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Competitive binding of Cd, Ni and Cu on goethite organo–mineral composites made with soil bacteria[☆]



Huihui Du^{a, b, *}, Qiaoyun Huang^b, Caroline L. Peacock^c, Boqing Tie^a, Ming Lei^a, Xiaoli Liu^a, Xiangdong Wei^a

^a College of Resources and Environment, Hunan Agricultural University, Changsha, 410128, PR China

^b State Key Laboratory of Agricultural Microbiology, College of Resources and Environment, Huazhong Agricultural University, Wuhan, 430070, PR China

^c University of Leeds, School of Earth and Environment, Leeds, LS2 9JT, UK

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ABSTRACT

Soil is a heterogeneous porous media that is comprised of a variety of organo-mineral aggregates. Sorption of heavy metals onto these composite solids is a key process that controls heavy metal mobility and fate in the natural environment. Pollution from a combination of heavy metals is common in soil, therefore, understanding the competitive binding behavior of metal ions to organo-mineral composites is important in order to predict metal mobility and fate. In this study, batch experiments were paired with spectroscopic studies to probe the sorption characteristics of ternary Cd–Ni–Cu sorbates to a binary organo-goethite composite made with *Bacillus cereus* cells. Scanning electron microscopy shows that goethite nano-sized crystals are closely associated with the bacterial surfaces. Sorption experiments show a larger adsorptivity and affinity for Cu than Cd/Ni on goethite and *B. cereus*, and the goethite–*B. cereus* composite. X-ray photoelectron spectroscopy reveals that carboxylate and phosphate functional moieties present on the bacterial cell walls are primarily responsible for metal sorption to the goethite–*B. cereus* composite. Synchrotron-based X-ray fluorescence shows that Cu and Ni are predominately associated with the bacterial fraction of the goethite–*B. cereus* composite, whereas Cd is mainly associated with the goethite fraction. The findings of this research have important implications for predicting the mobility and fate of heavy metals in soil multi-component systems.

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1. Introduction

Heavy metal pollution in soils has received a lot of attention over recent decades, due to the toxicity and persistence of heavy metals in the environment. A recent report shows that Cd, Ni and Cu rank among the top three most serious heavy metal pollutants on the Chinese mainland, with 7.0%, 4.8% and 2.1%, respectively, of Chinese soils exceeding the Environmental Quality Standard for Soils in China (Zhao et al., 2015). The mobility and fate of heavy metals in contaminated soils depends largely on their sorption to various solid components, namely clay-sized minerals and organic constituents such as humic substances, and bacterial and fungal biomass (Dai et al., 2017; Du et al., 2016a). Moreover, multi-metal

pollution is common, therefore, the competitive or synergistic sorption of metal ions needs to be better understood in order to properly predict heavy metal mobility and fate (Hughes et al., 2017; Yang et al., 2016; Zhu et al., 2017).

With the ongoing development of spectroscopy techniques, the binding characteristics of heavy metals on soil components have become increasingly clear. In general, heavy metals sorb on minerals and organic components through non-specific or specific sorption via the formation of either outer-sphere or inner-sphere complexes (Bradl, 2004). Sorption of heavy metals to minerals and organic components is largely dependent on pH, ionic strength, solid-to-metal ratio, temperature and the presence of anionic ligands that are abundant in soil solutions (Du et al., 2018a; Peng et al., 2017). In multi-metal contaminated environments, the sorption of individual heavy metals is also affected by competition for sorption sites from other heavy metals. For example, in clay sorption systems, Cu reduces Ni sorption on montmorillonite, but Ni exerts a negligible effect on Cu sorption (Yang et al., 2015). The

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* Corresponding author. 1st Nongda Road, Furong District, Changsha City, PR China.

E-mail address: duhuihui@hunau.edu.cn (H. Du).

selective sorption sequence of $\text{Cu} > \text{Ni}$ can be attributed to differences in metal properties and the affinity of each metal towards the montmorillonite binding sites. In organic sorption systems, Fowle and Fein (1999) showed that sorption edges for Cu on *Bacillus subtilis* bacterial cells occur at lower pH values compared to Cd, signifying the selective sorption sequence of $\text{Cu} > \text{Cd}$ for the organic bacterial cell surface sites. In mixed mineral and organic sorption systems, the presence of organics can change the sorption behavior of heavy metals. For example, in a calcareous soil, the selectivity sequence of metal adsorption is $\text{Cu} > \text{Cd} > \text{Ni}$ (Jalali and Moradi, 2013), however, when soil is rich in organic matter, the metal binding sites are more selective for Ni than Cd (Chorom et al., 2013).

