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journal homepage: www.elsevier.com/locate/envpolCompetitive adsorption of Pb and Cd on bacteria–montmorillonite composite[☆]

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ABSTRACT

The characteristics and mechanisms of competitive adsorption of trace metals on bacteria-associated clay mineral composites have never been studied, despite their being among the most common organic–mineral complexes in geological systems. Herein, competitive adsorption of Pb and Cd on *Pseudomonas putida*–montmorillonite composite was investigated through adsorption–desorption experiment, isothermal titration calorimetry (ITC), and synchrotron micro X-ray fluorescence (μ -XRF). From the experiment, stronger competition was observed on clay mineral than on bacteria–clay composite because more non-specific sites accounted for heavy metal adsorption on clay mineral surface at the studied pH 5. Both competing heavy metals tended to react with bacterial fractions in the composite, which was verified by the higher correlation of Cd (and Pb) with Zn ($R^2 = 0.41$) elemental distribution than with Si ($R^2 = 0.10$). ITC results showed that competitive adsorption exhibited a lower entropy change (ΔS) at the metal–sorbent interfaces compared with single-metal adsorption, revealing that Cd and Pb are bound to the same types of adsorption sites on the sorbent. The competitive effect on bacteria–clay composite was found to be helpful for a better understanding on the fixation, remobilization and subsequent migration of heavy metals in multi-metal contaminated environments.

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1. Introduction

Bacteria are widely considered as efficient bio-sorbents for heavy metals (Ding et al., 2015; Huang et al., 2005; Guiné et al., 2006). In soil systems, EPS/biofilms formed by microbes largely affect the speciation, toxicity and mobility of heavy metals, which are important components of their biogeochemical cycling (Gadd, 2010; Priester et al., 2006). Clay minerals are also a key component which governs trace metal immobilization and transport, due to their large specific surface area, high cation exchange capacity and reactive amphoteric hydroxyl groups (Celis et al., 2000). Clays are spatially associated with bacterial communities in natural environments (Huang et al., 2015; Marshall, 1975). This association is

ascribed to both bacterial clay authigenesis (Konhauser and Urrutia, 1999) and bacterial biofilm formation on clay mineral surfaces (Alimova et al., 2006; Lünsdorf et al., 2000). These processes give rise to bacteria-associated clay minerals that are composite solids, which consist of clay minerals intermixed with intact and partially degraded bacterial cells. Properties of the bacteria–clay complexes differ considerably from their end-member phases, exerting a diverse influences on the chemical reactivity of heavy metals (Chen et al., 2008; Du et al., 2016; Fang et al., 2010a; Flemming et al., 1990; Ohnuki et al., 2007).

Trace metals usually coexist in a range of concentrations in geological environments, e.g., soils and sediments exposed to leaching water from mine tailings and smelters (Buchauer, 1973). Under such circumstance, competitive adsorption effects need to be addressed. Researches dealing with the competitive adsorption of metals on clay minerals have been published over the past decades. For instance, Srivastava et al. (2005) reported that the selective adsorption sequence for multi-metal adsorption on kaolinite was $Pb > Cu > Zn > Cd$, which was positively correlated

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with their hydrolytic ability. de Pablo et al. (2011) observed the selectivity sequence adsorption of $\text{Hg}^{2+} > \text{Zn}^{2+} > \text{Ba}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$ on montmorillonite. The selective sequence of $\text{Cu} > \text{Ni}$ for binding on montmorillonite was proposed by Yang et al. (2005a,b) which can be interpreted by their metal properties such as electronegativity, Misono softness parameter, first hydrolysis constant, and electron configurations. A few studies on the competitive adsorption effect of heavy metals by bacterial biomass are available. For instance, Claessens and Van Cappellen (2007) observed that Zn (59 μM) had no measurable effect on Cu binding to *Shewanella putrefaciens* cells at a pH of 5.5. Micheletti et al. (2008) showed that *Cyanotheca* strain 16Som 2 is an effective sorbent for the selective removal of Cr and Cu from multiple-metal solutions. Moreover, binding was either non-interactive, synergistic, or competitive between metal ions. Wang et al. (2014) recently reported that EPS extracted from *Desulfovibrio desulfuricans* exhibited a higher binding ability with Zn than Cu. FTIR analysis showed that Cu bind with protein, whereas Zn combined with both protein and polysaccharides. In contrast, Yang et al. (2015a,b) observed that Cu decreased significantly Zn adsorption on EPS extracted from *Klebsiella* sp. J1, but the uptake of Cu was not influenced by Zn. They attributed this finding to the stronger complexation ability between Cu and the protein-like substances in EPS as shown by using FTIR and fluorescence spectrophotometry.

Most of aforementioned studies examined competitive adsorption behaviors of trace metals by individual soil components (e.g., mineral and bacteria). However, soils are more complex. Investigating competitive adsorption of metals on composite solids (e.g., bacteria-associated mineral complexes) is critical. Only one report on the competitive adsorption of heavy metals on goethite–*Bacillus thuringiensis* composite was found; the competitive sorption intensity between Cu and Cr was observed to be greater on the goethite–*B. thuringiensis* complex than on goethite (Zhu et al., 2012). The competitive effect of heavy metals on bacteria–clay mineral composites has never been studied despite their being the most common organic–mineral complexes in soils and sediments.

