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Competitive sorption of Cu and Cr on goethite and goethite–bacteria complex

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ABSTRACT

Sorption of Cu and Cr in single and binary sorbate systems on goethite and goethite–*Bacillus thuringiensis* complex was studied. It was observed that the initial sorption rate and sorption capacity of heavy metals on goethite–*B. thuringiensis* complex were greater than that on goethite in single system at studied pH. The competitive ability of Cr in the sorption on both goethite and goethite–*B. thuringiensis* complex was stronger than that of Cu in binary system. Greater intensity of competitive sorption between heavy metals was found on goethite–*B. thuringiensis* complex than on goethite. The percentage of sorbed metals desorbed by $Ca(NO_3)_2$ from goethite was lower than that from goethite–*B. thuringiensis* complex, conforming the higher sorption affinity of heavy metals for goethite than that for goethite–*B. thuringiensis* complex. For each sorbed heavy metal, the desorption ratio was slightly higher from single sorption system than from binary sorption system, indicating the release of loosely sorbed metal and the retention of tightly bound cation during competitive sorption. The results obtained in this study are of significant importance for the assessment and remediation of multi-heavy metal pollution.

1. Introduction

Environmental pollution by heavy metals such as Cu and Cr has received great attention in the recent decades. These heavy metals, which are released by natural processes or anthropogenic activities, are non-degradable in nature and highly toxic to plants, animals and human beings. In natural environments, these elements may be sorbed by soil components or sediments, dissolved in aquatic solution and/or accumulated by living organisms such as crops, vegetables and fish, and then may enter into the food chain. Therefore, the sorption of heavy metals on soil components or sediments relates closely to their mobility and bioavailability, and plays a vital role in relieving their threat to human beings and animals.

Quite a number of investigations have been devoted to the sorption of heavy metals by individual soil components including phyllosilicates, oxides, humic substances and microorganisms [1–3]. Specific sorption by the formation of inner-sphere complex and/or nonspecific sorption through the formation of outer-sphere complex have been suggested as the primary mechanisms for the sorption of heavy metals on soil constituents [1,2]. In natural environments, soil constituents are usually closely associated with each other through electrostatic or hydrophobic interaction, hydrogen bonding, van der Waals force, covalent bonding and so on [4–7]. Iron/aluminum oxide–bacteria complex is one of the most common types of complexes in terrestrial and aquatic environments with an abundance of negatively charged functional groups on bacterial surface and the relatively high point-of-zero-charge (PZC) of the oxide [8,9]. Several studies are available on the sorption of heavy metals on oxide–bacteria composite [9–14] and the characteristics of the sorption on the composite were observed to be markedly different from their individual components due to the differences in surface charge, electrical double layer property, amount and reactivity of sorption sites. However, these studies focused only on Pb, Cd, Cu and Zn, with little information on the sorption of Cr on oxide–bacteria complex.

In contaminated environments, different heavy metals are usually present together. The competition among these toxic metals for the sorption sites on the sorbent certainly affects their sorption kinetics, capacity and affinity, and then their mobility, bioavailability and toxicity towards living organisms. The competition in sorption among different heavy metals has been observed on most soil components, organo-mineral complexes, soils and sediments [15–21]. Many factors such as the first hydrolysis constant, electronegativity, ionic radii and softness of heavy metals, surface functional group, surface charge, surface area of sorbents have been proposed to explain the preference of the sorbent for the heavy metals in competitive sorption [16,19,22]. However, so far, scant attention has been paid to the competitive sorption of heavy metals on oxide–bacteria complex.

Goethite is a crystalline oxide and presents ubiquitously in natural terrestrial weathering environments. *Bacillus thuringiensis* is gram-positive bacteria and occurs typically in soils. In current study, goethite–*B. thuringiensis* complex was prepared by immobilizing bacteria on goethite through direct adsorption. The aim

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of the study was to investigate the sorption and competitive sorption of Cu and Cr on goethite–*B. thuringiensis* complex and compare the characteristics with that on pure goethite. The study might be useful in the remediation of soil pollution by multi heavy metals.

2. Materials and methods

2.1. Preparation of chemical reagent solution

Deionized distilled (DD) water was used to prepare all the solutions. Stock solution of each heavy metal was prepared by dissolving $Cu(NO_3)_2{\cdot}3H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ in DD water, respectively. Potassium nitrate (0.02 mol L^{-1}) was prepared as supporting electrolyte for all experiments. The pH of stock solution and supporting electrolyte was adjusted to 4.5 by 0.1 or 0.01 mol L^{-1} HNO_3 or KOH.

2.2. Synthesis and characterization of goethite

Goethite was synthesized according to Atkinson et al. [23]. Fifty grams of $Fe(NO_3)_3{\cdot}9H_2O$ in 825 mL of DD water was precipitated by the slow addition of 200 mL of 2.5 mol L^{-1} NaOH under vigorous stirring. After six days of aging at 60 °C, the precipitate was dialyzed, air-dried and then ground to pass through 100 mesh sieve. The final product was identified as goethite by X-ray diffraction (data not show). The specific surface area and PZC of goethite were 96.4 $m^2\,g^{-1}$ and 8.3 as measured by high speed automated surface area and pore size analyzer (Quantachrome Autosorb-1, USA) and Mehlich method [24], respectively.

