Cooperative and competitive adsorption of amino acids with Ca^{2+} on rutile

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Amino acids are highly soluble in water and do not spontaneously organize themselves. For these molecules, it has been recognized that mineral surfaces may potentially have played an important role in their selection, organization and concentration in the prebiotic era. Here, we investigated the adsorption of the oppositely charged amino acids glutamate and lysine with and without the addition of Ca^{2+}. Without Ca^{2+}, glutamate shows maximum adsorption at a pH of ~4 and lysine shows maximum adsorption at a pH of ~9.4. In comparison, with Ca^{2+} present, glutamate showed maxima adsorption at both pH ~4 and ~10, whereas lysine showed no adsorption at all. These dramatic effects can be described as cooperative adsorption between glutamate and Ca^{2+} and competitive adsorption between lysine and Ca^{2+}. Surface complexation model calculations indicate a purely electrostatic origin of these effects. Adsorption of Ca^{2+} at high pH makes the rutile surface more positive, attracting glutamate and repelling lysine. The cooperative or competitive effects show that biomolecules can participate in complex adsorption behaviour. A fundamental understanding of amino acids speciation and coordination chemistry to oxide mineral surfaces may provide valuable insight into biomaterial and bimolecular interactions and the fate of organic acids in natural environments, as well as the possible role of mineral surfaces in the chemical evolution of biomolecules in the origin of life.

Biogeochemical control on the dissolution/precipiation of fine suspended solids from mine drainage

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Mine drainage discharges fine suspended solids (SS), as well as trace metals. Although many abandoned mining sites adapt sand filter beds to treat the SS, improved system is still in demand, as often long-term operation clogs either the sand media or the porous filter installed underneath of the bed, dramatically degrading treating capacities. The first approach was to find better filtering mediums. Fly ash, mine tailing aggregates, metal scraps and the mixed medium were compared with the current sand bed filters in the laboratory, using the mine drainage from the field. Batch and column test of 7 days revealed sand media still outperformed to other candidates. Mixing with anthracite or activated carbon on the sand filter also improved the treatability, extending to some heavy metals, as well.

Possible bioleaching of the suspended solids was also investigated to ameliorate the system by manipulation the dissolution/precipitation processes associated with the solids in the filter media. The redox transformation and biogeochemical interactions of heavy metals in the solids were examined using facultative anaerobic bacterium *Shewanella* sp. (HN-41) in batch mode and with small scale columns. This is a preliminary study carried out to determine if such process is instrumental in preventing the coagulation of solid precipitates on the sand media and the porous media. In addition, bioleaching of the metals from the suspended solids is also considered. The organism HN-41 was not influenced by pH ranging from acidic to neutral and was able to metabolize all the metal elements from the suspended solids, with high contents of metals.

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