The present work aimed to investigate the competitive adsorption of Cd and Pb on bacteria–montmorillonite composite. Isothermal titration calorimetry (ITC) was employed for the first time to determine the mechanisms of competitive adsorption from a thermodynamic aspect. Synchrotron micro X-ray fluorescence ($\mu\text{-SRXRF}$) was used to quantify the distribution of Cd and Pb within the composite. New insight on the competitive binding of Cd and Pb at the bacteria–mineral interface enhances our fundamental understanding of the retention and release and thus increasing our knowledge on biogeochemical cycling and endpoint of heavy metals in soil micro-environments, where bacteria-associated clay mineral complexes are dominant or make up a significant proportion of reactive solid phases.

2. Materials and methods

2.1. Sorbents

Pseudomonas putida X4 is an aerobic soil gram-negative bacterial strain. Bacterial cells were cultured at 28 °C in a Luria broth medium (pH 7.2), containing 5 g/L of bacto-yeast extract, 10 g/L of bacto-tryptone and 5 g/L of NaCl, to the late-exponential growth phase as described by Wu et al. (2014). Bacterial cells were obtained by centrifugation and were washed three times with the electrolyte (0.01 M KNO_3) to remove excess media. Fresh bacterial biomass was used for the experiments. Montmorillonite (Mont) is a representative 2:1 type clay minerals, and is widely distributed in soil environments. Montmorillonite used in this work was purchased

from Zhejiang Sanding Group Co. Ltd. (Shaoxing, Zhejiang, China). Clay-sized fractions of montmorillonite (<2 μm) were isolated based on the procedures outlined by Rong et al. (2007). Montmorillonite and bacterial cells were all suspended in 0.01 M KNO_3 electrolyte. The bacteria–Mont composite was obtained by mixing bacterial and mineral suspension in a 1:1 ratio (dry-weight basis) and incubating it for 4 h at pH 5 to achieve equilibrium.

2.2. Adsorption isotherms of Cd and Pb in single and binary systems

Batch adsorption experiments were carried out by mixing the sorbent (*Pseudomonas putida*, Mont, and *P. putida*–Mont composite) suspension with different amounts of Cd and Pb solutions separately (single system) or together (competitive system; initial molar ratio of Cd to Pb was 1:1) in 0.01 M KNO_3 background electrolyte. The sorbent concentration was 1 g/L (dry-weight basis), and the initial metal concentrations ranged from 0 to 0.5 mM. All the sorbent concentrations shown below refer to dry mass unless it is specified otherwise. All pH measurements were made with a digital pH meter (PB, Sartorius, Germany) which has been calibrated successively by standard buffer solution (6.86, 4.01 and 9.18). The pH of the mixed suspensions was adjusted to pH 5 using minor additions of 0.1 M HNO_3 or 0.1 M KOH solution. The mixtures were then incubated on a rotary shaker for 4 h (28 °C). During this period, pH adjustments of the suspensions were made every 30 min. After equilibration, suspensions were centrifuged at 8000 g, supernatants were filtered through 0.45 μm nylon filter membranes and acidified with HNO_3 . Residual Cd and Pb were measured through atomic absorption spectrometry (AAS; Varin AAS240FS). Solid phases of the bacteria–Mont composite after adsorbing Cd and Pb in the binary-metal systems were collected for $\mu\text{-SRXRF}$ experiments.

2.3. Exchange of pre-adsorbed Cd and Pb

Pre-adsorption experiments were performed by mixing 1 g/L sorbent (*P. putida*, Mont, and *P. putida*–Mont composite) suspension with 0.5 mM of Cd or Pb solutions separately, with 0.01 M KNO_3 as the background electrolyte. The pH of the suspension was buffered to 5, and then the suspension was incubated for 4 h (28 °C). After equilibration, suspensions were centrifuged at 8000 g, supernatants were filtered through 0.45 μm membranes and acidified with HNO_3 for AAS analysis. The solid phase was re-suspended in 0.01 M KNO_3 background electrolyte, then an equal amount of the second metal (Pb or Cd, 0.5 mM) solutions were added to the mixture and incubated for another 4 h at pH 5. The mixtures were then centrifuged at 8000 g, and the concentrations of Cd and Pb remaining in solution were measured with AAS (Varin AAS240FS). During the adsorption–desorption experiments, the pH of the mixed suspensions was adjusted every 30 min. The experimental settings of the “exchange experiments” were to simulate the competitive-ITC experiment shown below, i.e., one metal was adsorbed (titrated) on the sorbent in the presence of another metal.

2.4. Isothermal titration calorimetry

A Thermal Active Monitor III (TAM III) system (Thermometric AB, Sweden) was used to measure the heat effect at 28 °C. For single-metal systems, the adsorbent (*P. putida*, Mont, and *P. putida*–Mont composite, 10 g/L, pH 5) were placed in a 1 mL stainless steel ampoule. Automatic titration with metal ion (Cd or Pb) in the syringe (2×10^{-2} M) was performed. For competitive-ITC, it was unable to obtain the competitive thermodynamic parameters if the two metals were titrated simultaneously. Therefore a new method was established according to Chekmeneva et al.

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