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Mobility and transport of copper(II) influenced by the microbial siderophore DFOB: Column experiment and modelling

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HIGHLIGHTS

- The microbial siderophore DFOB strongly enhances Cu mobility.
- Breakthrough and elution can be well described by surface complexation modelling.
- The mobilizing effect of DFOB is at maximum at a DFOB/Cu molar ratio of 1:1.

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ABSTRACT

Acid Cu leaching from the European Kupferschiefer ore deposits is a challenge e.g. due to its high carbonate content. In this study, we investigated the transport behaviour of Cu under conditions related to a biohydrometallurgical leaching approach using neutrophil microorganisms in neutral to slightly alkaline solutions. We studied the effect of the microbial siderophore desferrioxamineB (DFOB) as a model leaching organic ligand on Cu mobility in column experiments with kaolinite. The results revealed that DFOB strongly enhances Cu mobility. The breakthrough of Cu occurs considerably earlier in the presence of DFOB than in the absence of the organic ligand. Furthermore, complete elution of Cu was observed at 5 pore volume exchanges faster compared to elution with deionized water. The established geochemical transport model shows good agreement with the experimental data and suggests a maximum efficiency at a Cu to DFOB molar ratio of 1:1. In addition, results of modelling revealed that in the absence of the ligand, a pH increase from 6.5 to 8.5 significantly retarded Cu breakthrough, whereas in the presence of DFOB, Cu breakthrough curves were nearly insensitive to pH changes and close to the breakthrough curve of a non-reactive tracer.

1. Introduction

Understanding the processes governing the fate and transport of copper as an environmental contaminant is essential in the context of industrial waste disposal, hydrometallurgy and metal recovery from ores. Sorption and desorption on mineral surfaces and complexation with organic ligands are major reactions controlling the Cu concentration level and affecting its mobility in soil.

Natural organic molecules play an important role regarding the transport behaviour of copper in terrestrial ecosystems. Several studies have been conducted to investigate mobilization of metals by Low Molecular Weight Organic Acids (LMWOAs) (Najafi and Jalali, 2015; Wang and Mulligan, 2013; McLaren et al., 1981). Organic ligands enhance or diminish metal mobility via sorption and desorption processes in porous media depending on the interaction mechanisms among ligands, surfaces of solid phase particles, and metal ions. Previous studies have indicated that organic ligands might affect metal mobility by forming soluble or insoluble complexes. Wang and Mulligan (2013) studied the pH-dependent effect of aspartic acid, cysteine, and succinic acid on the mobility of As, Cu, Zn and Pb from mine tailing in column experiments. They found that in the presence of organic acids and under slightly acidic to neutral conditions, mobility of copper is slightly decreased, whereas at pH values above 7, organic acids considerably enhanced copper mobilization and transport. McBride (1981) studied the effect of several organic ligands on copper mobility. He showed that glutamic and fulvic acids elevated copper sorption at a given pH, whereas citric acid and EDTA prevented copper sorption to natural soil. It was reported that sorption of Cu

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on hematite in the presence of fulvic acid was increased at slightly acidic pH and was decreased above pH 6 due to the formation of dissolved metal–organic complexes (Christl and Kretzschmar, 2001). Karimzadeh et al. (2013) found that the microbial siderophore desferrioxamineB (DFOB) could enhance the mobility of Cd, Zn, and Pb in the presence of zeolites under alkaline conditions.

In this work, mobility and transport of Cu influenced by DFOB as a complexing organic ligand in the presence of kaolinite as a sorbent was investigated in column experiments. Transport of Cu in the column was modelled using the numerical approach for multiple element transport contained in the software COMSOL Multiphysics®, coupled with the chemical speciation programme PHREEQC by the interface iCP 1.2 (Nardi et al., 2014). The approach is based on the one-dimensional advection-reaction-dispersion equation and on the surface complexation model of Dzombak and Morel (1990) implemented in PHREEQC 2.18 (Parkhurst and Appelo, 1999).

2. Materials and methods

2.1. Materials

Kaolinite was obtained from Sigma-Aldrich Chemie GmbH, Germany. It was washed three times with 1 M NaCl (Merck, Germany) and 3 times with deionized water to avoid possible interferences caused by impurities. The copper stock solution (1.5 mM) was prepared by dissolving $Cu(NO_3)_2 \cdot 3\ H_2O$ (Merck, Germany) in ultrapure water (≥18 MΩ/cm). The exact Cu concentration was determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Scientific ELEMENT XR) using a Cu standard solution (Merck, Germany) for calibration. DFOB was provided as mesylate salt from Sigma-Aldrich and was used without any pre-treatment. A stock solution (1.5 mM) was prepared using ultrapure water. NaCl was used as a background electrolyte at a concentration of 0.1 mM. The pH of the solutions was adjusted to 6.5 using 0.01 M HNO_3 and 0.01 M NaOH.

