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Evaluation of the Mechanisms and Effectiveness of Nano-hydroxides, Wood and Dairy Manure-Derived Biochars to Remove Fluoride and Heavy Metals from Water

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Abstract

The development of effective treatment processes for the removal contaminants, such as fluoride and heavy metals, from polluted water have been urgently needed due to serious environmental health and safety concerns. In this dissertation, a variety of materials including various (hydro)oxide nanomaterials, biochars and surface modified biochar were studied to evaluate their effectiveness and mechanism on removing fluoride or mixed heavy metals from water.

In the Chapter 2, this study investigated the adsorptive removal of fluoride from water using various (hydro)oxide nanomaterials, focusing on ferrihydrite, hydroxyapatite (HAP) and brucite, which have the potential to be used as sorbents for surface water and groundwater remediation. The Freundlich and Redlich–Peterson adsorption isotherms better described the adsorptive capacity and mechanism than the Langmuir isotherm based on higher R^2 values, indicating better fit of the regression predictions. Additionally, the adsorption kinetics were well described by the intra-particle diffusion

model. Column studies in a fixed bed continuous flow through system were conducted to illustrate the adsorption and desorption behavior of fluoride on ferrihydrite, HAP, or brucite. The experimental results fitted well with the Thomas model because of the R^2 values at least 0.885 or higher. By comparisons of the adsorption capacity and the rate constant, columns packed with ferrihydrite exhibited not only faster rates, but also higher sorption capacity than those packed with HAP or brucite. The desorption tests in deionized water showed that the adsorbed fluoride could be desorbed at a lower efficiency, ranging from 4.0% to 8.9%. The study implicated that (hydro)oxide nanomaterials of iron calcium and magnesium could be effective sorptive materials incorporated into filtration systems for the remediation of fluoride polluted water.

In Chapter 3, the exploration of cost-effective sorbent for fluoride removal from water was continued with another promising material, biochar, because of its high surface area and diverse surface functional groups. This study explored the removal of fluoride from water using a calcium hydroxide-coated dairy manure-derived biochar (Ca-DM500). The Ca-DM500 showed 3.82-8.86 times higher sorption capacity of fluoride from aqueous phases than the original manure-derived biochar (DM500). This was mainly due to strong surface complexation between fluoride and calcium hydroxide. The Freundlich and Redlich–Peterson sorption isotherms better described the experimental data than Langmuir model. Additionally, the sorption kinetics were well described by the intra-particle diffusion model, indicating combined specifically and non-specifically chemisorptive interactions occurring on the heterogeneous surface of Ca-DM500. Ca-DM500 showed high reactivity per surface area for sorption of fluoride contributing to the importance of surface complexation. Furthermore, the co-presence of anions showed the effects on reducing fluoride removal on Ca-DM-BC, following the order of SO_4^{2-} ≈ PO_4^{3-} > NO_3^-. The Thomas model can reflect the sorption behavior of fluoride in a continuous fixed-bed column. Column studies demonstrated that the Ca-DM500 shows strong affinity to fluoride and low desorption potential as well as stable sorption capacity through regeneration and reuse cycles. From these results, we concluded that Ca-DM500 can be applied as an efficient and reusable sorbent for removing fluoride from water.

Heavy metal is another type of pollutant often found coexisting with fluoride, and biochar is increasingly being recognized as a promising, low cost sorbent that can be used to remediate contaminated water. Therefore, in Chapter 4 this study examined the competitive removal of heavy metals ions of Cd^{2+}, Pb^{2+} and Zn^{2+} from water using biochars derived from douglas fir (DF-BC) and dairy manure (DM-BC) and their removal efficacy and mechanism in both static and continuous flow through systems. DF-BC and DM-BC showed the removal of mixed metal ions following the preferential order of Pb^{2+} >> Zn^{2+} > Cd^{2+}. Among the various factors influencing the competitive removal, the solution pH played a decisive role in influencing the metal ion species in solution, surface charge and solubility of metal minerals, which consequently affects the electrostatic attraction/repulsion, surface complexation with functional groups and chemical precipitations of metal hydroxides and/or carbonate on biochar. Langmuir sorption isotherm better described the experimental results than the Freundlich or Redlich-Peterson models. In addition, the removal kinetics and model fitting elucidate that three steps of intraparticle diffusion might be the more representative to describe the immobilization processes of metal ions on the external surface and internal pores. Moreover, the column study showed DF-BC more consistent removal of mixed metals through regeneration and reuse, while DM-BC showed a greater pH buffering capacity for metal removal. In summary, both DF-BC and DM-BC prove to be an effective, reusable and stable materials for the long-term removal of mixed metals ions from water.