Soil minerals and organics are commonly found to interact with one another to produce organo-mineral composites (Kleber et al., 2015). For example, it is reported that 50–75% of soil organic matter exists within clay-sized organo-mineral aggregates (Christensen, 2001), and in particular ~21% of the organic carbon in sediments appears to be associated with reactive iron phases (Lalonde et al., 2012). Organo-mineral associations may arise through a number of processes, including the formation of authigenic minerals promoted by organics (Gauger et al., 2016; Liu et al., 2016), the coprecipitation of Fe/Al hydroxides in the presence of dissolved organic compounds (Du et al., 2018b; Gentsch et al., 2015; Otero-Fariña et al., 2018), and the adsorption of organics or formation of biofilms on mineral surfaces (Chen et al., 2014; Playter et al., 2017). These processes lead to the formation of organo-mineral composites, which exhibit different metal sorption behaviors compared to their isolated end-member components. This in turn has led to an increasing interest in the binding behaviors of trace metals on various organo-mineral composites such as organo-iron (hydr)oxides (Du et al., 2018a; Moon and Peacock, 2012, 2013; Otero-Fariña et al., 2017, 2018), organo-silicate clay minerals (Du et al., 2017a; Wang et al., 2016), organo-aluminum hydroxide (Du et al., 2018c), and organo-manganite oxide composites (Pena et al., 2011). Results have shown that the organics (e.g., humics, bacteria, etc.) play an important role in metal uptake at mid-low environmental pH (Moon and Peacock, 2012), and also influence metal distribution (Du et al., 2016a, 2017a; Moon and Peacock, 2012). However, to date, very little information is available regarding multi-metal sorption behavior on mineral-organic composites, despite the fact that soil solutions typically contain a mixture of metals. A recent study by Zhu et al. (2012) shows that the competition between Cu and Cr for sorption sites is stronger on a goethite-*B. thuringiensis* composite than on pure goethite. In contrast however, a similar study found that the competition between Pb and Cd on a pure clay mineral is stronger than on a clay mineral-*P. putida* composite (Du et al., 2016b). These few available studies, from a macroscopic point of view, suggest that mineral-organic interaction affects the competitive binding behaviors of metals. However, microscopic information necessary to better understand this competitive binding behavior, such as the metal coordination chemistry and the metal distribution between the organic and mineral components in these complex systems, is still poorly understood. Indeed, ternary-metal competition on organo-mineral composites has never been studied.

This work investigates the competitive sorption characteristics of ternary Cd-Ni-Cu sorbates on a model binary organo-mineral composite, i.e., a composite of goethite and *Bacillus cereus* cells. Goethite is the most common iron oxide in the soil environment and strongly interacts with various soil organic components including microorganisms. *B. cereus* is a heavy metal resistant bacterium isolated from a contaminated soil. Batch sorption combined with X-ray photoelectron spectroscopy (XPS) and synchrotron-based X-ray fluorescence (μ -SRXRF) are employed to

determine macro and micro-level sorption information, towards a clearer understanding of the metal-composite interactions. The results are important for better prediction of the transport and fate of heavy metals in complex soil systems.

2. Materials and methods

2.1. Sample preparation and characterization

Goethite was synthesized by hydrolysis of a 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution held at 60 °C for 24 h (Du et al., 2017b). *Bacillus cereus* is a Gram-positive bacterium, isolated from a heavy metal contaminated soil. Its GenBank accession number is MH345838 (NCBI). The Luria-Bertani liquid medium (10 g L⁻¹ tryptone, 5 g L⁻¹ yeast extract, 5 g L⁻¹ NaCl) was used for bacterial cultivation to the late-exponential phase. The cells were harvested by centrifugation (4000 g) and washed several times with 0.1 M NaNO_3 (the electrolyte used in the study). The goethite-*B. cereus* binary composite was prepared by adsorption of bacterial cells to the mineral surface. Briefly, goethite and *B. cereus* were first suspended in 0.1 M NaNO_3 under stirring. The bacterial suspension was then added slowly to the mineral suspension, and allowed to react for 2 h until adsorption equilibrium (Hong et al., 2012). The mass fraction of bacteria-to-mineral in the composite was 50%:50% (dry mass), in order to maximize comparison of the metal sorption behaviours between the composite and the isolated end-member goethite and *B. cereus* cells.

Before metal sorption, the *B. cereus* cells were stained with fixable viability dye and the fluorescence was measured using an Axio Imager A1M upright microscope (Carl Zeiss Shanghai Co., Ltd.) to determine their bioactivity behavior, following the method described by Wu et al. (2014). The results in Fig. S1 show that the *B. cereus* cells were alive before the sorption of metal ions. The Brunauer-Emmett-Teller (BET) specific surface area (SSA) of goethite was measured by nitrogen adsorption using an automated gas sorption analyzer (Autosorb-IQ, Quantachrome, US). The morphology of the goethite, *B. cereus* cells and goethite-*B. cereus* composite was characterized by scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (FE-SEM/EDS, Quanta F250, Germany). For SEM-EDS, the samples were fixed in 2.5% glutaraldehyde, subjected to an ethanol dehydration series, and dried in a freezer dryer at -53 °C.

2.2. Sorption experiments

Sorption isotherm experiments were carried out in a batch process at 25 °C. The stock solutions of Cd(II), Ni(II) and Cu(II) were prepared at 10 mM from analytically pure $\text{Cd}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$, respectively. Sorption samples were prepared by mixing known amounts of goethite, *B. cereus* or goethite-*B. cereus* composite suspensions with Cd(II), Ni(II) or Cu(II) solutions (single-metal sorption systems) and mixed Cd(II), Ni(II) and Cu(II) solutions (ternary-metal sorption systems; the initial molar ratio was 1:1:1). The final sorption suspension contained 1 g L⁻¹ sorbent and 0–0.5 mM metal ions. Suspension pH was set to 5.5 by minor additions of either HNO_3 or NaOH. This mildly acidic pH was chosen to best represent the pH of most common soil types (i.e., red soil) in southern China (Xu et al., 2003), where soil multi-heavy metal contamination is a serious environmental problem (Li et al., 2010). At this pH Cd, Ni and Cu occur predominantly as free aqueous divalent ions with no precipitation of metal (hydr)oxides (Du et al., 2017a; Moon and Peacock, 2012; Tan et al., 2011). The mixtures were shaken continuously for 24 h during which time the pH was recorded and subsequently adjusted to the set pH every 4 h. All sorption suspensions were separated by centrifugation (8000 g)

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