Thermodynamic Analysis of Heavy Metals Adsorption to Biochar

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Biochar is a carbon-rich solid produced through reductive thermal processing and/or pyrolysis of biomass derived from a variety of feedstocks, including straw, wood, and organic industrial wastes. Biochar is a cost-effective sorbent owing to its low production cost and its ability to efficiently remove metals and organics from water. While numerous studies have investigated metal uptake from solution by biochar, few of these have developed a mechanistic understanding of the adsorption reactions that occur at the biochar surface. In this study, we employed a combined modeling and spectroscopic approaches to describe the molecular level adsorption of divalent cations (Ni(II) and Zn(II)) and radionuclide (U(VI)) to biochar using different types of biochar. We applied two thermodynamic approaches, (i) surface complexation modeling (SCM) and (ii) isothermal titration calorimetry (ITC), supported by synchrotron-based X-ray absorption spectroscopy (XAS) to develop a predictive and mechanistic model of metal binding to biochar. Our results showed that the reactivity of biochar towards Ni(II) and Zn(II) directly relates to the site densities (mole sites/m^2) of biochar, and U (VI) uptake is strongly influenced by U(VI) aqueous speciation at different pH. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) studies along with synchrotron-based extended X-ray absorption fine structure (EXAFS) analyses, shows that Ni(II), Zn(II) and U(VI) adsorption occurs at proton-active carboxyl (-COOH) and phenolic hydroxyl (-OH) functional groups on the biochar surface. The SCM approach were able to predict the Ni(II), Zn(II) and U(VI) adsorption behavior across a wide range of pH, in the presence of solution Ca^{2+}, and at varying initial U(VI) and biochar concentrations. SCM combined with ITC analyses revealed that the enthalpies of protonation are exothermic and Ni(II), Zn(II) and U(VI) complexes with biochar surface are slightly exothermic to slightly endothermic depending on the protonation state of biochar surface functional groups to which the metals complex. The results obtained from these combined approaches contribute to the better understanding of molecular scale metal adsorption onto the biochar surface, and will

facilitate the further development of thermodynamics-based, predictive approaches to biochar removal of metals from contaminated water. Our resulting models can also be used to optimize pilot-scale experiments that could enable commercial exploitation of biochar as metal sorbents.