Glass beads (<0.5 mm, Sigmund Lindner GmbH, Germany), which were used as a matrix for kaolinite in the column experiments, were washed with $Na_2S_2O_4$ and H_2O_2. Sorption of Cu on beads was found to be negligible (<2%) in preliminary batch experiments.

2.2. Experimental

Column experiments were performed at ambient conditions using a glass column with an internal diameter of 1 cm and a bed length of 7.5 cm (Omnifit Labware, Diba Industries). Columns were packed with a homogenous mixture of 2 wt% kaolinite and 98 wt% glass beads, resulting in an average porosity of 0.37 ± 0.01. Two 0.2 μm cellulose acetate paper filters (Sartorius Stedim Biotech GmbH, Germany) were placed as supports at the top and bottom of each column. Solutions were pumped through the columns upwardly with a constant flow rate of 0.04 mL/min using a Harvard Apparatus Syringe Pump 11. The pH of the influent for all columns was adjusted to 6.5. The effluents were collected using a fraction collector (MLE GmbH, Germany) at a time interval of 15 min per fraction. The samples were checked for pH and then diluted with deionized water to get 10 mL solutions for Cu analysis by ICP-MS.

Three columns prepared as described above were used to investigate the influence of DFOB on copper mobility in the presence of kaolinite clay mineral. Two columns were charged with a 1.5 mM Cu solution, while the third was charged with a mixed solution of Cu and DFOB (1.5 mM each).

Elution experiments were performed with columns 1 and 2 (loaded with Cu only). After the solute concentration in the outflow reached the initial concentration, the influent was switched to deionized water (DW) for one column and to 1.5 mM DFOB solution for the other column.

2.3. Theory of reactive solute transport

The mass balance for multicomponent reactive transport of non-degradable solutes in homogenous non-sorbing porous media under steady-state flow conditions is described as

$$\frac{\partial C_t}{\partial t} = D\varnothing\frac{\partial^2 C}{\partial x^2} - j_w\frac{\partial C}{\partial x} \tag{1}$$

where C_t is the total mass of solute per unit volume of the porous medium, C is the solute concentration, t is time, j_w is the flow velocity in x-direction, $\varnothing$ is the porosity, and D is the diffusion coefficient of the solute.

Equation (1) can be extended to describe the transport of a solute through a sorbing porous medium. For a non-degradable compound, the total mass of solute C_t is the sum of the masses of dissolved and sorbed species per unit volume:

$$C_t = \varnothing C + \rho S \tag{2}$$

here, ρ is the medium bulk density, and S is the amount of sorbed solute per unit mass of sorbent. The combination of Eqs. (1) and (2) results in Eq. (3)

$$\frac{\partial C}{\partial t} + \frac{\rho}{\varnothing}\frac{\partial S}{\partial C}\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \tag{3}$$

where $v_x = j_w/\varnothing$ is the pore water velocity. For reversibly sorbing components, Eq. (3) can be rewritten as

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \tag{4}$$

In this equation, R is the retardation factor, given by

$$R = 1 + \frac{\rho}{\varnothing}\frac{\partial S}{\partial C} \tag{5}$$

Here, $\partial S/\partial C$ is the sorption relationship between the solute concentration in the liquid and solid phases.

In this study, we applied a surface complexation model to predict sorption of copper on kaolinite. Dzombak and Morel (1990) introduced the generalized double-layer model, which proved to be well applicable for surface complexation modelling on kaolinite. Since sorption onto this mineral is dominated by sites at the edge faces of the crystals, only one type of surface hydroxyl group (≡SOH) is defined. By means of the thermodynamic modelling program PHREEQC 2.18 (Parkhurst and Appelo, 1999), the distributions of aqueous and surface species of Cu and DFOB are explicitly calculated, using the LLNL database (Delany and Lundeen, 1991) and additional constants of surface and aqueous reactions. These constants are listed in Table 1 together with the surface parameters used for kaolinite. Specifically, the effects of pH and ligand concentration on Cu transport were investigated by the model.

3. Results and discussion

3.1. Influence of DFOB on Cu transport

Results of the chemical speciation modelling are presented in Fig. 1. At pH 6.5 in the absence of DFOB, almost the total amount of copper is present as aqueous ion, whereas in the presence of DFOB,