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Enhancing biochar uptake efficiency for 129-I and 99-Tc through acid activation prior to pyrolysis

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Biochar has shown great promise for the sequestration of several pollutants, including metals (e.g., Hg) and cationic radionuclides (UO_2^{+2}). It also has the potential to sequester anions although the anion exchange functionality of biochar is not well understood. Inexpensive and highly effective sorbents are needed for the *in situ* remediation of Department of Energy (DOE) contaminated sites, especially for two anionic radionuclides, ^{129}I and ^{99}Tc, which are common human health risk drivers in radionuclide-contaminated lands. However, the application of biochar for radionuclide sequestration under DOE waste conditions has not been investigated. To address this DOE complex-wide need, batch sorption experiments were conducted using biochar derived from pecan shells to examine the possibility of biochar as a low cost (<$2/kg) and high-capacity sorbent material for the sequestration of ^{99}Tc and three speciation of ^{129}I, including iodide (I^-), iodate (IO_3^-), and organic iodine (org-I). Two temperature pyrolysis (500 ºC and 700 ºC) and two acid-activation (H_3PO_4 and HCl) were conducted to prepare the biochar sorbents prior to sorption experiments. Besides, characterization of the biochars were also performed, including their morphologies using scanning electron microscopy (SEM), surface areas, and organic compositions by Nuclear magnetic resonance (NMR). Our results indicated that acid-activated biochar had much higher capacities (in terms of distribution coefficient, $K_d = [anion_{solid}]/[anion_{aq}]$) to sequestrate the ^{99}Tc and different iodine species, compared with the non-acid-activated biochar. In general, the H_3PO_4-activated biochar (500 ºC) was the most effective sorbent for two anionic radionuclides, with ^{99}Tc K_d of 49,390±14,268 mL/g, iodide K_d of 2,433±312 mL/g, and iodate K_d of 410±168 mL/g on average, respectively. The HCl-activated biochar (700 ºC) was also effective at sequestering ^{99}Tc (K_d of 7,864±5,585 mL/g) and iodide (K_d of 2481 ± 237 mL/g), but not for iodate. NMR analysis suggested that the strong sorption capacity for these two biochars may be due to the formation of abundant alkene, aromatic and heteroaromatic functional groups. Our study provided the evidence supporting the validation of functionalized biochar as a cost effective, long-term option for in situ sequestration of ^{129}I and ^{99}Tc for contaminated areas at several DOE sites.