine et al. [7] examined Cr(VI) sorption onto 35 soils from contaminated sites and developed an empirical linear regression equation that mostly related to SOM and soil pH. However, their X-ray absorption near-edge structure (XANES) spectroscopy data suggested that what was initially recognized as "sorption" was instead the primary reduction of Cr(VI) to Cr(III), with the redox potential increasing with increasing SOM. Perez et al. [8] developed a charge distribution surface complexation model (SCM) to describe the adsorption of chromate onto two ferrallic soils. Unfortunately, the binding constants determined in that study could not be extended to other soils. Thus, a more generic model to predict Cr(VI) partitioning in various soils is still needed.

Recently, assemblage or multi-surface models using published "generic" model parameters were shown to be a promising tool to predict trace-element partitioning in soils [9–12]. The models assume that trace-element adsorption in heterogeneous soils can be described by the sum of the individual reactive surfaces. Yet, predictions for oxyanions are not as good as those for cations, because the performance of this approach relies on the goodness of the model framework and the accuracy of the model's parameters [13], and cations like Cu^{2+} , Cd^{2+} and Pb^{2+} are more thoroughly investigated than anions. We previously developed a SCM of Cr(VI) adsorption onto goethite, in which the surface species were based on spectroscopic evidence. The model well-predicted Cr(VI) adsorption over a wide range of pH values, ionic strengths, and surface coverages [4], thus demonstrating its utility in soil speciation models.

The aim of the present study was to develop a multi-surface model using published model parameters to predict the solid-solution partitioning of Cr(VI) in various soils. The most important reactive surfaces in soils, goethite and hydrous ferric oxide (HFO), both of which are responsible for Cr(VI) retention, were considered, as were other modeling factors such as the reactive surface area and competitive ions, specifically, PO_4^{3-} . We then compared the performance of the multi-surface model with that of an empirical partitioning model.

2. Materials and methods

2.1. Materials and chemicals

The 12 surface (0–15 cm) soils tested in this study were collected from southern and central China (Fig. 1). Their properties are listed in Table 1. After collection, the soils were air dried and passed through a 2-mm sieve. Soil pH was recorded in 0.01 M CaCl_2 (1:2.5 w/w), and the soil cation-exchange capacity (CEC) using the NH_4Ac method at pH 7.0 [14]. The soil samples were ground to pass through a 60-mesh sieve and then used for further characterizations and experiments. SOM was removed using 1 M NaOCl at room temperature to exclude the reduction effect of SOM on Cr(VI) [7,15]. Briefly, 600 mL of 1 M NaClO was mixed with 30 g of soil, after which the suspension was stirred for 6 h at room temperature. The soil was separated by centrifugation at $2000g$ for 30 min and the process repeated three times. To remove extra salts, the soil was washed with deionized water three times; it was then freeze dried until further use. This method is better than the H_2O_2 oxidation method in maintaining the original type and surface area of the amorphous oxide minerals in soils [15].

The total amount of Fe hydroxides in soils was determined using the dithionite-citrate-bicarbonate (DCB-Fe) extraction method [16]. Amorphous Fe oxides was extracted with oxalic acid (Ox-Fe) [9].

Sodium chromate tetrahydrate (99% purity) was purchased from Sigma-Aldrich Co. (St. Louis, MO). Other chemicals were of A.R. grade and were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water (resistivity $>18 \text{ MX/cm}$) was used throughout the study.

2.2. Batch adsorption experiments

The partitioning of Cr(VI) in soils as a function of pH (3–10) and initial Cr(VI) concentration ($0.269\text{--}13.6 \times 10^{-5} \text{ mol/L}$) was examined in batch adsorption experiments. Briefly, 0.050 g of SOM-removed soil samples and 10 mL of background electrolyte solution (0.01 M NaNO_3) were added to 15-mL centrifuge tubes, together with a chromate stock solution (1000 mg/L) in an amount needed to obtain the desired concentration. The solution pH was adjusted using small volumes of 0.01 M HNO_3 or NaOH to cover the range from pH 3 to 10. After shake-incubation for 48 h at 25°C , the suspensions were centrifuged at $3000g$ for 20 min and the pH was

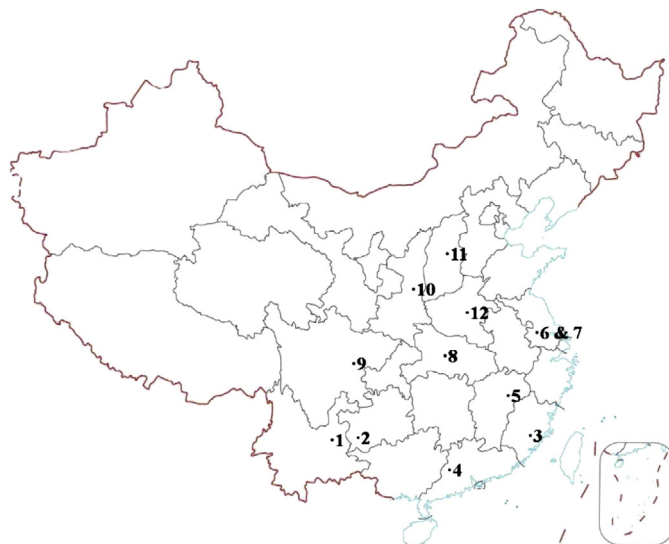


Fig. 1. Distribution of the sampled soil sites.

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