2.3. Preparation and characterization of bacteria

Biomass of *B. thuringiensis* was prepared according to Cai et al. [25]. The cells were initially cultured in 5 mL of beef-extracted peptone medium at 28 °C for 7 h. Two milliliters of the preculture was then transferred to 200 mL of the same medium and cultured for another 18 h to attain the stationary growth phase. Cells were harvested by centrifugation at 10,000 × *g* for 10 min. Bacterial biomass was then washed thrice by DD water and resuspended in a suitable volume of 0.02 mol L^{-1} KNO_3. The pH of bacterial suspension was adjusted to 4.5 by 0.1 or 0.01 mol L^{-1} HNO_3 or KOH. A known aliquot of cell suspension was centrifuged and dried at 60 °C to a constant weight for determining the concentration of the cell in suspension. The specific surface area and PZC of *B. thuringiensis* were 192.4 $m^2\,g^{-1}$ and 2.7 as determined by methylene blue adsorption method [26] and acid–base titration method (Automatic Potentiometric Titrator, Japan) [14], respectively.

2.4. Preparation of goethite–bacteria complex

Four grams of goethite was suspended with 195 mL of 0.02 mol L^{-1} KNO_3 in conical flask, and the pH was adjusted to 4.5 by adding 0.1 or 0.01 mol L^{-1} HNO_3 or KOH until reaching equilibrium. The final volume of the suspension was adjusted to 200 mL by adding suitable volume of 0.02 mol L^{-1} KNO_3. Preliminary experiment was carried out to investigate the sorption of *B. thuringiensis* on goethite as described by Rong et al. [7]. In a batch of centrifuge tubes, 2 mL of goethite stock suspension (20 mg mL^{-1}, pH 4.5) was mixed with different volumes of bacterial suspension to evaluate sorption isotherm. The total volume of each mixture was made 8 mL by the addition of supplemental volume of 0.02 mol L^{-1} KNO_3 (pH 4.5). The mixtures were shaken at 25 °C for 1 h. After the addition of 1 mL sucrose solution (60% by weight), unattached bacteria in the mixture was collected by centrifugation at 10,000 × *g* for 20 min. The final residue was goethite–bacteria complex. The amount of bacteria in the supernatant was determined directly by spectrophotometry, and the amount of bacteria sorbed was calculated by subtracting the amount of bacteria in the supernatant from that added initially. The experiment showed that sorption isotherm of *B. thuringiensis* on goethite was H-type [1]. A constant amount (43.6 ± 0.1 mg) of goethite–*B. thuringiensis* complex was prepared for the following experiments, the sorption of bacteria in the complex was saturated.

2.5. Sorption kinetics and isotherms of Cu and Cr in single and binary systems

Known amounts of goethite–*B. thuringiensis* complex prepared as described in Section 2.4 were resuspended by in 0.02 mol L^{-1} KNO_3 (pH 4.5) and premixed with 4 μmol of $Cu(NO_3)_2$ and $Cr(NO_3)_3$ individually (single system) or together (binary system). The total volume of the mixture was 8 mL. The mixtures were shaken at 25 °C for different time period from 0.083 to 24 h to investigate the sorption kinetics. Batch experiments were also carried out by mixing the same mass of goethite–*B. thuringiensis* complex with different amounts of $Cu(NO_3)_2$ or $Cr(NO_3)_3$ individually (single system) or together (binary system; the initial molar ratio of Cu to Cr was 1) in 8 mL supporting electrolyte solution. The mixtures were shaken at 25 °C for 24 h to construct the sorption isotherms. The pH of each sample was maintained at 4.5 by the addition of 0.1 mol L^{-1} KOH or HNO_3. After centrifugation at 10,000 × *g* for 20 min, the amount of heavy metal in each supernatant was determined by atomic absorption spectrometry (Varian AAS240FS). The sorption of each heavy metal was then calculated by the difference between the amount of the metal introduced initially and that remained in the supernatant. Similar experiments were also carried out on the same amount of pure goethite for comparison.

2.6. Desorption of sorbed Cu and Cr

Goethite–*B. thuringiensis* complex prepared as described in Section 2.4 was resuspended by in 0.02 mol L^{-1} KNO_3 (pH 4.5) and premixed with 4 μmol of $Cu(NO_3)_2$ and $Cr(NO_3)_3$ individually (single system) or together (binary system). The same experiments were carried on the same mass of pure goethite in 8 mL of total mixture volume. The mixtures were shaken at 25 °C at pH 4.5 for 24 h. After centrifugation at 10,000 × *g* for 20 min, the supernatants and the residues were collected separately. The heavy metal–sorbent complex was washed by DD water and then resuspended by 8 mL of 0.1 mol L^{-1} $Ca(NO_3)_2$. After shaking at 25 °C at pH 4.5 for 8 h, the desorbed heavy metals were collected and determined as described above.

All the sorption and desorption experiments were conducted in triplicate and the relative standard deviation was lower than 5%.

3. Results

3.1. Sorption kinetics of Cu and Cr in single and binary systems

Sorption kinetic curves of Cu and Cr in single and binary systems on goethite and goethite–*B. thuringiensis* complex are depicted in Fig. 1. These kinetic data were fitted by several kinetic models. The kinetics could be explained most satisfactorily by the pseudo-second-order model, which has been applied widely and satisfactorily in earlier investigations on the sorption of heavy metals on various sorbents [22,27–29]. The linear form of the pseudo-second-order model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

$$h = kq_e^2$$